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Edge and terrace structure of CoTPP on Au(1 1 1) investigated by ultra-high vacuum scanning tunnelling microscopy at room temperature

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ABSTRACT

Edge adsorption and terrace molecular domain structures of Cobalt(II) tetraphenylporphyrin (CoTPP) on Au(1 1 1) were investigated using STM at room temperature. Two different terrace domain structures were observed. These two arrangements were found to be enantiomorphous arrangements of the molecular assemblies, where the molecular rows rotate ±16° with respect to the [1 2 1] direction of Au(1 1 1). In both arrangements, most of the CoTPP molecules were imaged as one bright dot with four legs, corresponding to a planar conformation of the macrocycle. A small proportion of the CoTPP molecules appear as two bright dots, corresponding to a saddle shape of the macrocycle. Our results show that most of the saddle-deformed CoTPP molecules are distributed in the vicinity of the bridging sites of the reconstructed gold surface. Besides terrace domains, we found that several edge adsorption structures of CoTPP are also stable enough to be imaged and analysed in detail. Furthermore, the relationship between edge structures and terrace domains was revealed.

1. Introduction

Studying the adsorption behaviour of organic functional molecules on surfaces benefits multiple research topics over a wide range, from the over century-old fields such as catalysis, lubrication and corrosion to the relatively new-born fields of organic and molecular electronics; and from basic scientific problems such as electronic transport mechanisms at the nanoscale, to applications such as implementation of novel devices [1–6]. Amongst all of the common functional molecules, phthalocyanine and porphyrin derivatives are particularly relevant due to their chemical stability and excellent semiconducting properties which have found application in light emitting diodes as well as other devices [7–14]. Due to their extensive use in the body (in red blood cells, for e.g.), they are also of more fundamental interest [15].

Using scanning tunnelling microscopy (STM)-an imaging tool with high spatial resolution, numerous research works have been carried out on porphyrin derivatives, the results of which have given us insight into the molecular conformation [16–19], electronic orbital structure [20,21], assembled structures [22–42], metalation [43–46] and surface reactions [47] involving these molecules. For meso-substituted porphyrin, its conformation on a surface depends on the rotation angle (dihedral angle), the bending angle of the meso-substituents and the deformation of the macrocycle. For instance, tetrapyridyl-porphyrin (TPyP) adsorbs on the Ag(1 1 1) surface with a dihedral angle of 60° between the pyridyl and macrocycle planes [16]; whereas on Cu(1 1 1), the conformation of TPyP is more complicated with several possibilities. On this surface, within the pyridyl group, the C–C bonds rotate by an angle not larger than 10° and bending towards the substrate occurs within the angular range of 20–30°, causing significant distortion of the macrocycle [17]; for Cobalt(II) tetraphenyl porphyrin (CoTPP) on the Cu(1 1 1) surface, the dihedral angle is larger, at around 35° and the bending angle of the pyrrole rings is estimated to be 20° [21]. Furthermore, another report showed that Copper(II)-tetra[3,5 di-t-butylphenyl] porphyrin (Cu-TBPP) adopts a different conformation on Au(1 1 0) when annealed at different temperatures and times. Their results indicate that the conformation with a dihedral angle of 45° is the most thermally stable one [18]. Going beyond simple imaging of these molecules, a molecular switch was realized by rotating one leg of Cu-TBPP on Cu(2 1 1) by the STM tip [19]. Electronic properties of these molecules have also been explored. Scanning tunnelling spectroscopy (STS) results show that CoTPP has a band near 5.2 eV while Nickel(II) tetraphenyl porphyrin has no such band. The half-filled d_z2 orbital of Co(II) is responsible for the band of 5.2 eV [20]. Under different bias conditions, STS *dI/dV* maps revealed the orbitals near the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of CoTPP in saddle conformation [21]. As for assembled structures of porphyrin derivatives, many results have been published, varied from single component [22–24] to multi component [25,26], and from single-decker molecules [27,28] to double-decker molecules [29,30] and varied environments, including ambient

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[31,32], organic solution [33–35], conductive solution [36–39] and UHV [40–42].

Besides investigation of metal porphyrins, metalation of porphyrins has also been explored. An Iron atom beam was introduced into a vacuum chamber and reacted with a H_2-TPyP precursor layer on Ag(1 1 1), resulting in the formation of Fe(II) TPyP [43]. Similar results were obtained on Iron and Cerium with H_2-TPP forming Fe(II) TPP and Ce(II) TPP respectively [44,45]. A novel metalation mechanism was proposed based on these STM results and density functional theory (DFT). The results suggest metalation of H_2-TPP with Co, Fe and Ni are two-state reactions while for Cu and Zn are single state-reactions on the potential energy surface [46]. Due to involvement in many biological and chemical reaction processes, surface reactions of metal porphyrins attract wide interest in many fields. With low temperature STM (LT STM), it was found that Zn-TBPP could be capped with 1,4-diazabicyclo[2.2.2]octane (DABCO) [47]. Another report demonstrated the possibility of oxidization of Mn(III) porphyrin chloride into Mn(IV) porphyrin oxide by O_2 and reduction of Mn(IV) porphyrin oxide to its original state by cis-stilbene [15].

Most of these research efforts have involved investigating ordered domains of molecules on surface terraces, while not so many papers report adsorption of porphyrin derivatives on step edges. Cryogenic STM experiments revealed that Pt-TBPP tends to adsorb on step edges of Cu(1 0 0) at low coverage [48]. In another report performed under similar experimental conditions, freebase TBPP (H_2-TBPP) and Cu-TBPP were found to exhibit different conformation and adsorption behaviour around step edges [49]. At step edges, H_2-TBPP molecules form molecular chains that bridge the gap between upper and lower step edges. Due to the different molecular conformations found at step edges and on terraces, the H_2-TBPP domains formed on wide terraces are incommensurate with these molecular chains at the step edges so there is no apparent structural relationship. For the case of Cu-TBPP, it was found that upper edges of the step were the preferred adsorption sites. In stark contrast to H_2-TBPP, Cu-TBPP domains on terraces were found to have nucleated from edge adsorption, as the two structures in this case are commensurate with each other and appear identical in STM images. Nucleation of Zn-TBPP at step edges under the interaction of the electric field in STM was used to create gold nanofingers on the Au(1 1 1) surface at room temperature. In that case however, single ZnTPP molecules at step edges were not discerned [50].

Most investigations on single molecule edge structures with sub-molecular resolution were performed at low temperature (77 K or below). In this report we investigated the assembly behaviour of CoTPP on terraces and step edges at room temperature. Two different terrace domains were found in our experiments. A previously unreported contrast of CoTPP in terrace assemblies was observed as well as the conventional four-leg structure. Single molecular structures around step edges were studied at the sub-molecular level under room temperature. In the last part of the paper, the relationship between terrace domains and edge structures is discussed. Studies on this molecule are particularly relevant due to its wide use as an oxidising agent and a catalyst.

2. Materials and methods

Cobalt(II) tetraphenylporphyrin (CoTPP) was purchased from Fluka. Au(1 1 1) films on mica were purchased from Agilent. STM tips were made by electrochemically etching Tungsten wire (0.2 mm in diameter) in 4.5 M/L NaOH solution. The gold surface was cleaned by repeated cycles of Argon-ion sputtering and annealing and examined using our home-built ultra-high vacuum scanning tunnelling microscope (UHV-STM) before depositing molecules by sublimation from a K-cell. The CoTPP was degassed for several hours before being deposited on a freshly cleaned Au(1 1 1) surface, which was held at room temperature under UHV conditions during the deposition and subsequent STM imaging. Images were obtained using our home-built UHV (middle of 10^{-11} Torr) STM. Our STM was equipped with a low-current amplifier with a noise floor of the order 50 fA. Images were processed with Wsxm 4.0 develop 12.0 [51].

3. Results and discussion

The chemical structure of free CoTPP is illustrated in Fig. 1a. After sublimation onto a clean Au(1 1 1) surface in situ, it can be seen that the molecules form large, ordered domains, as shown in Figs. 1b and c. The herringbone reconstruction lines can also be seen in these two images lying under the molecular assembly. Following analysis of these and similar images, two kinds of domain were determined with different orientations relative to the substrate lattice. Representative images of each kind are given in Fig. 1b and c. Due to different imaging parameters, gold atoms and the CoTPP cannot be observed simultaneously. An alternative method to reveal the substrate lattice is via the herringbone reconstruction which is along the [1 2 1] directions of the Au(1 1 1) surface. In Fig. 1b and c, the [1 2 1] directions were marked with black lines. *A* and *B* point out the vector orientation of a unit cell of the CoTPP adlayer. Statistical results show that the *A* direction in Fig. 1b is rotated 16° ± 5° anti-clockwise relative to the [1 2 1] direction while in Fig. 1c the rotation is 16° ± 5° clockwise. In other words, Fig. 1b and c show molecular domains that are mirror images of each other with the mirror plane perpendicular to the substrate, and aligned along the [1 2 1] orientation of Au(1 1 1). Thus, nonchiral CoTPP molecules formed chiral domains similar to adlayers of Ni(II) porphine and TPyP on the Ag(1 1 1) surface [42,52]. Although ordered structures of CoTPP on Au(1 1 1) have been reported in UHV and electrochemical environments [20,53], our results reveal an additional domain chirality.

In the medium resolution image, Fig. 2a, most molecules appear as a bright spot with four legs. Molecules in this image were elongated slightly in one direction relative to its actual four fold symmetry, caused by thermal drift of the STM. In Fig. 2b, we present high resolution images. The unit cell of CoTPP is illustrated in this image, indicating that the molecules are organised in an almost square unit cell of angle 88° ± 5° and dimension 1.42 nm. Several CoTPP models are superposed on the STM image to show the adsorbing pattern.

As indicated by circles in Fig. 2a, a small proportion of CoTPP molecules were imaged as two symmetrical protrusions. Thus, in this conformation, these molecules show two fold symmetry. Two fold symmetry of CoTPP was also found on the Cu(1 1 1) surface [21]. In this adsorbing conformation, the whole macrocycle is buckled at the center, giving the molecules a butterfly appearance. More specifically, one pair of opposite pyrrole rings tilt upwards, while the other pair of rings bends down. It is also apparent that the deformed molecules have a different orientation on the surface, and in fact are rotated by 26° ± 5° clockwise relative to the other molecules within the domain, as illustrated in Fig. 2c. The vast majority of these distorted molecules are to be found at the bridging sites of the herringbone reconstruction. The degree of molecular deformation we have observed is unlikely to be due to the topography of the herringbone reconstruction, and is more likely to be due to the higher surface free-energy there. The molecules may be attempting to achieve as much overlap as possible between their unoccupied orbitals and the gold atoms to compensate for the lack of full co-ordination of the atoms at the bridging sites, with a severe deformation of the molecules occurring as a consequence.