

Face-on and Columnar Porphyrin Assemblies at Solid/Liquid Interface on HOPG

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Porphyrins having alkyl chains, each of which contains a diacetylene unit, were prepared to examine their self-assembled structures at the liquid/solid interface on graphite. The porphyrins with the longest alkyl chains form a face-on arrangement on the surface, while those with shorter alkyl chains form highly ordered one-dimensional columns. This work demonstrates that introducing a structural perturbation in the alkyl chain is a useful strategy to obtain novel surface assemblies.

Liquid/solid interface on highly oriented pyrolytic graphite (HOPG) provides a unique opportunity that one can observe molecular arrangements with scanning tunneling microscopy (STM) at molecular resolution under ambient conditions.^{1,2} This in turn gives detailed insights into how molecules assemble themselves into ordered two-dimensional (2D) patterns. The insights thus obtained will then form the basis of bottom-up fabrication of molecule-based materials and functional surfaces with controlled molecular arrangements.³ Surface assemblies of porphyrins are of particular interest because of their rich optical, electrical, and catalytic properties. Already, there are a number of 2D assemblies of porphyrins from simple derivatives to elaborate multiporphyrin compounds.^{4–8} Most of the monomeric porphyrins studied so far have alkyl chains attached to the porphyrin core to gain enthalpy of adsorption onto the HOPG surface.^{5–7} These alkylated porphyrins adsorb on HOPG in close-packed manners to maximize the surface coverage. Thus, *meso*-tetrakis(alkoxyphenyl)porphyrins form lamellar arrangements with alkyl chains from neighboring rows being interdigitated, leaving no void spaces on the surface.⁵ One way to obtain patterns other than close-packed ones on the surface may be using directional forces such as hydrogen bonds.⁶ Yet another way may be introducing a perturbation on part of the alkyl chain, a strategy that has rarely been attempted. Herein we report on the surface assemblies made from porphyrins bearing alkyl chains, each of which contains a diacetylene unit (Chart 1). The diacetylene moiety imparts kinks in the middle of the alkyl chains. In addition, the diacetylene units have a potential for topochemical 2D polymerization, given that they align properly on the surface.⁹

A drop of a 1-phenyloctane solution of porphyrin (0.1 mM) was placed on a freshly cleaved surface of a HOPG block (see

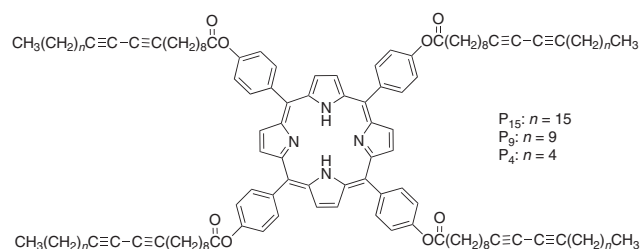


Chart 1.

Supporting Information¹⁰). Image scanning was conducted with a STM tip, which was mechanically prepared from Pt/Ir wire, immersed in the solution. The P_{15} molecules form a surface pattern with a face-on configuration (Figure 1). The four-leaf clover-like features appear brightest in the image. Each of these features is attributed to the tetraphenylporphyrin in the molecule. The four bright spots may correspond to the region around the phenyl groups in the molecule. The submolecular resolution suggests that the molecules are tightly immobilized on the surface. Undulation in contrast is recognized in the intervening area between the porphyrin moieties. Molecular models superimposed on the STM image nicely match the four-leaf features and the undulation in the intervening areas. The kinks introduced in the alkyl chains by the diacetylene moieties apparently prevent the alkyl chains from forming a closely packed layer as seen in the case of porphyrins with simple alkyl chains,⁵ giving rise to the new surface pattern with void spaces on the surface.

Unexpectedly, obtained images for P_9 were completely different from those expected for any face-on arrangements (Figure 2, left). Thin lines with a raised middle align side-by-side to make a straight striped column. Then the columns align side-by-side to fill the 2D surface. The stripe pattern is consistent with stacked porphyrins in an edge-on orientation.⁸ The interporphyrin distance (0.57 nm) is larger than typical π - π stacking separations (ca. 0.35 nm). This could be either due to steric repulsion by the phenylene groups, which are twisted from the porphyrin plane, or by the alkyl chains, each of which occupies a width of ca. 0.45 nm, or due to some tilt of the porphyrin planes from the surface normal. The intercolumnar separation of 5.0 nm is shorter than the length of a stretched-out P_9 molecule (ca. 7.0 nm) by 2 nm. There can be two explanations for this observation. One is that the alkyl chains are in folded conformations. The other is that the alkyl chains from neighboring columns may stack vertically, which is allowed because the porphyrin planes are in an edge-on orientation. The molecular models superimposed on the image show the extent of this overlap, assuming that the alkyl chains are in a fully extended conformation.

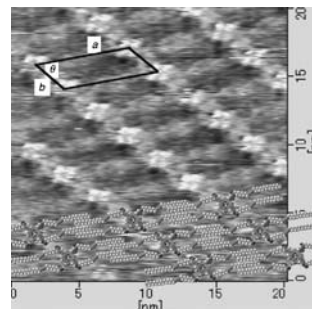


Figure 1. STM image of the array of P_{15} at the interface of 1-phenyloctane solution (0.1 mM) and HOPG: $V = -1.1$ V, $I = 10$ pA. $a = 7.0$ nm, $b = 2.9$ nm, $\theta = 49^\circ$.

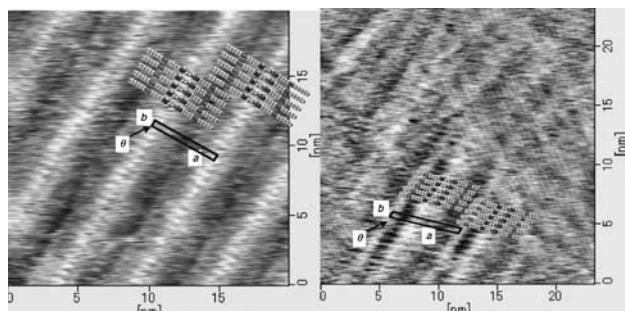


Figure 2. STM images of the array of P₉ (left) and P₄ (right) at the interface of 1-phenyloctane solution (0.1 mM) and HOPG. P₉: $V = -1.0$ V, $I = 20$ pA, $a = 5.0$ nm, $b = 0.57$ nm, $\theta = 87^\circ$. P₄: the brightness scales with residual tunnel current under near constant height scan,¹⁰ $V = -1.1$ V, $I = 10$ pA (average), $a = 6.0$ nm, $b = 0.57$ nm, $\theta = 67^\circ$.

The porphyrin with the shortest alkyl chains, P₄, also gave a striped pattern reproducibly (Figure 2, right). In this case, there are two raised portions, which we attribute to the porphyrin cores and the diacetylene groups, on the basis of a good fit of molecular models, as indicated in the figure. In this configuration, the intercolumn separation, $a = 6.0$ nm, nearly matches the extended molecular size. Therefore, the alkyl chains from neighboring columns are not overlapped as opposed to the case for P₉. The observation that the acetylene units only on one side of the porphyrin core are visible might be explained on the basis of different mobilities. It may be possible that strong adsorption of the acetylene units on one side of the porphyrin core on the surface prevents acetylene units on the other side from adsorbing in an optimal fashion onto the surface due to steric reasons.

Some attempts have been made to address the reasons for the difference in the surface patterns (i.e., face-on vs. column) depending on the alkyl chain length. The UV-vis spectra for these porphyrins in solutions identical with those used in the STM measurements (0.1 mM P_{*n*} in 1-phenyloctane) exhibit a sharp Soret absorption peak for each of the porphyrins at 420 nm, values identical with those in more dilute solutions, which indicates that every porphyrin molecule exists as monomeric species in the solution phase under the conditions of the STM measurements regardless of the length of the alkyl chains. This observation indicates that the 1D column formation is surface-induced.

All porphyrins exhibited sharp melting behavior mostly within 1 K and showed no sign of a liquid crystalline phase. The melting points of the P_{*n*} series increase as *n* decreases (P₁₅: 67.4–68 °C; P₉: 75.2–75.8 °C; P₄: 81.6–82.2 °C). This trend indicates that the association of molecules in the solid state is dominated by the attractive interaction of the porphyrin macrocycle and that the alkyl chains serve to alleviate the interaction. On the other hand, molecule–graphite interaction is dominated by the alkyl chains.^{1,2} Therefore, the porphyrins with the longest alkyl chains may prefer surface adsorption in a face-on fashion, while the porphyrins with shorter alkyl chains may prefer molecule–molecule association over molecule–surface adsorption, giving rise to the columnar assemblies.

In conclusion, we have studied surface patterns formed through self-assembly of porphyrins with alkyl chains each containing a diacetylene unit. These porphyrins afforded either face-on patterns or columnar structures at the 1-phenyloctane/HOPG

interface depending on the length of the alkyl chains as revealed by STM. This work demonstrates that introducing a structural perturbation into the alkyl chains is a useful strategy to produce novel surface patterns. The diacetylene units aligned along the columns could be used for polymerization,⁹ which forms the basis for our ongoing study. Furthermore, the highly ordered porphyrin columns obtained are very interesting as charge and exciton transport materials.¹¹

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