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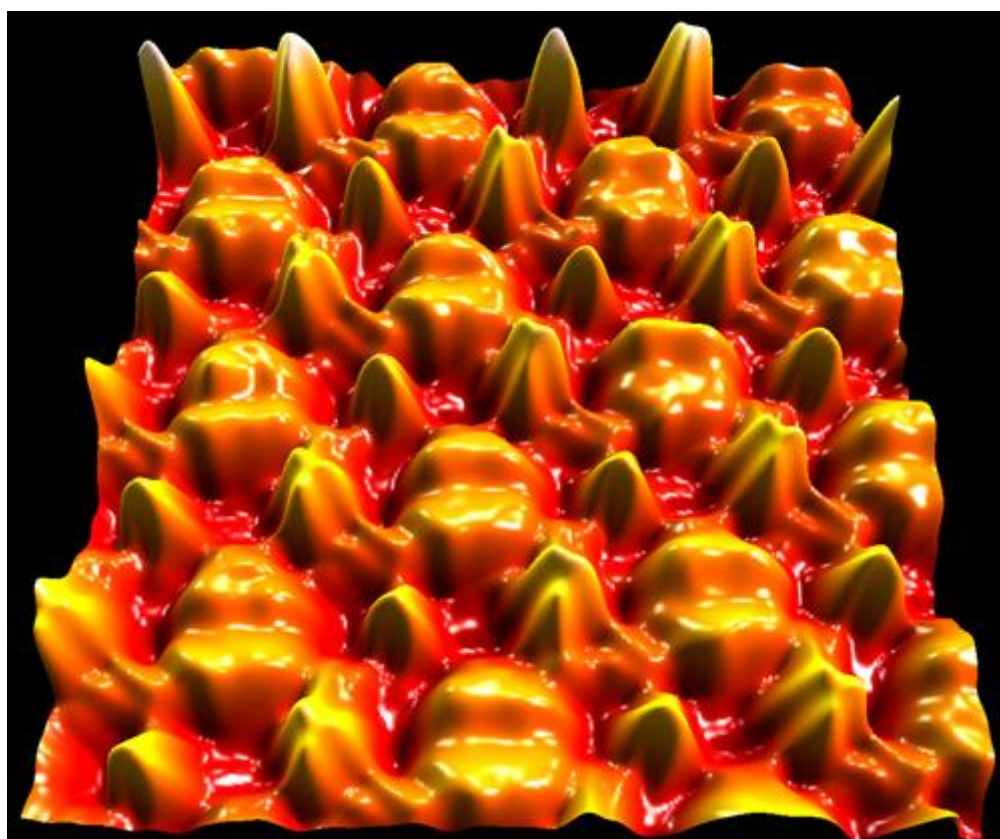
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COMMUNICATION

Little exchange at the liquid/solid interface: defect-mediated equilibration of physisorbed porphyrin monolayers†‡

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The transition from low to high density 2D surface structures of copper porphyrins at a liquid/solid interface requires specific defects at which nearly all exchange of physisorbed molecules with those dissolved in the supernatant occurs.

In the past decade, numerous studies have been reported that deal with the organisation of potentially functional organic molecules in highly organised monolayer structures on surfaces.[1] In particular, the self-assembly of molecules at a liquid/solid interface has become a popular approach, since it involves relatively mild conditions allowing a wide range of molecules to be employed. Scanning Tunneling Microscopy (STM) is a powerful method to monitor the formation and stability of such layers at the (sub)molecular level.[2] Only in recent years the first systematic STM studies have been performed to reveal the effect of the temperature and the supernatant solution concentration on the physisorption of molecules into monolayers at liquid/solid interfaces, to elucidate the thermodynamics behind this process.[3] A detailed understanding of such factors will be of paramount importance for the possible application of these self-assembled layers in future functional devices.[4]

Because of their rich chemical, catalytic, and photophysical properties, porphyrins are promising candidates for the creation of novel materials with applications in fields ranging from electronics and photovoltaics to catalysis and biosensing.[5] Here we report STM studies of the self-assembly behaviour of (5,10,15,20-tetraundecylporphyrinato)copper(II) (**(TUP)Cu**, Fig. 1a)[6] at the interface of 1-octanoic acid and a (0001) graphite substrate. In general, tetra-alkyl-functionalised porphyrins readily self-assemble into monolayers of extended lamellar arrays.[7] We will demonstrate that different 2D structures of **(TUP)Cu**
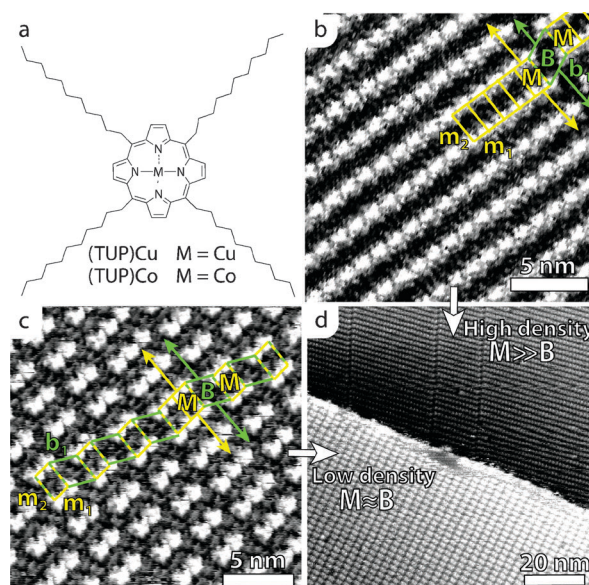
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‡ Electronic supplementary information (ESI) available: Experimental procedures, detailed analysis of the *M* and *B* unit cells by STM and molecular models, **(TUP)Co** insertion data, and additional STM images of the annealing process in time. See DOI: 10.1039/c1cc12569a

Fig. 1 (a) Molecular structure of **(TUP)Cu** and **(TUP)Co**. (b) STM topography of a high density monolayer of **(TUP)Cu** at the 1-octanoic acid/graphite interface, [**(TUP)Cu**] = 10^{-4} M, V_{bias} = −760 mV, I_{set} = 10 pA. Unit cells B and M are indicated. (c) STM topography of a low density monolayer of **(TUP)Cu** at the same interface, [**(TUP)Cu**] = 10^{-6} M, V_{bias} = −1000 mV, I_{set} = 15 pA. (d) STM topography of a monolayer of **(TUP)Cu** at the same interface, created by the successive application of a 10^{-6} M and a 10^{-4} M solution, V_{bias} = −870 mV, I_{set} = 10 pA. The lower terrace is covered by a high density monolayer resembling that in (b), while the higher lying terrace is similar to that in (c).

at the liquid/solid interface adjust differently to a sudden change in concentration of this compound in the supernatant solution in order to re-establish thermodynamic equilibrium. It will be revealed that the dominant exchange of molecules with the solution occurs at specific defect sites, with surprisingly little desorption/adsorption at other sites in the monolayer.

Monolayer formation of **(TUP)Cu** at the 1-octanoic acid/ graphite interface occurs fast: STM revealed that within seconds after applying a droplet of a solution of **(TUP)Cu** to the substrate, it is fully covered with lamellar arrays of these molecules. The molecules were found to self-assemble into

concentration-dependent surface polymorphs. The high density $(0.39 \pm 0.02$ molecules nm$^{-2})$ structure (Fig. 1b) is typically observed for a monolayer formed from a 10^{-4} M solution of **(TUP)Cu**, while lower density $(0.32 \pm 0.03$ molecules nm$^{-2})$ structures typically cover the entire surface when a 10^{-6} M solution is applied (Fig. 1c).

Both domains comprise the same two basic intermolecular binding motifs, which we name M and B,§ with the difference in monolayer density being related to the ratio in which these structures populate the surface. We determined the unit cell parameters of M and B by co-imaging the molecular overlayer and the underlying graphite (ESI‡). The M unit cell, which covers the majority of the high density domains, has vectors of $\mathbf{m}_1 = 1.26 \pm 0.05$ nm and $\mathbf{m}_2 = 2.05 \pm 0.05$ nm, at an angle of $79 \pm 4°$, resulting in a surface area of 2.54 ± 0.12 nm^2. This structure closely resembles the surface structure reported for 5,10,15,20-tetradodecyl-porphyrin on graphite.[7d] The B unit cells are spanned by the same $\mathbf{m}_2$ unit cell vector of the M unit cell, and a vector, $\mathbf{b}_1 = 1.92 \pm 0.09$ nm, at an angle of $71 \pm 4°$, yielding a surface area of 3.72 ± 0.26 nm^2. Both unit cells occur in rows along the common $\mathbf{m}_2$ unit cell vector, which is indicated by arrows in Fig. 1b and c. In a given domain, rows of **(TUP)Cu** comprising M and B unit cells can coexist in virtually any ratio. The low density domain of Fig. 1c consists of alternating rows of M and B unit cells, yielding a nearly equal ratio of the two $(M \approx B)$, whereas in a high density domain (Fig. 1b) rows of M unit cells dominate in larger patches $(M \gg B)$, which are only occasionally intersected by a single linear row of the larger B unit cells. The observation that **(TUP)Cu** self-assembles in low density, $M \approx B$, domains when the monolayer is created from a low concentration solution is in agreement with other STM studies in which the concentration of the dissolved compound and the architecture of the monolayer on the surface were correlated.[3a–c,8] Those studies suggested that the observed polymorphs represented the thermodynamically favoured surface structure for the applied concentration. However, we demonstrate here that thermodynamic equilibrium of the monolayer of **(TUP)Cu** is not easily reached, as the exchange of molecules with the solution phase is nearly absent and structural rearrangement requires the presence of certain defects.

When we prepared a $M \approx B$ monolayer of **(TUP)Cu** on the graphite surface with a droplet of a solution of concentration 10^{-6} M, and subsequently exposed it to a droplet of a 100-fold more concentrated solution (10^{-4} M), different $M \approx B$ domains appeared to adapt in a strikingly different way to the new situation. The STM image in Fig. 1d was recorded 16 hours after addition of the 10^{-4} M solution. During this time, the lower lying terrace had transformed into higher density, $M \gg B$, structures (ESI‡), while the structure of the $M \approx B$ domain on the higher terrace remained completely unaltered. The difference in surface density between the two terraces is ~25%. The observation that large fractions of the initial low density surface structures persist for such a long time under a solution with a concentration at which higher density structures are thermodynamically much more favourable indicates that physisorbed monolayers of **(TUP)Cu** on graphite are not necessarily in thermodynamic equilibrium with the supernatant solution. Clearly, some areas appear to

be trapped in thermodynamically unfavoured, low density structures, even though a large excess of porphyrins is available in the supernatant solution.

To understand this phenomenon, we examined the relationship between M and B unit cells in more detail. The single rows of B unit cells categorise patches of M unit cells into two sublattices, which are coloured blue and red in Fig. 2a. The equilibration of a $M \approx B$ domain into a $M \gg B$ domain with increased surface density involves the conversion of the larger B unit cells to the smaller M unit cells. A redistribution of molecules of **(TUP)Cu** on the surface annihilates rows of B and moves all the molecules to one of the two sublattices. The increase in surface density involves the adsorption of additional molecules of **(TUP)Cu** from the supernatant solution. Detailed inspection of STM images recorded in the course of the equilibration process revealed that a specific type of defect is required for the transition to higher density, $M \gg B$, domains. Two of such defects are indicated in dashed squares in Fig. 2a and b. At these defects, the two sublattices meet each other along the $\mathbf{m}_1$
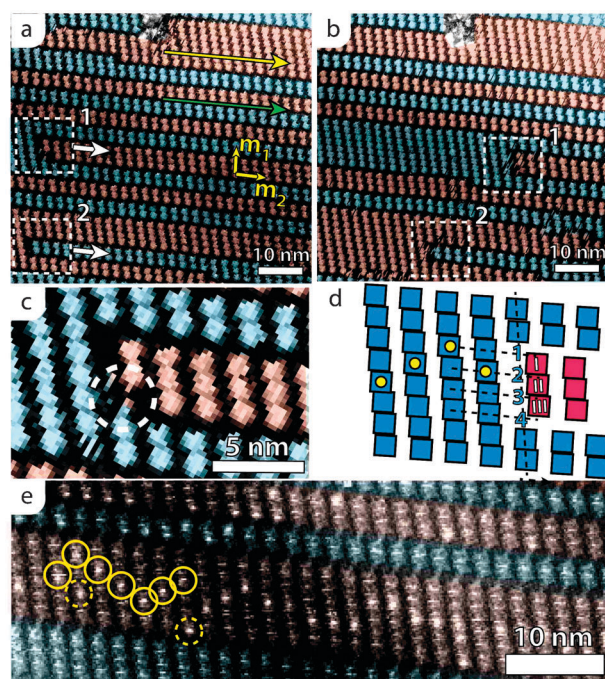

Fig. 2 (a–b) STM topography images showing the transformation of a domain of **(TUP)Cu** at the graphite/1-octanoic acid interface. Image (b) was recorded 15 minutes after image (a). The dashed squares indicate defects required for the transition of a low into a higher density domain. The arrows indicate the propagation of the annihilation of the low density structures. $V_{bias} = -850$ mV, $I_{set} = 10$ pA. (c) Enlargement of defect 1 in image (a). The dashed circle indicates a single molecule of **(TUP)Cu** moving from the red to the surrounding blue sublattice. (d) Schematic representation of the defect in (c), showing the shift of three molecules (I–III) from the red sublattice to three of the four lattice positions (1–4) of the blue sublattice. The fourth position is filled by an additional molecule from the supernatant. (e) STM topography image of a monolayer created by first applying a droplet containing 10^{-6} M of **(TUP)Cu** in 1-octanoic acid to the surface, followed by a droplet containing 10^{-4} M of **(TUP)Co** in the same solvent. $V_{bias} = -450$ mV, $I_{set} = 15$ pA. The solid circles highlight some of the inserted **(TUP)Co** species. The dashed circles indicate locations where a second **(TUP)Co** molecule is inserted in the same row.

direction (*i.e.* the termination line of a sublattice), *and in the* m_2 direction (indicated by yellow and green arrows).

The STM images in Fig. 2a and b were recorded at the same location with a time interval of 15 minutes, during which the two defects have moved along the monolayer in the direction of the white arrow. In the course of this motion, part of the red-coloured sublattice and its two flanking rows of *B* were annihilated, and additional molecules of **(TUP)Cu** must have been adsorbed from the solution phase. A magnification and a schematic of one of the defects in Fig. 2a are shown in Fig. 2c and d, respectively. Starting from this defect, the red-coloured sublattice is annihilated by the surrounding blue-coloured sublattice. We propose that during the annealing of a single row of *M* unit cells of the red-coloured sublattice, the three molecules in this row (I, II, and III) move, in a 2-dimensional fashion, to three of the four lattice positions of the blue-coloured sublattice (1–4), leaving the fourth position available for adsorption of an additional molecule of **(TUP)Cu** from the supernatant solution, as is indicated by yellow dots in Fig. 2d.

To test the proposed incorporation mechanism of porphyrins from the solution we used a molecular tracer.[9] **(TUP)Co**, the cobalt-containing sibling of **(TUP)Cu** (Fig. 1a), was chosen as a marker molecule, since the d_{z^2} orbital of the cobalt centre is known to give rise to an easily recognisable protrusion in STM height measurements.[10] The applied experimental procedure was similar to that described for the annealing of a low density monolayer of **(TUP)Cu**, with the difference that now a droplet of a solution with a concentration of **(TUP)Co** of 10^{-4} M in 1-octanoic acid was applied to the monolayer of **(TUP)Cu**. Because of the high similarity in both size and shape of **(TUP)Co** and **(TUP)Cu**, we anticipated that the density of the monolayer increases through the same mechanism as in the case of **(TUP)Cu**, albeit now by the insertion of the much more abundant **(TUP)Co** species. In the STM image shown in Fig. 2e, which was recorded 73 minutes after the addition of the solution of **(TUP)Co**, a clear trail of inserted **(TUP)Co** porphyrins is visible, some of which we encircled for clarity in the red sublattice. In the absence of desorption of **(TUP)Cu** during the transformation process, one single **(TUP)Co** adsorbate is expected to be incorporated in every annihilated row of this sublattice. For the vast majority of the rows, we indeed observe this expected insertion. More importantly, we found that only occasionally a second **(TUP)Co** adsorbate (indicated by dashed circles) was inserted in the same row, which is explained by the increased possibility of exchange of molecules around the location of the defect. The observation that **(TUP)Co** insertion in the absence of a defect occurs for only 2–3% demonstrates that desorption of **(TUP)Cu** only plays a minor role, and that the majority of the molecules of **(TUP)Cu** remains adsorbed.

In conclusion, we have shown that the concentration-induced transformation of a physisorbed monolayer of **(TUP)Cu**, from a low to a high density structure, is limited by 2D dynamics. In the absence of certain defects, metastable monolayer domains are unable to adapt to the new thermodynamic situation. From this observation and the experiments with **(TUP)Co** tracer molecules, we conclude that desorption of **(TUP)Cu** molecules occurs only rarely. Molecules from the solution can almost exclusively be incorporated through specific monolayer defects. As a consequence, the transformation of

monolayers of **(TUP)Cu** is slow and the initial monolayer formation, which occurs within seconds, determines the surface structure for hours or days. This implies that these physisorbed monolayers are not necessarily in thermodynamic equilibrium with the supernatant solution at all times. Future research will be directed to investigating the effect of extreme dilution of the supernatant solution on close-packed monolayers of **(TUP)Cu** at the liquid/solid interface.

Notes and references

§ A detailed account on the different surface structures formed by **(TUP)Cu** will be given in a forthcoming full paper.

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