Assembly of functional molecular nanostructures on surfaces

Elba Gomar-Nadal,†* Josep Puigmartí-Luis and David B. Amabilino

Received 11th September 2007
First published as an Advance Article on the web 5th November 2007
DOI: 10.1039/b703825a

This *tutorial review* discusses different techniques for the preparation and deposition on surfaces of organic nanostructures – monolayers, nanowires, nano-dots and other aggregates – with emphasis on the key role that chemical design and non-covalent interactions (between molecules themselves and molecules and surface) play in the definition of the final structure and its properties. The characterisation of the nanostructures and the important effects of post-deposition treatment are also touched upon. The tetrathiafulvalene (TTF) unit is used as the example to demonstrate the general principles that are applicable for these different nanoscale architectures, because of the interest of this family of compounds in molecular electronics.

1 Introduction

The preparation of any functional system, one which has a property of interest, requires not only control over the components of the system (their optical, magnetic or electronic characteristics) but also over the organisation of these pieces. The relative orientation of molecules in a material can influence very dramatically on the function. This statement holds true for bulk materials as well as for nanostructures – objects with at least one dimension less than 100 nm. It is in the latter area that great activity and excitement are apparent since the 1990's, because of the potential of molecular systems in the emerging nanoscience field in general, and especially molecular electronics. It is hoped that the bottom-up approach inherent to the use of molecular systems will lead to the fabrication of devices on scales unreachable through exclusive use of current top-down techniques,[1] but also that molecular materials have unique properties compared with their oxide and related counterparts.[2]

The toolkit of the chemist approaching the preparation of molecular nanomaterials contains a variety of pieces which can be incorporated into the final object (Fig. 1), and which must be arranged with the help of appropriate non-covalent interactions in the solid state.[3] Molecular nanostructures are attractive in such diverse fields because of the tunability of the properties of these materials by selectively modifying specific

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Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193, Bellaterra, Spain. E-mail: amabilino@icmab.es; Fax: 34 93 580 5729; Tel: 34 93 580 1853
† Current Address: Intel, Robert Noyce Building, 2200 Mission College Blvd., 95054 Santa Clara, CA, USA. E-mail: elba.gomar-nadal@intel.com

Josep Puigmartí-Luis Elba Gomar-Nadal David B. Amabilino

Elba Gomar-Nadal (Barcelona, Spain 1978) received her PhD in Materials Science in 2004 working with David Amabilino in the group headed by Jaume Veciana at the Barcelona Materials Science Institute (CSIC). As a part of her thesis, she visited Stuart M. Lindsay's group (Arizona State University, USA) and Frans De Schryver's and Steven De Feyter's group (University of Leuven, Belgium). Her work was focused on the design, synthesis and study of electroactive self-assembled monolayers (SAMs) and polymers with electrical and optical properties based on TTF derivatives. After her PhD, she joined Ellen D. Williams' group as a postdoctoral research associate at University of Maryland, College Park (USA). Her research interests included multi-functional molecular materials, organic field-effect transistors, supramolecular electronics, self-assembly and surface molecular organizations. She is currently working as a process technology development engineer at Intel, Santa Clara, CA.

Josep Puigmartí Luis (Artés, Barcelona, Spain 1978) received a degree in Chemistry from the Universitat Autònoma de Barcelona in 2001. Then he did a Master degree in Food Engineering and Chemistry at the Institut Químic de Sarrià (Barcelona, 2003). Presently he is engaged in his PhD programme in the group lead by Jaume Veciana at the Barcelona Materials Science Institute (CSIC) under David Amabilino's direction. His current research focuses on the development of new supramolecular organic conductors on and off surfaces.

David B. Amabilino (Hertfordshire, England 1966) is a tenured research scientist working in the group headed by Jaume Veciana at the Barcelona Materials Science Institute (CSIC). His experience is in Supramolecular Chemistry, having worked as a postdoc in Fraser Stoddart's group (then in Birmingham, England) and Jean-Pierre Sauvage's group (ULP, Strasbourg) after receiving both BSc (Hons) and PhD from Royal Holloway and Bedford New College (University of London). His current interests lie in the influence of supramolecular and stereochemical effects on molecular materials.

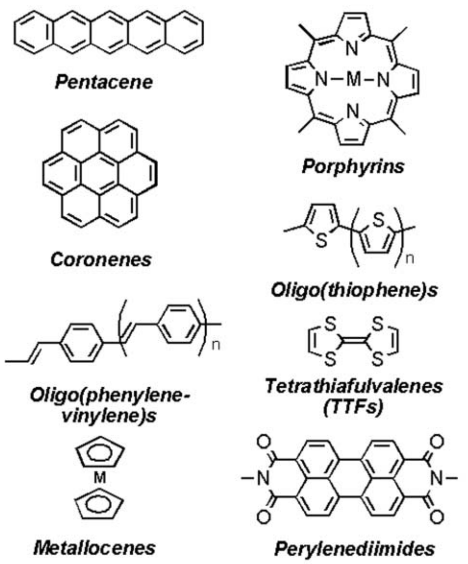


Fig. 1 Molecular units used frequently for the preparation of functional nanostructures.

functional groups while leaving the rest of the molecule unchanged. But immobilisation on a surface is required for many of the applications that these molecules are directed towards. Therefore, to achieve a suitable organisation one must consider not only interactions between the molecules themselves but also those with the surface, which play a role of varying importance according to the system.

This review will discuss different techniques for the preparation and deposition on surfaces of molecular nanostructures – monolayers, nanowires, nano-dots and other aggregates – with emphasis on the key role that chemical design and non-covalent interactions play in the definition of the final structure and its properties. The use of self-assembly – the aggregation of disordered molecules into an ordered structure under equilibrium conditions – is key to many of the systems which function best. While numerous functional molecules have been employed as the building blocks for nanostructures with varied properties (Fig. 1), here the tetrathiafulvalene (TTF) unit[4] will be used as a representative example to demonstrate the general principles that are applicable for these architectures.

2 Deposition methods, treatment and characterisation techniques

In view of the large number of molecular compounds known, and a correspondingly wide variety of molecular properties, it is not surprising that there are different routes for the preparation of molecular nanostructures.[5] Fig. 2 schematically shows some of the most common deposition methods, which we will now outline.

2.1 Deposition methods

2.1.1 Self-assembled monolayers (SAMs). Self-assembled monolayers (SAMs) can be divided into two broad classes: chemisorbed and physisorbed. In the former class, the molecules have a chemical functionality (or "headgroup") with specific affinity for a solid surface with which it forms covalent bonds (of limited reversibility) and drives the formation of the monolayer. This definition is the one referred to in the surface science community, although those from a molecular sciences training would consider physisorbed monolayers a class of SAM because they are formed spontaneously from a pre-designed building block on a solid surface and therefore meet the criteria of a self-assembly process. These SAMs are formed through weaker van der Waals interactions between monolayer and surface with stronger interactions (*e.g.* hydrogen bonding, electrostatic, *etc.*) within the layer between the molecules, and they are more dynamic because of the nature of the interaction between the molecules and the substrate.

The election of the substrate will depend on the class of SAM and desired final properties. For chemisorbed SAMs, for example, there are a number of headgroups that bind to specific metals, metal oxides, and semiconductors. The most extensively studied class of these SAMs are alkanethiols on Noble metals (*e.g.*, gold, silver). Both types of SAMs can be formed by spontaneous adsorption from either the liquid or the vapour phase (Fig. 2a)

2.1.1.a Solution phase deposition. The ease of preparation and the low cost of solution depositions make them convenient and sufficient for most applications of SAMs, especially for those requiring contact with other liquid phases in subsequent experiments. Provided that the substrate has been cleaned properly, in principle, it simply has to be dipped into the corresponding solution for a period of time – determined by the solvent and the reactivity of the head group – and the monolayer will assemble. It is very important to control carefully the purity of the solution, which can be difficult. In the case of silane-based systems, for example, the water content is crucial for the proper preparation of the SAM. Proper degassing of the solution is another important issue since oxygen could react with the molecules or the substrate's surface, affecting the SAM growth and ultimately its properties. After complete formation of the SAM an appropriate rinsing procedure has usually to be performed to remove unreacted amphiphiles and other impurities.

2.1.1.b Vapour phase deposition. The principle of gas phase deposition is also simple, although the practice can be difficult. The substrate is placed in a vacuum chamber equipped with a port with a valve through which the molecules are dosed with a controllable flux from a little container or glass bulb (Fig. 2a). For molecules with a low vapour pressure the container can be heated (see Section 2.1.4 Thermal evaporation).

Generic ultra-high vacuum (UHV) chambers allow for cleaning of the surface prior to SAM formation on single crystals of metals, for example. Both ion sputtering and annealing can be performed *in situ*. Besides work in UHV it is also possible to deposited SAMs using high or medium vacuum chambers or a nitrogen stream. Employing a UHV chamber is generally more expensive than growth from solution. The principal advantages of gas phase deposition in a UHV chamber over ambient conditions are the clean environment, the possibility to vary temperature over a wide

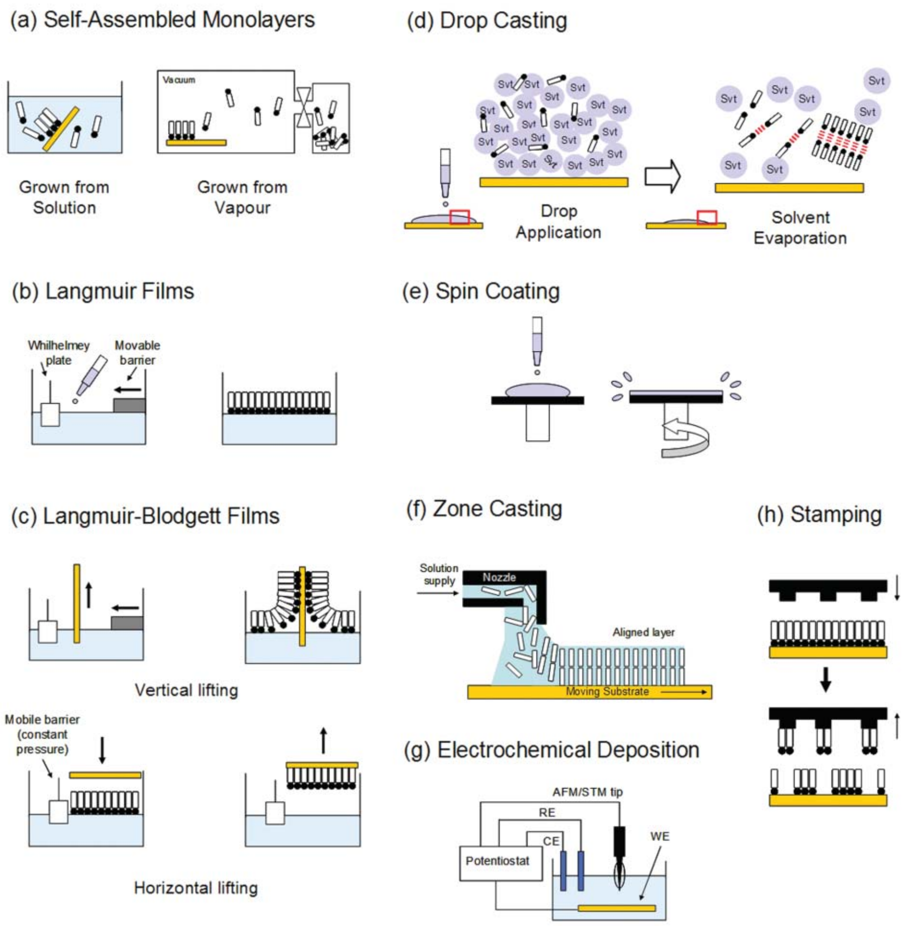


Fig. 2 Overview of the various preparation routes for the deposition of molecular nanostructures on surfaces. (a) Growth of SAMs can be done either in solution or in vacuum. (b) Langmuir films are formed by spreading amphiphilic molecules on a liquid surface. (c) LB films are prepared by transferring Langmuir films onto a solid substrate. (d) Generation of nanostructures as a result of combined self-assembly and dewetting when a drop-casted solution is evaporated on a surface. (e) In spin-coating, a residual layer remains on the substrate owing to surface tension when an excess of a solution is placed on the surface and then rotated at high speed. (f) Oriented, anisotropic layers of soluble molecular materials are prepared by zone casting which consist of casting a suitable solution, continuously supplied by a nozzle, onto a moving substrate. (g) Crystalline mono- and multilayer films can be grown on a substrate by electrochemical deposition. The sample is the working electrode (WE). The reference electrode (RE) and the counter electrode (CE) ensure the control over electrochemical processes within the cell and at the working electrode surface. This process and the resulting structures can be studied at the nano-scale if the cell is integrated in an AFM/STM microscope. (h) Schematic representation of the procedure for patterning a pre-formed SAM using stamps.

range, and the availability of a large number of *in situ* analytical surface science tools (see Section 2.2).

2.1.2 Langmuir–Blodgett (LB) films. *Langmuir* films[6] consist of amphiphilic molecules spread on a liquid surface (typically water (Fig. 2b)) rather than the solid surfaces used for SAMs. The hydrophilic headgroup of the amphiphile has an affinity to the water while the hydrophobic endgroup sticks out of the interphase between layer and water. To form a Langmuir monolayer, the molecule of interest is dissolved in a volatile organic solvent that will not react with or dissolve into the subphase. A quantity of this solution is placed on the surface of the subphase, and as the solvent evaporates, the surfactant molecules spread forming a two-dimensional gas. A moveable barrier then compresses the surface of the subphase, allowing control of the surface area available to the floating layer. Generally, the state of the monolayer on the water surface is monitored by measuring the surface pressure.

Langmuir–Blodgett (LB) films are prepared by transferring Langmuir films onto a solid substrate by vertical or horizontal lifting (Fig. 2c). Multilayers are prepared by repeated (periodic) dipping of the substrate in/onto compressed films on appropriate solutions. Both highly hydrophilic or highly hydrophobic substrates can be employed.

2.1.3 Solvent evaporation. Techniques based on a controlled solvent evaporation are another approach to deposit nanostructures from solution that exploit the principles of self-assembly. This section describes relevant examples of this type of technique.

2.1.3.a Drop casting. Drop casting consists of letting a small volume of solution of compound fall onto the substrate surface and leaving it to dry either in air or in an atmosphere of the solvent to ensure slower evaporation (Fig. 2d). The molecular self-assembly at the surface is highly influenced by the dewetting phenomena (or rupture of the thin solvent liquid film on the substrate), which depends on the solvent, the solution concentration and the substrate nature. A reduction of the dewetting contribution to the self-assembly organization of the molecules can be achieved by decreasing the rate of solvent evaporation, *e.g.* selecting a low volatility solvent, preparing the film in a sealed atmosphere saturated by the vapours of the solvent or cooling down the substrate.[7] Another similar deposition method is *immersion*. Here, the substrate is dipped into the solution for a certain period of time (minutes) and then extracted and left to dry in air.

2.1.3.b Spin coating. In spin coating, the solution of functional molecules is applied on the substrate which is then rotated on a spinning wheel at high speed so the centrifugal forces push the excess solution over the edge of the substrate and a residue on the substrate remains thanks to surface tensions (Fig. 2e). This technique has been optimized for deposition of thin layers of polymers but, as will be shown later, it can also be adapted to deposit thin films and nanostructures of small molecules.

2.1.3.c Zone casting. Zone casting is a method for preparation of oriented, anisotropic layers of soluble molecular materials on substrates that have not been pre-oriented.[8] The material in solution is continuously supplied through a nozzle onto a moving substrate and the solvent evaporation takes place from the surface of the meniscus formed between a special flat nozzle and the substrate (Fig. 2f). The gradient of solute concentration causes solidification in a narrow zone under highly anisotropic (or directional dependent) conditions. For each compound, stationary deposition conditions must be determined by choosing a suitable solvent, initial concentration, and adjusting casting parameters such as temperature and casting speed.

2.1.4 Thermal evaporation. Thermal evaporation represents one of the oldest thin film deposition techniques. Evaporation is based on the sublimation of a heated material onto a substrate in a vacuum. Generally, a crucible containing the organic material is placed inside a highly refractory metal containing structure (*e.g.* a tungsten basket) that is heated by passing a current through it. The deposition rate and film thickness is controlled with a crystal quartz monitor and ultra-thin organic films with thicknesses from less than one to several monolayers can be deposited. By applying electrical fields between pre-patterned electrodes on the substrate, it is possible to direct the deposition of the molecules. This type of deposition is called *electric-field assisted evaporation* and can be used to grow nanowires (see Section 6).[9]

2.1.5 Electrochemical deposition. Crystalline, molecularly thick organic films mimicking layer motifs observed in bulk crystals of conducting charge-transfer salts can be deposited by electrochemical oxidation of neutral molecules in the presence of an electrolyte that contains the appropriate counterion.[10] The electrodeposition is carried out in a three electrode electrochemical cell that contains a "working electrode" (WE), a "reference electrode" (RE), and a "counter electrode" (CE) (Fig. 2g). For electrodeposition to occur the conducting substrate – the working electrode – has obviously to conduct electricity. The resulting structures can be studied *in situ* at the nano-scale if the cell is integrated in an AFM/STM microscope.

2.1.6 Stamping. The use of functional molecules as ink on a rubber stamp is a conceptually simple and very attractive way to deposit molecules onto surfaces. Basically, the stamp is pressed into the "ink" (either the pure molecule or a solution of it) and is then removed and pressed onto a surface (Fig. 2h). The method has a very wide variety of guises within the field of soft lithography and printing, with microcontact printing being particularly popular, since it allows patterning over relatively large areas.[11] Also, the use of transfer printing seems particularly promising.[12] The resolution of the techniques are such that nanoscale features can be achieved, although within the patterned areas the organisation is not necessarily controlled. The beauty of the methods are that they can be combined with the formation of chemisorbed SAMs, solvent evaporation and electrochemical methods to achieve patterned nanostructures.

2.3 Post-deposition treatment

The layers that are formed on substrates using any of the techniques which we have just described are not necessarily generated in their most thermodynamically stable state, metastable situations are common.[13] The observation of phase changes at the nanoscale are few,[14] but in principle many of the molecular films can be modified *in situ* by annealing either with solvent vapours or heat, for example. The study of phase diagrams in these systems is not common at all, and their thorough investigation would be a valuable contribution to the field. In any case, the effects of time, temperature and atmosphere on nanostructured functional molecular nanostructures are critical.

2.3 Characterization techniques

A varied arsenal of analytical techniques is available for the study of the structure and properties of organic nanostructures on surfaces.[5,6,15] In addition to the material properties, discussed later, other characteristics that are typically of interest are surface topography, thickness, intralayer spacing, molecular orientation and packing, substrate coverage, and chemical composition. These are critical when a correlation between structure, composition and behaviour is attempted. In many cases, the only restrictions are the low conductivity of the materials and their sensitivity to electron beam damage, but there are a large number of studies that have been carried out successfully.[16]

The development of scanning probe microscopies (AFM and STM) provided powerful new capacities to study both the structural organization and the assembly process of nanostructures at a molecular level. While STM is limited to conducting materials, AFM has a wide variety of variants which can probe structure, morphology, and electrical properties,[17] although in general the resolution is lower than STM. The scanning probe methods give nanoscale information, generally over small areas (several microns) and frequently have better resolution than scanning electron microscopy

(SEM) and even challenge transmission electron microscopy (TEM) which is somewhat more restrictive and limited to vacuum chamber operation, although these electron beam techniques are extremely valuable for the study of fibres and particles especially.[18] Scanning near field optical microscopy (SNOM) is also a powerful tool in certain instances.[19]

These scanning probe and electron microscopy techniques have extended to the nanoscale the initial structural understandings derived on a wider scale mainly from spectroscopic techniques (*e.g.* RAIRS, XPS, ellipsometry, and Raman) and physical methods (*e.g.* studies of wetting with contact angle). More recently, diffraction methods (X-ray diffraction and electron diffraction from Synchrotron sources) have also started to play a lead role in shaping the understanding of these structures.[16] This statement is true where crystalline order is presented over several microns, but for sub-micron domains the scanning probe techniques have come into their own.

In the next sections, we will present specific examples of the application of the deposition methods and characterisation techniques described earlier to organic nanostructures, using the tetrathiafulvalene (TTF) unit as building block.[4] TTF and its derivatives are excellent molecular components because of: (i) their redox properties: The oxidation of the TTF ring system to the cation radical and dication species occurs sequentially and reversibly within a very accessible potential window and the corresponding oxidation potentials can be tuned changing the substituents attached to the TTF core; (ii) their rich supramolecular chemistry. TTF derivatives readily form dimers, highly-ordered stacks, or two-dimensional sheets, which are stabilised by intermolecular π–π interactions and non-bonded S···S interactions; (iii) their stability to many synthetic transformations and; (iv) the large number of conducting and superconducting charge transfer salts and complexes that have been described.[4]

3 Self-assembled monolayers (SAMs)

SAMs are an important vehicle for the development of nanoscience for several reasons: (i) they are easy to prepare, (ii) they can be grown on objects of all sizes and are critical components for stabilizing and adding function to preformed nanometer-scale objects, for example, thin films, nanowires, and colloids, (iii) they can couple the external environment to the electronic (current–voltage responses, electrochemistry) and optical (local refractive index, surface plasmon frequency) properties of metallic structures, and (iv) they link molecular-level structures to macroscopic interfacial phenomena, such as wetting, adhesion, and friction.[15] Examples of these capacities are presented in the next sections using TTF chemisorbed and physisorbed SAMs as a model.

3.1 Chemisorbed SAMS

Chemisorbed SAMs are a robust way to immobilize molecular systems on solid supports because of the limited reversibility of the ‘‘covalent’’ bond formed between the surface and the adsorbate. Self-assembly of electroactive molecular systems – like the TTF unit – is a promising approach for the preparation of systems which can be tested in the area of molecular optoelectronics. Organic synthesis allows the functionalization of electroactive units to form chemisorbed SAMs with a range of specific physical and chemical properties (*e.g.* ion sensing).

Fig. 3 shows a general synthetic design used to prepare these systems. The first requisite for SAM formation is the presence of the surface active group that will anchor the molecules to the substrate – *e.g.* thiol or disulfides groups for gold substrates. A spacer between the electroactive unit and the surface active group is generally used to promote intermolecular lateral interactions resulting in more dense SAMs and to ensure that the long axis of the molecule does not lay parallel to the substrate. Alkyl chains are the most common spacers and they are also used to insulate the electroactive unit from the substrate. On the other side of the electroactive unit, an extra-functionality can also be added to fine tune the SAM properties.

The observation of stable redox chemistry of TTF derivatives in SAMs[20] prompted the investigation of electrochemical sensors based on the cation-sensitivity of crown-ether groups, and particularly SAMs of crown-ether annelated TTFs on electrode surfaces.[21,22] The TTF thiols **1–3** in acetonitrile solution showed, by cyclic voltammetry (CV), a small but reproducible redox potential shift of the electroactive TTF group on Li^+ and K^+ ion complexation (10–20 mV), a

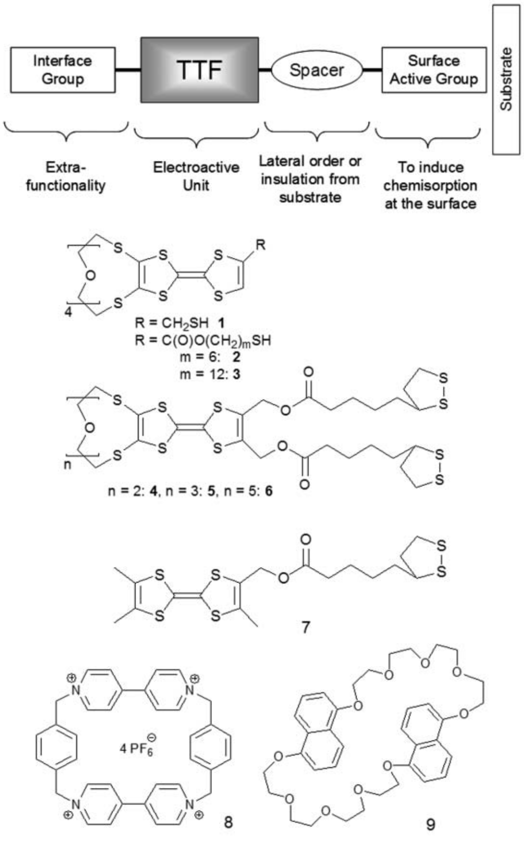


Fig. 3 Schematic structural representation of molecular electroactive systems for molecular optoelectronics and specific examples of TTF-based systems.

significant response to Na^+ and Ba^+ (45–55 mV) and a greater response to Ag^+ (60–90 mV). The same responses were obtained for the SAMs, showing for example a response to Ag^+ of 60–85 mV on platinum. The response was independent of the length of the thiol chain. However, these SAMs were not stable under various experimental conditions. Liu *et al.* prepared the bis-thioctic ester TTF derivatives **4**, **5** and **6** which formed remarkably stable SAMs on gold with very clear and reversible surface-confined electrochemistry.[23] These layers were able to recognize alkali metal ions (Na^+ and K^+). Compound **5** showed an anodic shift for the first and the second oxidation potential (Na^+: $\Delta E_{1/2}{}^1 = +60$ mV, $\Delta E_{1/2}{}^2 = +55$ mV; K^+: $\Delta E_{1/2}{}^1 = +20$ mV, $\Delta E_{1/2}{}^2 = +30$ mV) while the smaller crown **4** only showed a minor increase of +10 mV in the first oxidation potential in the presence of Na^+. This seemed to indicate that the monolayer was able to complex the metal ion even after the second TTF oxidation, perhaps as a result of either surface aggregation or cooperative effects between neighbouring crown ether rings on the layer.

Another interesting application of TTFs SAMs that relies on the TTF unit redox properties is the creation of molecular machines – such as switches and shuttles – using controlled redox-active host–guest complexes. Stoddart *et al.* have studied in detail the use of the TTF unit in solution or on surfaces for the preparation of molecular machines.[24] An example of this are SAMs of TTF **7**, in which the redox-active unit in its neutral state forms a pseudo-rotaxane with the electron deficient cyclophane **8**, whereas in the dicationic state a pseudorotaxane is formed with the electron-rich macrocyclic polyether **9**.[25]

SAMs of TTF derivatives have also been used as a platform to study the electrical characteristics of individual molecules using current-sensing AFM and STM.[26] In this study, the TTF unit was linked to the substrate directly through a dithiolate group attached to the TTF core (without using a spacer) and alkyl chains were instead present on the other side of the electroactive unit. The packing in lateral dimensions for these SAMs was not dense because of the lack of favourable interactions between alkyl chains resulting from the steric constraint at the dithio unit at the head of the TTF core. Current sensing AFM measurements allowed an estimation of the resistance on a single molecule in the monolayer (25.7 ± 0.3 GΩ), which was remarkably low for an organic molecule with mechanical contacts and compared to the resistance estimated for alkanethiols of equivalent thickness ($\gg 100$ GΩ). This result confirmed that TTF derivatives are good candidates for molecular wires.

3.2 Physisorbed SAMS

Physisorbed monolayers of small molecules have not received the same amount of attention as chemisorbed monolayers, probably because of the difficulty of controlling the exact location of the adsorbed molecules – among other factors – on account of the dynamic nature of the interaction between the molecules and the substrate. This shortcoming can be overcome by understanding the molecule–substrate and molecule–molecule interactions which would enhance the control over these monolayers. One of the main advantages of self-assembly is the possibility of encoding the information for building specific packing patterns on the surface in the chemical structure of the molecules, often by exploiting non-covalent interactions such as hydrogen bonding and coordination bonds.

Adsorption of molecules onto graphite from solution in a high boiling organic solvent gives physisorbed monolayers spontaneously at the liquid–solid interface. Scanning tunnelling microscopy (STM) has been employed to investigate the ordering of the molecules in this type of system at room temperature (Fig. 4). The interactions that are common to most examples of adsorbate are the alkyl chain–graphite ones. However, the cores 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 chains can lead to different packing forms, and if the cores interact strongly their orientation relative to the substrate can be influenced, as we shall see.[27–29] The orientation of the layers can be directly compared to images of the graphite substrate, which is recorded by lowering the tip of the STM. 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.

The study of simple series of alkyl chain substituted TTFs show that 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.[27] When no long chains are present, the TTF can also 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 (Fig. 5).

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 and even molecules stacked on top of each other. The system is a particularly interesting one from the molecular electronics point of view, because a rectifying current is observed when scanning tunnelling spectroscopy (STS) curves are recorded over the molecules in the monolayers as well as over the "isolated" molecules.[28] These organizations are not suitable to generate wires because the cores are lying coplanar to the graphite surface (Fig. 6a, left). In order to generate them, a coplanar orientation of the molecules is required, perpendicular to the surface (Fig. 6a,

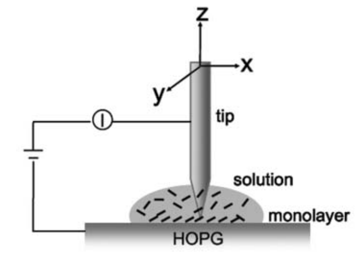


Fig. 4 STM set-up for probing physisorbed SAMs.

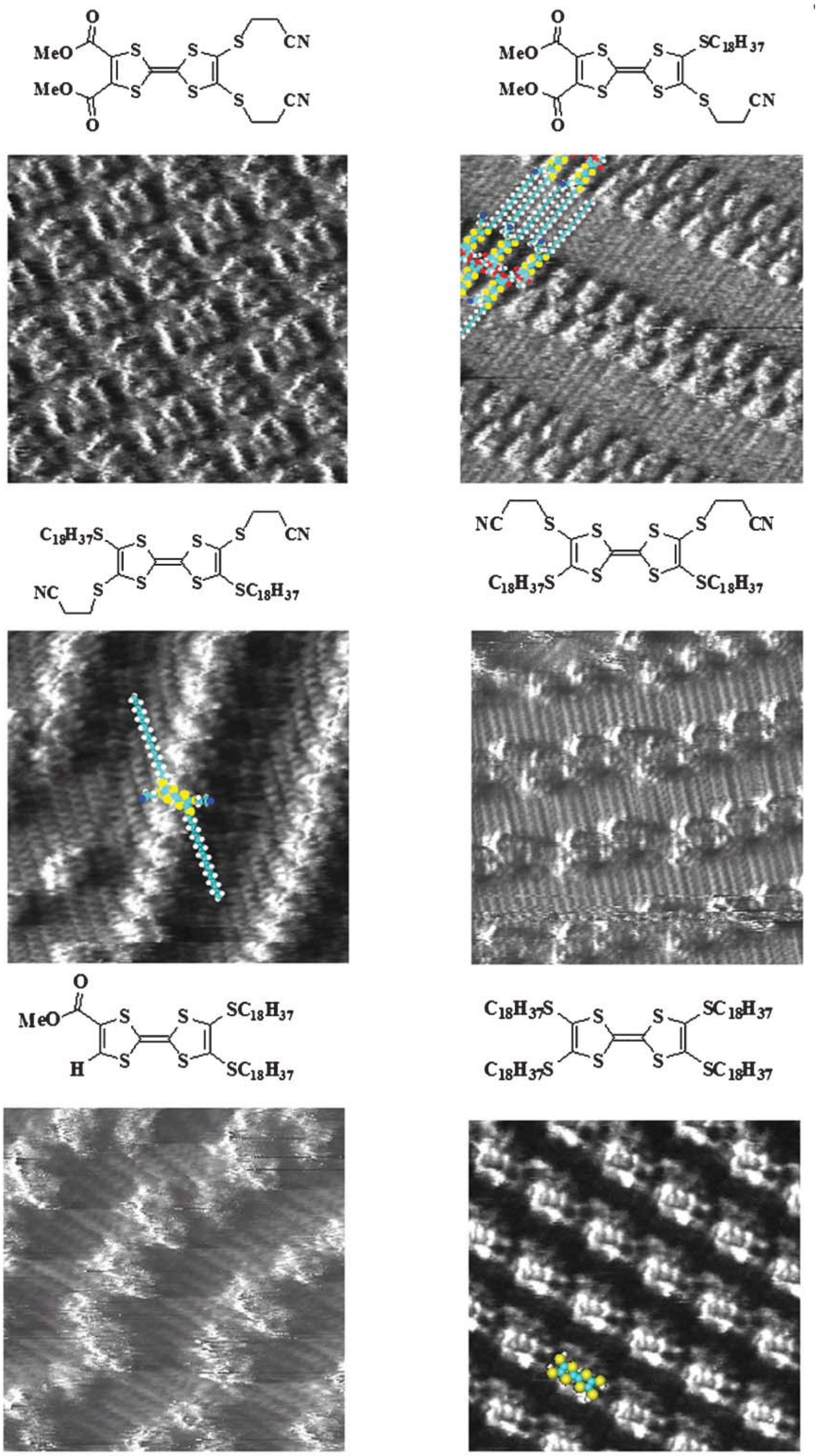


Fig. 5 STM images of TTF derivatives with different numbers and positions of alkyl chains.

right). Therefore, the molecule–molecule interaction has to be increased. An effective way to do this is using hydrogen bonds.[29]

Indeed, a TTF derivative including two amide groups in the chains emanating from the core orders very nicely at the graphite–octanoic acid interface (Fig. 6b).[29] The separation between the areas of bright contrast in the STM image shown coincides with a π–π stacking interaction, and molecular modelling of the compound on graphite supports this hypothesis.

The stacks are well separated from one another by the abutting alkyl chains which lay flat on the surface. The stacks also show wire-like electronic character. STS results show a small experimental gap, and calculations of the width of the valence band and conduction band give values of 0.54 eV and 0.44 eV, respectively. These large bandwidths indicate that the

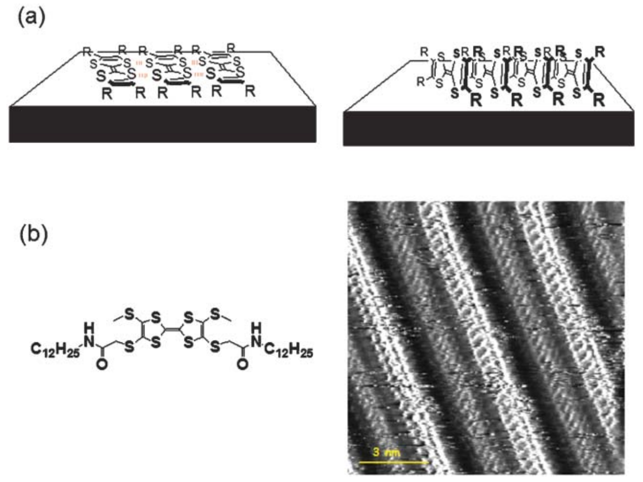


Fig. 6 (a) Arrangement of TTF on a surface in which surface–molecule interactions dominate the arrangement of the molecules (left) and the forced alignment of the π systems which can arise by making the molecule–molecule interactions sufficiently strong (right). (b) An STM image of the TTF shown which self-assembles through hydrogen bonds to give a stack of the electron-rich cores.

TTF stacks can act as molecular wires both for hole and electron transport.

4 Langmuir–Blodgett (LB) films

The LB film forming technique is a potent tool for the preparation of a variety of layers which exhibit interesting properties.[6] Its strength lies in the fact that nanometre-thick layers can be grown sequentially in a controlled way, where the orientation of the molecules is fixed with the long axis perpendicular to the surface, and the relative disposition can be determined by the dipping direction of the substrate (Fig. 2c).

The study of TTF-based Langmuir monolayers and LB films has been discussed in a comprehensive manner by Talham.[6] The vast majority of these films, and especially those showing the highest electrical conductivities when doped, are prepared from TTF derivatives bearing a single alkyl chain. Here, the TTF moieties are positioned parallel to each other and perpendicular to the surface, a situation which guarantees the correct general orientation for conductivity when charge carriers are introduced by doping (with iodine vapours usually).

LB films generally have granular morphology, in which different domains exist oriented in different directions. Therefore, the bulk conductivities in the doped films are always worse than those of crystalline materials, because thermally activated intergrain processes are required for the transport of charge in addition to the conductivity within the domains. However, it remains to be seen what the conductivity within the layers is over the scale of nanometres, a study which is technologically feasible today. One of the areas which has raised most interest in the area of TTF derivatives in molecular electronics has been the possibility of preparing molecular rectifiers. These systems, which allow current to pass more easily along the long axis in one direction rather than the other, are usually prepared in such a way that an electron accepting moiety is included in the molecule, to facilitate the directionality of charge transfer.

One example of these is molecule **10**, which incorporates an aliphatic TTF part and a trinitrofluorene moiety as the electron acceptor.[30] Note that two chains were attached to the TTF part to compensate for the large size of the fluorene head group. This compound forms Langmuir layers when spread from a chloroform solution onto a water surface followed by compression (Fig. 7). The surface pressure–area per molecule isotherm increases sharply below 60 Å^2 per molecule, has an inflection at approximately 50 Å^2 per molecule, and collapses below 30 Å^2 per molecule. The uneven curve was thought to arise from a conformational change in the molecule. A detailed analysis of the conformation of the molecules in the layer was possible thanks to infrared spectroscopy, which indicate that the TTF moiety forms a slight angle with respect to the perpendicular to the plane of the interface, where the fluorene moieties are located.

These monolayers were then transferred onto silicon or gold and top electrodes were deposited to generate tunnel junctions. A clear preference for current flow is seen in the current–voltage sweeps of these devices. The rectifying effect (the ratio

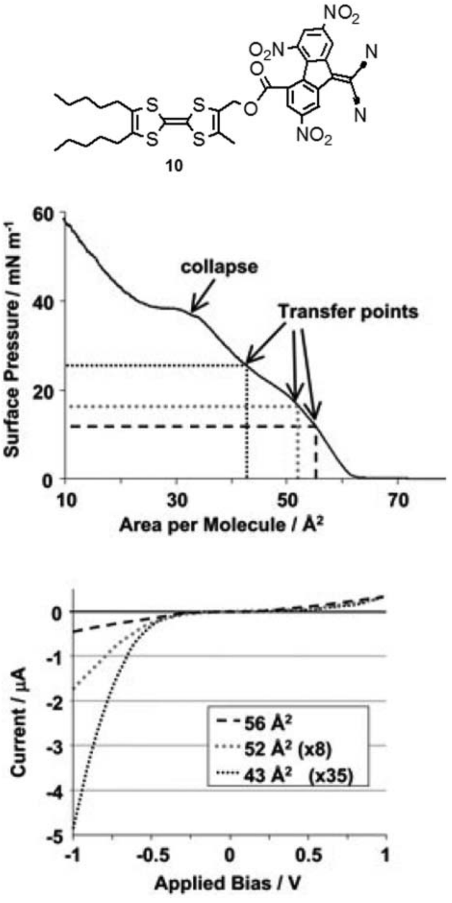


Fig. 7 Molecular structure of the molecular rectifier **10**, the Langmuir isotherm of **10** with the points of transfer of the film indicated (middle) and the corresponding current–voltage curves in an n-Si/molecule/Ti tunnel junction (bottom). (We thank Wiley-VCH for permission to reproduce the graphs.[30])

of current flow in the favoured direction over the unfavoured one) increases importantly when the compression of the layer is increased, because of the steeper alignment of the molecules with respect to the surface (Fig. 7). The molecular origin of the rectifying effect was proven by exploiting the possibility of the LB technique to cover a surface with the polar or apolar part of the molecule in contact with it.

A series of crown ether derivatives incorporating two TTF residues have proven to be particularly interesting regarding the nanostructures that they form in the Langmuir trough and then deposited onto surfaces, either by vertical or horizontal lifting.[31] As an especially nice example, the salt comprised of the dication radical of these bis-TTF macrocycles and the anion radical of F_4TCNQ (Fig. 8) shows a range of nanowires formed by vertical transfer onto mica from the surface of either pure water or dilute solutions of alkali metal salts.

For example, the sample from the surface of the NaCl solution shows a monolayer and a series of interwoven, curved nanowires, while that from KCl also shows these structures to some extent, but also a number of straight nanowires, aligned with the symmetry axes of the mica surface. On the other, when the horizontal lift-off technique was used from the sample on the KCl solution, mainly the straight wires aligned with the surface axes are observed by AFM (Fig. 8c) The hypothesis to describe this alignment involves recognition of the potassium ions which are present in the crown ether part of the structure in preformed wires with the potassium vacancy sites on the cleaved mica surface. The morphology of the nanowires depends on the potassium ion concentration in the subphase, as well as the temperature and the surface pressure at which the deposition is carried out. The bulk conductivity of multilayer films is of the order of the expected one for a salt of this nature (10^{-3} S cm^{-1}).

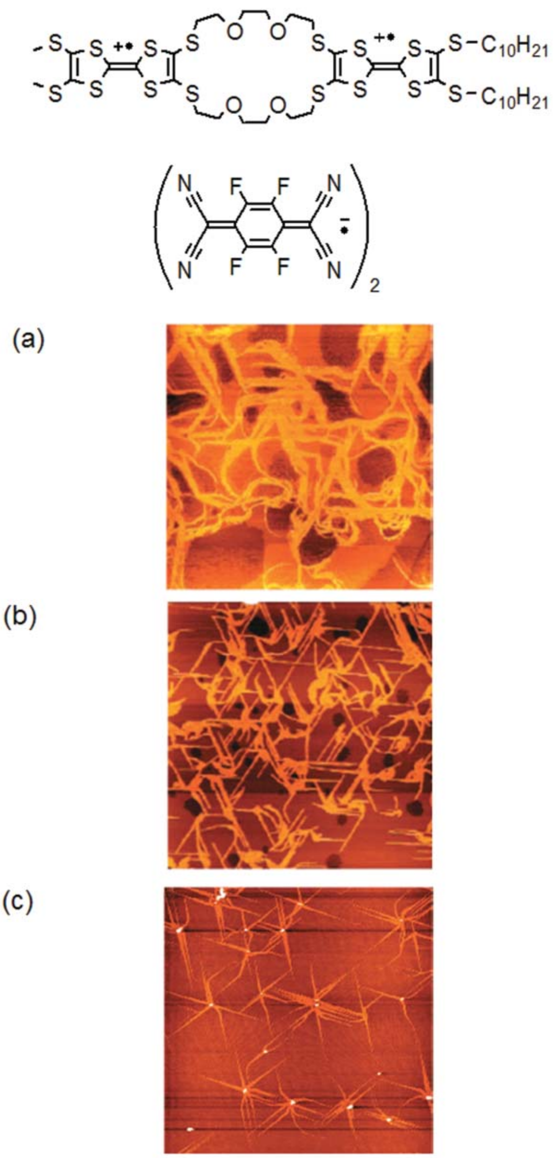


Fig. 8 Molecular structure of the salt X $(F_4TCNQ)_2$ and AFM images of the salt on mica substrates. (a) transferred by the vertical dipping method from 0.01 M NaCl (10 × 10 μm); (b) transferred by the vertical dipping method from 0.01 M KCl (10 × 10 μm) and; (c) transferred by the horizontal dipping method from 0.01 M KCl (30 × 30 μm). (We thank the National Academy of Sciences of the USA for permission to reproduce AFM images.[31])

5 Solution evaporation

The deposition of molecular materials from solution can result in the formation of well-defined nanostructures, but careful choice of the method and the different parameters involved, such as the polarity and volatility of the solvent, the concentration, the chain-length dependence in amphiphilic derivatives, and the nature of the surfaces is necessary. In this section we will focus on the influence that these factors play in the assemblies of functional π-electron-rich compounds.

5.1 Drop casting

A solvent-mediated drop-casting technique is a deposition method which allows one to vary the coverage of the film according to the concentration of the original solution. Moreover, the control of the supramolecular structures determined thermodynamically or kinetically is also allowed by this technique, when temperature, surface, solvent and molecular structures are considered. Therefore, unlike the Langmuir technique which in general is focused on complete monolayer formation, sub-monolayer coverages are easily achieved quickly, as well as thick film formation. However, the level of perfection of the films is in general not as great as that achieved with the Langmuir technique.

Recently, a group of related but dissimilar TTFs derivatives allowed the evaluation of the factors mentioned previously in their self-assembly into rod like structures when the solvent-mediated drop-casting technique was used.[32] Six different TTF derivatives (Fig. 9) were studied, three *trans* (**11a**, **11b** and **11c**) and three *cis* (**12a**, **12b** and **12c**), in which the lengths of the aliphatic chains were also varied.

When chloroform solutions of the *trans*-TTF isomers were deposited onto highly oriented pyrolytic graphite (HOPG), AFM images of the films revealed rod-like objects of varying length and breadth. In the case of **11a** and **11b** (Fig. 10a and 10b, respectively) no dependence on the concentration was observed in the formation of their structures but a clear

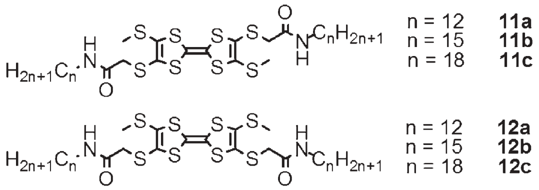


Fig. 9 Molecules studied to evaluate the influence of structure on nanofibre formation upon casting.

orientation with respect to complementary graphite axes was detected. For the *trans* TTF compound **11a**, the block-like objects have varying length, but more importantly the height and width of these aggregates were bigger than those of **11b**. This aspect could be accounted for by the different solubility of the compounds in the solvent used for deposition, which introduces a kinetic factor into the formation of such self-assembled structures. On the other hand, *trans* isomer **11c**, studied under same conditions, forms a dense mesh of very fine fibres with no well defined distribution over the HOPG (Fig. 10c). The small dimensions of the fibres observed by AFM and their random orientation point to precipitation in solution rather than on the surface, a result supported by fibre formation even when the surface is not present, on a transmission electron microscope grid.[32]

While **11a** and **11b** do not present differences in their morphologies, the *trans* isomer **11c** generates small aggregates (Fig. 10c) and very long isolated fibres (Fig. 10d) when lower concentrations (10^{-5} M) of the compound in chloroform are used. The big difference in the width of the fibres between high and low concentration deposition for **11c**, and the lack of orientation of the fibres when diluted, implies that the ones formed from more concentrated solutions of this compound are deposited under kinetic control rather than under a more thermodynamic influence seen at lower concentrations in chloroform. So the concentration, solubility of the compound (alkyl chain length), and the region of the evaporated drop which is under study are important factors when the dimension and morphology of the structure generated are of concern.

The surface onto which the solutions are cast also plays a central role in the formation of the finer structures. When the same casting experiments were performed on hydrophilic surfaces, instead of hydrophobic ones, the fibre-like structures were not observed, even when using the strong and directional amide group as the hydrogen bonding unit. As an example, we can consider again the TTF derivative isomers we focused on in the preceding paragraphs, where no fibres or blocks are observed in the AFM images when the casting experiments are performed from toluene on freshly-cleaved mica, independently of the concentration used. Instead, mono- and multi-layers are observed along with amorphous chunks of material (Fig. 11). Therefore, the ability of the amide to self-assemble as functional units in fibre-like aggregates on graphite is disturbed on hydrophilic surface, possibly on account of the interaction between the amide groups of the molecules with it, as seen for other amide derivatives.[33]

The solvent used for the compound deposition also shows an important role on the aggregation process on any surface. For example, when toluene was used to deposit compound **11c** on graphite, it did not generate well-defined fibres as were observed from chloroform, but in some areas a monolayer was imaged by AFM in which fibril morphology was evident (Fig. 11). These fibres have a width which corresponds to the length of a single molecule, very unlike the morphology seen from chloroform.

The constitution of the molecule is also of critical importance. When the *cis*-TTF derivatives (**12a–c**) were cast onto graphite from toluene or chloroform (at the same concentrations as the *trans* isomers), no well-ordered fibres or blocks were observed. Rarely, nanofibres of the type seen for the *trans* isomers were observed for the *cis* isomer, but in general with smaller dimensions, close to the molecular resolution, owing to the fact that now a stronger interaction of the TTF derivatives with the surface was active.

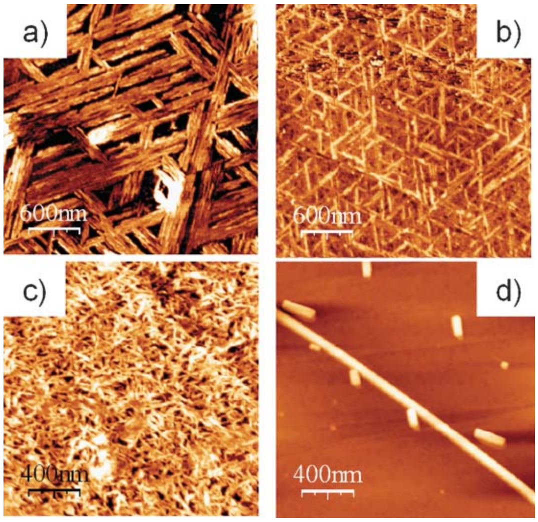


Fig. 10 AFM images of **11a** (a), **11b** (b), and **11c** (c and d) on HOPG after evaporation of the solvent. All images are from a 10^{-4} M chloroform solution except (d) which comes from 10^{-5} M.

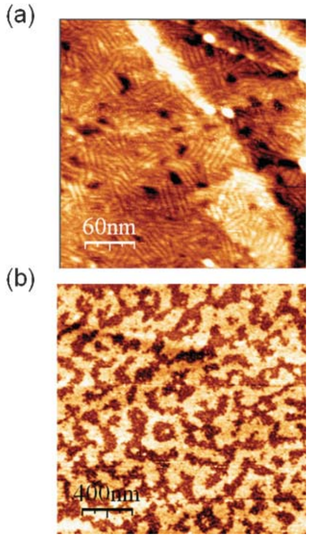


Fig. 11 Topographic AFM images of **11c** recorded on graphite (a) and mica (b) both from toluene solution 10^{-4} M.

The *cis* isomers have the possibility for both alkyl chains to adhere fully on the surface through van der Waals interactions, allowing the formation of short and small fibrillar domains, while for the *trans* isomers the contact of both chains is less favourable because of their S-shape.

Another physical process observed frequently in the solvent-mediated drop-casting method is dewetting. This phenomenon describes a rupture of a thin liquid film on the substrate and the formation of droplets which actually can be controlled to generate patterns (Fig. 12). For example, binary mixtures of two, polymers and dewetting, are accompanied by a phase ordering.[34] The final structures can be controlled by variation of the molecular weight of the polymer, volatility of the solvent used, and the diameter of droplet formed, which depends on both previous factors. At higher concentrations, the droplets fuse and worm-like structures are observed, as in the case of compound **11c** on mica (Fig. 11b).

5.2 Spin coating

Spin coating is a deposition technique which offers an easy and inexpensive process for mono and multilayer formation. This method has several technical advantages when compared with drop casting or immersion. In these techniques, the molecular units are allowed to diffuse around the substrate according to the chain and functional groups present. In contrast, for the spin-coating process the adsorption and rearrangement of adsorbed chains on the surface and the elimination of weakly bound molecular units from the substrate can be achieved almost simultaneously depending on the rate of rotation. The best-quality films are obtained by optimising the spin speed and the time of application, as well as the substrate and the solution concentration.

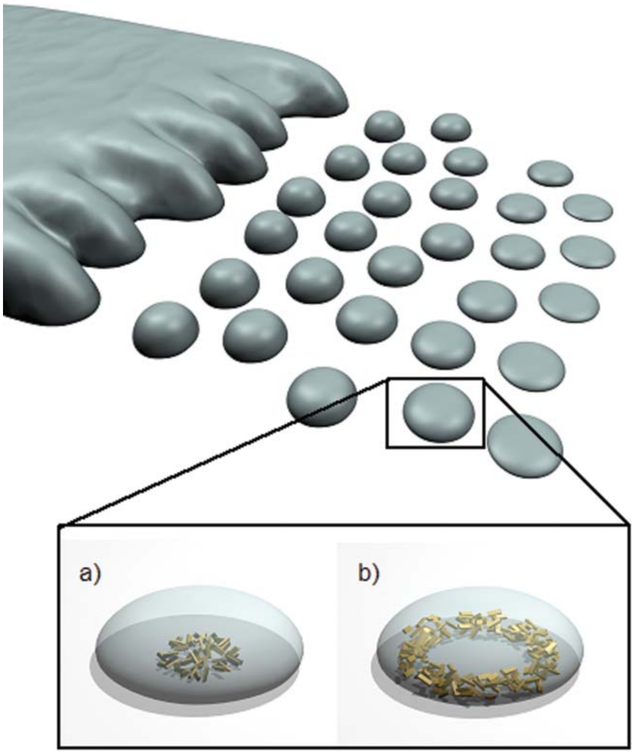


Fig. 12 Representation of a thin liquid film which ruptures on the substrate with the formation of droplets. In the bottom part of the figure a schematic representation of specific patterns that can be reached: (a) formation of spot-structure and in (b) nanoring structure.

By using the TTF electroactive core unit, semiconducting behaviour can be achieved by simple spin-coating technique instead of SAMs, Langmuir–Blodgett, sublimation, drop casting, zone casting and electrochemical deposition. This feat is possible because the spin-coating processes can yield a highly ordered internal structure. A recent example of this effect is the spin coating of arborol (tree-like) TTF derivatives (Fig. 13) which are semiconducting after doping (either chemical or electrochemical) on account of the significant degree of supramolecular order present.[35]

While the compounds terminated with ester groups (**13**, **14**, and **15**) did not form well-ordered films, the alcohol-terminated compounds (**16**, **17**, and **18**) do. The TTF derivatives containing four side-chains, each bearing two or more terminal hydroxyl groups, showed improved film quality

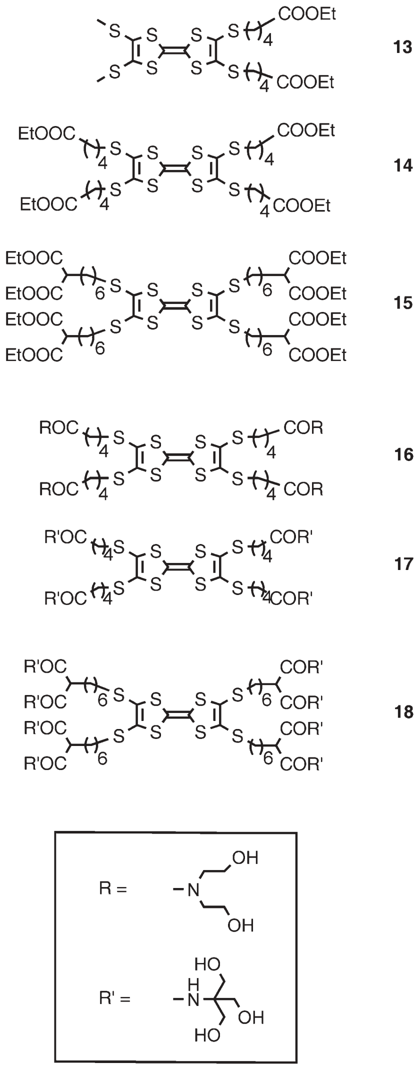


Fig. 13 Molecular arborol systems of TTF derivatives studied by spin coating method.

when the number of hydroxyl groups at the periphery of the molecules was highest.

These results emphasize the importance of the ordering on the properties of molecular systems, and show the possibility of using spin-coated films for the formation of semiconducting charge-transport layers.

Another proof of this statement is a study carried out by Akutagawa *et al.* where nanowires and size-controllable nanodots based on charge-transfer (CT) complexes of the amphiphilic TTF derivative **19** were achieved.[36] When an organogel of neutral **19** was cast the film surface morphology revealed fibrous shapes. In contrast, the CT complex formed isolated fibrous structures or nanodots. The electrical properties were analysed and observed in the case of the spin-coated film. The diameter and height of the nanodots clearly depended on the rotational speed of the spinner, with the nanodot diameter decreasing when increasing spin speed was employed (Fig. 14).

To conclude, spin coating is a technique which allows control of film formation where morphology can be varied by adjusting the spin speed and controlling the experimental conditions, such as the concentration, wetting angle of the substrate, and suitable positioning of groups inside the molecule to drive the organisation.

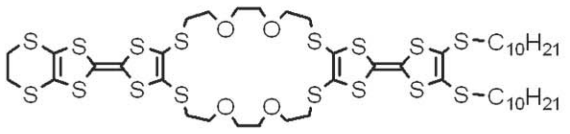
5.3 Zone casting

Drop casting and spin coating do not allow the preparation of films with complete anisotropy over large areas. An appealing one-step method for the preparation of large area anisotropic films from a solution-processible material is zone casting. This technique was originally designed to produce composites of conducting polymers, as was spin coating, but both of them have been successfully adapted to produce oriented layers for different molecular systems.

Recently, large area films of a TTF derivative with long alkyl chains have been obtained with this technique.[37] X-ray reflectivity scans and grazing incident diffraction revealed that the TTF molecules in these films were tilted with respect to the substrate surface and were well-aligned in the casting direction (Fig. 15).

These oriented film layers have a high one-dimensional electrical conduction path attributed to the intermolecular π–π overlapping of the closely packed electroactive cores, and have potential application as field-effect transistors (FETs). Tens of FETs were fabricated in a reproducible way when the casting parameters such as temperature and casting speed were optimised. In addition, it was observed that the charge carrier mobility improved considerably (close to 0.1 cm^2 V^{-1} from 0.006 cm^2 V^{-1} for a channel length of 100 μm) upon annealing the devices by heating.

Therefore, zone casting is a technique which allows the construction of highly oriented films covering large areas in two directions: parallel and perpendicular to the casting direction. Herein an alignment control along the solvent evaporation front is possible rather than an anisotropic flow toward the front.



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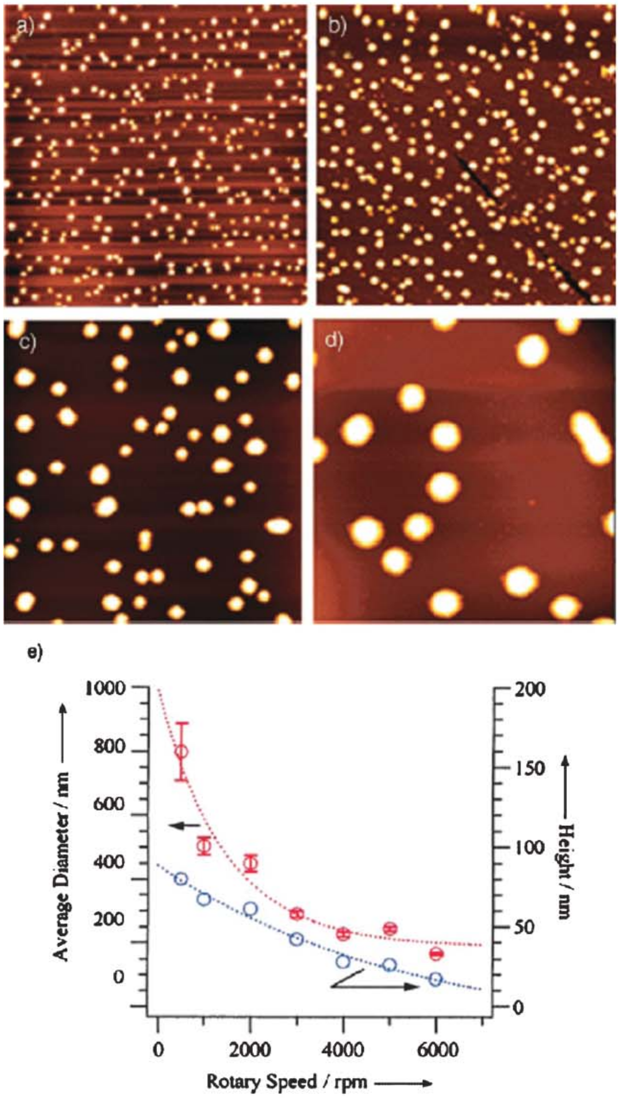


Fig. 14 Molecular structure of **19** and AFM images of size-controllable nanodots going from higher rotation speed substrate (a) to lower (d) based on charge-transfer complex formed from organogel on mica. The scale of all AFM images is 10 × 10 μm^2. In (e) average diameter and height of the nanodots obtained from statistical analysis of the AFM images. (We thank Wiley-VCH for permission to reproduce the graphs.[36])

6 Thermal evaporation

Vacuum deposition of small organic molecules by sublimation is another technique used to prepare thin films for organic electronics such as FETs. An advantage of this technique *versus* zone casting is that the thickness of the film can be fine tuned from less than one to several monolayers using a crystal quartz monitor during the deposition. This feature makes this technique convenient for thin film growth studies at different stages of the film formation together with complementary characterization techniques such as AFM, STM and X-ray diffraction. Factors that affect the molecule crystal growth are the purity of the organic material, the nature, cleanness and

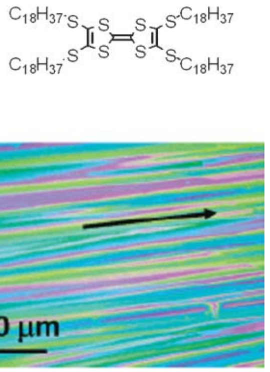


Fig. 15 Molecular structure of a TTF derivative studied by zone casting and optical micrograph image of the zone-cast film. The black arrow indicates the casting direction.

roughness of the substrate, the evaporation rate and the temperature at which the substrate is held during the evaporation. Disadvantages of this technique are that it is limited only to molecules that can sublime and are stable to the sublimation temperatures, and expensive high vacuum equipment is needed.

Although TTF had been widely used to prepare conducting and superconducting molecular materials, the application of TTFs in OFETs has only been initiated in the last years. Mas-Torrent *et al*. have recently reviewed the progress in the field.[38] The strong electron-donating properties of TTFs make their thin films labile to oxygen, resulting in poor FET performances. To enhance their air stability, a decrease in the TTF electron-donating properties is necessary. This can be achieved functionalizing the TTF unit with groups that increase the oxidation potentials. The introduction of fused aromatic rings or electron-deficient nitrogen heterocycles to the TTF skeleton has been proved to enhance the stability and high hole mobilities were obtained in the thin films.[39]

Compared to p-type semiconductors, the number of n-type semiconductors is still limited, and their FET performances are not satisfactory. The development of good n-type materials is crucial for the fabrication of p–n junctions, bipolar transistors, and integrated circuits. To obtain high electron mobility, organic semiconductors should have LUMO energy levels near the work function of electrodes. A strategy to obtain high performance n-type organic semiconductors is the introduction of electron-accepting substituents into electron-donating π-conjugated systems. TTF derivatives with halogeno-substituted quinoxaline rings have led to FET devices with excellent n- or p-type performances with high carrier mobilities by controlling the HOMO and LUMO levels of the molecules.[40]

By applying electrical fields between pre-patterned electrodes on the substrate, it is possible to direct the deposition of the molecules and to form nanostructures – such as nanowires – instead of uniform films. This type of thermal evaporation deposition is called *electric-field assisted evaporation*.

6.1 Electric-field assisted evaporation

Since the electrical wiring of nanometer-size organic semiconductors is difficult, it is necessary to fabricate conductive electrodes by self-construction. Sakai *et al*. have prepared organic conductive wires and nano-transistors using co-evaporation of TTF and tetracyanoquinodimethane (TCNQ) under an AC electric field.[9] Needle-like crystals of TTF–TCNQ charge transfer complex grow from the edge of gold electrodes along the electric field (Fig. 16). The frequency dependence of the growth time of molecular wires indicates that an AC electric field around 100 Hz is the most effective for making connected wires. Many connected wires were highly conductive and did not show any modulation of electrical conductivity with the gate voltage. However, n-channel field effect transistors were observed with improvements of growth sequence. This was attributed to the formation of a tiny semiconductor area formed at the connecting point of two conductive wires grown from opposite electrodes. The electrical conductivities of the conductive wires were 20–100 S cm^{-1} which are lower than that of the *b*-axis of single crystals (500 S cm^{-1}) but much higher than the inhomogeneous conductivity along *a*-axis (1 S cm^{-1}) and *c*-axis (3 S cm^{-1}). The long axis of the molecular wires corresponds to the *b*-axis of TTF–TCNQ segregated stacking crystal. A local nonstoichiometry at the connection of two wires could be the cause of the decrease of the total electrical conductivity. The total electrical conductivity of the semiconducting nanowires was 0.2 S cm^{-1} (1/500 smaller than for conductive wires) and increased when increasing the gate voltage behaving as an n-channel FET (Fig. 16).

Another technique that takes advantage of the application of an electric field between two electrodes is electrochemical deposition.

7 Electrochemical deposition

Unlike redox-inert systems, in the electrochemical technique the ability exists to produce films accurately in regard to nucleation and growth, by controlling the potential and current flow of the system. The construction of these films occurs under ambient conditions so that their assembly can be

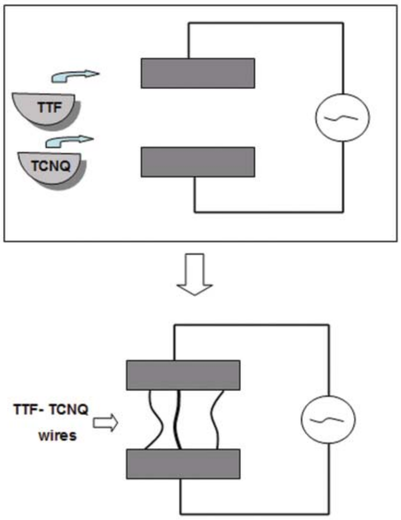
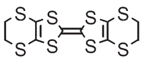


Fig. 16 A schematic representation of the formation of nanoscale wires of the conductor TTF–TCNQ formed in UHV between two electrodes with an alternation current between them.

examined directly with AFM or STM when using a three-electrode design adapted for electrochemical growth (Fig. 2g).

Many studies illustrate that the overlayer structure and orientation with respect to the substrate in a multilayer system is governed by interactions between the substrate and large ordered arrays of molecules rather than individual substrate–molecule interactions. Therefore, the appropriate control which this technique provides on the first crystals grown over the surface allows influences of the crystal nucleation, growth, polymorphism, and morphology. Such control also is governed by the electrocrystallization conditions and the characteristics of the electrode surface applied in the systems at the atomically level. Depending on the potentials and the crystallinity of the surface the selective formation of different polymorphs can be achieved.

An example of this effect is the random island formation of either α-(ET)$_2$I$_3$ or β-(ET)$_2$I$_3$ charge-transfer salts on HOPG substrate surface (working electrode), when oxidizing ET molecules by a three-electrode cell in acetonitrile containing also the I_3^- counter-ion.[10]



ET-TTF

These islands grow anisotropically along preferred directions on the HOPG surface, with the progression eventually terminating either at the boundary of another island or at the edge of a graphite step. Moreover, it is possible to selectivity create one or other polymorph by controlling parameters like the potential applied and working electrode make-up. The kinetically favoured α-phase is formed when high overpotentials or electrochemically etched HOPG working electrodes are used. If either low overpotentials or pristine HOPG are employed the β-phase can selectively be reached.

The result described here demonstrate that the organization of crystalline molecular overlayers on highly ordered substrates can be governed and formed by coincident epitaxy between the overlayer and substrate rather than by individual molecule–substrate interactions. At the same time the connection between the overlayer and the surface can be driven by electrochemical deposition as presented previously.[41] Recent work has also shown how nanowires can be generated,[42] and electrodeposited salts of TTF derivatives on silicon even show signs of superconductivity.[43]

8 Conclusions and outlook

The organisation and properties of molecular nanostructures on surfaces can be influenced greatly using the different techniques for the preparation and deposition and the supramolecular characteristics of the molecules. Key factors for the formation and properties of these structures are chemical design and the balance of the non-covalent interactions that direct the self-assembly of these molecules on surfaces (molecule–molecule, molecule–solvent, molecule–substrate and solvent–substrate). However, a major challenge is the formulation of quantitative rules for the understanding of the balance between these factors, as well as the role of annealing, to mention but two important effects. Thorough investigation of these effects in molecular systems is sure to be critical in the advancement of the area.

A large number of interesting systems have been described and the incorporation of these structures in working devices has been proved. But there are still important issues that need to be addressed to move toward device applications. The search for new molecules with improved stability processability and semiconducting, optical and/or magnetic properties is important. A noteworthy opportunity here is the use of self-assembly to prepare hybrid systems with predesigned pathways for interaction between components, for example the functionalisation of electrodes to fuse organic and oxide or metal-based structures.

It is also necessary to develop easier and more reliable methods to generate larger extensions of nanostructures with more control over their homogeneity and location. An interesting approach to solve this is the combination of top down microfabrication techniques with bottom down techniques. Examples of this are *templating self-assembly* where an element of pattern is introduced into the self-assembled structure to increase its order and the use of printing techniques.[44] If full advantage can be taken of these innovative methods, it seems only a matter of time before molecular nanostructures find functions in mass use devices.

Acknowledgements

We thank warmly all the coworkers who have contributed to our own work in this area, as well as Steven De Feyter (Katholieke Universiteit Leuven) and Mathieu Gonidec (ICMAB, CSIC) for illustrative material. We are grateful to the public bodies that have funded our Research, in Bellaterra the DGI (MEC, Spain Project CTQ2006-06333/BQU), the European Integrated Project NAIMO (NMP4-CT-2004-500355), and the Marie Curie Research Training Network CHEXTAN (MRTN-CT-2004-512161).

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