STM Observation of Labile Axial Ligands to Zinc Porphyrin at Liquid/Solid Interface

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Observation of labile axial ligand coordination to zinc porphyrins on a graphite surface at liquid/solid interface was achieved by scanning tunneling microscopy. The presence of an axial ligand is clearly manifested as an increased height from the basal porphyrin molecule. Further, the trans and cis isomers of the phenylazopyridine ligand can be distinguished on a statistical basis.

Self-assembly of molecules into organized arrays on surfaces may provide a basis for bottom-up nanofabrication of molecule-based materials and devices.[1] One of the popular substrates for such a purpose is highly oriented pyrolytic graphite (HOPG).[2] From the first scanning tunneling microscopy (STM) study on the self-assembly of liquid-crystalline molecules on HOPG surface[3] to recent flourishing studies on ordered arrays of various classes of compounds,[2] most of them are just two-dimensional (2D). Vertical extension of the 2D order, if achieved, would provide a powerful methodology to produce well-defined three-dimensional (3D) architectures on surfaces. One approach toward the goal is to use a tripod molecule that forms an ordered array on a surface.[4] Another approach is to use the axial coordination to metal porphyrins. Although there have already been a number of reports on porphyrin arrays on surfaces,[5] there are only a very few reports on porphyrin arrays bearing axial ligands. We prepared pyridine-coordinated rhodium porphyrins and observed its ordered arrays on HOPG at the liquid/solid interface.[6] The rhodium porphyrin is characterized by its kinetically inert, robust metal–ligand bond. In contrast, zinc porphyrin accepts one axial ligand in a reversible manner.[7] Amine coordination to zinc 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin on Ag(100) was investigated by an ultrahigh vacuum STM.[8] Herein, we report for the first time on the observation of labile axial coordination at a liquid/solid interface. Figure 1 displays the porphyrins and axial ligands used in the present study. $M(C_{18}OPP)$ ($M = H_2$[10] and Zn[11]) and Azo[12] were prepared according to the literature.

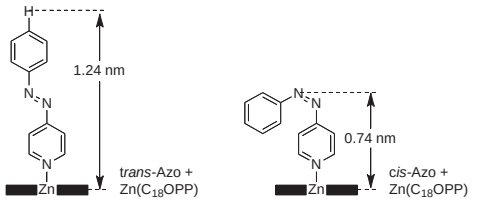

Figure 1. Porphyrins and axial ligands used in the present study ($C_{18}OPP$ = 5,10,15,20-tetrakis(4-octadecyloxyphenyl)-porphyrin; Azo = 4-(phenylazo)pyridine). The distances are the estimated values from crystal structures of related fragments.[9]

Figure 2a shows a representative STM image for the array of $Zn(C_{18}OPP)$ in a drop (1 μL) of porphyrin solution in 1-phenyloctane on HOPG.[13] In axial coordination experiments, a 1-phenyloctane or toluene solution (1 μL) of Azo was overlaid on the solution of $Zn(C_{18}OPP)$. A representative example for a sample comprising of 5 mM *trans*-Azo in addition to $Zn(C_{18}OPP)$ is shown in Figure 2b.[14] With the axial ligand, the apparent height becomes greater. Repetitive observations for different samples with different tips confirmed the height difference of $\geq$0.1 nm under the conditions specified in the figure caption.

Next, we used mixed solutions of $Zn(C_{18}OPP)$, $H_2(C_{18}OPP)$, and Azo in the observation. Azo coordinates to $Zn(C_{18}OPP)$ but not to $H_2(C_{18}OPP)$. The purpose of the experiments is to more clearly show the height differences between porphyrins with and without an axial ligand by capturing both types of porphyrins within the same frame of image by using the height of the free-base porphyrin molecules as an internal standard. Molecules of $Zn(C_{18}OPP)$ and $H_2(C_{18}OPP)$ in the mixed arrays are hardly distinguishable from each other. However, on addition of Azo, the zinc porphyrins become much brighter than the free-base porphyrins. Figure 3a shows an STM image for a 1-phenyloctane solution of $Zn(C_{18}OPP)$ and $H_2(C_{18}OPP)$ containing *trans*-Azo. A large difference in the contrast for the free-base porphyrins and the ligated zinc porphyrins is apparent. The apparent heights of porphyrin molecules collected from multiple images on different samples were put into the histogram shown in Figure 3c, which clearly shows two sets of clusters centered at 0.11 (the standard deviation in Gaussian distribution: 0.03) nm and 0.29(0.07) nm, corresponding, respectively, to $H_2(C_{18}OPP)$ and $Zn(C_{18}OPP)$•*trans*-Azo.

The same set of experiments were performed by using

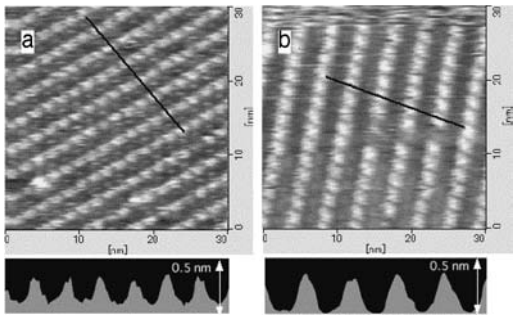

Figure 2. STM images and cross sections at the 1-phenyloctane/HOPG interface. (a) 20 μM $Zn(C_{18}OPP)$; $I = 26$ pA; $V_{sample} = -1.1$ V. (b) 10 μM $Zn(C_{18}OPP)$ and 6 mM Azo; $I = 30$ pA; $V_{sample} = -1.1$ V.

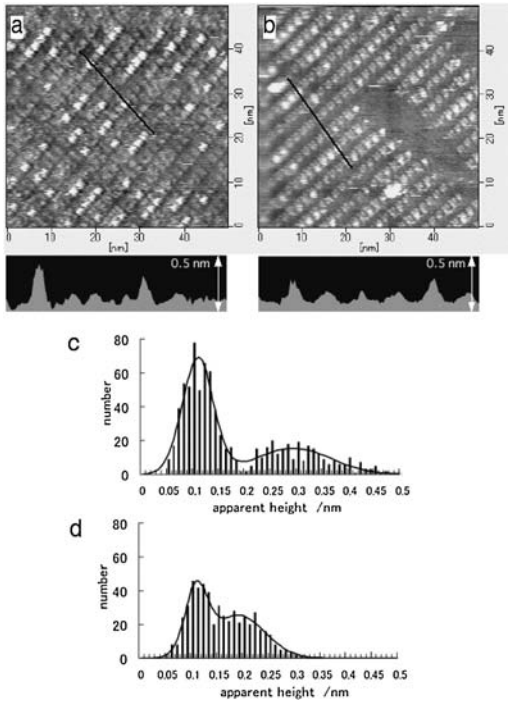

Figure 3. Ternary mixtures of 5 μM $Zn(C_{18}OPP)$, 5 μM $H_2(C_{18}OPP)$, and 5 mM Azo; $I = 24$–28 pA; $V_{sample} = -1.1$ V. (a) and (b): STM images and cross sections for samples respectively containing *trans*-Azo and a mixture of *trans*- and *cis*-Azo (2:3). (c) and (d): Histograms of the apparent heights for samples, respectively, containing *trans*-Azo and a mixture of *trans*- and *cis*-Azo (2:3). Least squares fit by Gaussian distributions is also shown.

solutions containing *trans*- and *cis*-Azo in a ratio of 2:3.[15] A representative image for this system is shown in Figure 3b. The histogram for the cis-rich solutions (Figure 3d) shows that the apparent height for the ligated $Zn(C_{18}OPP)$ is greatly reduced, while that for the $H_2(C_{18}OPP)$ molecules remains unaltered. The histogram can be fit by partly overlapping two Gaussian distributions, which give the mean heights of 0.11 (0.02) nm and 0.19(0.05) nm for the lower and higher clusters. The height of ligated zinc porphyrin is significantly reduced. Thus, it is possible to distinguish structural isomers with STM, though not on an individual molecular basis but on the statistical basis.

There are a couple of new findings. Firstly, the protrusions higher than 0.3 nm are rarely observed for the mixed solution, even though the solution contains 40% *trans*-Azo. This suggests that the association/dissociation kinetics is much faster than the STM time scale. Therefore, what we see in the STM image is averaged (in a loose sense) heights of *trans*- and *cis*-Azo. Secondly, the observed heights do not match the actual geometric heights. The zero point for the height is taken to be on the layer of alkyl chains. The higher appearance of porphyrin core (ca. 0.1 nm) is not due to its geometric height but due to its more conducting π system. The *trans*-Azo ligand appears higher than the basal porphyrin molecules, but only by ca. 0.2 nm, much less than the actual height of 1.24 nm (see Figure 1). The height in the mixed solution is significantly lower than expected from the trans/cis ratio (2:3). Interpretation of these observations requires information on the electronic decaying parameters[16] for respective molecular fragments, which warrants further study.

In conclusion, we have succeeded for the first time in the STM observation of axial ligands bound to porphyrin through labile coordination at a liquid/solid interface. This is a step toward the extension of 2D order upward into the 3D realm.

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