Monographs in Supramolecular Chemistry

Supramolecular Chemistry at Surfaces

David B Amabilino



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Supramolecular Chemistry at Surfaces

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Preface

for Lluïsa, Adrià, Brian and Mònica

The idea for this text came during a Master level lecture course that I was participating in at the *Universitat de Barcelona* on the Bottom-up Growth of Materials on Surfaces, especially focussing on molecular materials. I felt that in the nanoscience area, the vast body of work on mono- and multilayers had very good specific reviews but there was no overview of the area as a whole, showing the requirements or needs for any particular kind of assembly route and the advantages and disadvantages of the various strategies for surface assembly, or indeed the opportunities that existed should one route have been tried and not reached expectations. Where was one to turn for alternatives? This monograph modestly aims to help address this space and provide an (albeit highly personal and far from comprehensive) overview of supramolecular chemistry at surfaces.

The text aims to introduce the main concepts involved in the growth of layers of molecules on surfaces, and show the breadth of work that has been done, and the excitement that this growing area generates. It does not attempt to be an exhaustive treatment of supramolecular chemistry at surfaces, and I apologise in advance to those kind enough to read the work but feel their important research under-represented. It was simply impossible to give a totally comprehensive coverage of all the fields that are discussed here. The treatment is broad and is the author's view of the main principle concepts across strongly and weakly interacting systems at interfaces.

I have to thank all the people, mentors, students and colleagues I have worked with during my scientific career, in every aspect from my PhD through my postdocs up to the present time, and especially those who have carried out research into monolayers in my group in the Materials Science Institute of Barcelona (ICMAB-CSIC)—Elba Gomar-Nadal,

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Josep Puigmartí-Luis, Patrizia Iavicoli, Mathieu Gonidec, Wojciech Saletra, Magali Lingenfelder, Ángela Bejarano, Arántzazu González Campo, Cristina Oliveras and Marta Riba—because I've learned a lot with you. Also, I'm indebted to my collaborators and dear friends Steven De Feyter, Rasmita Raval, Roberto Lazzaroni, Mathieu Linares, Hans Elemans, Ángel Pérez del Pino, Ismael Díez-Pérez and Carmen Ocal who have taught me an enormous amount, as well as to people in their groups, André Gesquiere who taught me how to drive an STM, Mohamed Abdel-Mottaleb, Sam Haq, Wael Mamdouh, Shengbin Lei, Mendel In't Veld, Andrea Minoia and Hong Xu. To my present group and colleagues, Neil Champness, Peter Beton and Rob Jones, I thank them for their patience and kindness in answering the often stupid questions I posed to them!

Scientists like what they do too much (or at least they should do), but the strength from our loved ones is vital, and the most important thing; to my family I dedicate this book. To my wife Lluïsa, who is my soul mate and also professional confidante, you've helped me more than you know, and to Adrià, Brian and Mònica for making me the proudest Dad in the world.

Abbreviations

AES	Auger electron spectroscopy
AFM	atomic force microscopy
APTES	(3-aminopropyl)triethoxysilane
BAM	Brewster angle microscopy
CV	cyclic voltammetry
CyDs	cyclodextrins
DFT	density functional theory
FESEM	field emission scanning electron microscopy
GIXRD	grazing incidence X-ray reflectivity
HOMO	highest occupied molecular orbital
HOPG	highly oriented pyrolytic graphite
HWE	hot wall epitaxy
IRRAS	IR reflection absorption spectroscopy
ITO	indium tin oxide
LB	Langmuir–Blodgett
LbL	layer-by-layer
LEED	low energy electron diffraction
LUMO	lowest unoccupied molecular orbital
MBE	molecular beam epitaxy
MOF	metal–organic framework
μCP	microcontact printing
ML	monolayer
OMBE	organic molecular beam epitaxy
NEXAFS	near-edge X-ray absorption fine structure spectroscopy
PDMS	poly(dimethylsiloxane)
PEM	polyelectrolyte multilayer
PM-IRRAS	polarization modulation-infrared reflection-adsorption
	spectroscopy
QCM	quartz crystal microbalance

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RAIRS	reflection-absorption infrared spectroscopy
SAM	self-assembled monolayer
SEM	scanning electron microscopy
SFGS	sum frequency generation vibrational spectroscopy
STM	scanning tunnelling microscopy
STS	scanning tunnelling spectroscopy
SURMOF	surface grown metal-organic frameworks
TOF-SIMS	time-of-flight secondary ion mass spectrometry
UHV	ultrahigh vacuum
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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CHAPTER 1

Surfaces for Supramolecular Systems

1.1 Introduction

The non-covalent bond is omnipresent in molecular systems at surfaces and the frontiers between materials in general.^{1–5} This environment is distinct to either bulk materials or solution-borne aggregates, although as we shall see, the principles of supramolecular chemistry can be applied to great effect at surfaces. A great deal can be learned about supramolecular objects by studying them at surfaces where they can be probed with powerful techniques that allow precise information to be garnered about their structural and physical characteristics. Apart from the purely scientific fascination with these systems, opportunities are evident for their use in electronic devices including sensors, or for their optical or mechanical properties. While many of the phenomena apply to nanoparticulate systems with solid cores where supramolecular chemistry from the surface is extremely versatile,^{6–11} the most precise way to study these systems is on flat surfaces where molecules are attached at more or less specific locations. This kind of system is the subject of this book.[†]

The supramolecular chemistry in these environments can be complex, because, as is shown graphically in Figure 1.1, the molecules that form an eventual layer on a bulk material have interactions between themselves and also with the surface of the bulk material and whatever medium is over them. We must therefore consider conscientiously this kind of situation in

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[†]The frontiers between two bulk phases in colloidal systems are not covered here; the interested reader is recommended the following text for treatment of these equally fascinating areas: H.-J. Butt, K. Graf and M. Kappl, *Physics and Chemistry of Interfaces, second revised and enlarged edition*, Wiley-VCH, Weinheim, 2006.



Figure 1.1 Molecules at surfaces and the frontiers between the components of the system.

all its guises as a system, a whole rather than a sum of parts. The chemical characteristics of all components of the system can influence dramatically the relative importance of any particular non-covalent interaction. There is also the case where the surrounding medium contains other molecules capable of interaction with the layer of surface-bound molecules. It is desired to provide the reader with an understanding of surfaces and how supramolecular systems behave at them, and how one can characterise them. It will be shown why these systems are of interest from a fundamental point of view, but also in terms of materials with practical applications. In this sense, opportunities for surface-grown supramolecular systems will be given.

Surfaces surround us, literally, and play defining roles in the properties of all kinds of materials (Figure 1.2), and have done for millennia.¹² In natural systems, the interactions and reactions between molecules take place very often in heterogeneous media: at surfaces, or more properly at *interfaces*, the area between two continuous phases. The self-assembly of lipids and macromolecules at interfaces is widespread and intriguing.¹³ Indeed, it was in biological systems where scientists initially saw the importance of supramolecular chemistry and mentioned it in these terms in the context of collagen self-assembly.¹⁴ A recent book discusses in detail the fascinating topic of biointerfaces.¹⁵ All the frontiers between the combinations of solids, gases, and liquids are involved in important chemical processes, from the capture of oxygen by lungs or gills when animals breathe^{16,17} to the deposition of inorganic materials in processes such as bone formation. Supramolecular chemistry is of vital importance in the functioning of these systems. In man-made materials, "non-stick" surfaces in cookware have revolutionised the way we prepare food and the remarkable advances in adhesives have made fixing broken objects easy. Surfactants, natural and artificial, are perhaps the most frequently observed system where a molecule interacts through non-covalent bonding with itself and a surface to make bubbles or clean dirt.

The physical or chemical examples given so far refer principally to surfaces that are the contact point between two continuous materials (phases). The surface is the outermost layer of a material (Figure 1.3). However, this plane



Figure 1.2 Household interfaces in action; from top left, our fingers with the screens of mobile tactile devices for function and casing for grip and support, a label on a glass bottle held in place by an adhesive, a quite different sticky situation for a plaster that must adhere to damp fingers, and the wetting of paper by a drop of water (right) or a wax crayon coated area (left) where the drop stays intact and round.



Figure 1.3 The concepts of surface and interface, of each material and the system.

and even the region immediately below the surface of a material is not representative of the bulk, especially in the case of liquid systems or metals, for example. When considering phenomena such as the reflection light from solid materials or the properties of conductors or magnets near their surface, it is far more appropriate to speak of the interface between two bulk phases. The term implies that there is a region near the surface that is influenced by it in a structural and/or property sense. The properties of materials near their contact point with a different phase will change compared with the bulk. The same is true when considering liquids, water perhaps being the best known case,¹⁸ where the short range ordered structure

dominated by hydrogen bonds makes its surface tension high in contact with air and explains how it covers certain surfaces. The mobility of the atoms or molecules at the surface of a material will generally be different to that in the bulk and will depend on the strength of the interaction between them. Soft metals may have mobile surface atoms while the strong bonds in oxides on their surface will not favour motion. These characteristics will affect the nature of any layer forming on them.

It was perhaps Allara and Nuzzo that sparked the present interest in selfassembled systems on surfaces with a series of papers on the adsorption of alkyl adsorbents to different surfaces. In one of their seminal papers, "Spontaneously Organized Molecular Assemblies. 1. Formation, Dynamics, and Physical Properties of *n*-Alkanoic Acids Adsorbed from Solution on an Oxidized Aluminum Surface" published in the first issue of the then new journal Langmuir,19 they showed how long alkyl chain carboxylic acids formed layers spontaneously from solution. They also presented a scholarly perspective concerning the previous work on adsorption at surfaces. Indeed, in 1946 (in the first volume of *Journal of Colloid Science*!), the formation of monolaver films from non-polar liquids was established.²⁰ The authors of that work noted then that "the greater the chain length of the molecules the more condensed and rigid the film will be", a hypothesis that has truly stood the test of time, as we shall see. Remarkably, they also found that for platinum and Pyrex "while weight concentrations of only 10^{-7} M were required for primary aliphatic amines and monocarboxylic acids, roughly 1000 times more was needed for the aliphatic alcohols, esters and ketones and for cholesterol". This pioneering work already gave us the evidence that specific molecular and supramolecular chemistry can be used to control the formation of monolayers. Of course, all this work was surely inspired by Langmuir's work on monolayers on water²¹ and multilayers by transfer from it,^{22,23} the latter with his co-workers Blodgett and Schaefer that give their names to the films.

These methods of monolayer and multilayer (film) preparation and the subsequent very significant advances in complementary routes make a toolbox of unique techniques that allow the assembly of molecules on surfaces. Some of the main methods are represented in Figure 1.4, and they are the ones that will appear throughout this text.

Building on the shoulders of the pioneering scientists working on adsorption at surfaces and those of the founders of supramolecular chemistry,^{24–26} the development of supramolecular systems at surfaces has been spectacular in recent years. It is a truly interdisciplinary area with multiple potential and actual applications across a huge range of areas. One need only consider the following achievements observed at the molecular level to appreciate this: precise binding of molecules in host–guest systems at interfaces;²⁷ observation of reactivity of single molecules on surfaces;²⁸ the proof of spontaneous symmetry breaking on a surface;²⁹ the measurement of conductivity through single molecules,³⁰ and the self-assembly of single molecule magnets on surfaces.^{31,32}



Figure 1.4 Some routes to the formation of layers of molecules on surfaces and cartoon representations of the films they produce.

As specific landmarks in the development of supramolecular systems on surfaces (Figure 1.5), the observation of binding and formation of organised domains of a complex formed between a biotin-derived surfactant and streptavidin is paradigmatic of the way host–guest interactions can be used to assemble materials.³³ This biological recognition motif forms remarkably well defined monolayers at the surface of water. In a more purely synthetic example, the proof that resorcin[4]arenes adsorbed on a gold surface through thioether groups showed a remarkable selectivity and sensitivity (down to nanograms) for tetrachloroethene in a quartz microbalance oscillator (Figure 1.5).³⁴ This example shows how a host–guest system from solution can be turned into a device that does not require solution processing at all. Surface immobilisation is an excellent route for applying developed host–guest systems in a way where solution processing is not necessary and where the limits of detection of spectroscopy are avoided.

The observation of extended surface chirality when the enantiomers of tartaric acid are adsorbed on copper was remarkable.³⁵ It showed how modern imaging techniques at metal surfaces can give precise structural information—in this case, the chirality in extended areas—of molecules on surfaces to show their supramolecular organisation as well as proving the potential to probe heterogeneous catalysis in this kind of adsorbed system. The final example here is that of another biologically inspired system—duplex DNA—that when confined in a monolayer is capable of polarising electrons, an important feat for molecules within the context of spintronics.³⁶



Figure 1.5 Four examples of supramolecular systems on surfaces that were important breakthroughs for science. Top left, the binding of a biotin derived surfactant to a fluorescently-labelled streptavidin at the airwater interface; bottom left, the selective detection of tetrachloroethene by a self-assembled monolayer formed by a resorcinarene derivative; top right, the expression of structural chirality in monolayers of chemisorbed tartrate on metallic copper; and bottom right, the observation of spin-selective passage of electrons through a monolayer of double-stranded DNA.

The study of self-assembly on surfaces has led to an area referred to as "two-dimensional supramolecular chemistry",^{37,38} focused mainly on the plane parallel to the initial surface, which shares the feedback of information with crystal engineering that many supramolecular systems do. The difference now is that very precise information can be determined on surfaces, perhaps leading to insight that crystal science can sometimes not achieve and revealing the beauty and complexity of superstructures and complexes.³⁹ Merely by way of example, the observation of benzoic acid derivatives on surfaces reveals that the structures that they form can be very similar to those formed in the solid state. The dicarboxylic acid compound shown in Figure 1.6 forms a structure on the surface of graphite very similar to planes within the bulk crystals of the compound.⁴⁰ Chains of hydrogen bonded acids run parallel to one another and the alkyl chains attached to the phenyl ring interdigitate to give a crystalline packing. Apart from single-component systems whose structure can be studied precisely at surfaces,



Figure 1.6 Drawings of ordered supramolecular structures observed both in threedimensional solids and on certain surfaces. The top example shows chains of a phthalic acid derivative where the pendant long alkyl chains interdigitate and interact through van der Waals interactions. Below, the complex formed between melamine and cyanuric acid.

ordered multiple-component systems are also formed readily. The classic example from supramolecular chemistry and crystal engineering⁴¹ of the complex formed between melamine and cyanuric acid (Figure 1.6) forms the same bimolecular network on a surface.⁴² While not all adsorbates show identical two-dimensional structure to the solid state, there are factors in the molecular and supramolecular design that can be optimised to result in

remarkable similarities: pyrene-2,7-dicarboxylic acid and the tetrahydroanalogue crystallise in three and two dimensions with remarkable similarity, while biphenyl derivatives do not.⁴³ This effect was ascribed to the high planarity of the former. From these examples of strict assembly, it is possible to develop systems that show molecular recognition at interfaces,⁴⁴ as we shall see in forthcoming chapters.

Whether supramolecular structures on surfaces mimic what they would do in bulk or do something different depends in grand measure on the nature of assembly and surface. The foundation for the supramolecular "buildings" included here are all important. Let us then first consider the nature of surfaces and how they interact with molecules.

1.2 The Nature of Surfaces, Their Interactions with Molecules and Growth of Layers

Surfaces of materials are generally fascinating places to look at chemistry: the energy of the surface atoms or molecules is higher than in the bulk, because all the theoretically possible interactions that would give them their lowest energy state are not achievable.⁴⁵ Apart from their accessibility, surfaces are the part of a material where reactions and interactions take place first because of this higher energy. Their interaction with an incoming molecule lowers the energy of the system as a whole.

When an atom or molecule adheres at the interface between two bulk phases, the process is termed adsorption. The attached chemical is termed the adsorbate (while before it is attached, it is termed adsorpt or adsorptive, Figure 1.7) and the bulk phase it adheres to most strongly is the adsorbent. The amount of adsorpt that ends up attached to the adsorbent in the most simple case is a function of the concentration or vapour pressure of the adsorpt and the temperature of the system.



Figure 1.7 A schematic view of adsorption and the definition of the components in the system.

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The mobility of a molecule on a surface and the interactions it will be able to enter into with other like, or unlike, molecules will depend largely on the nature of the surface-molecule interaction. The wetting of surfaces by molecules, as in macroscopic systems, is determined by the balance between adhesive forces (between the adsorbent and the adsorbate) and the cohesive forces that tend to make the adsorpt aggregate homogeneously and not stick to the interface.

Surfaces are never perfect, therefore, it is important to consider the nature of a substrate's surface before the addition of any material to it as it will have an influence on the type of adherence that takes place. For all surfaces, be they liquid or solid, chemical impurities can influence dramatically the local surface energy. These impurities can affect the structural and therefore chemical and physical properties,⁴⁶ for bad or good: doping (introduction of cations or anions with chemical "impurities" sometimes through oxidation or reduction) can be essential for the optimisation of certain electrical⁴⁷ and thermal⁴⁸ properties and can affect beneficial growth modes.⁴⁹ It should also be noted that the purity of any adsorpt is similarly very influential in the self-assembly of surface-based structures, and on eventual properties.⁵⁰

For solid surfaces (that are never atomically flat on a micron scale), common defects are step edges, where the plateau of the surface rises or lowers by one atomic or molecular plane (Figure 1.8). The sizes of the plateaus can vary tremendously. Pits, trenches or simple vacancies can occur, just as adatoms and molecules and islands comprised of them can be present. The defects can attract adsorbates first, rather like the seats in a train where everyone sits down first, the seats correspond to the most favourable absorption sites in this simile. All of the seats are filled until no more are available. People will then sit on the floor, lean or stand as there are no predominantly favoured sites: the flat space fills up. Back to the molecular world, it is frequent to observe molecules and their assemblies aggregate first at step edges.



Figure 1.8 A lateral view representation of an adsorbent showing some common surface defects on otherwise atomically flat surfaces, where the density of defects is grossly exaggerated.

The reader will find references to "the" solid–liquid interface, but in fact this term is not precise because there are a multitude of solid–liquid interfaces, all with their own particular characteristics. It is obvious that the interface between water and fresh teflon is completely different to that between water and hydrophilic glass, yet both are solid–liquid interfaces.

The consecutive adsorption of molecules on surfaces can occur in several ways that can be distinguished from one another by their adsorption isotherms. The isotherms in Figure 1.9 show some of the contrasting behaviours that can occur, where the interfacial excess (Γ in mol m⁻²)—the amount of adsorbate in touch with the surface—is plotted against the concentration of adsorbate (either the pressure, in the case of a gas, or the molarity of a solute in a liquid). The linear relationship between interfacial excess and concentration, corresponding to Henry's rule, implies a proportional increase in adsorbate molecules on the surface with the surface pressure or concentration. Although this ideal kind of behaviour might be possible through isotropic interactions of a single material being grown from the vapour state, in the context of the systems described in this text, it is more likely only to be observed in the initial phases of adsorption of layers when the interfacial excess is very low. It can be regarded as the first term in many of the isotherms.



Figure 1.9 Examples of hypothetical adsorption isotherms: Henry-type adsorption is an ideal case seen in the early stages of adsorption (low). Langmuirtype adsorption results in a monolayer to which the adsorbate has negligible affinity. The cooperative type of sigmoidal curve shows the case where self-assembly can play a role. The BET-type curve results from the adsorption of a monolayer that subsequently has a weak affinity for further adsorbate growth, which does happen at higher concentrations or pressures.

The Langmuir isotherm shows a principally linear increase of surface excess at low concentration but then flattens and reaches a constant value despite any increase in concentration or pressure of the adsorpt. The molecule does not interact with itself: indeed, the Langmuir equation⁵¹ shown below assumes that there are no interactions between adsorbate molecules, or between adsorpts and adsorbates. In this equation, θ is the fraction of adsorbate on the surface compared to a complete monolayer, α is the Langmuir constant and *P* the pressure.

$$\theta = \frac{\alpha P}{1 + \alpha P}$$

This equation was derived starting with the assumption that there is an equilibrium between adsorbate and adsorpt with occupied and nonoccupied sites on the adsorbent, as shown in the following equation:

$$S^* + P \rightleftharpoons SP$$

which would remind many supramolecular chemists of any host-guest equilibrium in homogeneous media. Indeed, the Langmuir equation is analogous to the Hill equation used in biochemical systems in order to evaluate cooperative binding. Once all binding sites are occupied, no more material can enter in this model, and the Langmuir-type curve effectively corresponds to a self-limiting growth scenario. This situation is observed often for solution-based systems on solid substrates.

At this point, it is also important to consider the relative amounts of each component in the system. The stoichiometry of interactions between adsorbate and adsorbent accessible surface is usually quantified in terms of the *coverage*. More properly, this is termed the fractional coverage (θ as shown in the Langmuir equation above), and corresponds to the ration of N_s (the number of surface adsorption sites occupied by adsorbate) and N (the total number of adsorption sites on the adsorbent). A complete monolayer is often referred to as 1.0 ML ($\theta = 1$ for monolayer) coverage, corresponding to the plateau in the Langmuir isotherm. This situation corresponds to a particular molecular orientation with respect to the surface. Supposing half of the material with respect to the full monolayer were adsorbed: that would correspond to 0.5 ML coverage. A bilayer would correspond to 2.0 ML, and so on. The coverage is a key and useful concept in defining the formation.

The formation of layers can involve a very significant interaction between the adsorbate molecules, and in this case a cooperative binding curve (Figure 1.9) results for the formation of a monolayer. This type of curve is typical for systems where "all or nothing" adsorption takes place because of strong non-covalent bonds in-between the adsorbed molecules themselves as well as a significant interaction between their assembly and the substrate surface. For this kind of curve, after a monolayer is formed, no more adsorpt is incorporated into the layer because the interaction between the molecule in the layer and that in the bulk overlayer medium is very weak. Should a complete monolayer be formed through relatively strong adsorbent-adsorpt interactions (full monolayer coverage) but the resulting adsorbate is capable of forming relatively weaker but significant interactions with like molecules in the overlayer, the BET-type isotherm (after Brunauer, Emmett and Teller) will result. The layer will get increasingly thick as the adsorpt pressure or concentration in the overlayer medium is increased, until the isotherm becomes essentially that of the adsorpt condensing on itself as a bulk material. The effect of the interface is lost as the number of layers increases.

The different kind of adsorption curves can also be explained at the molecular level from a qualitative structural viewpoint. The phenomena that are manifested in the different growth models (Figure 1.10) of island (Volmer– Weber), layer by layer (Frank–Van der Merwe) or layer followed by island (Stranski–Krastanov) correspond to different kinds of adsorption isotherms. In the full layer growth model (Frank–Van der Merwe), one would expect an isotherm similar to that of the Langmuir isotherm. In the cartoon in Figure 1.10, this would correspond to a full monolayer as in the second drawing from the top. Should additional layers be formed specifically on top, at sufficiently high concentrations or pressures, subsequent Langmuir-type isotherms would come about. It would not be expected that this type of behaviour would proceed beyond many layers unless very specific and strong interactions were at play, though we shall see examples of this in this book.



Figure 1.10 Purely illustrative representations of the three contrasting situations for layer formation on an adsorbent when an adsorpt attaches to it.

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Should the interaction between adsorpt and adsorbent be of lower order to the interactions between adsorbate and adsorpt, islands of material will grow on the initial surface, as indicated in Figure 1.10 in the middle column. It will be appreciated that the number of interactions between adsorbate molecules themselves increases dramatically more than the interactions between adsorbate and adsorbent. Therefore, we would expect Henry-type behaviour with a negative deviation at very low surface coverages.

A combination of the two previous contrasting behaviours is at play in the Stranski-Krastanov type of film growth: the surface has a strong interaction with the adsorbate in the first layer, influencing the manner in which it organises itself in the single molecule thick film. This film interacts with adsorpt so that second layers form, but the interaction of this almost bulk-like second layer is not sufficient to make it adopt the packing of the molecules in contact with the adsorbent. Therefore, islands form on the monolayer with a packing similar to the bulk material.

The preceding discussion demonstrates that the result of adsorption of a molecule onto a surface and its subsequent organisation when more of the same molecule deposits on the surface will depend on the relative strengths of interactions between all the components of the system: surface, adsorpt, and overlayer medium. Indeed, the relative orientation of the adsorbate on the surface will be determined by the strength of interaction between the two in one orientation or another and the strength of interaction between the adsorbate molecules themselves. A strong adsorbate–adsorbate interaction (compared with adsorbate–adsorbent) can lead to a perpendicular arrangement of the molecules (Figure 1.11, top). If the surface. The situation is complicated further in solution, where the adsorpt is solvated prior to adsorption and likewise the surface (Figure 1.11, bottom). Thus, the relative interaction of the medium with both components plays a determining role in the formation of any layer.⁵²

Up to this point, equilibriums have been inferred, and, therefore, clearly we are dealing with situations where molecules are weakly bound—physisorbed—to the adsorbent. Under these conditions, the system reaches equilibrium rapidly, because the molecules diffuse with ease over the surface, and the desorption energy is low, in the region of 20–90 kJ mol⁻¹. Therefore, the molecules can be in a state of flux within the plane of the surface and can even de-adsorb and re-adsorb. On the other hand, when chemical bonds are formed (more or less reversibly), the energy associated with de-sorption is often considered to be in the range 100–400 kJ mol⁻¹, so molecules are much less mobile at room temperature and below. These cases will be discussed individually in the forthcoming sections, but some consideration is important at this point.

The chemical bonding between adsorbate and adsorbent determine many of the characteristics of the systems, and broadly they can be grouped into two classes: physisorbed and chemisorbed. In the following sections, these two classes of monolayers will be discussed in turn, but the general



Figure 1.11 The interactions and relative orientations of molecules on surfaces in a gas or vacuum (top) or in liquid solution (bottom).

characteristics are summarised in Figure 1.12. Broadly speaking, chemisorbed systems are robust and have the organisation of the molecules determined by specific bonds between adsorpt and adsorbent. While this type of layer is referred to as "self-assembled", it is in fact physisorbed systems that are much closer to what a supramolecular scientist might consider as such. The weaker interactions between adsorbent and adsorpt mean that structures that are generated are much closer to equilibrium. To emphasise this point, consider that the sizes of the domains (the areas with a certain type and orientation of structure) are usually much bigger in physisorbed systems. There is clearly a very thin line between what one might consider a chemisorbed or physisorbed species. For the purposes of this monograph, each system has been classified according to the reversibility of the adsorbate-adsorbent bond. If it is clearly reversible, the system will be considered physisorbed, despite the nature of the adsorbent.[‡]

There is an often quite heated debate as to what exactly is meant when referring to as a "self-assembled monolayer" (a SAM). Here, the term is used in its broadest sense, and no distinction shall be made into systems that are very close to or conversely far from equilibrium and dominated by kinetic factors, such as reactivity or mass transport. The variation of the relative

[‡]One might consider that a metal adsorbent always forms chemisorbed systems with organic adsorpts because of the strength of the bonds between them, but many of these systems are dynamic with no specific metal-adsorbate bonds, and the adsorbate can be desorbed intact.

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Figure 1.12 Some general characteristics of physisorbed and chemisorbed monolayers.

dominance of kinetic and thermodynamic factors can lead to a variety of structural outcomes. These can be controlled through temperature, adsorpt concentration and medium control.⁵³ While it is still complex to predict the behaviour that molecules have when they self-assemble at surfaces, it is important to be aware that, just as in solution, the assembly can be influenced by modulating these parameters for both physisorbed and chemisorbed systems.

The nature of the substrate—monocrystalline, polycrystalline or amorphous—also has a determining influence on the organisation of matter adsorbing at its surface. One might assume that order begets order, and disorder begets chaos, yet this extrapolation is not general. As shall be seen throughout this book, it is often true that crystalline layers of materials can be formed on monocrystalline substrates, but disordered layers are also frequent. A poorly-organised surface can lead to well-ordered overlayers if there is no strong interaction between the two materials. It is true that defects in surfaces can be translated into monolayers.

Crystalline surfaces with long range order are often the ideal place to look precisely at supramolecular phenomena because they can be extremely well defined which leads to huge simplifications when determining the structure of adsorbed molecules at the surface. The crystal face that is exposed to the



Figure 1.13 A schematic drawing of atoms in a face-centred cubic crystal exposing (111), (110) and (100) faces, with the unit cells of each surface indicated, and the dark lines indicating the edges of the crystal.

medium and to which adsorption takes place can be very important in determining what molecular organisation assembles at the surface of the material. The nature of the surface can be smooth, stepped, or corrugated. The smoothest surface of face-centred cubic metals, for example, is the (111) plane (Figure 1.13), of which a lot will be said during this book. The notation (111) refers to the Miller indices that indicate how the plane crosses the main axes of the crystal. Because it is the smoothest surface, it is also the most stable, since all surface atoms are surrounded in the plane. It has trigonal symmetry. Figure 1.13 shows this plane in a hypothetical object that also exposes the (100) surface (that has square symmetry and can be seen as a simple translation to a plane above the main cubic plane) and the (110) plane that is corrugated and has a rectangular unit cell with rows of atoms running along one direction. It is useful to remember these structures, as they are by far the most common in studies of self-assembled monolayers on metals. Apart from these very simple cases that suffice for our purposes, here, the surfaces of crystals can contain varying amounts of kink sites and atomic steps are defined by the Miller planes. A useful tool for visualising the different surfaces of crystals can be found at: http://surfexp.fhi-berlin.mpg.de/.

When a second material is deposited on the crystalline face of an adsorbent, the adsorbate can have its packing dictated by the surface. If the crystal structure is the same (as it can be in the case of certain metals deposited on other metals) then the growth is said to be *pseudomorphic*. In this case, the lattice parameters and crystalline orientation of adsorbate and adsorbent are the same. Molecules cannot take on the structure of metals, for example, but their packing can be influenced, with preferred orientations and distances between molecules different from the bulk. In this case, we can talk of *epitaxial growth*. The name epitaxy is derived from *epi* and *taxis* in Greek, meaning "above" and "in ordered manner", respectively. The adsorbent forces the adsorbate to adopt a structure that is not its preferred one as a pure material. A monolayer of a molecular material on a crystalline substrate is said to be *commensurate* when epitaxial growth leads to formation of a multilayer on a crystalline substrate where the new surface takes on the registry of the "template" surface. If the lattice positions of adsorbent do not match the adsorbate but the latter still has a preferred orientation, epitaxial growth takes place, but the nature is incommensurate. For all the examples in this book, we are dealing with *heteroepitaxy* where the deposited material and substrate are different.

The concepts of epitaxy and commensurate growth can apply to molecular layers formed under a variety of conditions, from ultrahigh vacuum (UHV) through different kinds of deposition—notably molecular beam epitaxy (MBE) where chemicals are sublimed onto the adsorbate—to solution state adsorption and electrochemically-grown films. The origins of epitaxial growth lie in the formation of inorganic and metallic films of compounds. Precise information on the growth modes of organic thin films was first developed using the MBE technique.⁵⁴

To understand commensurate structures in terms of molecules on surfaces, a couple of examples are called for. The first that has been chosen is that of *N*,*N*'-dimethylperylene-3,4,9,10-bis(dicarboximide) (DM-PBDCI) when adsorbed onto different crystal faces of metallic silver.⁵⁵ This case also shows how the surface to which an adsorpt attaches can influence dramatically the structural outcome (and as a consequence the eventual properties). Consider the layer of the DM-PBDCI molecules on an Ag (110) surface, shown in cartoon form in Figure 1.14 at the top. It is immediately obvious that the long molecular axis is perfectly perpendicular to the silver atom rows of this corrugated surface. Furthermore, the oxygen atoms of the adsorbate are located over silver atoms in the rows, as are the central bonds of the naphthalene residues. One could draw a unit cell on these molecules that would coincide with a multiple of the unit cell of the silver surface exactly, and therefore the structure is commensurate. The structural outcome of adsorption onto the Ag (111) crystal face is quite different: inspection of the lower cartoon in Figure 1.14 will make clear that the symmetry of the adsorbate packing and its unit cell cannot be brought to coincide or put into register with the metal underneath, and therefore an incommensurate structure is formed.

More than one commensurate structure can be formed by a given molecule on a given adsorbent. A fine example is that of coronene on gold (111).⁵⁶ When this compound was physisorbed from heptanoic acid at relatively high concentration (8×10^{-6} M), a regular dense hexagonal packing of the compound was observed, with a separation between the centres of the molecules of approximately 1.19 nm (Figure 1.15). This distance is in accord with a dense hexagonal packing matching the symmetry of the adsorbent, with the molecules spaced every fifth gold atom in each symmetry direction. Lowering the concentration to 3×10^{-6} M resulted in a more open structure (described as epitaxial) with the molecules located every sixth gold atom (with a distance of 1.45 nm between the centres of the molecules), a structure



Figure 1.14 The packing of the commensurate phase of DM-PBDCI on Ag (110) at the top (the repeat spacings of the molecules coincide with the same symmetry points on the surface), and below the incommensurate packing of the same molecule on Ag (111) (where the unit cell of the molecule does not match in any way that of the substrate).



Figure 1.15 Representations of the three commensurate packing arrangements of coronene on an Au (111) surface when physisorbed from heptanoic acid at different concentrations or treatments. Top left, the hexagonal dense-packed phase. Top right, the hexagonal loose-packed phase. The dots represent the centres of the gold atoms.

stabilised by the solvent that is co-adsorbed to the gold surface, rather like a crystalline solvate in bulk crystals that might be familiar to the reader. When the low density phase was exposed to additional solvent (or sometimes when more dilute solutions were used), a third structure was formed—also hexagonal in line with the adsorbent symmetry—but with three molecules per unit cell, as shown schematically in Figure 1.15 below the other two structures. The difference in energy between the two structures was assigned to surface–solvent and coronene–adsorbed solvent interactions, since the coronene–gold interactions must be practically identical in the two phases.

The reason that molecules can have a preference for the formation of commensurate epitaxial monolayers is the gain in potential energy that the system has when the adsorbates are located at preferred adsorption sites on the surface.⁵⁷ It is clear that any particular surface will have a potential energy map that effectively acts as a template for the adsorbed molecule to locate itself in, a local energy well. Provided that the interaction between molecules is not sufficient to overcome this energy—usually the case when

the molecules lay flat and provided the interaction between the edges of the molecule are not strong—the adsorbates will arrange themselves into the most favourable situations for a given density of molecules on the surface, as we saw in the previous example.

Polymorphism—the formation of two or more solid forms with different crystal structures—is abundant in monolayers and thin films formed on adsorbents by molecules, just as it is in the solid state for molecular materials.^{58–61} The previous examples show different structures that may come about because of the coverage of the surface by the adsorbate. But even under apparently identical conditions, thin films can grow with polymorphic character. Epitaxial films of pentacene 30 nm thick grown on a Cu (110) surface show two types of packing in different experiments (Figure 1.16).⁶² In the standing up form, a herringbone-type packing is seen with an angle of 3° in-between the plane perpendicular to the surface and the long axis of the molecules. In the polymorph, where the angles formed between the molecules and the lamellae they form are larger, the long axis of the pentacene is parallel to that of the surface. This result is of importance because such a subtle change in angle can change the overlap between the π orbitals in the material and therefore its properties. These forms are a result of a delicate balance in the non-covalent interactions taking place at the interface of the metal and organic systems, and the polymorphism manifests itself because of kinetic factors during the growth of the films where the pentacene has a certain flexibility in the π stacking interactions it can form with itself. It is a good example of how a surface can influence the packing of molecules in a supramolecular fashion. Therefore, metastable phases—those that are not at the absolute thermodynamic minimum-can exist in mono- and multilaver growth.

A recurring theme in surface supramolecular systems is that of chirality,⁶³ which is of interest regarding the preparation of chiral materials⁶⁴ and has



Figure 1.16 Representations of the polymorphic forms of pentacene on a Cu (110) surface. On the left is the standing up conformation viewed parallel to the copper surface and on the right is the packing parallel to the surface viewed from the direction perpendicular to the plane.



Figure 1.17 Cartoons showing the formation of chiral lines of prochiral objects (that can appear as an L or an r on the surface) on a (110) crystal face, and the mirror plane that relates them.

even been inferred in the origins of natural homochirality.⁶⁵ Even achiral molecules can adsorb to achiral adsorbents to give chiral structures, with the proviso that the adsorpt is prochiral. The origin of this emergence of chirality is the angles that are formed between the molecules and the symmetry axes of the underlying surface (Figure 1.17). In the case of chiral molecules, this leads to an intrinsic preference for one chirality or the other, while for achiral molecules, the local chiral chance preference can be propagated through lines (as in Figure 1.17) or to complete domains. Single molecules of cysteine adsorbed onto a gold (110) face show the kind of three-point interaction that can give the L or r shape shown in Figure 1.17 at the single molecule level.⁶⁶ There is a hierarchy of levels in the formation of chiral monolayers, ^{67,68} from the single molecules that are chiral at the surface or can form diastereomeric conformations if intrinsically chiral, to the domains, to the surface as a whole. The only way at present to have a homochiral surface is through the use of intrinsically chiral molecules.

The reason that chirality has a special significance in surface chemistry in general is the reduced symmetry operations available when compared with three-dimensional crystals.^{69,70} Molecules restricted to a plane have considerably fewer possible packing arrangements than in three-dimensional crystals. There are fewer 2D space groups: 17 compared with 230 for 3D, but the proportion is similar. Five of the 2D space groups are chiral when laid on a surface (while in 3D there are 65 chiral space groups), that constitute about 29 and 28%, respectively.⁷¹ But the real key is the symmetry operations available for packing on a surface, because an adsorbate on a surface cannot be related to another by inversion symmetry. Similarly, the glide plane parallel to the surface is not likely. The nature of the surface and molecular orientation provide more specific restrictions.⁷² This fact was demonstrated

in dramatic fashion in the construction and analysis of a particular subset of monolayers that showed a dramatic preference for the *p*2 space group.⁷³

The atoms on a crystalline surface of an adsorbent are not necessarily totally immobile, but can move slightly to remove surface stress experienced by the atoms if the crystal face has a particularly high energy or if there is a strong interaction between adsorbate and the surface atoms.⁷⁴ This situation is particularly true for metal adsorbents, and especially for crystal faces with more open structures. Following on with the topic of chirality to give an example, when tartaric acid adsorbs onto an Ni (110) crystal face, bis-tartrate is formed, which makes a highly strained complex with four nickel atoms.⁷⁵ The interaction between the Ni atoms and the OH groups of the adsorbate causes a distortion of the molecular skeleton and the Ni atoms bonded to it are twisted and pulled apart resulting in a chiral surface structure (Figure 1.18). The strong bonds between adsorbate and surface if an ordered monolayer is formed.

Should crystalline monolayers of adsorbate be formed, the size of the crystalline domains is an important characteristic of the overall surface. The minimum in energy, assuming an optimal packing match between adsorbent and adsorbate, will comprise a single crystalline surface domain. This situation has not been reached in molecular systems: domains of differing sizes are seen, and therefore the surface is polycrystalline, irrespective of the nature of the adsorbent mostly. Just as bulk crystals can undergo Ostwald ripening, so do "two-dimensional crystals". The phase boundaries are minimised in order to minimise the energy of the system. This phenomenon was shown in alkyl derivatives of anthraquinone and octathiophene adsorbed on graphite from solution,⁷⁶ where domains with edges tens of nanometres were seen to disappear at the expense of larger domains on a timescale of less than a minute! Subsequently, this effect has been shown to be general, though the timescale depends on the temperature and the strength of the molecule–surface interaction.



Figure 1.18 The adsorption configuration of (S,S)-bis-tartrate on Ni (110). The cartoon on the right shows the restructuring of the metal surface atoms to adapt to the strong coordination bonds.

For polycrystalline surfaces—where areas of crystalline material, each of them oriented in a random manner, make up the surface—the adsorbate can follow the same kinds of adsorption as for crystalline materials. In the case of epitaxial growth, the adsorbent crystallites in each area will dominate the packing, especially at low temperatures. However, for incommensurate films or those where epitaxy is lacking totally, the crystal domains can be bigger. Returning to pentacene on copper (which was discussed above, see Figure 1.16), for the polycrystalline metal surface, the nature of the epitaxy and adsorbate crystallite size depend on the temperature at which the surface is held.⁷⁷ At higher temperatures (333 K), crystallites of the organic molecule are over 100 nm long, but at the same time, polymorphism is again evident. At 77 K, long range order is not present in the film. As we have discussed for Ostwald ripening, heating (during deposition or postdeposition annealing) can influence greatly the quality of self-assembled monolayers, both in terms of adsorbate and adsorbent. This has been demonstrated, for example, in the case of monolayers of thiols on gold where the surface was annealed to give the flat metal⁷⁸ or in the preparation of silane layers on silicon oxide on silicon where increasing the temperature during deposition increases greatly coverage and molecular order.⁷⁹

An emerging area of great potential is that of what has been termed organic-organic heteroepitaxy or "weak epitaxial growth"⁸⁰ (WEG) of organic materials on organic surfaces (that are themselves surface-supported, Figure 1.19). Layers of iron porphyrins on a phthalocyanine⁸¹ proved the idea that matching of packing types of aromatic compounds could lead to heterostructures.⁸² This kind of organic-organic heterostructure is of interest for the preparation of materials with a variety of properties.^{83,§} Some examples of supramolecular influence in this kind of directed growth will be



Figure 1.19 The principle of organic–organic heteroepitaxy or weak epitaxial growth. The purely hypothetical molecules in the first layer on the substrate are ordered and induce epitaxy in the (equally hypothetical) second layer, and subsequent ones.

[§]While the idea of organic–organic heteroepitaxy and heterostructures is not general, one could extend this idea to molecule–molecule heteroepitaxy and heterostructures to include all kinds of coordination molecules, organometallics and clusters.

shown in Chapter 7, although the use of non-covalent bonds to direct specifically and selectively is underexploited at present.

Amorphous adsorbents—such as glasses or amorphous silica—will usually result in the growth of poorly structured layers of adsorbate when compared with flat crystalline substrates. As far as applications of films go, however, that characteristic can be irrelevant: consider the coatings of glass, silica support materials for chromatography or treated textiles. Many of these rely on chemisorbed molecules that have a function as the new surface of the material. However, if the interaction between the adsorbent and the adsorbate is weak, the non-covalent interaction between molecules on the surface becomes dominant in their organisation. Thus, the π stacking between large flat aromatic molecules can give rise to highly-ordered selfassembled structures, as is the case with certain materials that aggregate on the surface of polymers.⁸⁴ A similar situation arises when the substrate is a liquid, as is the case for Langmuir layers of molecules on water, which will be discussed in Section 1.5. Provided the interactions of supramolecular synthons with the amorphous substrate are weak, the self-association can lead to very ordered systems where the surface merely acts to orient the sample, something absent in three dimensions and an opportunity for the organisation of molecules.

All of the cases of surface-based supramolecular systems can be subject to analysis using phase diagrams, where the layers can change their structure as a function of two principle factors when adsorbate composition is held: temperature and coverage. Returning to the case of tartaric acid on Ni (110), the adsorption phase diagram is shown in Figure 1.20.⁸⁵ At low temperature, the molecules are physisorbed to the surface; increasing the amount of compound on the surface by evaporation merely makes multilayers.



Figure 1.20 An adsorption phase diagram as a function of temperature and coverage for (R,R)-tartaric acid deposited onto a Ni (110) face in vacuum.

At 170 K and above, however, a chemical reaction takes place; hydrogen is lost and the tartrate is formed. The monotartrate is formed only between 170 K and 270 K up to monolayer coverage, and also at 300 K when coverage is high. However, at less than half monolayer coverage, the molecule has sufficient space that the bistartrate form is generated. Thus, structure and bonding are controlled by temperature and coverage.

In the case of adsorption from a solution, the coverage is affected by concentration, and obviously the solvent will play a role in the nature of the layer that is formed. An interesting case in this regard is that of a mixture of triacontane and triacontanol adsorbed onto graphite from different solvents.⁸⁶ Firstly, regarding the phase diagram, it was observed that the two adsorbates form separate domains and have clearly different adsorption energies, and a difference of only 0.5 kcal mol^{-1} is sufficient to generate a 2:1 bias. The solvent is important: phenyloctane allows formation of the alcohol layer predominantly, while incorporation of a different alcohol into the solvent makes adsorption of triacontanol less favourable because it is solvated more favourably. Evidently, changing the proportion of the adsorbates will influence the surface coverage, and it is clear from the results on the system that solution composition does not correspond to monolayer composition when the adsorption energies are different. Another interesting case of solvent effect is that of monolavers of 3,5-di(4-ntetradecyloxyphenyl)pyrazole on graphite. When pure toluene was used as a solvent, rod-shaped molecules were observed with an achiral structure.⁸⁷ On the other hand, the packing of the molecules was chiral when a 1:3 toluene-chloroform mixture was used. More cases shall appear in Chapter 4, although the prediction of how solvent will affect the structure of monolayers remains difficult, and empirical testing is usually required to obtain optimum conditions for monolayer formation.

Supramolecular approaches to assembly on adsorbents very often use neutral components assembled on formally neutral surfaces. However, many surfaces have formal charges, particularly where ionic species are involved and where water is present in the medium, charging can become very important. While a full description is beyond the scope of this text, the importance of charged interfaces is enormous and the science rich: the reader is encouraged to explore more specific texts related to these matters.⁸⁸ When oxides are in contact with aqueous media, their surface is often anionic because of protonation of water. This feature presents an opportunity for the assembly of cationic species on the surface of oxides, as we shall see (particularly in Chapter 6). Mica is another widely used surface that presents a charged surface, where sheets of aluminosilicate are held together by cations in the mineral that is easily cleaved. In an appropriate medium, the cations can dissociate away from the surface leaving a net negative charge locally. Also, charges can be introduced by binding ions at interfaces as well as during electrochemical experiments. Evidently, these polar surfaces cause an electric dipole that attracts oppositely charged ions. In order for adsorption to take place, it is clear that an interchange of counter ions must take place. Formally, the layer of ions linked directly to the bulk material is referred to as the Stern layer, which is regarded as immobile. Counter ions are attracted to the surface by the electric field, but are mobile, and are referred to as the diffuse layer. Together, these areas comprise the electric double layer. This layer can be replaced, taking advantage of strong interactions between surface- and solution-borne counter ions that are drawn to the surface because of their multiply-charged nature or specific bonds. The former corresponds to the layer-by-layer formation of polyelectrolytes and the latter to chemisorption at interfaces.

In the following sections, the general characteristics of physisorption, chemisorption, and assembly at liquid interfaces shall be discussed, to provide the reader with an initial understanding of the characteristics of each class of system.

1.3 Physisorption

When molecules bind reversibly to an adsorbent—and can diffuse freely over it without the formation of significantly strong bonds-the adsorbate is considered to be physisorbed. The general characteristics have been compared and contrasted with chemisorption in Figure 1.12. The energy of sublimation (typically considered to be approximately 20–90 kJ mol⁻¹) of a molecule adsorbed onto the surface in question is of the order of that required for the breaking of typical non-covalent interactions. Particularly, van der Waals interactions are very important in determining whether molecules will physisorb to a surface or not. This reversible attachment of molecules to a surface—which is a general phenomenon—can be made specific through the use of non-covalent interactions between adsorbate molecules. Classic examples are alkanes and their derivatives adsorbed onto graphite-like materials. Here, the methylene groups of the aliphatic component form van der Waals interactions (of the $[C-H \cdot \cdot \pi]$ type) with the surface where there is near perfect registry for a commensurate epitaxial layer.⁸⁹ The all trans conformation of the alkanes is preferred, with each alternate methylene hydrogen atom interacting with neighbouring six membered rings in the graphitic surface (Figure 1.21). Typically, the alkanes are surrounded by their like neighbours generating close packed lamellar-like structures. Submonolayer coverages do not habitually show ordered material (except at very low temperatures) because diffusion takes place. Clearly, the larger the molecule, the more interactions that can take place, and the adsorption enthalpy increases while the entropic importance of liberating any adsorbed solvent or gas molecules at the surface is considerable. This strategy can be exploited to adhere individual molecules to a surface in solution. The tetrathiafulvalene derivative in Figure 1.21 adsorbs onto graphite from solution to give not only close packed layers but also individual molecules adsorbed onto the surface.⁹⁰ The adsorption is favoured by the 72 methylene and methyl groups that anchor the central unit parallel to the graphite surface.



Figure 1.21 The quasi-commensurate arrangement of all-*trans* alkyl chains on graphite showing the hydrogen atoms perfectly located for $[C-H\cdots\pi]$ interactions, and the chemical structure of a tetrathiafulvalene derivative with four octadecyl chains that allow adsorption as an apparently isolated molecule on graphite interfacing with a solution.



Figure 1.22 Part of the two-dimensional metal-organic framework nanocrystals formed by a porphyrin with metallic copper on the (111) surface of gold (these sheets lie parallel to the interface).

The mobility of molecules in physisorbed systems can be very high, especially at low coverages (below a complete layer) but even when complete monolayers are formed. This diffusion is important in the growth of ordered regions of molecules. A beautiful example of this phenomenon is the formation of two-dimensional supramolecular assemblies of metal-organic frameworks based on porphyrins and copper atoms (Figure 1.22) on a gold (111) surface.⁹¹ This study, performed depositing the components under ultrahigh vacuum conditions onto a surface, showed that by varying the deposition rate and the temperature of the gold and measuring the sizes of

the supramolecular grids, the molecular diffusion barrier could be derived. The formation and disappearance of very small aggregates was observed at temperatures below 373 K, showing that diffusion is possible, characteristic of a truly physisorbed system even though it involves a metal substrate, and that Ostwald ripening takes place, for clusters below a critical size.

A particularly elegant example demonstrating molecular diffusion on a surface showed how C_{60} molecules forming a non-covalent chain around the edge of a silver metal island fluctuate in their position over time,⁹² and emphasised the dynamic nature that molecule–metal contacts can have. The amplitudes of the fluctuations in this system are largest in the frequency range of 1.3–105 Hz in the modes resulting from Ag motion and 0.01–0.08 Hz arising from C_{60} movement.

Iust as in the crystallisation of molecular materials in bulk, metastable phases can be formed in self-assembled monolayers, where they are most clearly identified as polymorphs or solvates, as seen for the case of the polymorphs of pentacene earlier. In physisorbed monolayers, where in principle molecular diffusion and reorganisation are facile especially at liquid-solid interfaces, metastable phases present themselves, an example being the compound 3.5-tris(4'-biphenyl-4"-carbonitrile)benzene as shown in Figure 1.23.⁹³ The two structures correspond to metastable phases that upon heating convert into a more dense structure where all the voids are compacted, and all of the inferred interactions between the nitrile groups and the hydrogen atoms attached to the aromatic rings are optimised. In fact, it is probable that the two metastable structures are in fact solvates, where the heptanoic and nonanoic acid used as the solvent are incorporated in the voids, thus explaining the different nature of the voids, whose contents could not be observed in the experiments. This example is a particularly nice one in that the structure of the physisorbed layer was also observed under UHV conditions, and a structure corresponding to the thermodynamic structure from solution was obtained.

Porous materials in bulk form are potentially useful for the physisorption of molecules to the internal surfaces of the materials from the gas phase, and is of special relevance today with the hive of activity related to porous materials derived from molecules, be they based on coordination chemistry^{94–97} or on covalent frameworks.^{98,99} Physisorbed monolayers at interfaces can also form network-like structures with spaces in the layers. Jürgen-Hinrich Fuhrhop championed the idea of "yoctowells"¹⁰⁰ with volumes of 1–10 yoctolitres (1 yL) (10^{-24} L or 1 nm³), and other groups have demonstrated the formation of frameworks by physisorption of disc-shaped molecules, as shown for the formally C_3 symmetric compound in Figure 1.24.¹⁰¹ At the interface between graphite and 1,2,4-trichlorobenzene, this molecule, like others with long alkyl chains, favours interdigitation of the oligomethylene fragments thanks to their alignment and quasicommensurate layering on graphite and the dispersion interactions between them. The open structure only covers the surface after heating to 353 K (at a concentration of 2.87×10^{-5} M), after which a highly ordered layer with very



Figure 1.23 The two-dimensional metastable phases of the compound shown at the liquid–graphite interface, with the unit cells of the structures indicated. The top structure corresponds to that from heptanoic acid, and the bottom one to nonanoic acid.

few domain boundaries exists. The spaces in the layer are occupied by solvent molecules. At room temperature, the vast majority of the monolayer comprises the lamellar structure that is densely packed. Interestingly, the lamellar phase does not have all the alkyl chains adsorbed to the graphite, and they are presumed to be solvated above the layer, a not uncommon situation in this kind of physisorbed system where dense packing can be achieved without part of the molecule. The inter-conversion between the two phases can be performed reversibly by raising and lowering the temperature, showing a true thermodynamic process. An analysis of the changes of coverage with concentration and temperature showed the importance of both entropy and enthalpy in determining the relative coverage, and pointed to a



Figure 1.24 Representations of two phases formed by the C_3 symmetric molecule on graphite at its interface with 1,2,4-trichlorobenzene. Higher temperatures favour the porous phase while the lamellar structure is predominant at room temperature. Note that in the lamellar form, the grey alkyl chains represent those not adsorbed to the surface, and probably solvated above the layer.

significant entropy gain upon desorption of the adsorbate thanks to the degrees of conformational freedom it gains upon dissolution. At a lower concentration $(2.30 \times 10^{-4} \text{ M})$, the equilibrium is shifted toward the porous phase, that occupied more than half of the interface (while at higher concentration, less than 10% was present), showing how the nature of the supramolecular can be influenced by parameters commonly used in studies of self-assembly in solution.

Reversibility and therefore the thermodynamic effects associated with it are the hallmark of physisorbed layers. While metastable systems are formed, annealing can interconvert surface-based structures. When there is a very strong bond in-between adsorbate and adsorbent, the situation is quite different.

1.4 Chemisorption

Specific strong bonds between a surface and an adsorbed molecule lead to robust chemisorbed structures that are usually very different to physisorbed systems both structurally and chemically. On the one hand, chemisorption tends to produce structures which are to a large extent imperfect because the outcomes of adsorption are determined kinetically, predominantly. Once a strong bond between surface atoms and an adsorpt is formed, there is generally little movement of one with respect to the other. On the other hand, these monolayers are far more robust than physisorbed layers precisely because strong bonds unite adsorbent and adsorbate. Because of the very localised bond that links the two, and its geometric restrictions, the orientation of the molecule can be in any direction, allowed by the conformations of the bonds in the rest of the adsorbate molecule. At low coverages, most adsorbates would tend to interact weakly with the surface in a non-covalent manner away from the point of strong bond formation. In other words, the part of the adsorbate away from the point of covalent attachment is "physisorbed", meaning it can be mobile, although it can't escape to the surroundings, it is anchored. At low temperatures, this part of the molecule may be slumped next to the connection point. But at high coverages, the molecules would tend to align perpendicular to the plane of the surface of the adsorbent so that the maximum number of strong bonds can be made by the surface atoms of the adsorbent.

During the chemisorption process, the first step is usually considered to be physisorption where the molecule adheres to the surface but is able to diffuse in the plane to a degree determined by the substrate temperature (Figure 1.25).¹⁰² This situation is clearly witnessed in the case of molecules adsorbed onto surfaces from the vapour state under vacuum conditions. A paradigmatic case is that of alkanethiols on gold, where the compounds physisorb (they have a vaporisation enthalpy 20% greater than their bulk values) with an enthalpy of the order of 6.1 kJ mol⁻¹ per methylene unit, with a physisorption enthalpy of 33 kJ mol⁻¹ from the thiol group.¹⁰³ The chemisorption enthalpy is 126 kJ mol⁻¹ regardless of chain length



Figure 1.25 The processes leading to chemisorption.

and activation energy is approximately 29 kJ mol⁻¹. Therefore, for chain lengths longer than fourteen carbon atoms, the physisorption enthalpy is higher than the chemisorption enthalpy. Thus, detailed studies of these processes paint a precise picture of how molecules adhere to surfaces.

The magnitude of interaction locally is determined by the strength of the chemical bond between adsorbent and adsorbate. The bigger the molecule gets, provided there is one anchoring point, there is little influence on the local interaction energy between adsorbent and adsorbate, as was mentioned for the case of thiols on gold. Non-specific van der Waals interactions will increase the overall adsorption enthalpy for larger molecules though. There will also clearly be kinetic effects on the growth of the layer, because of the slower diffusion of the molecules.

The most frequent cases of chemisorbed molecules are those involving the bonding of organic molecules to metals, inorganic semiconductors or their oxides, and they are the basis of the development of a variety of selfassembled monolayers¹⁰⁴ with a gamut of processing methods.¹⁰⁵ The bonding is typically fully covalent, between oxygen or carbon atoms of the adsorbate and the surface atoms most commonly, or is essentially covalent through coordination between heteroatoms and inorganic surface atoms. Two examples are shown in Figure 1.26, the first layers of thiols on gold and the second siloxanes on silicon oxide. The latter are particularly common because of the ease of preparing this oxide on silicon wafers. Self-assembled monolayers are often distinguished from systems that are grafted covalently-through carbon-carbon bond formation for instance (Figure 1.26)—because in SAMs, non-covalent interactions influence film structure greatly. Yet both involve an adsorption and a covalent bond formation between substrate and "chemisorpt", the molecule that attaches to the surface. Grafting organic compounds to organic materials, organic layers or inorganic materials^{106,107} (Figure 1.26) normally implies a limited influence of non-covalent interactions during the film formation. Grafting is a term used especially when polymers are formed on surfaces.^{108,109} That said. "self-assembled layer" and "grafted layer" are sometimes used interchangeably, but all agree the films are chemisorbed! Whether non-covalent interactions play a large role in the adsorption or not, the surfaces that result can clearly be of interest from a supramolecular perspective.



Figure 1.26 Chemisorbed monolayers of organic compounds to the surfaces of oxides (silicon oxide is shown), metals (for thiolates on gold) and organic surfaces where the term "grafting" is used frequently. The grey shaded region indicates the covalent bonds that are created during chemisorption.

The tremendous advantage of chemisorbed layers, when compared to physisorbed layers especially, is their robustness. The stability of the films provided by the chemical bond between adsorbate and adsorbent often makes the films cleanable, manipulable in air, and they can be taken between different analytical characterisation methods without a need for vacuum transfer techniques. The chemical and thermodynamic stability also makes chemisorbed layers more suitable for incorporation into useful products. In addition, the surfaces can be built using covalent or noncovalent assembly. An early example of this approach that has been exploited widely is the chemisorption of a siloxane bearing a terminal amino group in its "tail" (the now commercially available 3-aminopropyltriethoxysilane) to a laver of silicon oxide on silicon (Figure 1.27).¹¹⁰ This work showed many interesting features of the formation of the layers, and came up with an ingenious way to avoid the formation of particulate silicates that can arise in solution treatments: the substrates were placed in an inert atmosphere with refluxing toluene or xylene solutions of the siloxane, that gave a smooth monolayer thanks to the low vapour pressure of the adsorpt in this mixture. Furthermore, the reaction of the amine group in the resulting monolayer was transformed using a number of reagents, building up grafted levels on top of the initial one. This possibility is available because of the stability of the bonds between the surface and initial adsorpt.

Of course, chemical bond forming reactions on the surface of silica and other hydroxyl terminated supports including different varieties of polymers, natural and not, are responsible for the application of certain particles for biological separation and studies,^{111,112} chromatography of different types,¹¹³ solid phase synthesis¹¹⁴⁻¹¹⁶ in chemistry, and the modification of surfaces for improved adhesion.¹¹⁷ An early example of the "insolubilisation" of a catalyst is the functionalisation of glass beads with 3-amino-propyltriethoxysilane. Reaction with 4-nitrobenzoic acid and formation of the diazonium salt gave a surface that was reacted with an alkaline phosphatase enzyme that provided a material that maintained the catalytic



Figure 1.27 The chemical steps leading to the functionalisation of semiconductor surfaces by chemisorption of a siloxane followed by covalent modification.

activity of the biological compound.¹¹⁸ A nice example of the supramolecular immobilisation of a functional unit is the binding of iron porphyrins to silica gel particles functionalised with a siloxane bearing an imidazole group: the resulting material is reversibly bound oxygen.¹¹⁹ Carbon monoxide was also proven to be bound. The surface configuration of the iron porphyrin prevents the dimerisation of the system that leads to decomposition in solution in an atmosphere containing oxygen, demonstrating the special properties of the interface.

Often, the function of surface-modified solids requires that the reactive groups are separated from the substrate so that they end up in a solvated situation—for example in the use of polymeric supports for solid phase synthesis—and are therefore immobilised but in a liquid environment. Similarly, the grafting of polymers on surfaces is a noteworthy activity^{120,121} but only certain examples of special relevance to supramolecular surface effects will be given in this text. Rather, emphasis shall be given to systems where the proximity to the interface provides an insight and application that are not necessarily evident in solution.

A nice example of the incorporation of supramolecular ideas into functional self-assembled monolayers is the preparation of a caesium sensor on gold-coated microcantilevers.¹²² The monolayer formed on the gold was made by co-depositing 1,3-alternate 25,27-bis(11-mercapto-1-undecanoxy)-26,28-calix[4]benzocrown-6 (the selective ion binding component) and decane-1-thiol (Figure 1.28). The alkyl thiol was added to ensure a dense monolayer and so as not to interfere with the binding site of the crown ether. Microcantilevers can be used generally for the detection of analytes because they undergo bending—that can be detected optically—because of the binding of molecules or ions to the layer that generates in-plane stress.^{123,124} In this case, deflection of the device is caused by the binding of the caesium ion in solution, and a deflection is clearly seen at 10^{-10} M, three orders of



Figure 1.28 A self-assembled monolayer that senses caesium selectively, as shown by the deflection of the cantilever to which it is attached. Reproduced from ref. 125 with permission from the Royal Society of Chemistry.

magnitude before potassium ions are detected clearly. While the achievement is remarkable, and the approach quite universal,^{125,126} it is generally true that these studies are focussed on the functionality of the device, and in the sensor area by and large the precise nature of the monolayer is not studied in depth. After all, the application matters. However, notice that in Figure 1.28 the thiol is still intact on the gold, something that today would be ascertained precisely using analytical techniques to ensure film structure. And the structure under different processing conditions can lead to different properties: durability, and so on. That said, the detection of nerve agents using the complexation of copper(π) to a cysteine monolayer on gold to detect dimethyl methyl phosphonate from a concentration of 10^{-15} M shows the power of the technology.¹²⁷ It is hard to imagine a solution-based recognition method that could provide this sensitivity, showing the huge potential of interfaces for sensing and based on the robustness of chemisorbed monolayers.

1.5 Assembly at the Surface of Liquids

The spontaneous formation of supramolecular systems at the interface between liquids and other media is perhaps the most intuitive and general assembly method for molecules. The overriding requirement of the molecular components is that they are poorly soluble in the liquid(s). The main driving force is the assembly of the surfactant-called so because it affects the surface tension of the liquid-at the interface between the two media because of the ability of *part* of the molecule to interact strongly with at least one of them. If the surfactant is applied to water, the most common case with this kind of film, it can be done in a solvent that is lost through evaporation from the interface into the bulk phase, usually to the air that is over the water. A drop of soap on an oily water surface causes an instantaneous change in the appearance of the liquid-air interface. Therefore, the assembly of molecules at the surface of water should have been noticed by the majority of the people reading this text! Indeed, it was in experiments on oil on water systems performed by Agnes Pockels^{128,129} then by Lord Rayleigh¹³⁰ and Henri Devaux¹³¹ that were later recognised by Langmuir in his historic paper in 1917.¹³² In this paper, it is pointed out that castor oil begins to have an appreciable effect on the surface tension of water "when it is in sufficient quantity to form a layer 1.3×10^{-7} cm thick". That is, 1.3 nm, the thickness of a single molecule, as pointed out by Devaux who also observed the formation of monolayers on mercury. In many ways, these results have led the way to nanoscience, as shall be detailed in Chapter 3.

Liquid surfaces present a completely different environment for noncovalent interactions when compared with solid substrates.¹³³ Apart from the huge mobility of the surface atoms compared with other substrates, an adsorbate can enter into the liquid—affecting directly its surface tension and can be solvated by it. Thus, the interface region is potentially wider than for an adsorbate–solid interaction and the number of interactions are greater, if not very strong or directional. The reason that water is so effective for the formation of layers of organic molecules is the hydrophobic effect coupled with the lower density of organic materials that means they can be manipulated at the water surface (they do not sink). The formation of layers at the air-water interface has also been studied most widely because of the tools available to "see" formation of films as well as the possibility of transferring these assemblies onto solid surfaces from the liquid, mainly based on simple optical methods (see Chapter 3). From its beginnings where the formation of layers could be studied in relative detail for molecule-thick films, the study of molecular systems at the surface of water has implications ranging from the origin of life to new materials for nanotechnology.¹³⁴

The apparatus that today we call the Langmuir trough is the tool that allows precise measurement of the formation of molecule-thick layers on water.¹³⁵ The original drawing of the equipment is shown in Figure 1.29. Habitually, the layer-forming molecule is deposited in a suitable solvent on the dust-free surface of water (the dust would cause imperfections in the film) with the two barriers far apart, and the solvent is allowed to evaporate. The mobile barrier (A in Figure 1.29) is moved so that the surface area available to the sample is reduced, until a monolayer film is formed.



Figure 1.29 Diagram showing the Langmuir trough from the original paper in 1917, where T is the enamel tray container (60 cm long and 15 cm wide), K a knife edge lying on a glass plate G, attached to a support (S). Glass rods (R) attached to the knife edge extend down and pass through holes in a paraffin-coated paper strip (B) that is on the surface of the water. Treated paper strip A is a mobile barrier.Reprinted with permission from ref. 135. Copyright 1917 American

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