Function Follows Form: Exploring Two-Dimensional Supramolecular Assembly at Surfaces

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ABSTRACT Two-dimensional surface structures formed by organic self-assembly offer an efficient route to bottom-up assembly of tailored nanostructures. Organic building blocks are especially interesting because of the wide variety of structures and properties that can be "built-in" at the synthesis stage. Well-controlled studies of these systems under ultrahigh vacuum conditions allow a careful look at the fundamental properties and relevant kinetic growth limitations. Further work will develop our understanding of the functionality of the systems and their potential use in technological applications.

Highly ordered, self-organized assemblies of organic molecules at surfaces have seen an explosion of interest in recent years. This is fueled by an interest and drive to develop efficient and effective methods for the patterning of surfaces with functional nanometer-scale structures.[1,2] Organic building blocks are of obvious interest because of the vast (virtually limitless) library of species that can be synthesized for formation in extended structures. Solution-based (three-dimensional (3D)) coordination chemistry is itself a growing field where researchers have demonstrated supramolecular structures of increasing complexity that can be "designed" by selection and synthesis of a specific building block molecule.[3–5] Analogous surface-supported structures utilize similar noncovalent intermolecular bonding interactions, *e.g.*, hydrogen bonding,[6–9] coordination bonding,[10–12] or a combination of the two.[13]

Much of the excitement surrounding surface studies of two-dimensional (2D) supramolecular assemblies is due to the observed analogies to efforts in 3D supramolecular crystal engineering.[14] Organic species at surfaces can pack in extended systems by interaction of the molecules, but with the additional influence of the molecule−surface interactions. Extended open network architectures have been produced with a wide variety of structural motifs using diverging ligands with well-defined binding locations at functional groups: one-dimensional (1D) chains,[6,15] honeycomb networks,[7,8] 2D rectangular grids,[11,12] and even chiral structures,[16] to name a few. The ability to design and produce tailored systems in a predictable way has been demonstrated in some cases (for examples, see Figure 1 and refs 11, 17, and 18), but, as for the 3D systems, there remains much to be learned about the design of 2D supramolecular architectures at surfaces.

The report by Weigelt *et al.*[19] in this issue makes significant advances in this field of study. Preparation of supramolecular assemblies at surfaces under ultrahigh vacuum (UHV, $<10^{-9}$ mbar) conditions usually requires deposition of the molecular building blocks by thermal sublimation from a crucible. Therefore, there is a limit to the range of molecular building blocks that can be utilized in these studies: a sufficient sublimation rate of the molecules must be obtainable at a temperature below which the molecules would fragment and decompose in the evaporation crucible. Most UHV studies have therefore focused on relatively small organic molecules, the few exceptions being studies that utilized highly specialized deposition methods, such as electrospray ionization deposition.[20] In the study by Weigelt *et al.*, an elegant strategy is demonstrated that effectively circumvents this dilemma: a larger molecular building block is synthesized *at the surface* from two smaller organic components (Figure 2). In this case, the reaction at the surface is imine formation by the covalent bonding of three octylamines to a trialdehyde core. The trialdehyde was evaporated onto the surface from a glass crucible, and the octylamine was dosed to the surface through a controlled leak valve. The resulting product has a mass much greater than that of each of its subunits.

Surface Studies of Model Systems. The surface synthesis strategy demonstrated in the paper by Weigelt *et al.* opens up possibilities for the study of a greater range of supramolecular systems at surfaces under UHV conditions.[19] Larger molecules have already

See the accompanying Article by Weigelt *et al.* on p 651.

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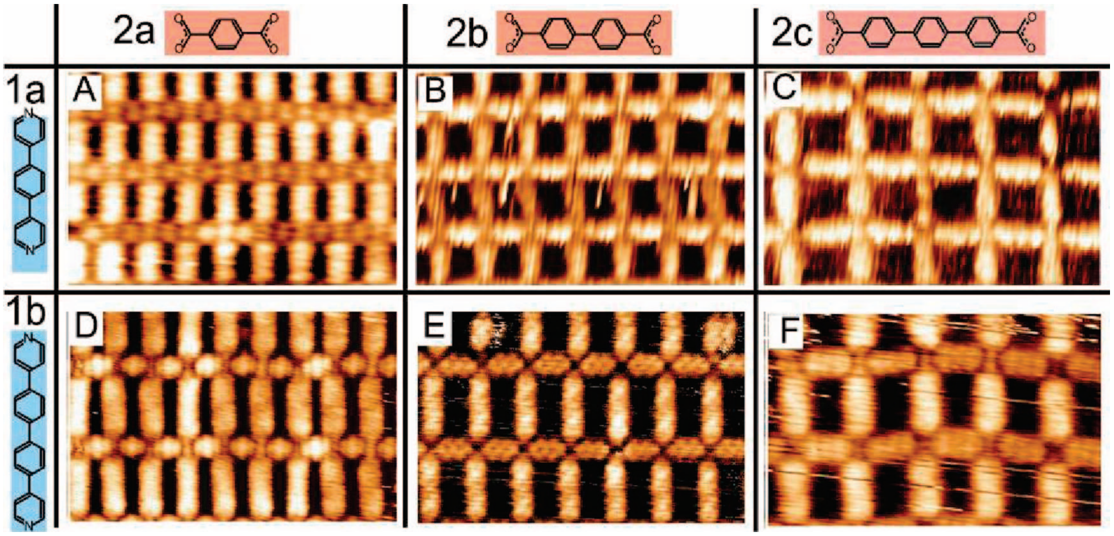

Figure 1. Steering the size and aspect ratio of rectangular molecular-scale compartments *via* the backbone length of two ligands in self-assembled metal−organic coordination networks. The ability to design such nanopore grids and a wide variety of other structures opens opportunities for designed functional structures at surfaces by supramolecular assembly. STM images (each 9.4 nm × 6.0 nm) here show six possible binary combinations $[(\mathrm{Fe}_2)(\mathbf{1})_{2/2}(\mathbf{2})_{2/2}]_n$ of two bipyridine (1a,b) and three bis-carboxylic acid (2a−c) ligands. Reproduced with permission from ref 17. Copyright 2007 National Academy of Sciences, U.S.A.

been studied at surfaces using liquid cell systems,[21] where molecular adsorption from solution is possible. These studies have revealed much about molecular organization at surfaces (in many cases producing structures remarkably similar to those obtained in UHV studies).

The key advantage in the UHV-based studies is the extraordinary degree of control available in the experiments. Starting from atomically clean and flat single-crystal surfaces with low defect densities, followed by deposition of highly purified organic (or inorganic) species, one has excellent control over what components are available to participate in the supramolecular assembly. The final stoichiometry at the surface is precisely controlled simply by the shutter open-time for the evaporators. This is a significant advantage over liquid deposition methods: the concentration of a molecular component at the surface can be far from the saturation value and can be precisely controlled.

UHV-based studies enable excellent control of kinetic processes that are very relevant for molecular self-organization and supramolecular growth or crystallization.

Highly controlled studies at well-defined surfaces offer the possibility for the careful examination of the physical and chemical aspects of these "model" systems. Especially, the scanning tunneling microscope (STM) and atomic force microscope (AFM) have allowed a spectacular (atomic/molecular resolution) view into surface structures. This will allow greater insight into application of these methods for the development and optimization of functional systems. For example, Langner *et al.*[17] studied multiple-ligand mixtures in controlled ratios that exhibit local self-selection and error correction in a complementary binary metal−organic coordination, demonstrating fundamental steps for molecular self-organization using very simple organic species.

Although we have seen an upsurge of groups using the STM to look at 2D molecular crystallization at surfaces, there is a growing recognition of the value of combining scanning probe studies with other methods to gain a better understanding of the interactions involved in producing the observed structures. For example, insight into the intermolecular bonding in supramolecular systems can be obtained by turning to photoemission studies, which have demonstrated clear coordination bonding for iron–dicarboxylate networks on Cu(100) surfaces[22] and evidence for hydrogen bonding in trimesic acid networks.[8] Complementary studies combining high-resolution STM studies and synchrotron-based near-edge X-ray absorption studies have more clearly elucidated the adsorption state and geometry of trimesic acid on Ag(111)[8] and of terephthalic acid on Pd(111).[23] Also critical in these studies is a close interaction with theoretical work to find the physical and chemical mechanisms that lead to the rich nanostructures observed in molecular assemblies at surfaces.[8,16,24]

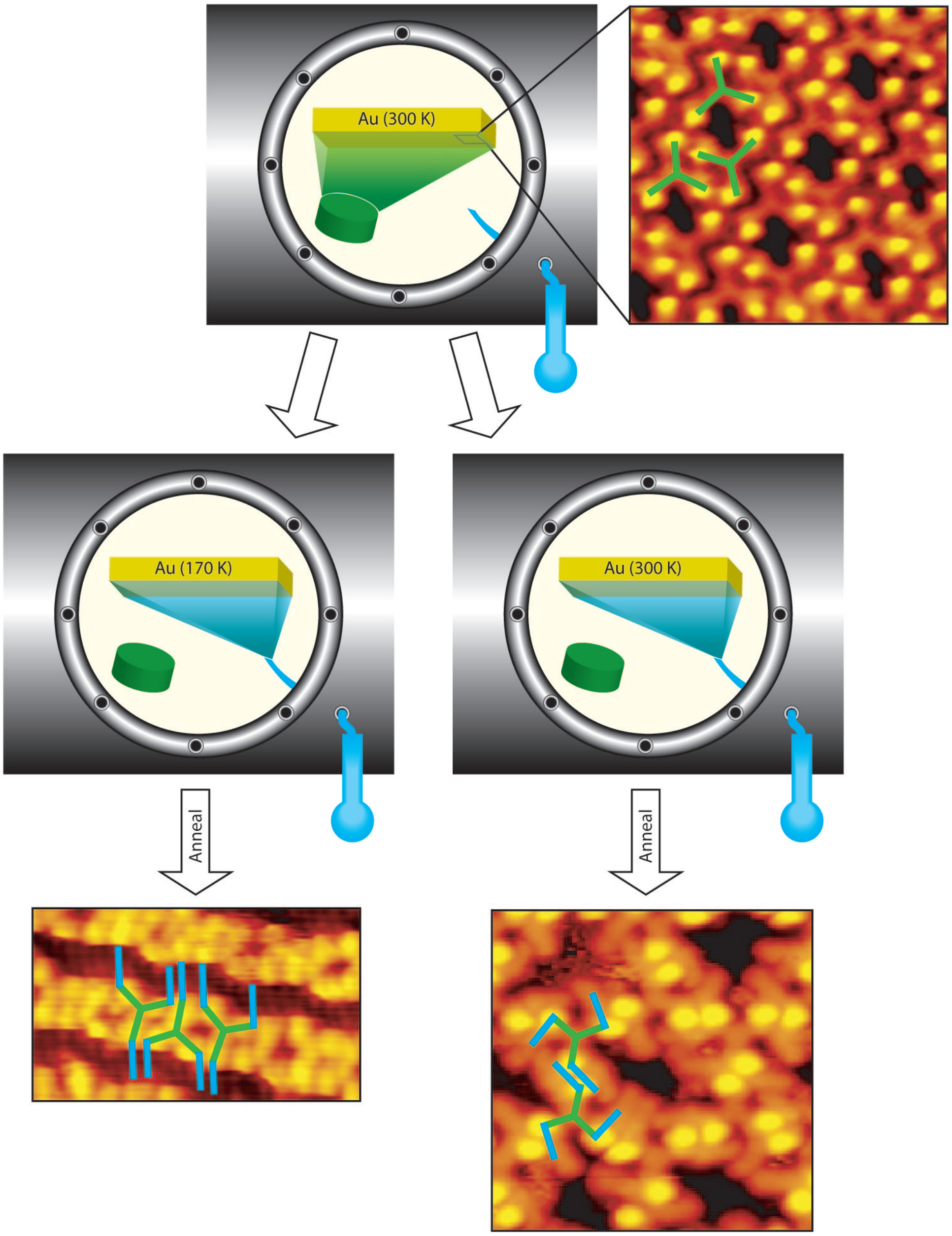

Figure 2. Triimine production in a two-step deposition process at a Au(111) surface under ultrahigh vacuum conditions, as reported by Weigelt *et al.*[19] In the first step (top), trialdehyde is deposited to the sample from a glass crucible. This results in the formation of highly ordered structures, as demonstrated by STM. In the second step (middle), octylamine molecules are deposited through a leak valve. Large kinetic effects in the ordering of the 2D triimine structure are demonstrated by experiments at different surface temperatures (bottom left and right), *i.e.*, varying the ratio of trialdehyde diffusion to octylamine deposition rate. STM images reproduced with permission from ref 19. Copyright 2008 American Chemical Society.

Aside from issues of system cleanliness and the availability of surface analysis methods, UHV-based studies also enable excellent control of kinetic processes that are very relevant for molecular self-organization and supramolecular growth or crystallization. For example, in studies of organic species at surfaces, one has a high degree of control over the relevant kinetic rates that can have dramatic effects on the growth of nanostructures.[25] The deposition rate of species to the surface is well-controlled by adjusting the evaporant temperature (and thus the sublimation rate). The growth kinetics are, in many cases, determined by competition between this incident flux of molecules to the surface and the kinetic diffusion of the molecular components across the surface. The diffusion of the molecules at the surface is a 2D Brownian-type motion (hopping between adsorption sites on the surface) and can be controlled by the surface temperature during deposition as well as *via* post-deposition annealing. The temperature range that can be achieved in modern surface analysis systems typically extends well beyond the range of interest for the study of molecular assembly (*i.e.*, above molecular decomposition temperatures and below temperatures where molecule mobility is essentially frozen, although studies at extreme cryogenic temperatures are very important for local tunneling spectroscopy measurements[26]).

Careful temperature-controlled studies of kinetic effects have revealed fascinating phenomena at surfaces: to name a few, kinetically limited growth of organic nanostructures,[25] diffusion-limited heteroepitaxial adatom aggregation,[27] and effects of rotational entropy in adsorption/desorption kinetics.[28,29] A study by Cañas-Ventura *et al.*[23] illustrated 1D and 2D supramolecular ordering of terephthalic acid on Pd(111), where the difference in structural dimensionality was related to whether the molecule had deprotonated at the metal surface, and therefore could be controlled to some degree by the sample temperature.

Kinetic Effects on Supramolecular Structure. In their report in this issue, Weigelt *et al.* have taken full advantage of the kinetic control possible in UHV surface studies in order to demonstrate a remarkable variety of organic supramolecular structure formation under different kinetic conditions[19] (Figure 2). They demonstrate significantly different supramolecular organization of the triimine, depending on the temperature of the surface during deposition. More critically, this can be thought of as varying the ratio of the molecular diffusion frequency on the surface with the arrival rate of new molecules. In the case of high flux of octylamines, the structural order of the preformed trialdehydes persists through the short time for the triimine formation; therefore, the resulting organizational motifs are related to the prior structure. The result is a high degree of conformational order. In the second case, at higher substrate temperature, the trialdehyde structure is not completely stable, and so the triimine formation occurs between molecules that are freely diffusing across the surface terraces. When the temperature is lowered, the triimines condense into a conformationally disordered hexagonal structure (higher entropy).

> Weigelt *et al.* have reported two key advances in this field: surface synthesis of large organic building blocks and kinetic control over supramolecular structure of the larger components.

Studies such as the one highlighted here are further expanding the available 2D surface structures that can be generated from organic ligands. Weigelt *et al.*have reported two key advances in this field: surface synthesis of large organic building blocks and kinetic control over supramolecular structure of the larger components.[19] Work will continue in understanding the growth and formation of these and other organic systems and how we can better develop design rules for planning and tailoring these systems.

Functional Characterization. Studies of well-controlled supramolecular assemblies at surfaces will not be the exclusive route to the development of functional organic nanostructures, but they do offer invaluable insight into the physical and chemical properties of these systems. The motivation for these studies is not purely a fundamental interest in supramolecular assembly of well-controlled model systems. Wide views of the potential impact of nanopatterned surfaces have been described in the literature, ranging from applications in molecular electronics to selective sensors to tailored templates for thin-film growth.[1,10,24,26,30] These surface-supported systems have potential impact in a wide variety of technical fields.

In the next stages of research, we will see more and more functional characterization of these systems. We started this discussion by describing the vast variety of organic ligands available and the ability to tailor these building blocks. The greatest promise of these systems lies in the potential to tune functional aspects of the supramolecular assemblies at surfaces by tailoring the structure of the networks through selection of the organic building blocks. Such derivation of supramolecular function from molecular building block design (form) is a fundamental goal of supramolecular research and lies at the heart of the expectations for nanoscience.

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