

Desorption Kinetics and Activation Energy for Cobalt Octaethylporphyrin Solution from Graphite at the Phenyloctane-Graphite Interface: An STM Study

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Supplemental Section

Tip-induced effects and their avoidance: Tip-induced effects have been used in the reversible isomerization of azobenzene¹, polymerization of organic molecules,^{2,3} manipulation of the reconstruction of Au(111),⁴ inducing chemical reaction at the organic-metal interface,^{5,6} and many other applications. Most relevant to our study was the tip-induced surface desorption of porphyrins and porphyrin like materials at the solution-solid interface. In porphyrins, it has been shown that this desorption process can occur via two different mechanisms; (i) either by applying a pulse of high voltage ($>|2|$ V) to the tip,⁷ (ii) or by scanning at a low bias voltage such that the tip-surface separation is very low in which case the adsorbed molecules are scrapped off by the tip.⁸ The adverse effects of tip-surface interaction in our experiments can be easily detected in ex-situ experiments. First, deposit a certain mixture or only one species on HOPG. Then, add a solution with an excess of the other species such that any compositional changes in the

monolayer due to tip effects can be easily detected by STM imaging. For example, a sample was prepared with $X_{\text{NiOEP}} \approx \Theta_{\text{NiOEP}} = 0.42$. Excess NiOEP was then added to the solution cell such that $X_{\text{NiOEP}} = 0.80$. When a pulse of -3 V was applied between the tip and the sample, the resulting surface appears as in Figure S1. We can clearly see the changes in Θ_{NiOEP} ($\approx X_{\text{NiOEP}} = 0.80$) within the yellow oval clearly demonstrating the surface desorption of MOEP induced by the voltage pulse (followed by rapid adsorption reflecting the concentration of species in the second solution). In general, pulsing affected an area of radius up to 50 nm in size, consistent with similar studies done in the past.¹²⁷

Figure S2 shows the effects of a second mechanism by which tip-induced desorption occurs. In S2(a), there are very few ($\approx 5\%$) NiOEP on the HOPG surface. Then, an excess of NiOEP is added on top such that the $X_{\text{NiOEP}} = 0.80$. As described in (ii) above, a series of sequential STM images are taken of with a low bias of +0.2 V, one of which is seen in S2(b). The fuzzy areas appear due to the fast adsorption/desorption process. Finally, after reversing the set point conditions back as in S1(a), the compositional changes in the monolayer can be easily seen in S1(c), where Θ_{NiOEP} changes from roughly 0.05 to 0.80.

In order to verify that these tip-effects do not occur during each scan and have an effect on the composition of the surface monolayer, we continuously recorded sequential STM images of the area where a tip-induced change had occurred. A portion of such a sequence is shown in Figure S3. While there is some small thermal drift, it is none the less clear that each CoOEP molecule (bright molecule) in S3(a) is present in the entire sequence. Moreover, no new bright molecules replace NiOEP molecules. Thus, the monolayer composition is kinetically stable immediately

after a tip-induced desorption event (but at a coverage consistent with the current covering solution).

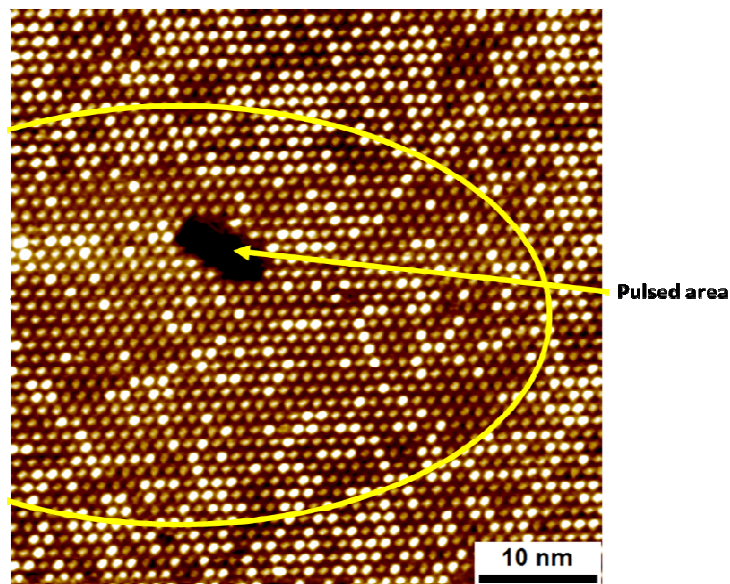


Figure S1. STM image of “tip-induced” desorption by pulsing the tip with -3 V. Prior to the pulse, $\Theta_{\text{NiOEP}}=0.42$ and $X_{\text{NiOEP}}=0.80$. After the pulse, area within the yellow curve is $\Theta_{\text{NiOEP}} \approx X_{\text{NiOEP}}$.

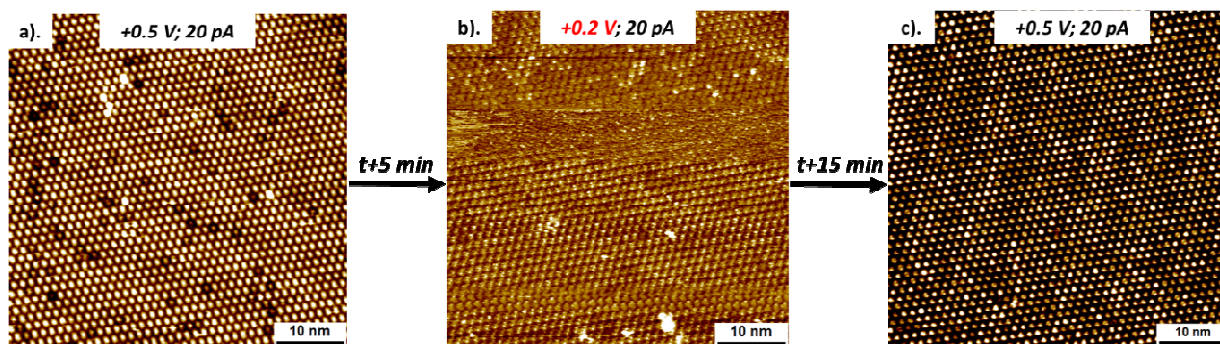


Figure S2. STM images of tip-induced desorption of CoOEP from HOPG caused by scanning at low bias; (a) STM image (at +0.5 V and 20 pA) of nearly 100% CoOEP monolayer covered bat a solution with excess NiOEP; (b) STM image after few scans (5 min) of (a) imaged at a lower

bias: +0.2V and 20 pA; (c) STM image showing changes in monolayer composition after few scans (15 min) at +0.5 V and 20 pA.

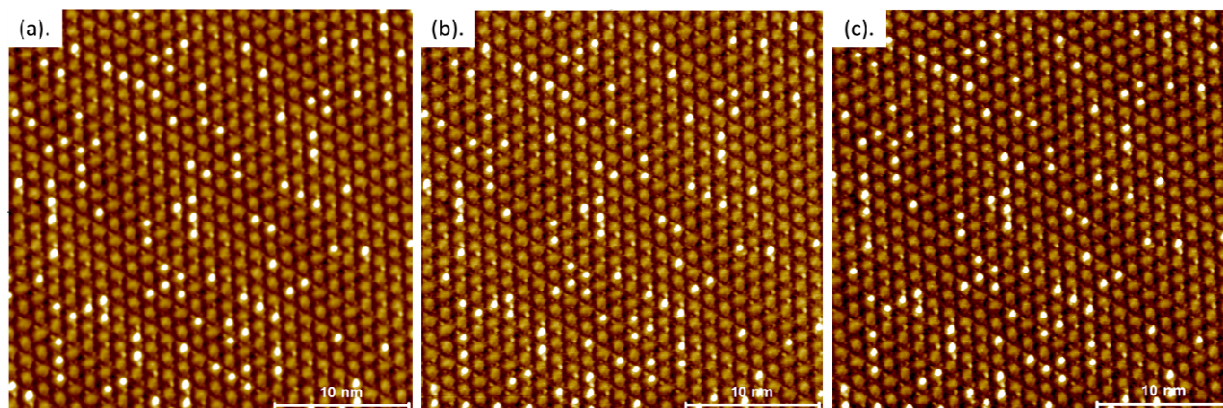


Figure S3. Sequential STM images of CoOEP/NiOEP on HOPG of an area after tip-induced desorption. Each image is separated by 108 sec. Set point conditions were +0.5 V bias voltage and 50 pA tunneling current.

Additional to these deliberate tip-induced desorptions, very rarely a random spike in voltage or current during scanning would induce desorption followed by rapid repopulation of the surface with species in proportion to the existing solution concentration. Because these changes are localized they are fairly easy to spot. Our response was always to move to a new area of the sample to continue measurement.

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