

Monolayer self-assembly at liquid–solid interfaces: chirality and electronic properties of molecules at surfaces

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Abstract

The spontaneous formation of supramolecular assemblies at the boundary between solids and liquids is a process which encompasses a variety of systems with diverse characteristics: chemisorbed systems in which very strong and weakly reversible bonds govern the assembly and physisorbed aggregates which are dynamic thanks to the weaker interactions between adsorbate and surface. Here we review the interest and advances in the study of chiral systems at the liquid–solid interface, and also the application of this configuration for the study of systems of interest in molecular electronics, self-assembled from the bottom up.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Molecules associate and organize in beautiful and amazing ways, but the way they do so is only really revealed to us and understood by us when we are able to visualize them. How can a curve on a graph, an equation or a spectrum compare with a spectacular scanning probe microscopy image or an inspired illustration resulting from a computational experiment? Representation and imagery are necessary to

capture the imagination and inspire new science, as well as to communicate it [1].

Beyond this superficiality, functions can be bestowed upon molecules in assemblies and upon the ensembles as a whole, provided that the function of the individual components is appropriate and that the supramolecular arrangement is fitting [2–4]. Back at the surface of things, the interface of a solid and a liquid is an excellent place to probe the assembly and function of molecules, for the following reasons: (i) the system is able to organize under equilibrium conditions at room temperature, leading to a thermodynamically stable system, (ii) a variety of sensitive molecular species can be probed with no limitation of molecular weight, and (iii) the structure of the organization can be imaged down to the atomic level thanks to scanning probe microscopies [5–7].

The adsorption of a molecule in a liquid to a surface in contact with the solution is governed by the series of

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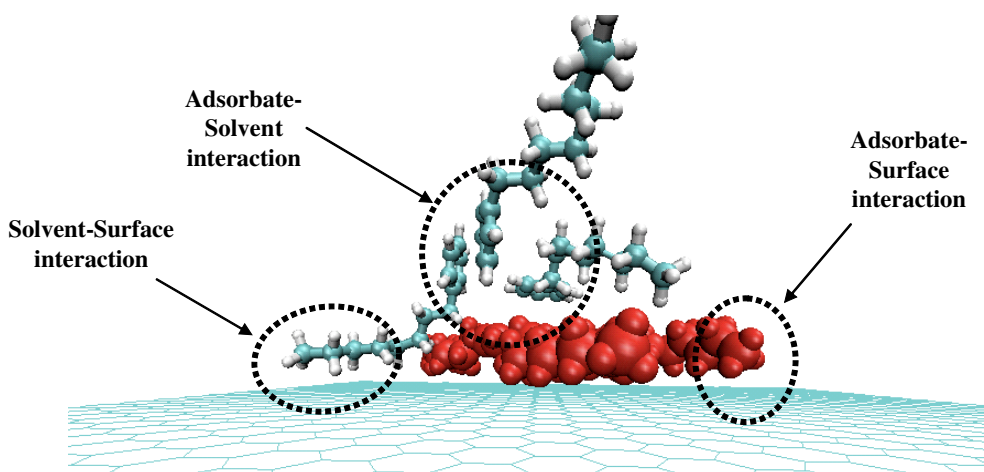


Figure 1. A schematic representation of the interactions at play in self-assembled monolayers at solid-liquid interfaces.

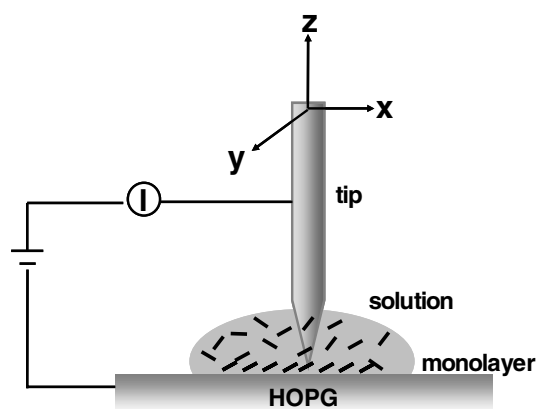


Figure 2. Scanning tunnelling microscope setup for probing self-assembled monolayers.

interactions shown in figure 1. In the situation that a ‘covalent’ bond is formed between the surface and the adsorbate, the process is referred to as chemisorption, and when van der Waals and other interactions (including π - π stacking and C-H $\cdots\pi$) are the principal actors then physisorption is said to occur. In both these cases, the packing of the molecules on the surface very often gives a stabilization which leads to a regular packing, so that the monolayers can truly be considered as two-dimensional crystals.

All the factors that make the adsorption favourable under an ambient setting mean that not only structure, but electronic

properties, dynamic processes, reactivity, redox processes and sequential non-covalent assembly can be monitored in real time in a liquid, under very soft conditions. Scanning tunnelling microscopy (STM) is the technique of choice when a conducting surface can be used for the system under study. The tip of the microscope penetrates into the liquid and images the adsorbed species while sweeping through the fluid (figure 2).

The number of ‘off-the-shelf’ molecules which can be employed in the study of interesting phenomena at the nanometre scale in monolayers is relatively limited, because they must have appropriate affinities for each other and the surface as well as having the property in question. The combination of design, synthetic chemistry, scanning probe microscopy and molecular modelling is therefore a powerful line-up of disciplines, and one which defines and determines the approach we use towards the two areas that we highlight in this review.

2. Chemisorption and physisorption

The differences in the nature of the chemisorbed and physisorbed systems may appear trivial at first sight, but there are very important features of the monolayers that are characteristic of each that are just because of these distinctions (figure 3). To begin with, the strength of the molecule-surface bond determines directly the dynamics of the system: physisorbed systems are in constant equilibrium with the overlying solvent, and molecules can desorb and adsorb freely [8]. The stronger the molecule-surface and

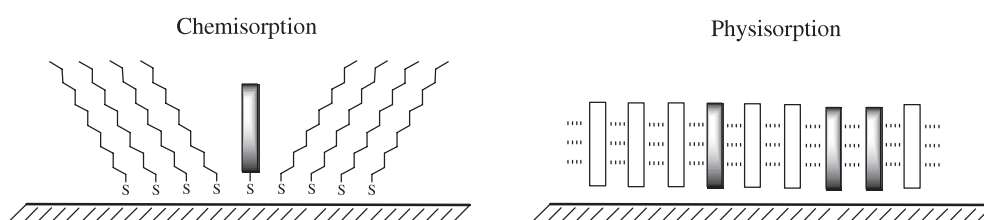


Figure 3. A representation of the isolation of electroactive units (in grey) in ‘insulating’ chemisorbed and physisorbed monolayer matrices.

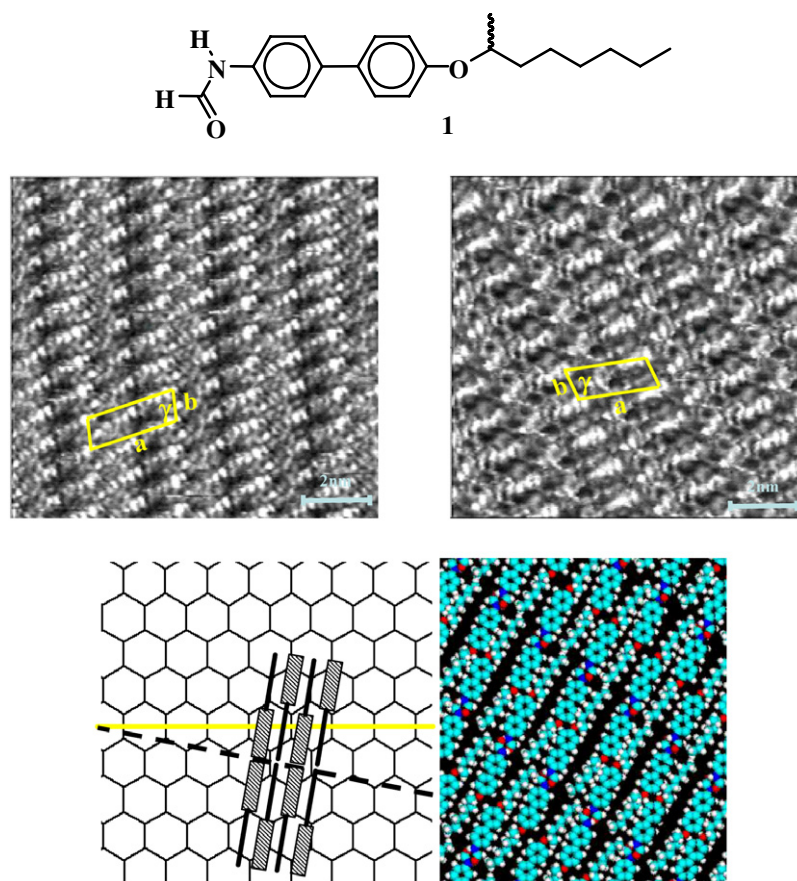


Figure 4. STM images of the enantiomers of **1** at the graphite–1-phenyloctane interface (top) and a schematic view of the packing of the molecules with respect to a graphite symmetry axis and an approximate molecular model (bottom).

molecule–molecule interactions are, the slower this process will be. Therefore, the ‘healing’ of the physisorbed system is usually fast on the experimental timescale. On the other hand, chemisorbed systems involve adsorbate–surface bonds of limited reversibility [9]. In comparison with the surface–molecule bond, the molecule–molecule interaction is weak, but is nonetheless important for the formation of a well-ordered monolayer [10].

One apparent advantage of the chemisorbed systems is their relative kinetic inertness, which means that electronic properties can be probed reliably. It is possible to insert molecular ‘wires’ into ‘loose’ and electronically poorly conducting monolayers such that the electroactive molecules are practically isolated from each other [11, 12]. However, this situation can also be achieved in physisorbed systems, provided that the electroactive molecule contains functional groups that can interact with the inert matrix through interactions such as hydrogen bonds (figure 3, right) [13]. The system contains a random distribution of electroactive molecules, such that they can occur as dimers and trimers, as well as isolated molecules.

The latter example shows the versatility of the systems which are driven by physisorption, an aspect which has drawn us to them, and is the reason for which we will dedicate the rest of this review to them. In particular, we will concentrate on the adsorption of molecules on graphite, which is observed

more often than not by STM at the interface of the substrate and a high boiling organic solvent [14]. The interactions that are common to most examples are the alkyl chain–graphite ones. These interactions, also called CH– π interactions [15], are weak hydrogen bonds between soft acids and soft bases: each CH– π interaction contributes about $1.0 \text{ kcal mol}^{-1}$ to the binding energy [16]. However, the moieties which are attached to the alkyl chains in physisorbed systems play a definite role in the packing of the monolayers: the symmetry and number of alkyl chains can lead to different packing forms [17] and, if the cores interact strongly, their orientation relative to the substrate can be influenced, as we shall see. The orientation of the layers can be compared directly to images of the graphite substrate, which is recorded by moving the tip of the STM closer to the surface. When the tip is brought back up, the monolayers can usually be imaged as they were before the approach of the tip to the graphite, showing their self-healing nature. Two aspects of this type of monolayer shall be discussed: chiral structures and systems with relevance for molecular electronics.

3. Chiral monolayers

Chirality—the mirror image relationship between objects—is important and interesting across the sciences: in biological systems (e.g. stereospecific interactions [18]), the chemical industry (e.g. stereoselective synthesis [19]), materials

(e.g. liquid crystal displays [20]) and in physics (e.g. chiral magnetic systems [21]). In chiral monolayers, a distinction must be made between systems formed from inherently chiral molecules (because of stereogenic centres or atropisomeric conformations) and the occurrence of chirality in achiral or racemic systems, in which case spontaneous resolution has taken place—to give some domains of right-handed molecules and others of left-handed molecules in equal amounts [22–24].

The adsorption of the chiral molecule **1** in its enantiopure form to graphite leads to the formation of chiral monolayers, as revealed by the STM images recorded using 1-phenyloctane as the solvent (figure 4) [25]. The chirality is expressed at two levels in these superstructures, first in the oblique nature of the unit cell (indicated on the images) and second with regard to the angle that the overlayer forms with respect to the underlying graphite, as shown in the schematic representation under the images.

The mixture of the enantiomers described in the previous paragraph also shows spontaneous resolution, and we say that a conglomerate is formed. The proportion of two-dimensional chiral space groups (five chiral space groups of the 17 available, 29.4%) is very similar to that in three-dimensional (3D) systems (65 space groups of the 230 available, 28.3%), but the spontaneous separation of enantiomers of both chiral and achiral molecules at ordered surfaces is frequent [26, 27]. This situation can be rationalized by taking into account the mutual symmetry relations that adsorbate and surface must satisfy [28, 29]. A molecule confined in a monolayer on a surface cannot be related to another by inversion symmetry, and the glide plane parallel to the surface is similarly excluded. Specific restrictions depend on the nature of the surface, because of symmetry, molecular orientation, and the strength of the molecule–surface and molecule–molecule interactions.

However, formamides similar to **1** which have 2-octyl terminated aromatic groups can form pseudoracemates rather than conglomerates at the graphite surface. The formamide **2**—in which the functional group is separated from the alkyl chain by a phenyl benzoate moiety—in its enantiopure form self-assembles at the graphite-1-heptanol interface to yield chiral monolayers in which the vast majority of the supramolecular tapes that are generated form an angle with the nearest graphite axis, although, importantly, a small percentage coincide with it [30]. When the racemic mixture of enantiomers is applied to the graphite surface the lamellae that are formed have a random chirality, as judged by the angle formed by the areas of bright contrast with the lamellar principal axis, as shown in the lower part of figure 5. In some areas of the domains that are formed (which are larger in the case of the racemate than in the enantiopure compounds) tapes with the same handedness are adjacent, and in others they alternate with their enantiomers. The packing is not that of a true racemate, where *R* and *S* enantiomers alternate, but rather it is a pseudoracemate, where the two are situated in a non-periodic fashion. This random distribution of chirality arises because, whereas the enantiomers form an angle with the graphite axes, the racemate has lamellae that are virtually collinear with one of the main graphite axes. Therefore, there is essentially no difference in the incorporation of either right- or left-handed

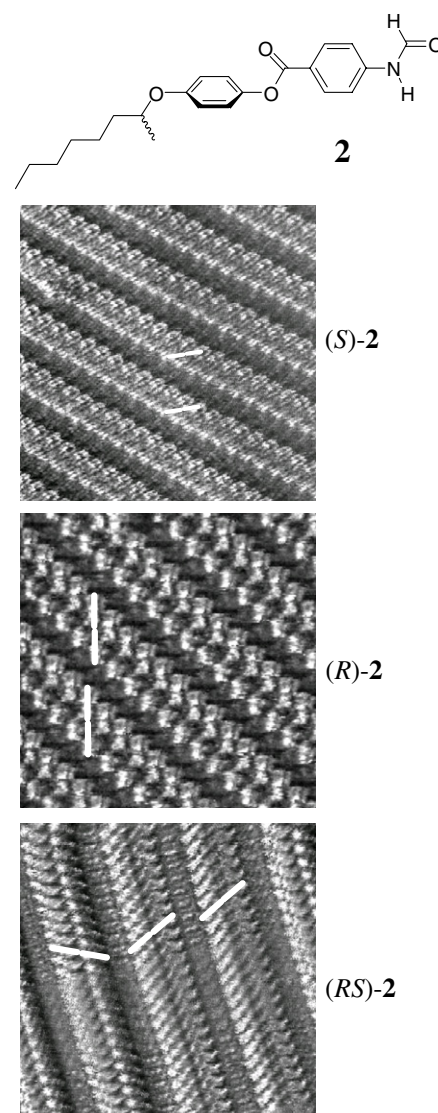


Figure 5. STM images of the enantiomers of **2** as well as its racemic mixture at the graphite–1-heptanol interface (*S* enantiomer image is 16.1 nm × 16.1 nm, *R* image is 12.0 nm × 12.0 nm and *RS* image is 13.6 nm × 13.6 nm).

enantiomers, whose alkyl chains can interdigitate anyhow (as shown schematically in figure 6). This situation could not occur if the enantiomers favoured an angle with the graphite axes; the alkyl chains would not be able to interdigitate, as implied at the top of figure 6.

The ability of the enantiomeric tapes to adjust to the surroundings is caused by the multiple conformations that the 2-octyl chain can adopt, as shown in the x-ray structures of the enantiomers [30]. This flexibility is seen in some of the domain boundaries in a biased racemic mixture of **2**, where the angle formed by a lamella and the graphite axis varies smoothly along its length (figure 7).

So, changes in molecular structure can tip the balance between racemic compound formation and spontaneous resolution in these physisorbed systems. One of the determining factors in reaching this conclusion is a structural basis obtained from x-ray crystallographic analysis of the

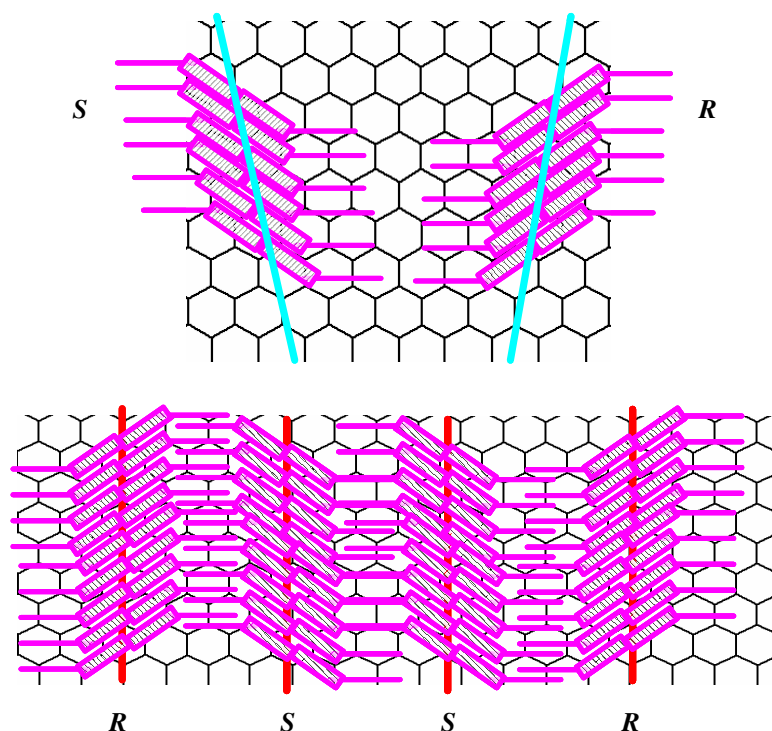


Figure 6. Schematic representation of the packing in the tapes of the enantiomers of **2** (which form angles with the graphite axes) and of the racemic compound (whose axis is coincident with that of graphite).

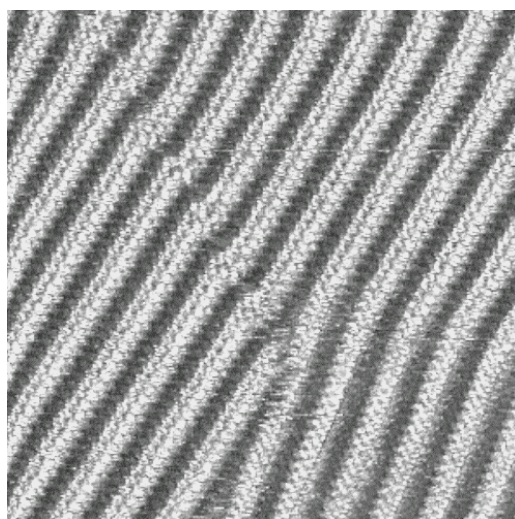


Figure 7. STM image of a 68:32 mixture of *R* and *S* enantiomers of **2** at the graphite–1-heptanol interface (image size 36 nm × 36 nm).

formamides, in which the lamellar superstructure is also present. In fact, the structure of the racemic mixture of **2** has a structure which is remarkably similar to high-resolution images of the same at the graphite–heptanol interface. In the STM image it is clear how the alkyl chains interdigitate (figure 8) as they do in the solid, and even the orientation of the phenyl rings appears to be similar.

A present challenge that we have is to study the effects of the number of stereogenic centres on the chiral expression in self-assembled monolayers, paying special attention to the

symmetry relationship between the surface and the adsorbate. With this goal in mind, we have prepared a C₄ symmetric porphyrin derivative with four identical stereogenic centres and we have studied its self-assembly at the graphite–heptanol interface using STM [31]. Unlike other porphyrin derivatives which are achiral and form either racemic domains or achiral monolayers [32–34], this compound forms monolayers with a single handedness in all the domains, as seen in the unique sense in the angle formed by the lamellae with the graphite axes and the angle formed by the alkyl chains with the axis of the tapes formed by the porphyrin cores (figure 9). The consequences of this chirality on chemical and physical properties will be investigated by our groups in the near future.

4. Physisorbed monolayers as a vehicle for studying electronic properties of molecules on surfaces

The use of organic molecules for electronic devices is an area of research which is gaining increasing impetus [35–38]. The junction formed between the STM tip and a surface with molecular species in between is a very interesting configuration in which to probe electronic properties using scanning tunnelling spectroscopy (STS) [39]. Tetrathiafulvalene (TTF) derivatives (see figure 10) are a particularly attractive family of molecules because of their electronic properties, as numerous recent publications show [40–46]. We were therefore drawn towards their study at the nanometer scale at the liquid–solid interface.

At the outset, we probed a simple series of alkyl chain substituted TTFs in order to develop a kind of grammar for

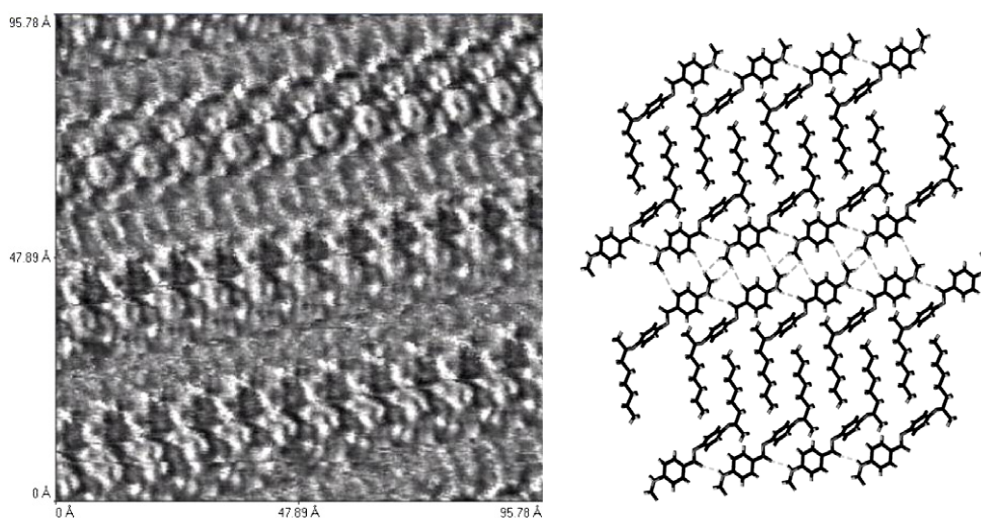


Figure 8. STM image of the *RS* mixture of **2** at the graphite–1-heptanol interface (image size 9.6 nm × 9.6 nm).

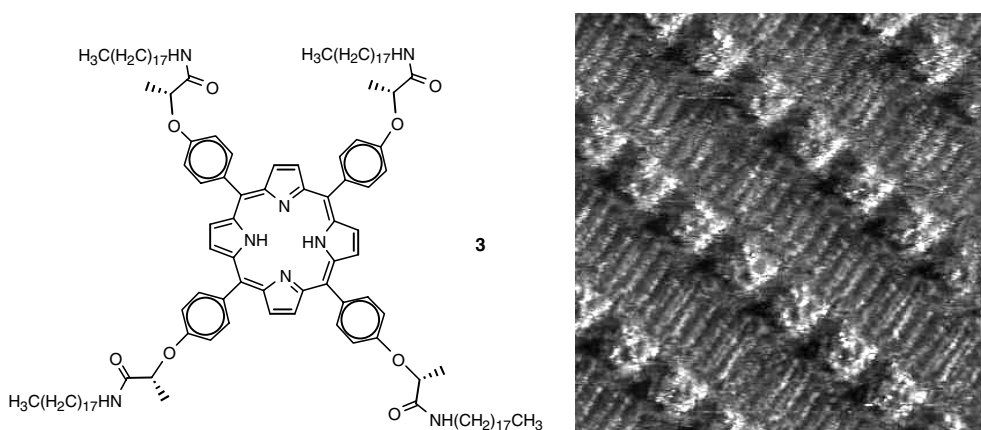


Figure 9. STM image of the homochiral porphyrin **3** at the graphite–1-heptanol interface (image size 11.7 nm × 11.7 nm).

the assembly language, and thus prepared and studied by STM (among others) the molecules shown in figure 10 [47]. Polymorphism and solvent dependence do play a role in the packing patterns which were observed, but the dominant factor is the number and constitution of the alkyl chains attached to the TTF core. When no long chains are present, the TTF can adsorb to the graphite from solution, showing that there is an inherent attractive binding between the core and surface. The isomerism of the molecules can lead to dimer-type structures or to continuous lamellae, thanks to abutting or interdigitation of the alkyl chains [48].

The TTF bearing four octadecyl chains is an interesting and quite unique case, because it forms extended monolayers in which the cores are essentially isolated from one another, as well as areas in which apparently isolated molecules are observed on the surface (figure 11) [49] and even molecules stacked on top of each other [47, 50]. The system is a particularly interesting one from the molecular electronics point of view, because a rectifying current is observed when STS curves are recorded over the molecules in the monolayers as well as over the ‘isolated’ molecules [49].

The long-term objective of the research on the TTFs is to generate supramolecular wires. The organisations reported above are not suitable in this context because the cores are lying parallel to the graphite surface (figure 12). In order to generate a wire, i.e. an object able to transport charges, the π -electron-rich TTF cores must face each other in a one-dimensional (1D) stack, which implies that they must be perpendicular to the surface. Therefore, the molecule–molecule interaction has to be increased. An effective way to do this is by using hydrogen bonds [51, 52].

Indeed, a TTF derivative including two amide groups in the chains emanating from it orders very nicely into 1D structures at the graphite–octanoic acid interface (figure 13) [53]. Density functional theory (DFT) calculations [54] and force-field-based molecular mechanics (MM) and dynamics (MD) simulations [55] have been used to study these TTF structures and the role of hydrogen bonding, which takes place between the amide groups, on the stability of those stacks. The separation between the bright spots along the 1D structure in the STM image of figure 13 coincides with a π – π stacking interaction, and molecular modelling of the compound on graphite

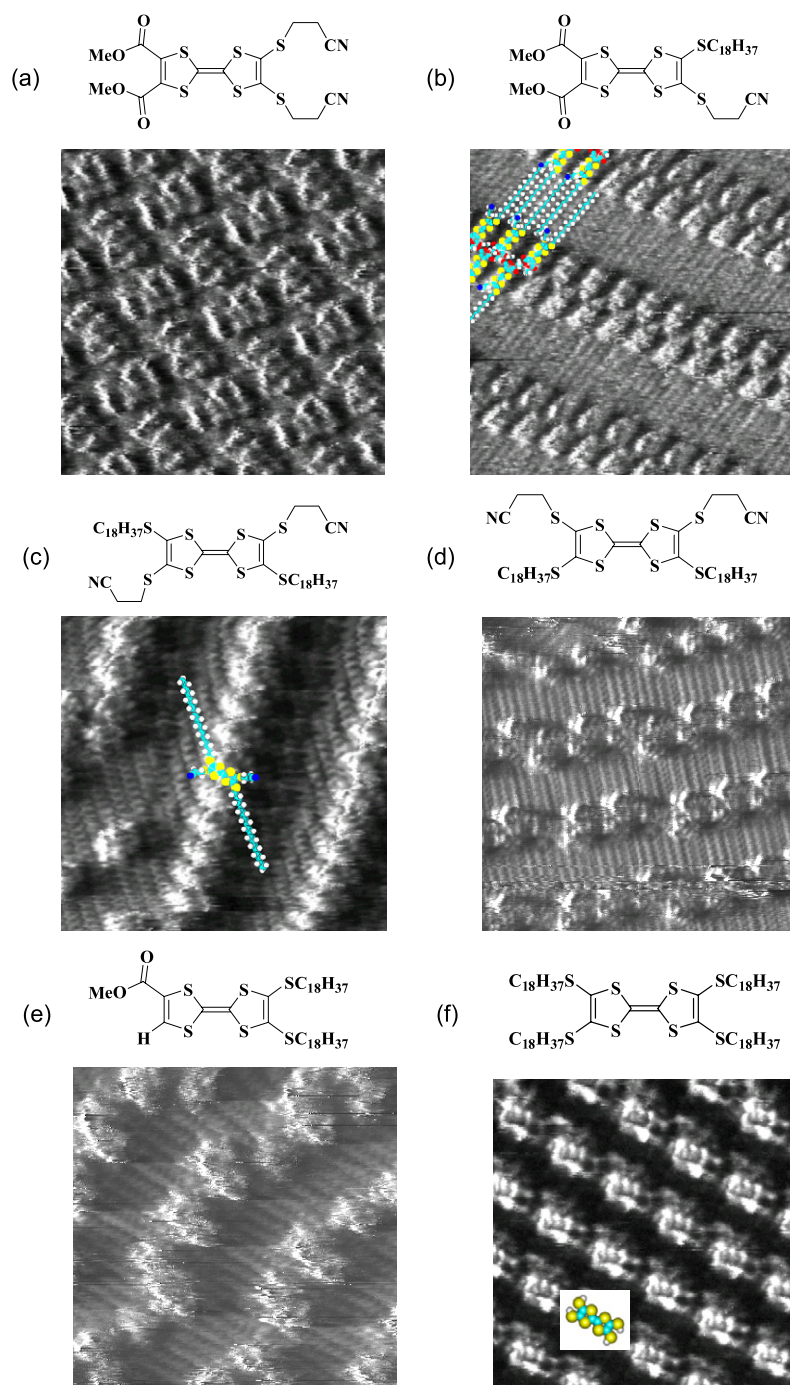


Figure 10. STM images of TTF derivatives with different numbers and positions of alkyl chains. Image sizes: (a) 5.1 nm \times 5.1 nm; (b) 11.9 nm \times 11.9 nm; (c) 10 nm \times 10 nm; (d) 13.8 nm \times 13.8 nm; (e) 10.9 nm \times 10.9 nm; (f) 10.1 nm \times 10.1 nm.

supports this hypothesis. The model indicates that molecules are adsorbed with the TTF cores ‘edge-on’ on the surface, having the electron-rich TTF moieties co-facial to each other. The molecules are kept aligned in the structure thanks to both π - π stacking interaction between the molecular cores and the hydrogen bonding patterns involving the amide groups. This geometry for the stacks can promote the formation of a possible pathway for one-dimensional charge transport. The stacks are well separated from one another by the abutting alkyl chains which lie flat on the surface.

The STS experiments performed on the TTF cores show a small experimental conductance gap when compared with other systems, indicating that the stacks are capable of performing with wire-like electronic character, because of the increased density of states that is implied [53]. Indeed, in parallel to the STS measurements, quantum chemical calculations [56] have been used to study the charge transport capabilities for the hydrogen-bonded TTF stacks, based on the strength of the electronic coupling between adjacent molecules in the modelled structures. The large bandwidths obtained for

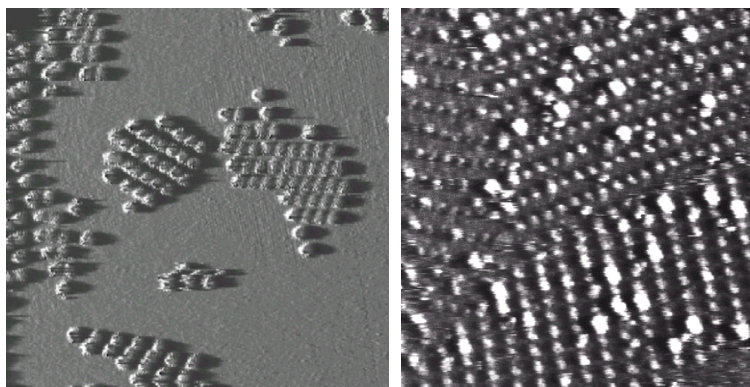


Figure 11. STM images of a TTF derivative bearing four octadecylthio chains at the graphite–1-phenyloctane interface. Left: image size is 55 nm × 55 nm; right: image size is 50 nm × 50 nm.

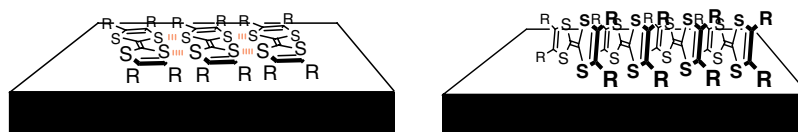


Figure 12. Arrangement of TTF on a surface in which surface–molecule interactions dominate the arrangement of the molecules (left) and the forced alignment of the π systems which can arise by making the molecule–molecule interactions sufficiently strong (right).

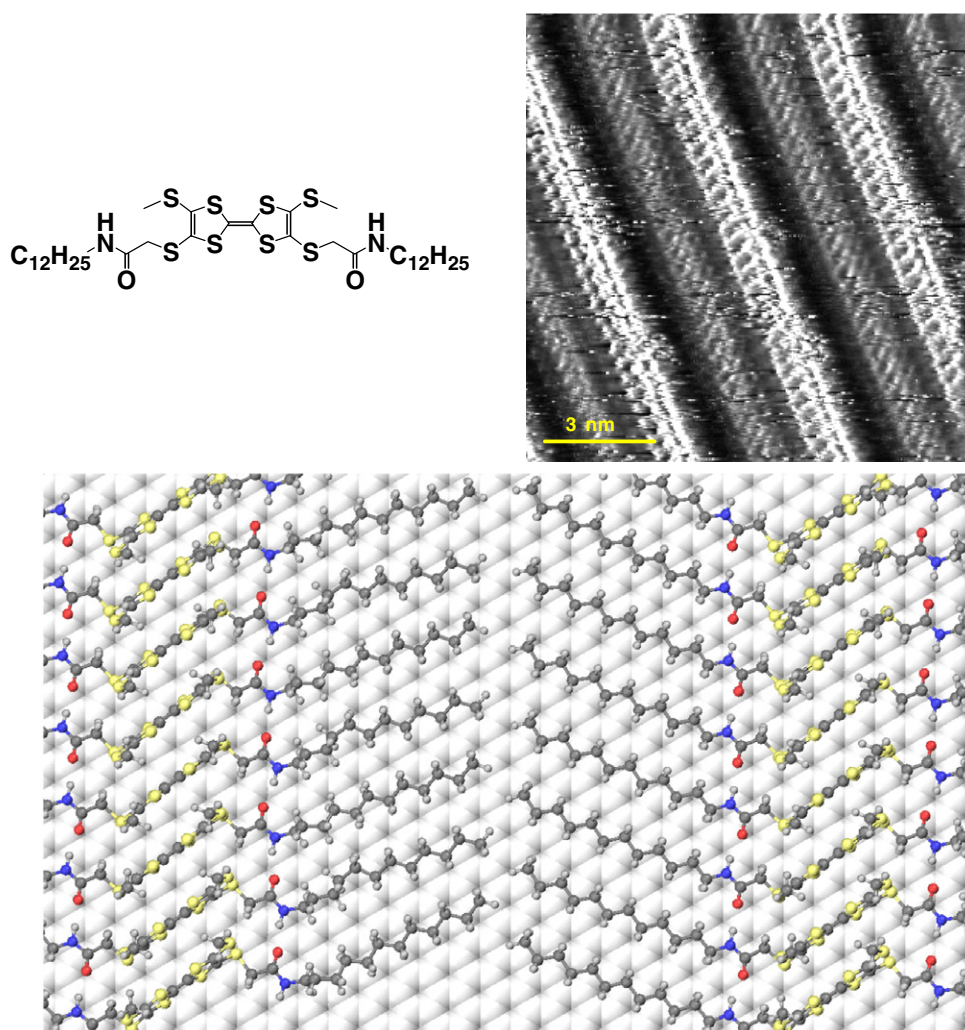


Figure 13. An STM image of the bis-amide TTF shown which self-assembles through hydrogen bonds to form stacks of the electron-rich cores, as confirmed by molecular modelling (lower image).

the valence band and the conduction band (0.54 and 0.44 eV, respectively) clearly show that those TTF stacks can act as molecular wires both for hole and electron transport [53].

5. Conclusion and outlook

The visualization of self-assembled monolayers at the liquid–solid interface using the scanning tunnelling microscope can lead to extremely high-resolution images with sub-molecular resolution, a fact which aids the study of transfer of chirality in self-assembled monolayers under equilibrium conditions. The dominant role that the alkyl chain and aromatic moiety–graphite interactions have on the structure of the monolayers in many cases can be overcome by incorporating hydrogen bonding groups in the structures. This feature facilitates research into the electronic properties of molecules at the liquid–solid frontier using scanning tunnelling spectroscopy. The present challenges in the area include the realization of working reversible devices in such an environment, as well as the creation of multicomponent systems that can perform some function and be subject to all the advantages of self-assembly, including repair.

Acknowledgments

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- [56] Quantum chemical calculations for the charge transport has been performed using a DFT approach as implemented in the ADF code <http://www.scm.com/Welcome.html/>