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A Self-Organized 2-Dimensional Bifunctional Structure Formed by Supramolecular Design

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Noncovalent interactions are critical to an understanding of a wide range of disciplines from molecular biology to materials science.[1] In crystal engineering, supramolecular synthesis utilizes hydrogen bonding and other interactions including halogen−halogen, halogen−nitrogen, halogen−oxygen, electrostatic interactions, and weak electron donor−acceptor complexation to organize molecules within a crystal.[2−4] Among the systems exhibiting electrostatic interactions, the most thoroughly studied are the fluorine-substituted aromatic−aromatic interactions, with perfluorophenyl−phenyl interactions playing a featured role.[3−6]

When the concepts of 3D supramolecular synthesis are applied to the 2D realm of physisorbed molecules on metal surfaces, the adsorbate−substrate interaction plays a role of equal importance with that of the intermolecular interactions. The weak lateral forces exerted by the surface upon physisorbed molecules, and the image charges that occur in metal substrates, allow the weak intermolecular forces to play a significant role in the formation of long-range order in the adsorbed phase. Once a desired monolayer structure is generated, it may be possible to build 3D layered structures based on that initial template. Note that we have restricted our consideration to systems where the interaction with the substrate is weak (physisorption). This is to ensure that lateral intermolecular interactions can play a significant role in adsorbate ordering. Strongly ordering chemisorbed systems such as CO + benzene adsorbed on Pt, Rh, and Pd[7−10] are not appropriate models for the noncovalent interactions envisaged here because both species undergo significant bonding with the metal substrates studied. An example of weak intermolecular interactions combined with physisorption comes from the STM study of DNA base molecules on Cu(111).[11] DNA bases form novel superstructures on Cu(111) surfaces through intermolecular hydrogen bonding and their planar orientation on the surface. The relative inertness of Cu(111) allows the molecules to diffuse over the surface to spontaneously self-assemble into small clusters and chains. Very recently, Yokoyama and co-workers have observed similar small clusters and chains on Au(111) at 63 K.[12] In this study, cyanophenyl-substituted porphyrins were found to form 3-molecule clusters in the case of single substitution, 4-molecule clusters for asymmetric double substitution, and branching chains for symmetrical double substitution.

While these reports on DNA bases and substituted porphyrins are encouraging for 1D aggregation, they do not represent practical examples of 2D supramolecular structures. There are reports of highly ordered 2D structures at the solution−graphite interface where solvent and solute adopt well-defined bimolecular structures.[13−15] In this report we provide the first example of a bimolecular self-assembled 2D structure formed by vapor-phase deposition onto a metal surface. The system reported here is a two-component structure reminiscent of the fluorophenyl−phenyl system, but modified to reflect the 2D nature of the problem. The materials studied in this report include cobalt(II) hexadecafluoro-29*H*,31*H*-phthalocyanine [F16CoPc], nickel(II) tetraphenyl-21*H*,23*H*-porphine [NiTPP], and the fully protonated form of cobalt(II) phthalocyanine, CoPc. They were first purified by sublimation and then vapor deposited onto Au(111) from quartz crucibles. To calibrate the thin film monitor a density value of 1.4, 2.4, 1.6 g/cm^3 was used for NiTPP, F16CoPc, and CoPc, respectively. The temperature of the crucibles was monitored with an iron−constantan thermocouple both to ensure a uniform deposition rate and to eliminate thermal decomposition due to over heating. Residual gases during deposition were also monitored with a quadrupole mass spectrometer.

Constant current STM images of submonolayer films obtained under UHV conditions at room temperature are shown in Figure 1. The top row shows large- and small-scale images of NiTPP adsorbed on Au(111). Embedded in the higher resolution image are space-filling models of the compound. Note that densely packed monolayer islands are observed with a simple 2D crystal structure having one molecule per unit cell. This structure and its electronic properties have been discussed in some detail, previously.[16,17] Isolated NiTPP molecules are never observed at room temperature due to surface diffusion, demonstrating the weak interaction between adsorbate and substrate. The parallel striations seen in all the lower resolution figures are due to the underlying Au(111) reconstruction.

Low- and high-resolution STM images of F16CoPc are shown in the center row of Figure 1. Although these molecules tend to aggregate, they do not form an ordered structure when deposited on Au(111). Further, there is considerable thermal motion on the surface causing the high-resolution images to appear with no submolecular resolution. The disorder and lack of submolecular resolution for F16CoPc is in dramatic contrast to what occurs for the protonated complex, CoPc. Films of CoPc form large 2D crystalline islands and individual molecules can be imaged with exquisite submolecular resolution.[18] This significant difference in packing between the proto and fluoro phthalocyanine is probably due to the difference in van der Waals attraction and electron affinities. The fluorinated compound, for example, is an n-type semiconductor whereas the protonated species is p-type. We find by UPS that there is a vacuum level shift (0.45 eV) upon F16CoPc adsorption that does not occur with CoPc.

The bottom row of images was obtained from a film that results when NiTPP and F16CoPc are deposited in a 2:1 molar ratio onto room temperature Au(111). This sample was prepared by alternately exposing the substrate for 1 and 2 s to F16CoPc and NiTPP vapor, respectively, for a total exposure time of 21 s at a deposition rate of about 0.01 nm/s. The low resolution image shows that under

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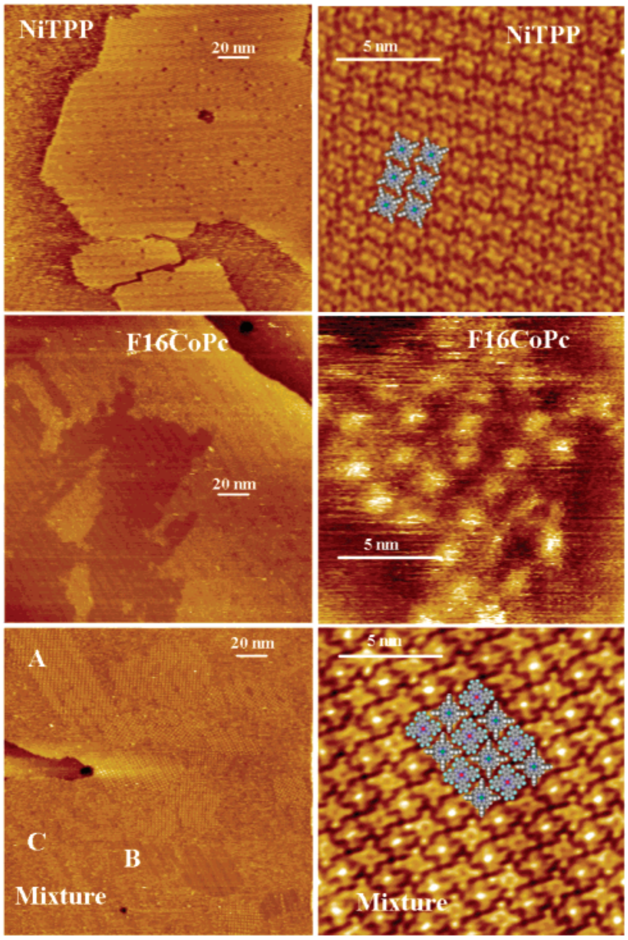

Figure 1. Comparison of room temperature constant current STM images of roughly one-half monolayer of different organometallics adsorbed on Au(111) imaged under UHV conditions. The upper row is low- and high-resolution images of NiTPP acquired at a −1.4 V sample bias and 0.4 nA. The middle row is low- and high-resolution images of F16CoPc acquired at a 0.9 V sample bias and 0.15 nA. The deposition rate for both compounds was 0.01 nm/s for a total exposure of about 0.2 nm. The lower row of images was acquired from a 2 to 1 mole ratio deposition of NiTPP and F16CoPc on Au(111). A constant current of 0.35 nA and a sample bias of −0.6 (left image) and +0.4 V (right image) was used. The high-resolution NiTPP and mixture images were Fourier filtered.

these conditions three types of regions result: disordered regions containing both F16CoPc and NiTPP (region C), well-ordered domains of NiTPP (as in B), and well-ordered regions of an entirely new structure with 1:1 composition, A. The nature of each of these is verified by high-resolution imaging. A small segment of region A is shown in high resolution on the bottom right of Figure 1. Also shown are space filling models of F16CoPc and NiTPP superimposed on the actual STM image.

With submolecular resolution, the F16CoPc molecules are easily identified by the strong tunneling current that results from orbital mediated tunneling through the half-filled d_{z^2} orbital of the Co^{2+} ion: they appear to have high spots in the center.[16,18] The remarkable contrast in tunneling current afforded by the difference in electronic configurations of transition metal ions allows one to clearly label molecular species for chemical identification at the molecular level. Unlike the films that result when F16CoPc alone is deposited on Au(111), the mixture has ordered regions where the individual F16CoPc molecules are clearly seen with submolecular resolution. Even the orientation of the phenyl groups in NiTPP is easily observed. Similar films made from the all protoforms, CoPc and NiTPP, are densely packed and appear to have a well-defined structure, but are compositionally disordered. This type of disorder can be found in the literature.[18] Clearly, the *intermolecular interactions between F16CoPc and NiTPP are producing an entirely new 2D crystalline structure that is more stable than the films resulting from either parent compound*.

More work is required to identify the principle driving force for the remarkable ordering seen in the 1:1 compound layer. However, one can enumerate some of the interactions which may drive this ordering. These include the ability of the two types of molecules to interlace, the up to 4 kJ/mol attractive energy for each close-approach H•••F interaction,[19] and reduced electrostatic repulsion between F16CoPc molecules due to the increased spacing forced by the NiTPP units. Attraction between the dipole moments normal to the surface at the periphery of each molecule that result from image charge formation in the substrate must also be considered. Finally, there is the destabilizing but weak quadrupole repulsion between the vertically oriented phenyl groups and the horizontally oriented fluorinated Pc ring.

Figure 1 shows islands of this new material that are ~100 nm in extent. Analysis of many such images taken from several samples indicates that these ordered regions represent about 25% of the surface. Preliminary experiments indicate that it should be possible to grow these islands much larger, perhaps to entirely cover a metal support. Parameters that produce changes in island size are (1) deposition rate, (2) relative rates of arrival of the components, (3) substrate temperature during deposition, and (4) postdeposition annealing. Modifications of these layers in terms of both electron transport properties and the addition of vertical substituents through changes in the central metal ion are easily engineered. We believe this is only the first in a broad new class of materials based both upon weak intermolecular interactions and image charges associated with adsorption on metal surfaces. What remains to be seen is whether these structures can be extended upward by sequential deposition to produce new three-dimensional materials.

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