

# Supramolecular Chemistry at Surfaces

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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 Saletta, 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
$\mu$ CP	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*

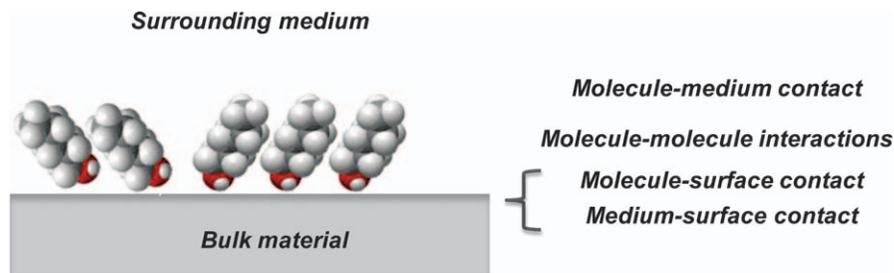
## 1.1 Introduction

The non-covalent bond is omnipresent in molecular systems at surfaces and the frontiers between materials in general.<sup>1–5</sup> 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,<sup>6–11</sup> 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.<sup>†</sup>

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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<sup>†</sup>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.

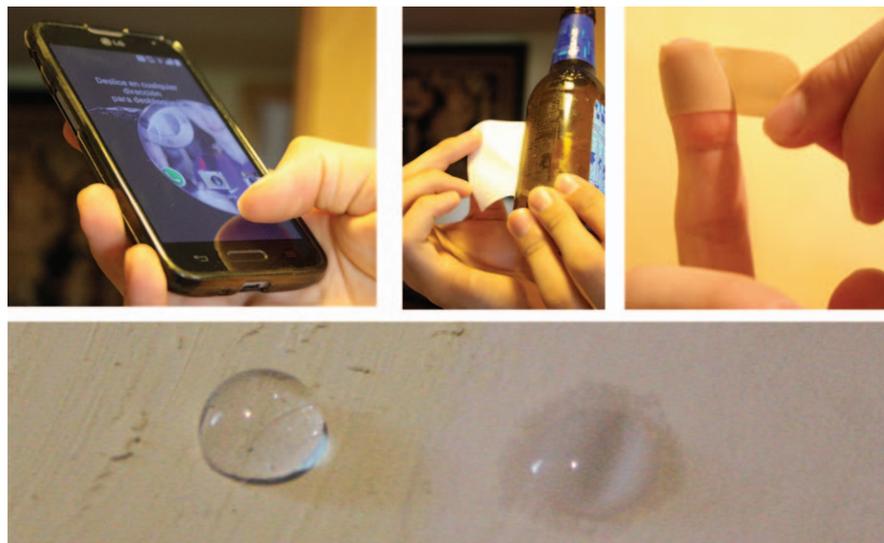


**Figure 1.1** Molecules at surfaces and the frontiers between the components of the system.

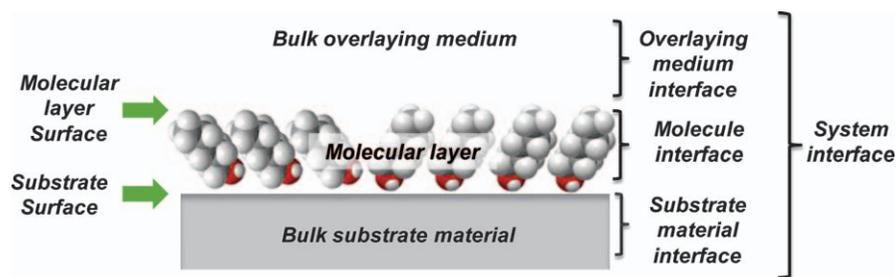
all its guises as a system, a whole rather than a sum of parts. The chemical characteristics of all components of the system can influence dramatically the relative importance of any particular non-covalent interaction. There is also the case where the surrounding medium contains other molecules capable 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.<sup>12</sup> 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.<sup>13</sup> 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.<sup>14</sup> A recent book discusses in detail the fascinating topic of biointerfaces.<sup>15</sup> 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<sup>16,17</sup> 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.

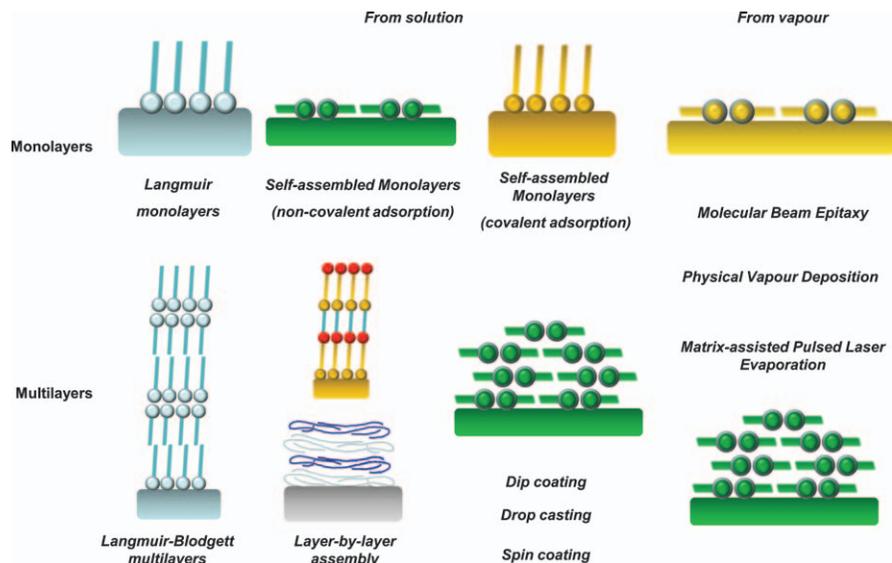
and even the region immediately below the surface of a material is not representative of the bulk, especially in the case of liquid systems or metals, for example. When considering phenomena such as the reflection light from solid materials or the properties of conductors or magnets near their surface, 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,<sup>18</sup> 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 self-assembled 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*,<sup>19</sup> 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 monolayer films from non-polar liquids was established.<sup>20</sup> 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 water<sup>21</sup> and multilayers by transfer from it,<sup>22,23</sup> 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.

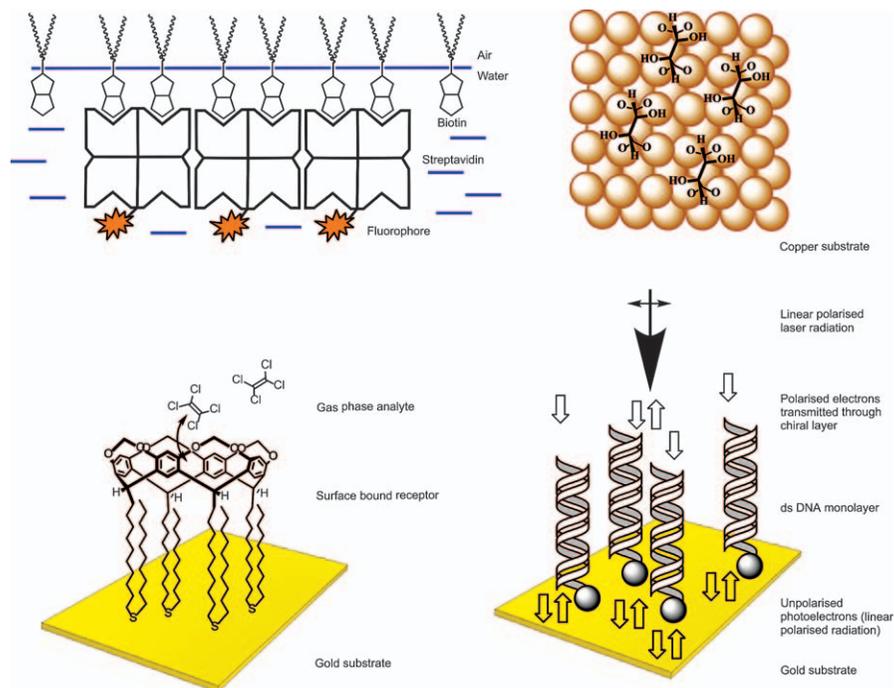
Building on the shoulders of the pioneering scientists working on adsorption at surfaces and those of the founders of supramolecular chemistry,<sup>24–26</sup> the development of supramolecular systems at surfaces has been spectacular in recent years. It is a truly interdisciplinary area with multiple 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;<sup>27</sup> observation of reactivity of single molecules on surfaces;<sup>28</sup> the proof of spontaneous symmetry breaking on a surface;<sup>29</sup> the measurement of conductivity through single molecules,<sup>30</sup> and the self-assembly of single molecule magnets on surfaces.<sup>31,32</sup>



**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.<sup>33</sup> 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).<sup>34</sup> 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.<sup>35</sup> 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.<sup>36</sup>



**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 air-water 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”,<sup>37,38</sup> 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.<sup>39</sup> 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.<sup>40</sup> 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,