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Self-assembly of melem on Au(111) and Ag(111): the origin of two different hydrogen bonding configurations[†]

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were also obtained to compare the different natures of the intermolecular bonding configurations.

We studied the self-assembly of melem on the Au(111) and Ag(111) surfaces. By scanning tunneling micro-

scopy imaging, we observed two different STM appearances of the melem molecule within the selfassembled nanostructure on Au(111), which resulted from the different intermolecular bonding configurations.

Moreover, further DFT details including the intermolecular charge density difference and bonding energy

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Introduction

The self-assembly of molecules presents an efficient approach to form novel nanostructures on surfaces, which has aroused significant interest in the past few decades. Generally speaking, the formation of desired surface nanostructures depends on delicate control over the molecule-substrate interactions and molecule-molecule interactions. The molecule-molecule interactions, which include hydrogen bonding, van der Waals forces and π - π interactions, often play a decisive role in the formation of self-assembled nanostructures on noble metal surfaces.¹⁻⁸ Thus, using different functional groups to regulate the intermolecular interactions has become the most popular way to control the surface nanostructures. Among others, hydrogen bonding interaction has been one of the most intensively employed ones.^{9,10} By functionalizing precursor molecules with specific functional groups, including -COOH, -OH, -CHO, -CN, -NH2 and so on, vast numbers of different self-assembled nanostructures have been achieved on inert surfaces of noble metals.¹¹⁻²³ It should be noted that the particular interactions between the hydrogen bond donor and acceptor are the underlying driving forces, which can be designed to construct desired nanostructures on the surface.

In this work, we investigated the self-assembly of melem on Au(111) and Ag(111) surfaces. Melem has a planar triangular heptazine group with three amino substituents at the corners of

the triangle (shown in Fig. 1a). It was found that melem was the precursor of graphitic carbon nitride.²⁴ The amino and heptazine groups fulfill the requirement of the hydrogen donor (H_{NH}) and hydrogen acceptors (Nheptazine) to construct hydrogen bonded surface nanostructures. It was previously reported that the selfassembly of melem could form five different porous and two densely packed polymorphs on Ag(111).²² Here, we have used the Au(111) surface, which is generally considered as a less active surface, to investigate the two-dimensional self-assembly of melem on the surface. Note that in this study we mainly focused on a relatively low molecular coverage, typically below 0.5 monolayer (one monolayer is defined as 1660 melem molecules per 100 nm²). By scanning tunneling microscopy (STM) imaging, we found one kind of porous structure on Au(111). Interestingly, from the highresolution STM image we resolved two different STM appearances of the melem molecule within the self-assembled nanostructure. However, there is only one kind of homogeneous melem molecule if we deposit the molecule on Ag(111) with the same coverage.²³ From further DFT calculations combined with STM imaging, we identified that the different single-molecule morphologies on Au(111) resulted from the different intermolecular bonding configurations due to the alternative double hydrogen bond between the hydrogen donor $(H_{NH_{\star}})$ and hydrogen acceptors $(N_{heptazine})$. Further DFT data including the intermolecular charge density difference and binding energy were also obtained to compare the different natures of their intermolecular bonding configurations.

Experimental

STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable temperature "Aarhus-type" STM purchased from SPECS, a molecular evaporator,

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Fig. 1 (a) Large-scale STM image shows the formation of a porous network structure by melem molecules on Au(111) at room temperature (300 K). (b) Closed-up STM image allows us to distinguish the sub-molecularly resolved topography of the porous structures. Green and white dashed ellipses indicate the two different configurations. The close-packed directions of the surface are indicated by white arrows. (c and d) Top and (e and f) side views of the DFT optimized models of two kinds of hydrogen bonded motifs on Au(111). (g and h) The electron density difference plots of the two different motifs, respectively, calculated at an isosurface value of 0.014 e Å⁻³. Blue and red isosurfaces indicate charge depletion and accumulation, respectively.

and standard facilities for sample preparation.^{25,26} After the system was thoroughly degassed, melem which was prepared according to our previous work was deposited by thermal sublimation at ~475 K onto Au(111) and Ag(111) surfaces.²⁷ The sample was thereafter transferred within the UHV chamber to the microscope, where measurements were carried out at about 100-150 K unless specified, and the typical scanning parameters were $I_t = 0.5-1.0$ nA and $V_t = \pm 1000-2000$ mV. All of the calculations were carried out within the DFT framework using the Vienna Ab Initio Simulation Package (VASP).^{28,29} The projector augmented wave method was used to describe the interaction between ions and electrons.^{30,31} We employed the Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation functional, and van der Waals (vdW) interactions were included using the dispersion corrected DFT-D3 method of Grimme.^{32,33} The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in VASP until the forces on all unconstrained atoms were \leq 0.03 eV Å⁻¹. Considering that different sites such as fcc and hcp in the Au(111) unit cell are known to have different influences on the adsorbate, we chose three atomic layers on Au(111), and two atomic layers on Ag(111).

Results and discussion

As shown in the STM image in Fig. 1a, after deposition of melem on Au(111) at room temperature, porous network structures are observed. However, it is also visible that some bright features are distributed within the network structure, which is not likely to be the consequence of the Au(111) herringbone reconstruction underneath the melem layer as seen in other self-assembled structures on Au(111).²¹ A close inspection of the high-resolution STM image clearly reveals the molecular arrangement and single-molecule STM topography of the melem molecules as shown in Fig. 1b. Interestingly, two different triangle features are found within the porous structures, that is, a brighter one (indicated by green ellipses) and a dimmer one (indicated by white ellipses).²³ Both of the triangles should be attributed to the melem molecules due to their similar sizes, STM shapes and packing modes. Moreover, one can tell that the three amino groups show clear contrasts at the corners. We also note that the bright melem molecules always appear in pairs.

Furthermore, the high-resolution STM image provides us with a more in-depth analysis. As shown in Fig. 1b, we could resolve the intermolecular arrangement and interaction between the melem molecules. Overall, the melem molecules are connected to each other in a three-fold fashion to form porous network structures on the surface. Notably, the dim features are linked with each other in a more staggered way compared with the bright features. To gain further insight, we performed extensive DFT calculations of the two motifs on the Au(111) surface (Fig. S1, ESI⁺), and the two models stand out as shown in Fig. 1c and d. Both of the melem molecules in the two motifs adopt a flat-lying geometry with a similar height in Fig. 1e and f. In addition, we have not reproduced the different contrasts from their Tersoff-Hamann STM simulations in Fig. S2 (ESI[†]), where the top figure shows experimental data and the bottom figure (showing no difference in contrast) shows simulated data. Their flat geometries imply that hydrogen-bonded intermolecular interaction among melem molecules determines the formation of the observed melem network, whereas the surface serves primarily as a template to accommodate the molecules. At the same time, we found that both of them are intermolecularly interlinked through two N···HN hydrogen bonds. Motif-1 is different from Motif-2 due to the different linking nature of the hydrogen bond acceptor at the heptazine core, which further results in a more staggered arrangement of Motif-1 than that of Motif-2. We have also calculated that the binding energy of Motif-1 is 0.83 eV and that of Motif-2 is 0.39 eV, which implies that Motif-1 is more favourable than Motif-2. Therefore, we conclude that Motif-1 should be attributed to the dim triangle feature and Motif-2 to the bright one. This conclusion is also in agreement with the fact that the bright dimers

account for a minority within the self-assembled nanostructures, that is, 5–10%.

To gain further insight into the two different motifs, we also performed DFT calculations of the electron density difference plots of the two dimers on Au(111) (shown in Fig. 1g and h). From their charge density difference maps, we clearly identify that both of the dimers are intermolecularly interlinked through two $N \cdots HN$ hydrogen bonds. However, as for Motif-2 shown in Fig. 1h, there is an additional repulsive interaction due to the proximity of the two N of the heptazines, which accounts for the lower stability of Motif-2 than Motif-1 (indicated by the red dashed ellipse).³⁴

Interestingly, the STM contrast of melem in Motif-1 is apparently different from that of Motif-2. Motif-1 consists of dim molecules, while Motif-2 consists of bright molecules. As shown in the line profile in Fig. S3 (ESI†), the dim and bright species appeared to have a height difference of 0.47 Å.² It is noteworthy that the dimmer melems which constitute Motif-1 always account for the majority; nevertheless, the bright melems which constitute Motif-2 still exist in the nanostructures even after annealing the sample until the molecules are desorbed from the surface. At the same time, we calculated the statistical distributions of the isolated or aggregated Motif2 dimers at different temperatures (Fig. S4, ESI†). In addition, we also controlled the coverage, and then found that the proportion of bright to dim dimers showed no significant dependence on the molecular coverage (Fig. S5, ESI†).

In addition, we could divide the porous structure into hexamers which consist of six melem molecules to further analyze the porous structure. As shown in the STM images of Fig. 2, we find four different hexamer structures. One is formed exclusively by the dim melem, *i.e.*, Motif-1 (Fig. 2a and e). One is composed of four dim molecules and a pair of bright dimers (Fig. 2b and f). One is composed of two dim molecules and two pairs of bright dimers at the opposite position (Fig. 2c and g). And the other is composed of two dim molecules and two pairs of bright dimers at the neighboring position (Fig. 2d and h). In the last case, the interaction between two Motif-2 units is in a staggered form as that of Motif-1. Based on these STM images, we performed the corresponding DFT calculations for the four hexamer structures in the gas phase. The optimized structural models are superimposed on the relative STM images in Fig. 2e-h, and a good agreement is achieved in all cases. Moreover, we also performed DFT calculations of the charge density difference maps of the four hexamer structures in the gas phase as shown in Fig. 2i-l, which clearly illustrate the cyclic double hydrogen bonds between the amino groups and heptazine groups.

To gain more insights into the influence of Motif-2 on the stability of the self-assembled structures, we calculated the formation energy of six possible hexamers which consist of different numbers of Motif-2 units as shown in Fig. 3. The relative binding energy as a function of the number of Motif-2 units is plotted as a linear relation:

$$E_{\rm hex}$$
 = -4.91 + 0.35 \times N

wherein E_{hex} indicates the binding energy of the hexamer, and *N* is the number of Motif-2 units involved in the hexamers.



Fig. 2 (a–d) The STM images of four types of melem hexamers which have been observed within the porous nanostructure, where the brighter ones are indicated by the green dashed ellipses. (e–h) The STM images (a)–(d) and their corresponding DFT-optimized structural models are superimposed. (i–l) The charge density difference maps of the corresponding STM images, where red and blue isosurfaces indicate charge accumulation and depletion, respectively (an isosurface value of 0.016 e Å⁻³).

The linear fit indicates a slope of 0.35. As expected, the hexamer formed purely by Motif-1 is the most stable. By placing two Motif-2 units at different positions in the hexamers, we constructed *para*-position, *meta*-position, and *ortho*-position hexamers (H-2-*p*, H-2-*m*, H-2-*o*). Of these hexamers, only the *para* and *meta*-position hexamers are found in the experiment. The hexamers with more than three Motif-2 units are not found presumably because of the fact that they are less stable. When the hexamer is purely formed by Motif-2, the binding energy is as low as 2.81 eV (H-6), and it is not observed either. In addition, a statistical distribution of the different hexamers that observed on Au(111) at 350 K and 450 K is provided in Fig. S6 (ESI†).

Despite their different stabilities, the proportion of the dim to bright dimers is almost fixed regardless of the annealing process. We speculate the possibility of spontaneous tautomerization of melem, which might yield the melem tautomer as a result of the hydrogen transfer from the amino group to the



Fig. 3 The DFT calculated binding energy as a function of the number of Motif-2 units in different hexamer structures. The red dashed line is fitted to the calculated values.



Fig. 4 (a and b) STM images of melem molecules on the Ag(111) surface. (c) The side views of the DFT optimized model of the hydrogen bonded dimer structure on Ag(111). (d) The electron density difference plot of the corresponding dimer structure, calculated at an isosurface value of 0.014 e Å⁻³. Blue and red isosurfaces indicate charge depletion and accumulation, respectively.

heptazine N site.²² Thus, to gain further insight into the origin of the two different melem molecules on the surface, we also performed the experiment on Ag(111) surface. As shown in Fig. 4a, we observed only one homogeneous phase with one kind of uniform molecular morphology of melem on the surface. A closer inspection of the self-assembled nanostructure shows that all of the molecules are composed of thermally stable Motif-1. As illustrated in Fig. 4c, the DFT calculated model of the dimer structure on Ag(111) shows a flat-lying geometry, which is the same as that on Au(111). In addition, we also annealed the sample at different temperatures, and no significant changes in the formed nanostructures were observed. On Au(111), we have calculated that Motif-1 is 0.22 eV more stable than Motif-2. However, Motif-1 is 0.31 eV more stable than Motif-2 on Ag(111). By comparison, there is an excess of 0.09 eV on Ag(111) for Motif-2. So, it is invalid that the bright dimer is due to the formation of the special interaction which is caused by the spontaneous tautomerization of melem.

Thus far, the origin and generality of the different contrasts between Motif-1 and Motif-2 are still confusing. Due to their similar adsorption geometries on the surface, the different contrasts of the molecules in the two different motifs might be attributed to the altered electronic states induced by the two different hydrogen bonding interactions. This phenomenon still remains an open question and warrants further theoretical explanations.

Conclusions

In summary, we have shown the two-dimensional self-assembly of melem on Au(111) and Ag(111). The self-assembled nanostructures are formed by the hydrogen bonded interactions between the melem molecules, where we observe two different basic dimer motifs within the nanostructure on Au(111). Surprisingly, the two different motifs also result in different contrasts of the STM images of the melem molecules. DFT calculations have been performed to illustrate the geometries and stabilities of the two different motifs on the surface. In addition, we have also studied the hexamers within the self-assembled structures which could be considered as the building blocks using the high resolution STM image and DFT calculations. An understanding of such self-assembled structures can provide fundamental insight into distinct intermolecular hydrogen bonding configurations, and the formation of porous structures may serve as growth templates of scientific or practical interest.

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