

## COMMUNICATION

## A self-assembled molecular nanostructure for trapping the native adatoms on Cu(110)

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**The native copper adatoms get trapped in a self-assembled molecular nanostructure which is mainly formed by the intermolecular van der Waals interactions, and two dominating specific binding modes between the adatoms and the molecules are revealed at the atomic scale by high-resolution STM imaging.**

Within the rapidly emerging field of surface nanoscience and nanotechnology, metal surfaces as templates always play a vital role in building up on-surface functional nanodevices and nanostructures, which is mainly attributed to the surface-mediated effects including restricted dimensions, charge transfer between adsorbates and metal substrates, substrate orientation and native metal adatoms, *etc.*<sup>1–4</sup> Native adatoms that mostly originate from the surface steps and defects upon thermal activation<sup>5</sup> have participated in the field of surface chemistry as building blocks of nanostructures or catalysts and received considerable attention in recent years. By introducing various strategies (*e.g.* STM manipulation, molecular templating, surface coordination), a variety of surface nanostructures involving native adatoms such as metallic chains, metallic clusters, metal oxides and metal–organic assemblies have been reported.<sup>6–9</sup> However, due to the high mobility and elusive concentration of the adatoms (depending on the surface defects and substrate temperature), one key issue lies in tracing the footprint of the native adatoms and further investigating the role and the properties of the adatoms. To date, a number of studies have reported that metal adatoms could be easily trapped in metal–organic coordination structures/networks on surfaces, in which strong charge transfer occurred between the trapped adatoms and the molecules.<sup>9–11</sup> It is still of general interest to find a simple way to trap the metal adatoms in a structure

wherein there is no strong interaction between the adatoms and the molecules to keep the intrinsic properties of the adatoms, and to explore the electronic or magnetic properties of the adatoms.<sup>12–14</sup>

In this work, we have investigated the spontaneous trapping of the copper adatoms *via* organic molecules on the Cu(110) surface by means of high-resolution STM imaging under ultrahigh vacuum (UHV) conditions. The molecule (3,4-bis(phenylethynyl)hexa-3-en-1,5-diyne-1,6-diyl)dibenzene, shortened as PEDB in the following, was chosen because there is no potential metal–ligand interaction, and the molecule–molecule interaction is also limited to weak van der Waals (vdW) force. The Cu(110) substrate, well known to supply freely diffusing adatoms,<sup>11,15</sup> was chosen as a resource for providing the copper adatoms. In such a model system we tackle the problem of whether it is possible to trap the copper adatoms by the adsorbed molecule in a moderate way, *i.e.* in a relatively weak interaction mode between the molecules and the adatoms. The STM results reveal the scenario that the native copper adatoms get trapped in a self-assembled molecular nanostructure in two dominating specific binding modes. These findings indicate that the mobile copper adatoms on the surface are able to enter into the weakly bonded molecular nanostructure and eventually get trapped inside the nanostructure at specific binding sites even without strong interactions with the molecules, and this novel system may have further implications for designing molecules that are capable of trapping single metal adatoms or even metallic clusters in a more delicate manner.

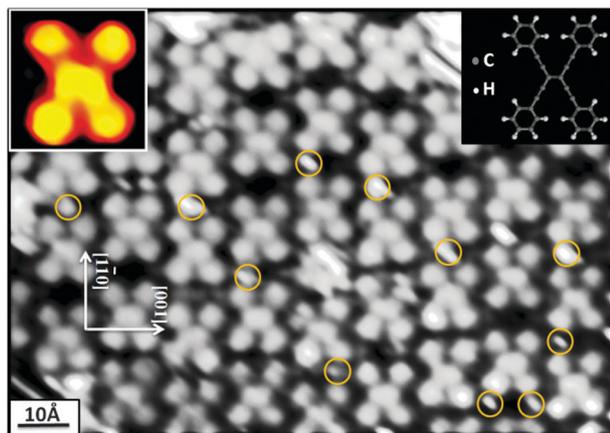
The experiments were performed in a UHV chamber (base pressure  $2 \times 10^{-10}$  mbar) equipped with a SPECS variable-temperature STM.<sup>16,17</sup> The PEDB molecules were loaded into a glass crucible which was mounted in a molecular evaporator. After the system was thoroughly degassed, the PEDB molecules were deposited by thermal sublimation onto a Cu(110) substrate held at 250K.

After deposition of PEDB molecules on Cu(110) held at 250 K, a self-assembled loosely bonded nanostructure consisting of random voids inside is formed as shown in Fig. 1. The upper-left panel shows the high-resolution STM image of a single PEDB molecule that exhibits a rather similar profile to

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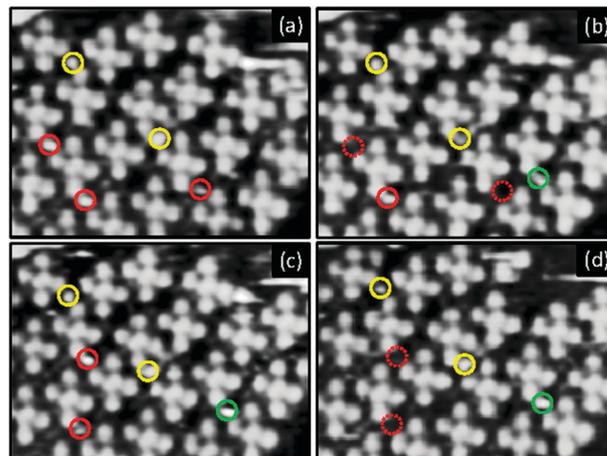
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**Fig. 1** STM image of PEDB molecules adsorbed on Cu(110) at 250 K. A close-packed structure was formed with random pores inside. The close-up STM image of a single PEDB molecule and the ball-and-stick model are shown in the upper-left and upper-right panels, respectively. Some copper adatoms observed as protrusions are indicated by the yellow circles. The lattice direction of the substrate is indicated in the image. Scanning conditions:  $I_t = 0.47$  nA;  $V_t = -2500$  mV;  $T = 215$  K.

the molecular model suggesting that the PEDB molecules adopt a flat-lying geometry on the Cu(110) surface. The single PEDB molecule is imaged as five distinct protrusions. By comparing the STM image and the dimensions with the molecular model we assign the peripheral four protrusions to the phenyl groups and the center one to the vinyl group of the molecule. All the molecules inside the structure are arranged with their long axis aligned along the  $[1\bar{1}0]$  direction to maximize the compactness of the structure, and we speculate that the observed molecular nanostructure is most likely driven by the intermolecular vdW interactions.<sup>18</sup> Interestingly, inside the formed nanostructure some bright protrusions (marked by the yellow circles) can be identified as shown in Fig. 1. According to the literature in which metal adatoms were involved,<sup>4,6,13</sup> we assign these protrusions to the copper adatoms originating from the Cu(110) substrate. This assignment can be further demonstrated by a series of STM observations as discussed below. Also, the high-resolution STM image reveals that the sizes of the circled protrusions are not quite uniform, which indicated that the protrusions could be composed of different numbers of adatoms. And, some of the protrusions appeared as blurred shapes, which is a sign of the high mobility of the copper adatoms, an indication of weak binding between the adatoms and the molecules.

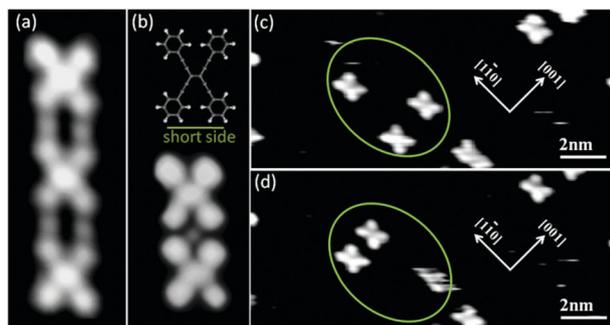
To gain further insight into the mechanism of the formation of such a complex metallosupramolecular nanostructure, we performed sequential STM imaging to investigate the stability of the adatoms involved in the nanostructures, as shown in Fig. 2. Since we know that the copper adatoms are mobile on the surface even inside the formed molecular nanostructure as we mentioned above, in this experiment we first chose an area that initially contained several distinct adatoms and then kept on scanning the same region at an interval of about 10 seconds, in such a way we hoped to get some dynamic information about the adatoms inside the confined nanostructure. The target



**Fig. 2** (a–d) Sequential STM images scanned in the same region at an interval of 10 seconds. The copper adatoms inside the structures are circled and different colors indicate different states of the adatoms. The scanning conditions remained the same as above.

adatoms inside the nanostructure are marked with solid circles in three different colors. Let us look at the ones in solid red circles first (Fig. 2a). They were found to be unstable (as shown in Fig. 2b–d, the dashed circles indicate the adatoms disappeared from the original sites). This observation indicates two points: first, there is enough space inside the molecular nanostructure allowing the adatoms to move around. Second, the adatoms are highly mobile but still can be detected by STM, which may be attributed to the confinement by the formed molecular nanostructure in comparison with the situation on the bare surface. At the same time, the ones in solid yellow circles (Fig. 2a) remained at the initial sites during the whole scanning process (Fig. 2b–d). More interestingly, the one in solid green circle suddenly appeared (Fig. 2b) and remained at the site during the following scanning process (Fig. 2c and d). This experiment indicates that the copper adatoms have enough freedom inside the loosely bonded molecular nanostructure and some of them can be trapped at specific binding sites by the adsorbed PEDB molecules on the surface.

A thorough and detailed analysis of a number of STM images is performed to get further understanding on the binding modes between the copper adatoms and the PEDB molecules. From the close-up STM images depicted in Fig. 3 we can distinguish two kinds of dominating elementary structural motifs. The elementary motif depicted in Fig. 3a demonstrates that two protrusions get trapped on the short sides between the PEDB molecules. Note that sometimes there is only one protrusion trapped in between the short sides on either the left or the right side. The elementary motif depicted in Fig. 3b demonstrates that one protrusion gets trapped in the middle of the short side between two adjacent molecules. These two binding motifs were mostly observed, and accounted for nearly 95% of the total trapping motifs. All these findings conclude that the copper adatoms are prone to locate in the voids inside the formed nanostructure. In comparison to the case of trapping metal adatoms through metal–ligand interaction, in this case we demonstrate that a weakly bonded two-dimensional



**Fig. 3** (a) and (b) STM images of two dominating specific binding modes for trapping the copper adatoms by the PEDB molecules. For a clear description, the short side of PEDB is defined in (b). (c) and (d) sequential STM images show PEDB molecules freely diffused on the Cu(110) surface with the time interval of 50 seconds between two STM images. The scanning conditions remained the same as above.

(2D) molecular nanostructure can also trap the adatoms (or even metallic clusters) in a more flexible manner.

The sequential STM images shown in Fig. 3c and d demonstrate that the isolated PEDB molecules have a high mobility to freely diffuse on the surface. This also supports our speculation that the formed molecular nanostructure and the trapping phenomenon were predominately determined by the intermolecular interactions rather than molecule–substrate interactions. Thus we could speculate the trapping scenario as the following: firstly, the weak intermolecular vdW interactions led to the formation of a 2D molecular nanostructure with large enough interstitials in between the adjacent molecules. Secondly, the highly mobile copper adatoms were able to travel around even inside the formed nanostructures until they reached more stable binding sites then got trapped by the molecules as mentioned above. There could be another possibility like this: after molecular adsorption on the surface both the molecules and the adatoms diffused around on the surface and in the process of forming the molecular nanostructures meanwhile the copper adatoms were caught by the adjacent molecules and confined inside the formed nanostructure, which would need to overcome a prohibitively large energy barrier to move away from it. Such dynamic effects were considered to be the primary factor in trapping gold adatoms in a similar system reported in the literature.<sup>19</sup>

In conclusion, by using the high-resolution UHV-STM imaging we have demonstrated that the native copper adatoms could be trapped in a 2D self-assembled molecular nanostructure in which there is no strong interaction between the adatoms and the molecules. The high-resolution STM images reveal that there are two dominating binding modes for the molecules to trap the copper adatoms where the dynamic effects were considered to be

the dominating factor in the process. These findings may have further implications for designing molecules that are capable of trapping metal adatoms in a more delicate manner.

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