



Dynamics of porphyrin adsorption on highly oriented pyrolytic graphite monitored by scanning tunnelling microscopy at the liquid/solid interface

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ABSTRACT

Scanning tunnelling microscopy (STM) at solid/tetradecane interface is used to study the dynamics of zinc(II)-octaethylporphyrin (ZnOEP) and zinc(II)-*meso*-tetradodecylporphyrin (ZnTDP) adsorption on the surface of highly oriented pyrolytic graphite (HOPG). ZnOEP exhibits a polymorphic behaviour, with a first metastable phase remaining for the first 2 h. This initial α -phase is then converted into a β -phase, where all porphyrins lie parallel to the substrate with a hexagonal arrangement, in agreement with previous reports. At variance with this behaviour, no metastable phases are found during ZnTDP adsorption under the same conditions. We consider that this different behaviour is due to the combination of a stronger interaction and lower mobility of ZnTDP on the HOPG surface.

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1. Introduction

Nanostructured surfaces, formed upon deposition of molecules on a substrate as organized monolayers, are of primary importance for bottom-up technologies [1–8]. The formation of such monolayers is governed by molecular self-assembly/self-organization. Many parameters, such as type of solvent, concentration, molecular interactions, size and structure of adsorbing molecule, type of surface and temperature, influence adsorption rate and monolayer formation. It is often the case that the adsorption process involves the appearance of polymorphs before the molecules eventually achieve a thermodynamically stable organization on the substrate surface [9–12]. In some cases such intermediate metastable structures do not live long enough to be characterized [13]. Fortunately, there are systems where, due to exhibiting long lifetimes (up to hours), switching between different polymorphs can be identified [14].

Scanning tunnelling microscopy (STM) at the solid/liquid interface has been used to study polymorphism on surfaces [15–19]. This technique allows the imaging of molecules adsorption in real

time. The molecules are added into a droplet of an electrically insulating solvent located between the STM tip and the surface. The tip scans the surface starting from the time these molecules are added, enabling the observation of the molecules organization on a conductive substrate and their evolution in time. For instance, Fichou et al. [20] reported the structural evolution of hexakis(*n*-dodecyl)-*peri*-hexabenzocoronene (HBC- C_{12}) on monolayers of *n*-pentacontane ($n-C_{50}H_{102}$) on highly oriented pyrolytic graphite (HOPG). They observed two metastable phases before the stable one is formed, over a period of time that extended up to 8 h. The weak interaction between HBC- C_{12} and the *n*-pentacontane monolayer is proposed to be at the origin of the HBC- C_{12} structural evolution. Samorì et al. [21] have also reported phase transitions in [5,5′]-bisphenyl-[2,2′]bithiophenes adsorbed on HOPG, where the final phase takes ca. 12 h to be formed, as a result of molecular arrangement modifications due to Ostwald ripening [22].

STM studies at the solid–liquid interface of zinc(II)-octaethylporphyrin (ZnOEP) adsorption on HOPG have also shown this to be a dynamic process [23]. The adsorption starts with the nucleation of ordered molecular domains, evolving into a fully packed 2D structure by Ostwald ripening. In the sequence of that first study, we have now been able to follow the details of ZnOEP adsorption on HOPG during the first minutes, evidencing a polymorphic monolayer formation. This result is compared with

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the adsorption of a porphyrin with longer alkyl chains, the zinc(II)-*meso*-tetradodecylporphyrin (ZnTDP), for which no polymorphism or phase transitions were observed, a fact that we attribute to a combination of lower molecular diffusivity and stronger molecular interactions (intermolecular and/or with HOPG).

2. Materials and methods

Zinc(II)-octaethylporphyrin (ZnOEP) was purchased from Sigma–Aldrich and used as received. Zinc(II)-*meso*-tetradodecylporphyrin (ZnTDP), was synthesized following previously reported procedures [24,25]. Further details are provided in supplementary information. Self-assembled monolayers were formed on freshly cleaved HOPG substrates (Micromash). 5 μL of a porphyrin-saturated solution in *n*-tetradecane (Sigma–Aldrich) is added with a microsyringe to a *n*-tetradecane droplet on the HOPG surface, as described in Ref. [23]. Room temperature STM measurements were performed at the HOPG/tetradecane interface in a constant current mode using a Pico-STM (Molecular Imaging). A mechanically etched Pt/Ir wire, $\varnothing=0.25$ mm, purchased from Goodfellow, was used as tip.

3. Results

Fig. 1 shows a set of sequential STM images obtained during the first 10 min, starting right from the first minute after the ZnOEP addition to the tetradecane droplet (time zero). These images are characterized by the presence of parallel rows with alternating brightness, being clearly identified regular rows of brighter dots. We name this early molecular arrangement as α -phase. The sequential STM images show also domains with ill-defined molecular positions, suggesting the existence of molecular disorder.

In the image obtained at $t=6$ min it is possible to observe a region with a molecular organization different from that observed in the α -phase, identified in Fig. 1 by a dashed line, being similar to a hexagonal structure, that we name β -phase. This β -phase is converted back into the α -phase 10 min later, indicating that these early β -phase domains are not stable.

Fig. 2(a) shows, in greater detail, the two-dimensional organization of ZnOEP in the α -phase, which consists on rows of ZnOEP dimer-like motifs, with different brightness. A detailed analysis of Fig. 2(a) reveals that the ZnOEP molecules within each dimer have different structural conformations. The molecules with lower intensity signals have 4 visible protrusions that we attribute to the ethyl groups that are oriented towards the graphite. The ethyl groups that are facing up are not visible in the STM image because they move during the STM scan. Therefore, according to the distance between the protrusions (see Figs. S2 and S3 of supporting information), the molecules are in a *trans* conformation (ZnOEP *trans* 1) with the two ethyl groups of the same pyrrole moiety pointing towards the same direction but opposite to those of the nearby pyrrole unit, as shown in Fig. 2(b) and (c). The brighter molecules are planar and closer to the graphite, with ill-resolved ethyl groups. In some molecules it is possible to identify 4 ethyl groups of adjacent pyrrole moieties pointing down while the 4 ethyl groups of the other two adjacent pyrrole units are likely pointing up (ZnOEP *trans* 2, in Fig. 2(b) and (c)). The unit cell parameters are $\alpha=(1.41\pm 0.06)$ nm, $\beta=(2.64\pm 0.23)$ nm and $\gamma=(83\pm 4)^\circ$. Fig. 2(c) shows the ionization potential maps of the ZnOEP in the two conformations, supporting the observation that the core, that is, the conjugated central part of the molecule, has the lowest ionization potential, giving rise to higher currents, in agreement with previous studies on other conjugated molecules [26].

Two hours after the addition of ZnOEP, we observe that the initially identified α -phase coexists with stable β -phase domains and with a third poorly resolved γ domain, as shown in Fig. 3. We note that, as mentioned above, metastable β -phase domains are already present at the early stages of the adsorption process ($t=6$ –8 min) (Fig. 1(d)). The sequence of images shown in Fig. 3(a)–(c), evidences the growth of the β -phase domains, via conversion from the α -phase, with the disappearance of the dimeric motifs. Fig. 3(c) is a proposed model for that growth process. While the brighter molecules are left unchanged, the dim partners in the dimers gain in brightness and appear to move, filling the gap that initially separated the rows of the α -phase. We find that the distance between the brightest molecules of adjacent rows of the α -phase remains constant. The third region (γ) is not well resolved, which might be due to molecular disorder.

The characterization of zinc(II) *meso*-tetradodecylporphyrin (ZnTDP) adsorption on HOPG revealed a very different behaviour with respect to that of ZnOEP, in the sense that no polymorphs were observed. The high resolution STM image of Fig. 4(a) shows the molecular packing of ZnTDP on HOPG, with unit cell parameters $\alpha=(2.08\pm 0.09)$ nm, $\beta=(1.34\pm 0.07)$ nm and $\gamma=(80\pm 3)^\circ$. The bright squares, with dimensions of about 1.13 ± 0.11 nm, correspond to the core of ZnTDP that are arranged side by side. The alkyl chains are not well resolved in the STM images due to the high ionization potential energy (as shown in the ionization energy map of Fig. 4(b)). Other authors [27,28] reported that the alkyl chains positions alternate between in and out of the plane of graphite, those lying on the HOPG surface forming a uniform, interdigitated alkane row that corresponds to the dark stripes with 0.94 ± 0.10 nm of width.

4. Discussion

The adsorption of ZnOEP on HOPG proceeds via an intermediate metastable phase, before reaching the equilibrium phase, which requires a nucleation time of ca. 2 h. In fact, the first STM images (Fig. 1) show the formation of α -phase, which takes place within the first minute after addition of ZnOEP solution to the tetradecane droplet. β -phase nucleation centres appear during these first minutes, but they are not viable (to initiate the growth of the β -phase domains) and are converted back to α -phase.

The high-resolution image of α -phase (Fig. 2) shows that the ZnOEP molecules are organized as dimer-like units, with different brightness, aligned along regular rows. We attribute the difference in brightness of the two ZnOEP units of the dimer to their different coupling to the HOPG. The current flowing between the molecule and HOPG depends on the spatial overlap between the electronic states of the adsorbate (ZnOEP) and those of the substrate (HOPG). Therefore, the weaker the electronic coupling between the two, the lower the current and the lower the intensity of the signal [26]. The fact that the dimer units of each dimer gain in brightness, as they evolve into the final stable structure, supports our assumption that the brightness difference found in the α -phase dimers is related to the electronic coupling between the ZnOEP molecules and the HOPG substrate. The β -phase “growth” is thus associated to the movement of the dimer partner molecules to achieve the 2D structure with minimum energy, as suggested by the model of Fig. 3(d).

ZnOEP molecules within each dimer have different structural conformations, ZnOEP *trans* 1 and ZnOEP *trans* 2, which differ by the relative orientation of the ethyl side groups, as described above. In the supporting information we provide the detailed characteristics of this structure, comparing experimental dimensions with the corresponding theoretical ones obtained by DFT/RB3LYP quantum calculations using SPARTAN'08 software, that support that conformation assignment.

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