Polymorphism in porphyrin monolayers: the relation between adsorption configuration and molecular conformation

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Throughout the article different font weights and types are used to distinguish between different properties of unit cells, unit cell vectors and adsorption configurations. “M, B, L, S” are used to indicated the four different polymorphs as well as their unit cells. Unit cell vectors are indicated in bold face (m1, b2, ...). In the article we use the term “adsorption configuration” to refer to the combination of unit cell vectors at which the four nearest neighbours of a given porphyrin adsorbate are found. Several different adsorption configurations were encountered at the graphite/l-octanoic acid interface and calligraphic symbols “M S, M, ...” were used to label them.
Figure S1. STM image from which the image in Figure 2b was cropped (dashed square).
Figure S2: STM images of (TUP)Cu at the HOPG/decamethyltetrasiloxane (a) and HOPG/1-octanoic acid (b,c) interfaces in which the equality of the shared unit cell vectors can be assessed. In image (a) it is shown for the shared $m_1 = s_1$ unit cell vectors that upon translating over 50 $s_1$ unit cell vectors (white arrow), the registry of molecules in the S domain compared to the molecules in the single array of the M polymorph is the same. The black lines are visual guides which pass exactly between the molecules in the S domain, and go right through the center of a molecule in the M array. This is not only the case at the endpoints of the white vector, as indicated by small grey arrows, but throughout the entire domain. The same argument is applied to domains in which the M polymorph coexists with the B polymorph (images (b) and (c)) to demonstrate the equality of $m_2$ and $b_2$. Image parameters: (a) 30 x 90 nm$^2$, $V_{bias}$ = -890 mV, $I_{set}$ = 7 pA; (b) 37 x 125 nm$^2$, $V_{bias}$ = -780 mV, $I_{set}$ = 8 pA; (c) 75 x 315 nm$^2$, $V_{bias}$ = -870 mV, $I_{set}$ = 13 pA.
Figure S3: STM image of the S polymorph of a self-assembled (TUP)Cu monolayer at the HOPG/decamethyl tetrasiloxane interface. A moiré structure, with a periodicity of $8 \times s_2$ and $6 \times s_1$ along the two unit cell vectors of this polymorph can be distinguished. $V_{bias} = -650\text{mV}$, $I_{set}=10\ \text{pA}$.

Figure S4: STM image of a self-assembled monolayer of (TUP)Cu at the HOPG/1-octanoic acid interface showing alternating patches of the M and B surface structures (a)
and a cross section (b) taken along the arrow in the STM image. $V_{\text{bias}} = -760 \, \text{mV}$, $I_{\text{set}} = 25$, $32 \times 19 \, \text{nm}^2$

**Figure S5:** STM image in which the L polymorph formed by (TUP)Cu (bottom) is co-imaged with the underlying HOPG substrate (top) at the graphite/1-octanoic acid interface. A grid with spacings of twice the graphite unit cell vectors, i.e. $2g_2 \times 2g_1$, was fitted over the top part of the image, while a grid with spacings of $l_1$ and $l_2$ was fitted over the lower half. By extending the graphite grid over the molecular grid, the unit cell vectors of the molecular overlayer have been determined in terms of the lattice parameters of the graphite substrate. $12 \times 17 \, \text{nm}^2$, $I_{\text{set}} = 11 \, \text{pA}$, $V_{\text{bias}} = -770 \, \text{mV}$ (bottom), $V_{\text{bias}} = -5 \, \text{mV}$ (top).
Figure S6: (a) The same STM image as in Fig 4 and 9 in which the same unit cell vectors are indicated. (b) Part of the unit cell grid of (a) is schematically drawn. The molecule marked “MS” in the STM image corresponds to the molecule marked “MS2” in (b) and (c). The MS2 adsorbate is surrounded by eight direct neighbours (M1, MS1, S1, S2, S3, MS3, M3 and M2). Four of these neighbours (MS1, S2, MS3, and M2) can be found at positions that are reached by translating over a single unit cell vector from the central MS2 molecule. In the left column of the table in Fig. (c), the four vectors by which each of these four neighbours is reached (−m1, +m2, +m1 and −s2) are indicated in their respective colours. The right column of the table shows that these four vectors also completely define the locations of the remaining four neighbouring adsorbates. The molecule labelled “M1” is, for instance, found at −m1+m2, i.e. the sum of the vectors that link MS2 to the neighbours that M1 and MS2 have in common (MS1 and M2). The same holds for the other three neighbouring adsorbates (M3, S1 and S3). The adsorption configuration of the molecule labeled MB in the STM image is explained in (d) and (e). In these two figures this molecule is labeled MB2. Part of the unit cell grid is drawn in (d) in which all direct neighbours of MB2 are numbered. The relevant unit cells m1 (red), m2 (green) and b1 (orange) are indicated. In figure (e) the four direct
neighbours that are connected to $MB_2$ by single unit cell vectors i.e. $MB_2, M_2, MB_3, MB_5$ are indicated, the four connecting unit cell vectors are used to color the quadrants of the representing square. The column marked “combi vectors” is meant to indicate that the other 4 surrounding adsorbates ($M_1, M_3, MB_6, MB_4$) are also defined by making combinations of this set of four vectors.