Supporting information:

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

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Contents:

1. Experimental Procedures
2. Figure S1: Overlay of a domain of the M structure and the underlying graphite
3. Figure S2: Overlay of a domain comprising a 1:1 ratio of M and B lamellae
4. Figure S3: STM image showing a location where it can be seen that B is a polymorph of M. Discussion is included underneath the figure.
5. Figure S4: Proposed molecular models of M and B structures.
6. Figure S5: The same STM images as in Fig. 2 but without sublattice colouring and annotation
7. Figure S6: Time evolution of the domains depicted in Fig. 1d.
8. Figure S7: The same STM image as in Fig. 2e with cross sections.
**Experimental Procedure:**

Scanning Tunneling Microscopy was performed using a home-built STM setup.\(^1\) Tips were mechanically cut from 0.5 mm diameter Pt\(_{0.8}\)Ir\(_{0.2}\) wire and freshly cleaved ZYB-grade HOPG (NT-MDT) was used as a substrate. All measurements were performed at solid/liquid interfaces created by the application of a droplet of the solution of a porphyrin molecule in 1-octanoic acid (Aldrich ≥ 98%) under investigation between the tip and the substrate. Because the transformation studies were performed by the addition of one or several droplets of a more concentrated solution to a previously applied, lower concentration, droplet, the concentration of the final solution mixture is not exactly known, but will, given the large difference in concentration between the applied solutions, closely resemble that of the highly concentrated one. During these manipulations at the surface the tip was electronically retracted.

**Synthesis of [5,10,15,20-tetra(undecyl)porphyrinato]cobalt(II)**

To a solution of 5,10,15,20-tetra(undecyl)porphyrin (0.12 g, 0.125 mmol) in chloroform / methanol (2:1) (75 mL) was added cobalt (II) acetate tetrahydrate (0.13 g, 0.53 mmol). The reaction mixture was heated gently at reflux under nitrogen for 1 h. Dichloromethane (50 mL) was added and the solution washed with sodium hydrogen carbonate solution (sat., 3 × 100 mL), then water (3 × 100 mL). The organic layers were dried over anhydrous sodium sulfate and the solvent removed to give the crude product as a dark red-brown solid. Purification of the crude product by column chromatography on silica (hexane : dichloromethane [2 :1] – [1 : 1]) gave a dark red-brown solid. Further recrystallisation from dichloromethane / acetonitrile gave [5,10,15,20-tetra(undecyl)porphyrinato]cobalt(II) as a dark red solid (60.7 mg, 49 %), mp. 74 - 78 °C. 

\[ m/z \text{ (ESI+)} \text{ Found: (M+) 983.89 (983.73 required). } \nu_{\text{max}} \text{ (CHCl}_3\text{)} / \text{cm}^{-1} 3020s, 2926m, 2843w, 1230w, 1223s, 1207m. \lambda_{\text{max}} \text{ (CHCl}_3\text{)} 583 \text{ nm (ε 3,520)sh; 539 nm (ε 10,450); 412 nm (ε 175,178).} \]

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Figure S1 STM image of \((\text{TUP})\text{Cu}\) on HOPG which formed a domain consisting purely of lamellae of \(M\) unit cells. The molecular overlayer was co-imaged with the graphite substrate by switching between a bias voltage of \(V_{\text{bias}} = -770\) mV (overlayer) and \(V_{\text{bias}} = -4\) mV (HOPG). The tunneling current was 22 pA during the whole image. The vectors of the \(M\) unit cell, \(\text{i.e.}\ \vec{m}_1\) and \(\vec{m}_2\), have been determined relative to the unit cell vectors of the HOPG, \(\vec{g}_1\) and \(\vec{g}_2\). The white lattice is spanned by \(2\vec{g}_1\) and \(2\vec{g}_2\). This lattice is drawn at double the graphite lattice spacing for clarity. The black/white dashed lattice is the lattice of the vectors of the overlayer \((\vec{m}_1\text{ and }\vec{m}_2)\). By combining the results of 6 overlay images these vectors were found to be

\[
\vec{m}_1 = \begin{pmatrix} -2.9 \pm 0.1 \\ 3.0 \pm 0.1 \end{pmatrix}, \quad \vec{m}_2 = \begin{pmatrix} 9.1 \pm 0.2 \\ 7.3 \pm 0.2 \end{pmatrix}
\]
on a basis of \(\vec{g}_1\) and \(\vec{g}_2\). The values in terms of nanometers are given in the paper.

Figure S2 STM image of \((\text{TUP})\text{Cu}\) on HOPG showing a domain consisting of alternating lamellae of \(M\) and \(B\) unit cells. Imaging conditions: Overlayer: \(V_{\text{bias}} = -770\) mV, \(I_{\text{set}} = 10\) pA. HOPG: \(V_{\text{bias}} = 5\) mV, \(I_{\text{set}} = 10\) pA. The \(\vec{b}_1\) unit cell vector has been determined with respect to the underlying HOPG lattice.

\[
\vec{b}_1 = \begin{pmatrix} -0.2 \pm 0.2 \\ 7.7 \pm 0.3 \end{pmatrix}.
\]
**Figure S3** STM image showing a location where two consecutive lines of $B$ unit cells are present on the surface. The green and yellow lines mark $M$ and $B$ unit cells, respectively.

**Discussion**

In Fig. 1c in the manuscript it might seem that the $B$ boundaries are mere phase boundaries between domains of the $M$ polymorph instead of a true polymorph of $(TUP)Cu$. We propose that this structure is not a mere phase boundary, because all the $B$ structures are identical, whereas in the case of phase boundaries one would expect a certain variation in width and in the relationship between the lattices of the domains at both sides of the boundary. Furthermore, if it were a phase boundary, the $B$ structure would always be found between two patches of the $M$ polymorph, i.e. domains in which $(TUP)Cu$ molecules are adsorbed in lattices spanned by $M$ unit cells. In the STM images in the article (Figs. 1b-d, and 2a-c,e) this is indeed always the case, but in Fig. S3, two consecutive lines of $B$ unit cells can be observed. The marked molecules are fully surrounded by $B$ unit cells and thus not part of a $M$ domain. Regarding $B$ as mere phase boundaries would not explain the formation of these structures and therefore the $B$ structure is treated here as a stable surface structure of $(TUP)Cu$ at the HOPG/1-octanoic acid interface.
Figure S4 (a) High resolution STM image of a monolayer of (TUP)Cu on HOPG containing both M (yellow) and B (red) unit cells; $V_{\text{bias}} = -770$ mV, $I_{\text{set}} = 10$ pA. (b) Proposed molecular models showing the intermolecular interactions and the interactions between the molecules and the underlying HOPG lattice. The red alkyl chains are proposed not to be adsorbed on the HOPG surface but on top of neighbouring molecules.
Figure S5 STM images of Fig. 2 of the paper without sublattice coloring and annotation.

Figure S6 Series of STM images showing the time evolution of the area depicted in Fig. 1d of the paper, with sublattice coloring (blue and red). Images were taken 4, 8.5 and 16 hours after the addition of a $10^{-4}$M droplet to a sample which was, until that moment, exposed to a $10^{-6}$M solution of (TUP)Cu in 1-octanoic acid. Image c is the same STM image as Fig 1d in the article. The same transformation process as described in the article can be identified.
Figure S7 (a-b) additional STM images showing the sparingly occurring insertion of (TUP)Co molecules into a monolayer of (TUP)Cu; (a) -489 mV, 13 pA; (b) -489 mV, 15 pA. (c) The same STM image as in Fig. 2e in the article, but now with a cross section through each array of porphyrins along the unit cell vector $m_1$. Below the image each cross section is shown.