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# Organic thin films:

From monolayers on liquids to multilayers on solids **J. E. Greene**

What began as curious ritual in the ancient world led to studies of surface tension, interface properties, phase transitions, and, eventually, sophisticated deposition techniques and a wealth of devices.

The recorded history of organic thin films spans some four millennia, with the early literature dating back at least to the time of Hammurabi, the sixth king of Babylonia, around 1800 BC. Translations of the era's ancient cuneiform tablets, such as the one above, indicate that a form of divination involved pouring oil on water and observing the way it spreads on the liquid surface and the rim of the bowl. As Assyriologist Leo Oppenheim noted, "The movements . . . could portend for the king peace and prosperity or war and rebellion: for the private citizen it might portend progeny, success in business, the recovery of health, and the right girl when he was about to marry—or the opposite."<sup>1</sup> That is, the fate of common people, royalty, and even entire nations was thought to rest on the morphology—or more fundamentally, on the density and surface tension—of a thin oily film.

Early mariners and fishermen were also familiar with the effect of oil on water. Roman philosopher Pliny the Elder (AD 23–79) wrote that divers added oil to water to make it smoother and thus easier for them to see the bottom. Benjamin Franklin, in a 1773 letter to physician and scientist William Brownrigg, wrote of an occasion when he had been sailing with a fleet near what is now Cape Breton Island off eastern Canada and had observed that the wakes of two of the ships were remarkably smooth, while all the others were rebuffed by the wind. After pointing that out to his ship's captain, Franklin was

told with disdain that "the cooks . . . have, I suppose, been just emptying their greasy water through the scuppers, which has greased the sides of those ships a little."<sup>2</sup>

Brownrigg noted that "Sir Gilford Lawson, who served long in the army at Gibraltar, assures me, that the fishermen in that place are accustomed to pour a little oil on the sea, in order to still its motion, that they may be enabled to see the oysters lying at its bottom . . . the same was practised on other parts of the Spanish coast."<sup>2</sup>

Franklin later confessed that he at first slighted Brownrigg's explanation but couldn't think of another. Familiar with Pliny's account, Franklin continued to collect anecdotes of oil's calming influence on choppy waters, cataloged the stories in a 1774 *Philosophical Transactions* article, and resolved to conduct experiments on the effect himself. (See the article by Joost Mertens, *PHYSICS TODAY*, January 2006, page 36.) After one such experiment near Clapham Common, south of London, he wrote,

I fetched out a cruet of oil, and dropt a little of it on the water. I saw it spread

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**Figure 1. Agnes Pockels (1862–1935).** Although lacking a formal university education, Pockels was supplied with scientific papers by her brother Fritz and was helped in publishing her own by Lord Rayleigh. In 1932, on her 70th birthday, she became the first woman to receive an honorary doctorate from the Technical University of Braunschweig. (Image courtesy of the Technical University of Braunschweig.)

itself with surprising swiftness upon the surface; but the effect of smoothing the waves was not produced; for I had applied it first on the leeward side of the pond, where the waves were largest, and the wind drove my oil back upon the shore. I then went to the windward side, where they began to form; and there the oil, though not more than a tea spoonful, produced an instant calm over a space several yards square, which spread amazingly, and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking-glass.<sup>2</sup>

### Kitchen chemistry

Taking Franklin's description of the Clapham experiment literally, one can estimate that a teaspoon of, say, olive oil spread over half an acre (2000 square meters) thins to about 20 Å. That's roughly the thickness of one monolayer of oleic acid, a primary constituent of the oil. Lord Rayleigh made the calculation, first as an approximation in 1890 and then more accurately a decade later based on his own experiments. Armed with his results, he proved Avogadro's theory for the number of particles in a mole.

Although Thomas Young had measured the wetting angles of liquids that ball up on solids as early as 1805, it was Agnes Pockels, shown in figure 1, who made the first direct measurements of the surface tension of a liquid. Surface tension at a liquid–air interface arises from an asymmetry in the inter-

action forces that surface molecules experience with the bulk liquid and with the air. Because forming the interface requires work against liquid cohesive forces, the surface has a higher free energy per molecule than the bulk liquid; the excess energy per unit area is the surface tension. (See the Quick Study by Laurent Courbin and Howard Stone in *PHYSICS TODAY*, February 2007, page 84.)

Having to care for her sick and disabled parents and unable to attend college, Pockels nonetheless devoured the scientific reading material her brother Fritz sent her while he attended the University of Heidelberg. In 1880, at the age of 18, presumably while spending time cleaning oily dishes with soap, she noticed a rapid motion of the water when initially brought into contact with the soap and wanted to understand the underlying science.<sup>3</sup> Using ordinary household items, she constructed a balance, now known as the Pockels trough, and carried out experiments in her kitchen sink. As she describes her procedure, “a rectangular tin trough, 70 cm long, 5 cm wide, 2 cm high, is filled with water to the brim, and a strip of tin about 1½ cm laid across it perpendicular to its length, so that the underside of the strip is in contact with the surface of the water, and divides it into two halves. By shifting this partition to the right or the left, the surface on either side can be lengthened or shortened in any proportion, and the amount of the displacement may be read off on a scale held along the front of the trough.”<sup>4</sup>

Having read Rayleigh's papers on the topic of liquid surfaces, Pockels wrote to him on 10 January 1891, describing her results. After reading her letter (translated from German by his wife), Rayleigh wrote to the journal *Nature* on 2 March, requesting that they publish her results, which they did on 12 March, 1891; the journal included both Rayleigh's and Pockels's letters.<sup>4</sup> In her first paper, summarizing 10 years of work, Pockels described, among other findings, the change in the surface tension of water containing varying concentrations of household soaps, oils, and “spirits of wine.”

The soaps and oils were surfactants composed of molecules with a hydrophobic long-chain hydrocarbon attached to a hydrophilic head group, such as an alcohol, carboxylic acid, or amine. Pockels also measured surface pressure, the difference between the water and organic-layer surface tensions, and reported that small amounts of oil on the surface of water have no appreciable effect. However, she did find that the surface pressure rose suddenly when the oil's concentration per unit area was increased—by shifting the trough partition—beyond a certain sharp limit. Thus Pockels was the first to demon-

strate a compression-induced phase transition in what today is labeled a compression isotherm (see figure 2).

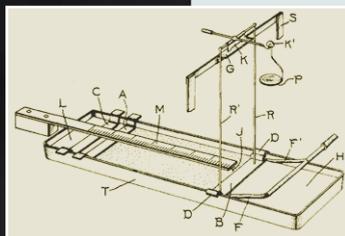
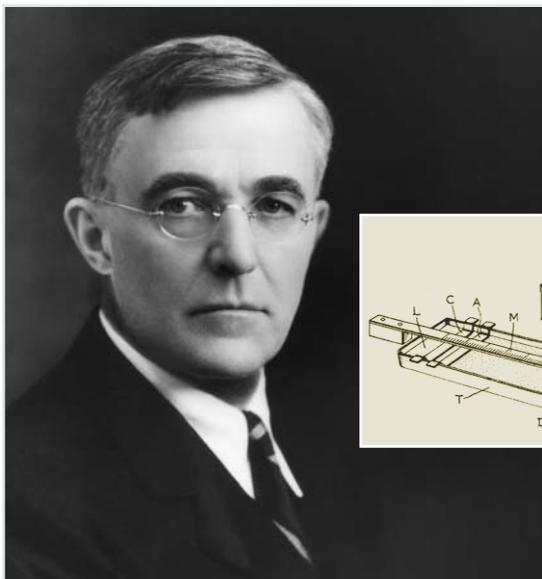
The surfactant molecules at low concentrations in Pockels's experiments behaved as a two-dimensional gas with essentially no lateral interactions. But as the trough partition was moved to decrease the average area per molecule and thus increase the surfactant concentration, lateral interactions began to exert an influence, and the molecules appeared as a spatially disordered liquid and then as an ordered 2D organic monolayer solid.

In later papers, Pockels discussed the required purity and cleanliness necessary to obtain accurate surface-tension measurements, determined the required concentrations of several household oils to form a monolayer, and examined the effects of varying the ratio of the number of hydrophobic molecules to the number having both hydrophobic and hydrophilic end groups.

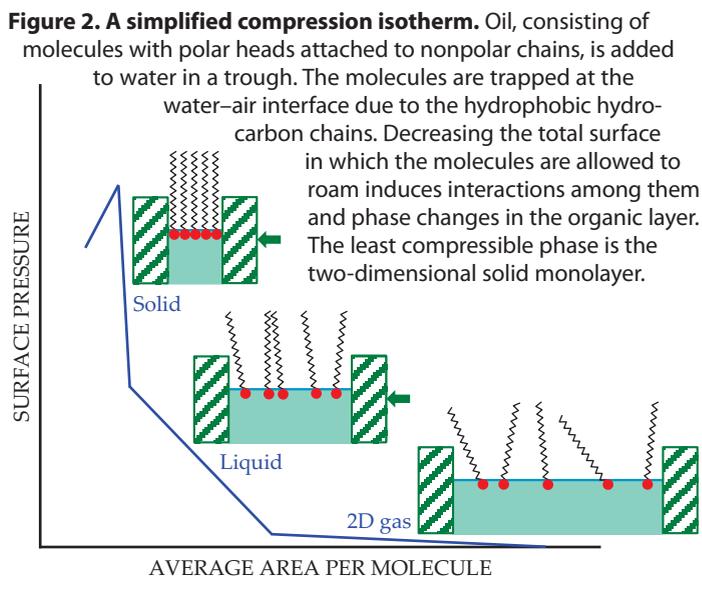
### Langmuir-Blodgett films

Irving Langmuir, shown in figure 3, was the next major contributor to liquid-organic interface science. He spent most of his career at the General Electric Research Laboratory in Schenectady, New York, and is well known for his research on the high-temperature behavior of tungsten and the dissociation of molecular hydrogen, work that culminated in his invention of rare-gas-filled incandescent light bulbs with greatly enhanced lifetimes. During the same period, the mid 1910s, he extended Pockels's pioneering work using what is now termed the Langmuir trough, an updated version of her own, to determine the fundamental properties of organic films on liquids.

In 1917 Langmuir published in the *Journal of the American Chemical Society* a seminal paper on organic films on water, in which he determined the spatial range of van der Waals forces between film molecules and described the nature of amphiphilic molecules—those having polar heads and nonpolar chains—and the physical basis for their behavior.



**Figure 3. Irving Langmuir (1881–1957)** in 1932. The first industrial chemist to become a Nobel laureate, Langmuir focused his early work on light bulbs—specifically, hydrogen dissociation on tungsten filaments. He also measured the surface tensions and surface pressures of numerous organic oils on water and in 1917 formulated a general theory of adsorbed films.<sup>5</sup> Using an updated version of a Pockels trough, shown in the inset and adapted from that seminal paper, he measured the pressure on a paraffin-dipped strip of paper B floating in an enamel tray filled with water. In the experiment, oil is added between strips A and B. As A is moved toward B, the oil film exerts a force on B, which tips a balance beam K having a counterweight on one side and a hanging pan P on the other.



The following passage captures a central issue he was addressing:

Let us consider oleic acid as an example. There is no doubt but that the carboxyl group [–COOH] has a marked affinity for water. The solubility of the organic acids in water, as compared with the insolubility of the corresponding hydrocarbons, is a clear indication of this fact. . . .

Therefore, when oleic acid is placed on water, it is probable that the carboxyl groups *do actually dissolve* in water. . . . The long hydrocarbon chains have too much attraction for each other, however, and too little for water, to be drawn into solution merely because of the affinity of the carboxyl for the water.

As a matter of fact, by the spreading of the oil on the surface as a monomolecular layer, the carboxyl group can combine with all the water it requires, without causing the hydrocarbon chains to separate from one another.

The spreading of an oil upon water is thus due to the presence of an “active group” in the molecule; that is, some group which has a marked affinity (secondary valence) for water. This leads



**Figure 4. Katharine Blodgett (1898–1979),** photographed in 1938, demonstrates an early version of the Langmuir–Blodgett trough. Turning a hand pulley repeatedly dips the glass slide into a solution of fatty acids on the surface of a water bath. The dips coat the glass with successive monolayers. (Image from the Smithsonian Institution Archives.)

directly to the prediction that an oil without active groups, such as pure paraffin oil, should not spread at all. Experiment shows that this is actually the case.<sup>5</sup>

In the same paper, from experiments carried out with a broad range of fatty-acid-based monolayer films, he determined the cross-sectional areas of the constituent molecules and their near-vertical orientation relative to the surface. He thus could deduce molecular configuration long before the development of modern spectroscopic techniques. Following Pockels's earlier work, Langmuir also showed that as the films continue to be compressed, they undergo phase transitions from a 2D gas to a liquid to a solid.

A year later Langmuir was introduced to Katharine Blodgett during her senior year at Bryn Mawr College. A former colleague of her father arranged a tour of the GE laboratories at Christmas break, during which Langmuir convinced her to pursue graduate work. After graduating from the University of Chicago in 1918 with a master's degree in physics, she was hired as the first female research scientist at GE. For six years she worked with Langmuir on a variety of projects, including electric current flow under restricted boundary conditions. Later, after leaving to work with Ernest Rutherford at Cambridge University on a doctorate, again at Langmuir's encouragement, she followed Langmuir as he resumed studies of organic films on liquids.

The pair's breakthrough in organic film growth came when Blodgett realized that multilayer films can be synthesized by repeatedly dipping solid substrates into suitable polar liquids.<sup>6</sup> Initial experiments, utilizing what is today called a Langmuir–Blodgett trough, involved the deposition of calcium stearate films on glass substrates, as shown in figure 4. Cal-

cium stearate,  $(C_{17}H_{35}COO)_2Ca$ , is insoluble in water, and its  $(-COO)_2Ca$  head groups attach to the glass substrates. By lifting and lowering the glass repeatedly, the pair produced films more than 200 monolayers thick. Subsequently, they produced birefringent coatings of barium stearate,  $(C_{17}H_{35}COO)_2Ba$ , more than 3000 monolayers thick and measured their optical properties, which allowed them to accurately infer a layer thickness of 24.4 Å. (See the article by Vijendra Agarwal, *PHYSICS TODAY*, June 1988, page 40.)

Blodgett quickly found a practical and important early application for Langmuir–Blodgett films on glass: antireflection coatings. The coated product was termed “invisible glass” in the popular press because the clearest uncoated glass available in the late 1930s had 8–10% reflectivity in visible light. While the original coatings based on fatty-acid salts were too soft for commercial purposes, durable coatings were soon developed. GE realized the importance of anti-reflective glass for such applications as eyeglasses, microscopes, telescopes, cameras, and binoculars; Blodgett filed for a patent—granted 16 March 1938—prior to her landmark publication on the coatings.<sup>7</sup>

### Self-assembled monolayers

As important as the midcentury organic monolayer and multilayer films were—and still are in some contexts—they are often amorphous and fairly weakly bound to the surface. In addition, almost all the literature dealt with systems in which the interesting polar part of the molecule was bound at the surface, leaving a less interesting hydrocarbon dangling on the outside. Organic chemists Ralph Nuzzo and David Allara at Bell Labs overcame both limitations in 1983 by showing how to prepare organic films that bond strongly to the surface and assemble themselves spontaneously with each molecule's chemically functional end group pointing outward. More specifically, they demonstrated the spontaneous growth of thiol monolayers—organosulfur compounds that contain a carbon-bonded  $(-SH)$  group—on gold.<sup>8</sup>

Thiols are the sulfur analogues of alcohols, in which sulfur takes the place of oxygen in the hydroxyl group. Like oxygen, sulfur has a valence of two, and organosulfur compounds have a strong affinity for metal surfaces<sup>9</sup> such as gold, silver, platinum, palladium, and copper. As a relatively inert material whose surface does not form a stable oxide, Au is often the metal of choice. Strong chemisorption bonds between the sulfur head group and Au substrates render the monolayers more stable than the early, physisorbed Langmuir–Blodgett systems.

When a clean metal is immersed in a dilute thiol

solution to make a self-assembled monolayer (SAM), two distinct kinetic regimes are observed. In the first step, comprising adsorption, surface diffusion, nucleation, and growth, the surface becomes densely covered in seconds to minutes, depending on the thiol concentration. Then follows a slow step, which can require several hours at room temperature, during which the layer reorganizes itself to maximize its packing density and minimize the defect density.

To decrease the influence that the sort of common defects shown in figure 5 have on physical properties, SAM growth kinetics are generally studied using single-crystal substrates. Reactions between the surface and head groups determine the speed of the first step, and fluctuations among the chains' conformations determine the rate of the second step. Ordering kinetics are faster for longer alkyl chains, probably due to increased van der Waals and dipole-dipole interactions.

Properties of a SAM can be tuned by forming mixed monolayers—a 2D analogue of 3D alloys—through coadsorption from solutions containing mixtures of, for example, two or more different thiols.<sup>10</sup> Unlike Langmuir-Blodgett films, which have been observed to exhibit phase segregation into macroscopic islands, the resultant SAM consists of a reasonably homogeneous mixture of the components. Nonetheless, scanning tunneling microscopy studies reveal a domain structure rich in individual components at the nanoscale.

Various patterning techniques now exist to control the spatial positioning of the different components for biosensors and molecular recognition applications.<sup>11</sup> One approach,<sup>10</sup> known as microcontact printing, is outlined in figure 6. Basically, the desired pattern is transferred from a solid template to an elastomeric stamp that is covered with a thiol “ink.” The stamp is then placed on the substrate, onto which the ink diffuses, and molecules assemble into the patterned SAM structure. The process can be repeated with other stamps, wetted with different

thiols, on bare regions of the substrate to construct complex patterns consisting of several different components. Features with size scales of the order of 500 Å can be fabricated by microcontact printing; even finer patterns can be achieved with UV, x-ray, electron-beam, and scanning probe lithography.

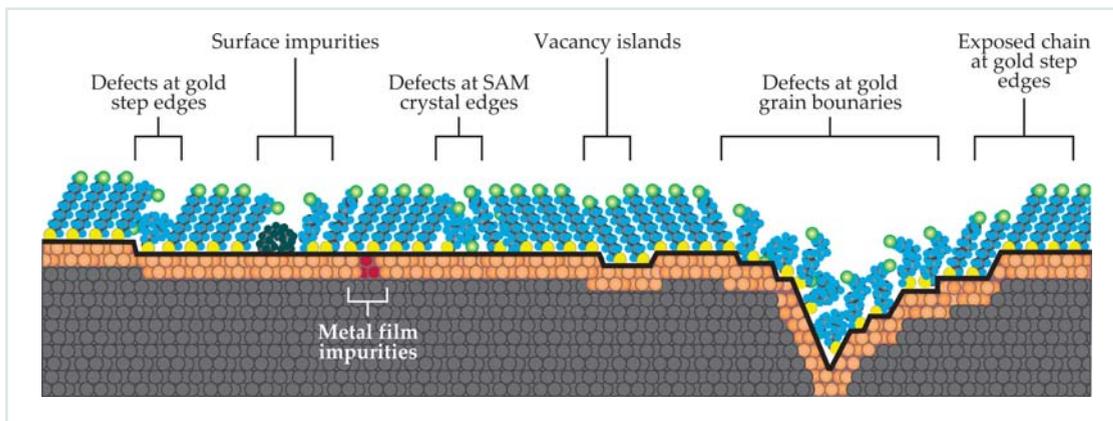
A disadvantage of thiols, however, is that they can quickly degrade in light, air, and some common solvents. Fortunately, they are not the only molecules that bind readily to a metal surface and form functionalized SAMs. Another important class of SAMs, used in the fabrication of molecular electronic devices, is based on organosilane precursors—alkane chains containing SiCl<sub>3</sub> head groups—deposited on substrates such as silicon oxide, aluminum oxide, and alloys of indium oxide and tin oxide.<sup>12</sup>

In the case of SiO<sub>2</sub> surfaces, the driving force for self-assembly is the formation of siloxanes, which connect the precursor silane to surface silanol Si-OH groups via strong Si-O-Si bonds. Because oxide substrates are typically amorphous, the packing and ordering of chemisorbed organosilanes are determined by the siloxane network, interchain interactions, and the reaction temperature.

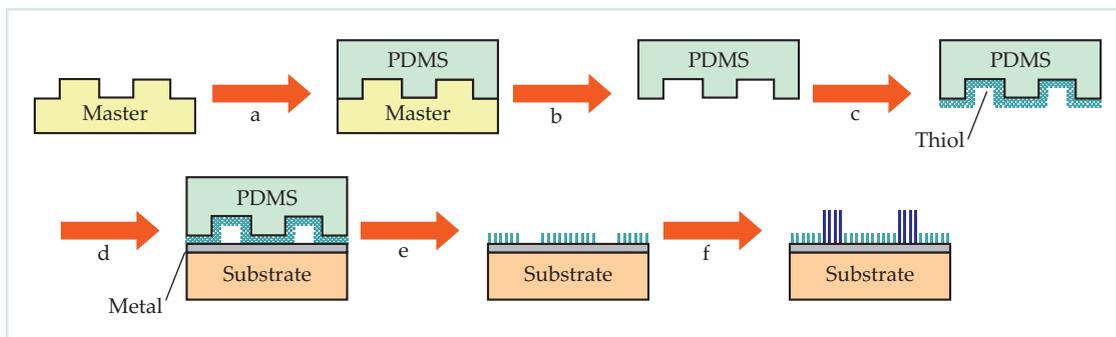
Recently another class of molecules called N-heterocyclic carbenes (NHCs) has emerged as yet another stable alternative to thiols. NHC-based SAMs form stronger bonds with metals than their thiol-based cousins and can tolerate boiling solvent, electrochemical cycling, and a wide range of pH levels (see page 20 in this issue).

### Designer films

Self-assembled monolayers and a subclass of multilayers known as self-assembled nanodielectrics, or SANDs, are of increasing interest for the fabrication of organic thin-film transistors and organic FETs (see reference 13 and the article by George Malliaras and Richard Friend, *PHYSICS TODAY*, May 2005, page 53). Some molecular electronic applications require SAMs to be deposited directly on Si after



**Figure 5. Intrinsic and extrinsic defects** in a self-assembled monolayer (SAM) on a polycrystalline substrate. SAMs are often thiols—organosulfur compounds with (–SH) head groups (yellow) that bond to a metal substrate (orange)—whose hydrocarbon chains (blue) follow the crystalline symmetry of the lattice and protrude outward. Such monolayer chains may also be terminated with a functional end group (green) that endows them with particular properties. In this schematic, the dark line marks the gold–sulfur interface and reveals the atomic-scale topography of the substrate. (Adapted from ref. 9.)



**Figure 6. Microcontact printing.** (a) A solid template is lithographically produced with the desired relief structure and coated with an elastomer, here polydimethylsiloxane (PDMS), a constituent of bathtub caulk. (b) The elastomer is removed from the master and becomes the stamp, which is then (c) inked with a thiol solution and (d) placed in contact with the substrate. (e) The thiol is transferred to the metal surface in the regions of contact to produce a pattern consisting of exposed metal and thiol-covered regions. (f) The patterned surface can be stamped with other thiol solutions to produce a surface patterned with different, spatially distinct thiols. (Adapted from ref. 10.)

the substrate's native oxide is removed. Other applications—primarily biosensors, probes, and molecular-separation techniques—call for self-assembled monolayers and multilayers to be selectively deposited on metallic and semiconducting nanostructures, such as quantum dots, nanowires, nanorods, and nanotubes.

Nanostructures are smaller than cells, the basic functional unit of living tissues, and thus can be functionalized to probe subcellular features. Functionalized nanorods, for example, have been shown to be capable of delivering DNA plasmids to cells.<sup>14</sup> SAMs on metallic “barcodes,” nanowires patterned with sections of different metals, are used to perform DNA hybridization assays and immunoassays—biochemical assessments that measure the concentration of macromolecules such as proteins.<sup>15</sup> Selective molecular recognition and the separation of proteins by size have been accomplished using gold nanotubes whose inner surfaces are functionalized with thiol groups.<sup>16</sup>

Clearly, although interest in organic materials started with curiosity over the spreading shapes of oily water, it has matured into a search for practical uses, controlled experiments, and scientific understanding, along with the development of sophisticated deposition techniques and device structures. One measure of success is the fact that a significant fraction of the modern literature in organic films is applied science. In addition to molecular electronics, organic thin films form the basis of a very broad range of subfields: Controlled wetting, adhesion, electrochemistry, solar cells, and magnetic memory storage are just a few.

Several factors are driving the success of organic thin films. One is the relative ease and favorable economics of their production. The films are typically grown from solution rather than from the expensive high- and ultrahigh-vacuum systems often used to deposit inorganic layers on substrates.<sup>17</sup> Other important factors include the amazingly rich chemistry of organic molecules, which offer a seemingly infinite palette for engineering new

materials, and the enormous range of bio-inspired processing routes available for designing unique, and in many cases self-organized, manufacturing processes. Thus it is an exceedingly safe bet that rapid progress in the field of organic monolayers and multilayers will continue well into the foreseeable future.

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