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Supramolecular organization of highly conducting organic thin films by the Langmuir–Blodgett technique

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The optimization of organic materials in semiconductor devices or as electrical conductors in devices is closely related to the optimization of electroactive molecular structures which can self-assemble into highly ordered solid films when cast from solution. This supramolecular optimization problem is dissected in the present feature article by focusing on self-assembly of thin films at the interface between water and air (Langmuir films). Recent advances towards fabrication of highly conducting Langmuir–Blodgett (LB) films is reviewed. Owing to new accurate structural methods, including synchrotron X-ray diffraction and scanning probe microscopy (in particular atomic force microscopy, AFM), the steps in the assembly process of Langmuir-Blodgett films can now be studied in unprecedented detail. This is exemplified for the electroactive molecular surfactant 2-octadecylsulfanyl-*p*-benzoquinone, and for amphiphilic derivatives of regioregular polythiophene. In the first case control over the packing of the electroactive part of the molecule is lost because the alkyl chains dominate the packing. For amphiphilic regioregular polythiophene the ability to π stack is the important feature that controls the assembly process leading to highly conducting polycrystalline films ($\sigma \approx 100$ S cm^{-1}). Comparisons of prototype systems such as disks, boards and rods dressed with alkyl chains show that in cases where π stacking is allowed to dominate over alkyl chain packing the structures formed at the air–water interface resemble bulk structures of similar molecules. Based on these analogies the link between the LB-assembly process and other solution based methods for film fabrication (such as spin coating) is discussed.

1 Introduction

In order to take advantage of tailor-made organic molecules for devices it is of paramount importance to control the supramolecular structure of the molecules in functional nanostructures and materials since functions such as electrical conductivity or chemical sensing depend crucially on the supramolecular arrangements of the material. In this context the assembly of molecular architectures that possess high electrical conductivity is very ambitious because electrical conductivity depends on the supramolecular (or intermolecular) contacts all the way from the source to the drain electrode. The challenge is hence to control not only nearest neighbor interactions but also the nano- and micro-scale morphology of the sample by proper molecular design and choice of sample preparation method. In addition, controlled introduction of charge carriers is also necessary. These challenges have to be met because self-assembled organic materials with good electrical conductivity (or equivalently high carrier mobility) are very important for future improvement of organic materials for electronic devices.

Owing to restrictions set by the preferred film fabrication methods (*e.g.* spin casting from solution) highly conducting organic materials should ultimately consist of molecules which are flexible enough to be soluble. In addition, the molecules should be coded in a way which allows them to find their way from a disordered state in solution into a highly ordered solid state through proper recognition of their nearest neighbors. The current focus on research involving nanoscale devices further emphasizes the need to control the micro- and nanoscale structure of molecular architectures.[1–6]

The present paper focuses on the status of rational assembly of conducting organic thin films by use of the Langmuir–Blodgett (LB) technique. This area of research offers a unique opportunity for studies of the supramolecular assembly process because the air–water interface provides a very well defined experimental situation in which the individual steps of the pseudo 2-dimensional assembly process can be addressed. By including highly accurate structural methods such as diffraction of synchrotron X-rays[7,8] and, after transfer to solid supports, scanning probe microscopy,[9] unprecedented insight into the assembly process can be obtained.

Systematic studies of the assembly process in general, including assembly at the air–water interface, will hopefully evolve with time into general rules for rational design of molecules suited for self-assembly into specific target structures.

1.1. Status of supramolecular (crystal) engineering

Organic synthesis has presently reached a stage where almost any molecule can be synthesized. This tremendous deed has been accomplished by systematic dissection of the synthesis of complex molecules into steps where prototype chemical transformations are made. Compared to this advanced level of scientific craftsmanship, our ability to organize organic molecules, once made, into larger predetermined 'supramolecular' architectures is almost non-existent. Of course important new developments have emerged[3,4] since the field of supramolecular chemistry[10] was initiated by the Nobel laureate from 1987, Jean Marie Lehn. Nevertheless, the basic control of for example the supramolecular complex that initiates crystal growth is not yet achieved, as evidenced by the tremendous difficulties encountered in the field of crystal engineering.[11,12] In practice it is still impossible to predict the crystal structure of even simple molecules.[13] The difficulties arise because the intermolecular interactions that hold non-ionic crystals together are so weak and spatially complex that very subtle effects, which are difficult to control, become decisive in determining the overall structure (Fig. 1).

In view of this level of complication the need to divide the problem of 3-dimensional assembly of molecular architectures into less complicated sub-tasks becomes evident. In analogy to organic synthesis, the supramolecular chemistry probably has to be performed in steps in order to identify the important interactions that govern the assembly process. As a starting point, one approach consists of separating the intermolecular from the intramolecular degrees of freedom,[13] another in reducing the effective dimensionality of the system to undergo assembly.[11] Using the first approach, predictions of the 3-

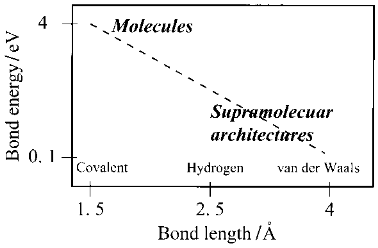


Fig. 1 Schematic illustration of the relation between bond strength and bond length (and type) for molecular structures on various scales.

dimensional crystal structures of non-flexible organic molecules have been made with some success.[13] The second approach offers numerous examples of successful design and assembly of structures in which the main interactions occur in one dimension.[11,14–16] With regard to pseudo 2-dimensional assembly, interfaces play an important role. Among these the air–water interface offers some advantages as discussed in the next section.

1.2 Assembly at air–water interfaces—the Langmuir–Blodgett technique

The Nobel prize in chemistry was awarded to I. Langmuir in 1932 for his pioneering studies of the physical–chemical properties of organic surfactants spread from solution onto an air–water interface of a simple trough.[17] Langmuir and his co-worker K. Blodgett found that for example long-chain fatty acids form a mono-molecular layer at the interface, in which the carboxylic acid moieties are submersed in the water phase, resulting in an overall orientation of the molecules perpendicular to the water surface. The molecules can be pushed together by moving barriers, initially placed at the ends of the trough. The area available per molecule on the surface can hence be controlled by the barrier positions. At the same time the 2-dimensional pressure, π, exerted on the barriers by the fatty acids, can be measured, allowing the pressure–area relationship to be obtained. In particular, it is possible to compress the monolayer into a dense film, which, if stable, can be transferred to solid supports. Different techniques are used for the monolayer transfer. That most frequently used for films of low viscosity is the Langmuir–Blodgett technique, in which the solid substrate simply is dipped and raised (Fig. 2A–D) vertically through the surface while maintaining constant surface pressure.[18,19] This process can be repeated several times resulting in multilayer films. In the normal Langmuir–Blodgett transfer process centrosymmetrical films of the Y type (Fig. 2, right) will be built up. Other multilayered structures are possible: If the film is only transferred at the upstroke, films of the Z type are built up, while X type films will form if the monolayer is only transferred at the down stroke. The normal vertical dipping technique is usually most successful for liquid-like monolayers of for instance long chain acids or phospholipids. If the Langmuir film on the water surface is more viscous, comprised of crystallites or aggregates, transfer by the vertical technique can be difficult because the high viscosity of the film prevents it from flowing towards the substrate. In these cases a horizontal dipping of the substrate can lead to monolayer transfer by the so called Schaefer method[20] (Fig. 2E).

The early work by Langmuir and Blodgett revealed a simple way to control molecular organization at the air–water interface. In the '60s Kuhn and co-workers exploited these possibilities to study exciton formation in LB films of dye-containing surfactants.[21,22] Later, as the field of molecular electronics gained pace through the '80s and '90s, the Langmuir–Blodgett technique has seen a true renaissance as evidenced by numerous reviews and books.[23–25]

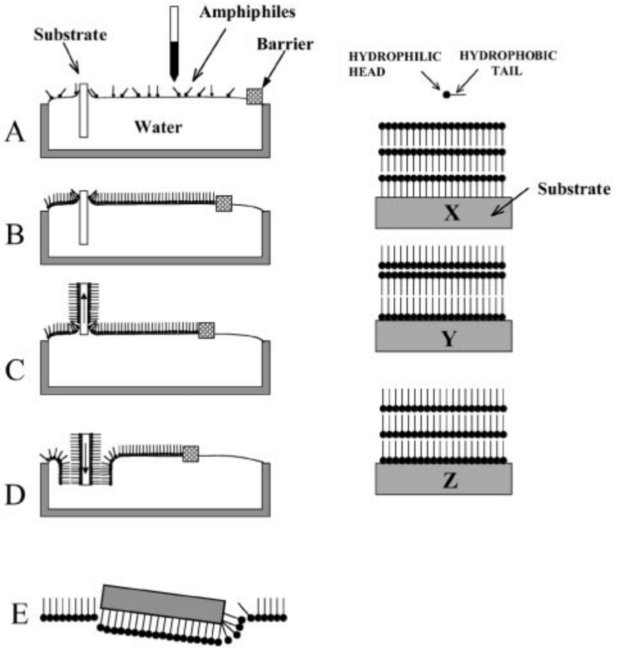


Fig. 2 The Langmuir–Blodgett technique. Left side: A, deposition of the amphiphiles on the water subphase with a solid substrate submerged; B, by action of the barrier the monolayer is compressed; C, by pulling out the substrate vertically a monolayer is transferred to both sides of the substrate; D, a multilayered structure is built up by repeated up and down strokes of the substrate; E, transfer of monolayer by horizontal lifting (Schaefer method). Right side: examples of different types of multilayer structures (X, Y, and Z) which can be built up by the LB technique.

Typical examples of the molecules employed in the beginning of this period to produce molecular electronic systems are shown in Table 1. Included are key examples of surfactant derivatives of dyes, of electron donors and acceptors as well as of molecular push-pull systems; all of them have been used in connection with the Langmuir–Blodgett technique.

Intriguing and important physical properties have been demonstrated from films of such molecules including (i) fair electrical conductivity,[23,26,27] (ii) sizeable second order non-linear optical response,[28] and (iii) rectification of electrical currents.[29,30]

The recent development of synchrotron sources, providing very high X-ray intensities, has allowed diffraction experiments to be performed directly on monomolecular films.[7,8,31] This experiment allows the in-plane structure of the films to be elucidated for the first time. Once transferred to solid supports, local probe methods such as atomic force microscopy[9] may also be used to study the in-plane structure of the surface of the films.[32–38] In combination these two methods have provided the missing link which allows the molecular structure of the individual amphiphiles to be related to the resulting in-plane structure of the films assembled at the air–water interface, as further addressed below.

2 Conducting Langmuir–Blodgett films

2.1 Background

The Langmuir–Blodgett technique has been proposed as a possibility to achieve thin films which are conducting and processable at the same time[23,26,27] and this goal has been pursued by several groups. As shown in Table 2 the guiding structural motif in the first generation of functionalized surfactants for conducting LB films has been taken from the π-stacked organic crystals (Fig. 3). By grafting alkyl side chains to either electron donating or accepting head groups, Langmuir–Blodgett films of *e.g.* the TTF moiety can indeed be fabricated and subsequently doped by iodine vapor. The

Table 1 Examples of a fatty acid (A) and 1st generation molecules for 'molecular electronic' LB films (B–E). References: A,[17,18] B,[40] C,[29,30] D;[21,22,34,54] Review[23]

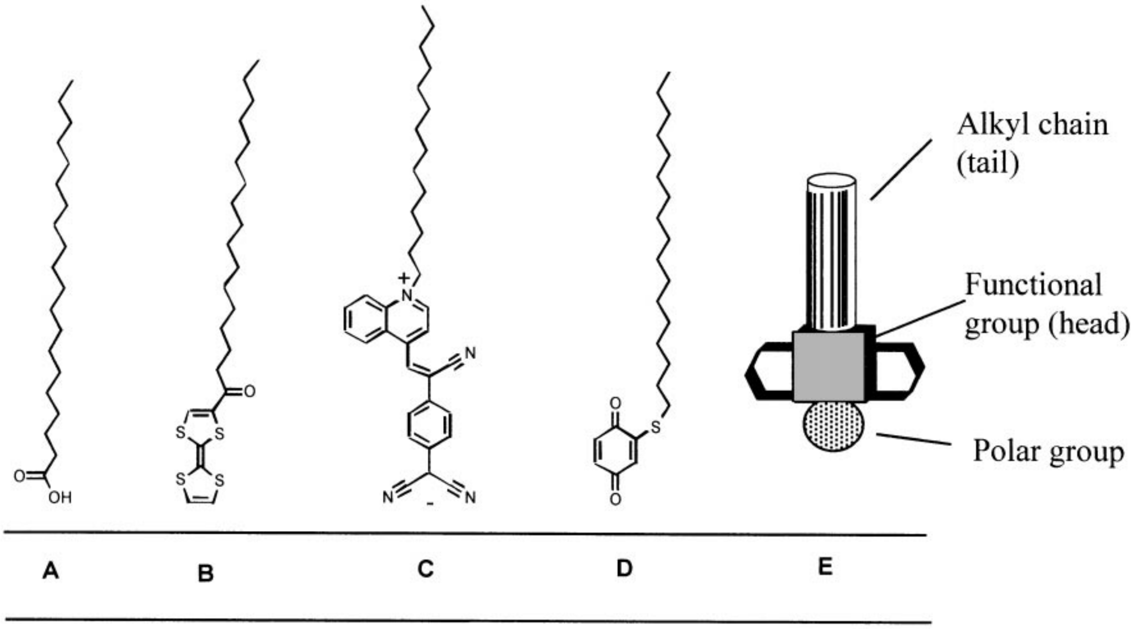
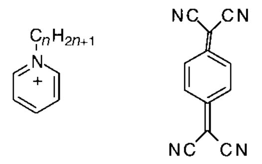
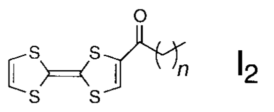
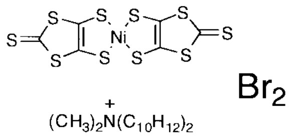
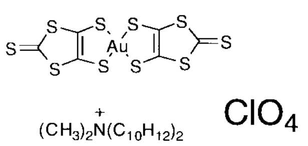


Table 2 Examples of 1st generation molecules for electrically conducting LB films

Molecules	Conductivity	Ref.
	0.1 S cm^{-1}	85-86
	0.01 - 0.1 S cm^{-1}	39,87-90
	0.01 S cm^{-1}	91
	30 S cm^{-1}	92-94

conductivity of these and similar systems lies in the range between 10^{-2} and 20 S cm^{-1},[23,39,40] *i.e.* orders of magnitude lower than the perfectly crystalline parent structure depicted in Fig. 3 which in the following serves as a reference, showing two important structures that are excellent organic conductors in their standard 3-dimensional crystal forms.

Polyacetylene, depicted in Fig. 3A, consists of extended rows of overlapping π orbitals which can promote carrier mobility intramolecularly along the conjugated backbone. Tetramethyltetraselenafulvalene hexafluorophosphate ($(TMTSF)_2PF_6$), shown in Fig. 3B, contains π-stacked molecules which allows charge to delocalize intermolecularly along the π stack. In both materials chemical or electrochemical doping is necessary to create charge carriers on the conducting backbones. The difference between the two materials lies in part in the different band widths resulting from the two

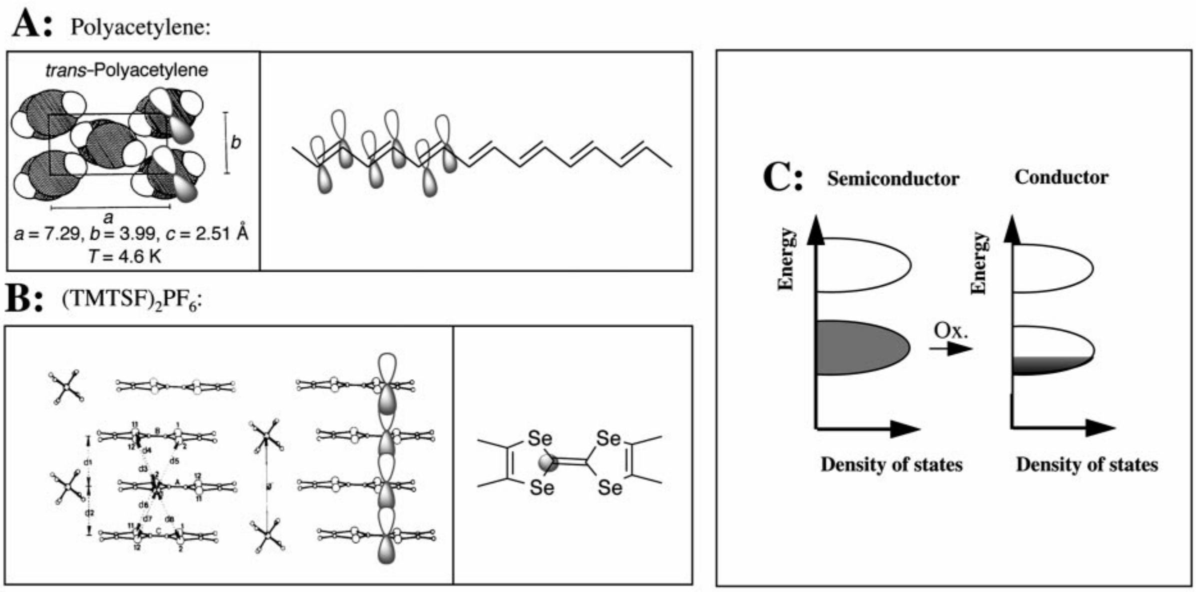


Fig. 3 Structure of the organic conductors polyacetylene (A) and, $(TMTSF)_2PF_6$ (B). C: Schematic representation of the electronic band diagram represented as the density of states for the materials in the undoped (semiconducting) and doped (conducting) state.

different types of π overlaps encountered and the magnitude of the on-site electron–electron repulsion (see Fig. 4). For polyacetylene the π overlap is intramolecular, resulting in an electronic coupling element, $t \approx 3$ eV.[41] By contrast the coupling is only ≈ 0.1 eV in $(TMTSF)_2PF_6$[42] due to the intermolecular nature of the interaction as discussed below (see Fig. 4). The room temperature conductivity, σ, of doped polyacetylene is $\approx 10^5$ S cm^{-1} [43] and ≈ 1000 S cm^{-1} for $(TMTSF)_2PF_6$.[44]

Electrical conduction in these systems is a result of the interplay between the key interactions illustrated in Fig. 4. Electronic overlap between adjacent molecules results in tight binding (Hückel) matrix elements 't' defined as $\langle \chi_i | \boldsymbol{H} | \chi_j \rangle$ with χ_i and χ_j being molecular orbitals of molecules in direct contact and $\boldsymbol{H}$ the effective Hamiltonian. The coupling element t_{parallel}, for example, represents a delocalization energy of charges within a well ordered array of molecules (Fig. 4). The local structure of the system will determine the size of the matrix elements and the extent of the delocalized states. As mentioned above $t \approx 0.1$ eV is a typical value for π stacks and $t \approx 3$ eV for the intramolecular coupling between adjacent atoms in conjugated polymers.

In a periodical system the electronic couplings will result in band formation, which, according to the tight binding model,[45] gives a dispersion of the local energy levels defined by

$$E_{\text{k}} = E_{\text{local}} + 2(t_{\text{parallel}} \times \cos(\boldsymbol{k}_{\text{parallel}}\boldsymbol{a}) + t_{\text{perpendicular}} \times \cos(\boldsymbol{k}_{\text{perpendicular}}\boldsymbol{b})) \quad (1)$$

for the 2-dimensional system shown in Fig. 4. Here E_{local} denotes the energy of the local orbitals, t the nearest neighbor coupling element as above, $\boldsymbol{k}$ the crystal orbital quantum number ($\boldsymbol{k} \in (-\pi/a; \pi/a)$), and $\boldsymbol{a}$ or $\boldsymbol{b}$ the periodicity in the 2-dimensional lattice. The corresponding density of states diagram is shown in Fig. 3C for the uncharged and the charged system.

The repulsion between electrons in the material counteracts the delocalization effect promoted by the 'transfer' matrix element, t, because mutual repulsion makes it difficult for electrons to pass each other in the solid. Electron–electron repulsion hence drives the system towards localized electronic states as described in a simple model by Hubbard[46,47] who took the electron–electron repulsion into account by introducing the on-site repulsion element, U (Fig. 4B). The transition between a delocalized regime (metallic) and a localized regime (magnetic) occurs at $U/t \approx 1$ according to this simple model.

On a macroscopic scale the conductivity, σ, is defined as

$$\sigma = n\mu q \quad (2)$$

where n is the concentration of charge carriers, μ their mobility and q their nominal charge. Since the charge carriers are created by thermal or external excitations in undoped neutral systems, conductivity increases with temperature as for semiconductors, while the doped systems, having a temperature independent concentration of carriers, can be metallic according to the tight binding model. Metallic conductivity is indeed observed in single crystals like $(TMTSF)_2PF_6$ but rarely in polycrystalline samples of conducting polymers.[48] This is because the highly ordered (and highly conducting) crystalline grains of the polymer most often are connected through more disordered regions with lower conductivity. As recently reviewed,[49] the relation between the interaction within grains (intragrain) and between grains (intergrain) is still a central question in the field of conducting polymers. This again emphasizes the need to control the structure of the sample not only on the molecular scale but also on the nano- and micrometer scales.

In summary, the molecules in an ideal thin film conductor should consist of low Hubbard U moieties which organize in highly regular arrays allowing efficient electronic overlap between neighboring moieties. Preferably the interactions should extend in 2 or 3 dimensions to maximize carrier mobility and to avoid instabilities typical of 1-dimensional systems.[50] These crystallites should further connect efficiently across domain boundaries allowing high mobility across boundaries. For use as semiconducting elements in field effects transistors or light emitting diodes such films can be used directly.

To achieve high electrical conductivity, charge carriers must be incorporated in the structure in a way that does not disturb the requirements mentioned above. Expressed in terms of Eqn. 2, high conductivity is reached by introducing a maximum number of carriers without degrading the carrier mobility governed essentially by the extend of the perfectly ordered local structures, and intergrain contacts.

2.2 Status of conducting Langmuir–Blodgett films—overview over design strategies

Since research in conducting Langmuir–Blodgett films was last reviewed in 1995[23] a number of new studies have been per-

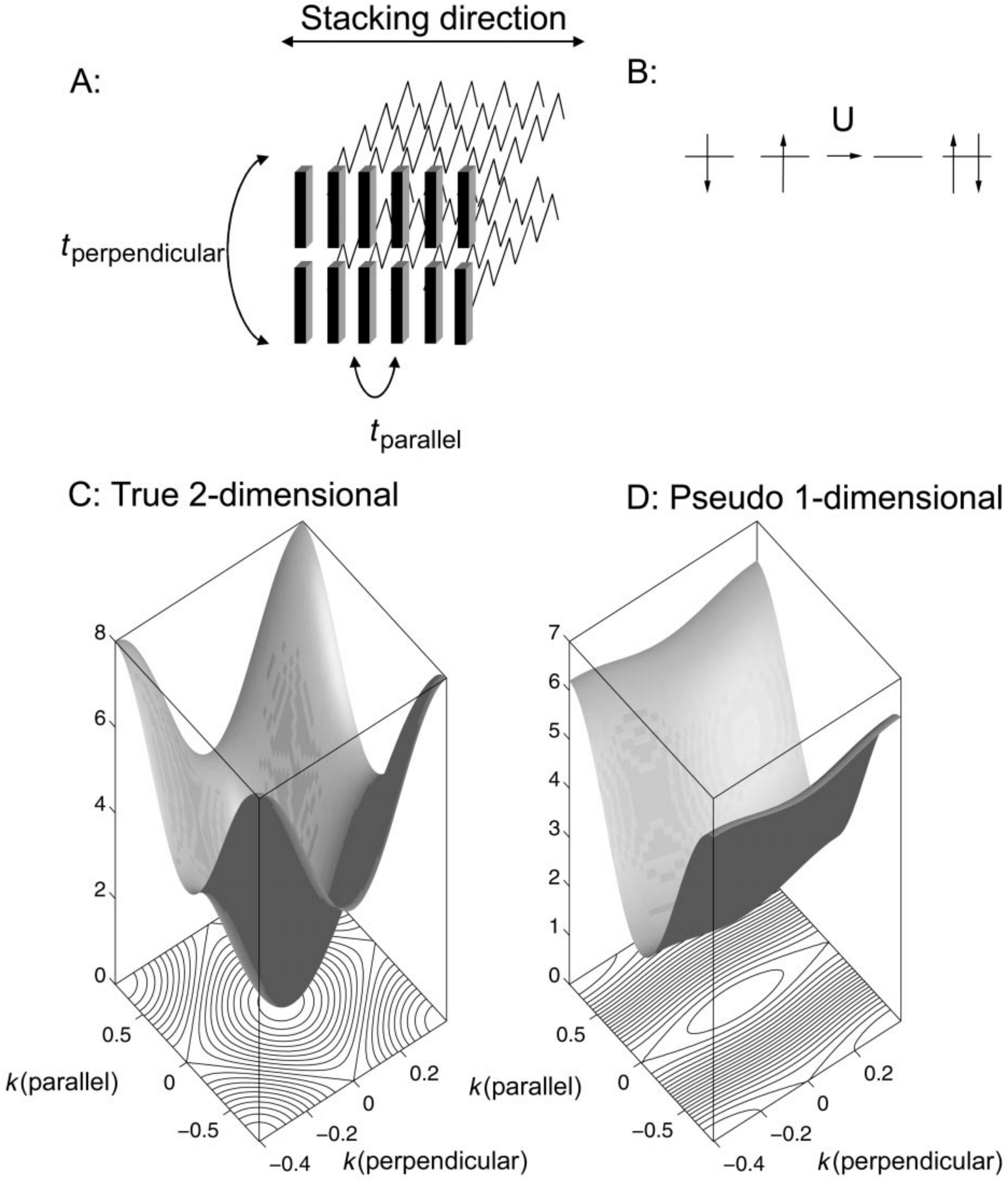


Fig. 4 A: Schematic diagram showing the electronic interactions (t) parallel and perpendicular to the stacking direction of electroactive molecules in a LB film. B: Definition of on-site repulsion 'U'. C: Band structure diagram of a 2-dimensional system, having $t_{\text{parallel}} = t_{\text{perpendicular}}$. D: Band structure diagram of a 2-dimensional structure having $t_{\text{parallel}} = 10t_{\text{perpendicular}}$ resulting in a pseudo 1-dimensional band.

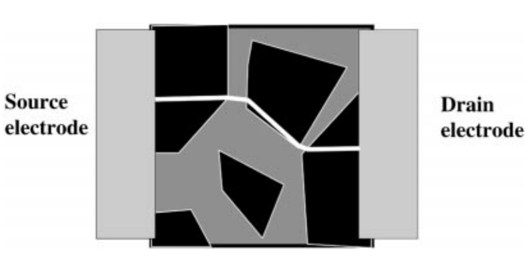
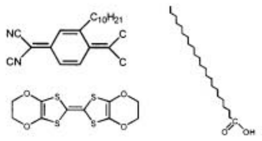
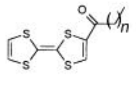
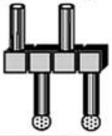
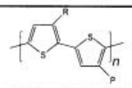
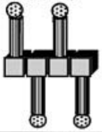
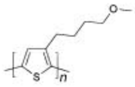
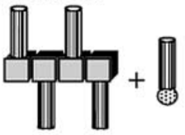
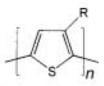
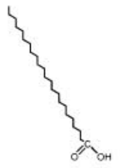
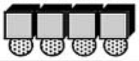
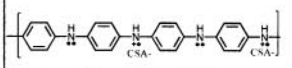
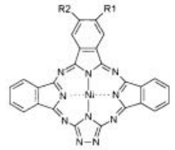
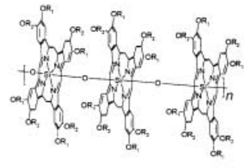
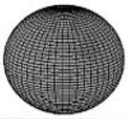


Fig. 5 Schematic model of the conductivity hierarchy in polycrystalline samples. Highly ordered domains are shown in black, being separated by disordered areas shown in gray. Charge carriers will follow a path minimizing the path length in the disordered areas as indicated by the white line.

formed in which conductivity plays a central role. As a brief review of the more recent work Table 3 summarizes studies performed after 1995 which involve conductivity measurements. The Table is ordered according to the prototype molecules encountered. Selected results from before 1995 are also included.

The prototype molecular structures have been included to emphasize the gross design strategies which have been used in various studies. Category (b) summarizes work where organic charge transfer complexes have been mixed with simple amphiphiles to produce composite LB films. As a natural extension of this design category (c) summarizes work where the surfactant and the electroactive group has been covalently linked as a molecule. By further linking the electroactive groups together into oligomers or polymers which resemble 'boards', conjugated

Table 3 Examples of 2nd generation molecules of conducting LB films

Prototype Molecules	Compounds (Examples)	Typical Conductivity/ S cm^{-1}	Ref.
(a) Simple amphiphiles 		$<10^{-10}$	95
(b) Charge-transfer molecules (typically mixed with long-chain acids) 		1-40	52,96-102
(c) Simple amphiphiles with electroactive head group 		≤ 0.1 (I_2 – doped)	40,88-90,103,104
(d) Amphiphilic hairy board polymers 	 R = alkyl P= polar group	50-100 (I_2 / $AuCl_3$ doped)	63
(e) Board polymers with polar substituents 		—	105,106
(f) Non-amphiphilic hairy bord polymers mixed with long-chain acids 	 R = alkyl 	**Undoped:** $\leq 10^{-3}$ **doped:** 10-100 ($NOPF_6$, I_2, $SbCl_5$)	66,67,107-109
(g) Non-hairy ionic polymers 		$< 10^{-2}$	110-113
(h) Hairy disks 		10^{-4}	114
(i) Hairy rigid rod polymers 		$< 5.2 \times 10^{-6}$	115
(j) Buckminster Fullerenes 		≤ 0.01 (RT, K-doped)	116,117

Legend
- ▯ = Alkyl chain
- ■ = Electroactive group
- ● = Polar group
- D = Van der Waals space

systems have been produced and studied either as pure compounds (d, e, g) or as mixtures with simple surfactants (f). Lamellae structures have been organized at the air–water interface either by grafting substituents directly onto molecular disks (h) or by preorganizing the disks in lamellae through covalent bonds as in so-called hairy rods (i). Finally globular structures in the form of Buckminster fullerenes have been studied (j). As a gross structural guide, typical local packing patterns of the prototype molecules are illustrated in Fig. 6. Leading references to the proposed structures are found in the figure caption.

From the values of the conductivity representing each prototype structure it is clear that not all systems are well suited for producing highly conducting films. For some categories the reason for this is quite clear: Hairy rigid rods for example (i) are coated with an insulating cap (the hair) which insulates the individual rods from each other (Fig. 6). Clearly such systems have not been designed with an optimization of efficient 2-dimensional electronic contacts in mind. In other cases the low values of the conductivity, as compared with bulk systems of the same molecules, are most likely due to the lack of order in the LB films (*e.g.* polyaniline shown for example in category (g)) or formation of a highly irregular polycrystalline film as in the case of C_{60} in category (j).[51]

In effect only two categories have provided conductivities which approach the values measured for prototype crystals shown in Fig. 3. These are solid solutions of highly conducting (non-surfactant) molecular or polymeric systems in simple amphiphiles (b, f) or conjugated amphiphilic hairy board polymers (d). In the composite films, crystallites of highly conducting grains are most likely connected by a percolation path through the non-conducting host.[38,52] In terms of understanding the packing of the molecules in the conductor these mixed systems therefore offer little new insight compared to the pure crystalline or polycrystalline samples of the native conductors. In the following emphasis will hence be on non-composite systems.

Extensive spectroscopic studies of many of the conducting LB films shown in Tables 2 and 3 (see refs. 23,27 and refs. therein) as well as X-ray scattering from the layers in the films provide information about the average orientation of the molecules. In general the results are in rough agreement with the anticipated overall structures expected to be obtained in the Langmuir–Blodgett preparation procedure (Fig. 2). These experiments do not explain in general the relatively low conductivity found in these films compared with the bulk structures of the same electroactive moieties due to the average nature of the structural methods employed. This therefore calls for a more thorough structural characterization, as suggested in 1992,[53] because conductivity depends strongly on the detailed interactions between neighboring molecules as well as the nano- and micrometre-scale morphology of the sample. Such studies have now been performed for a member of the simple amphiphiles with electroactive head groups (c) and for a member of the amphiphilic hairy board polymers (d) as described in some detail in the next sections.

2.3 Structural studies of Langmuir–Blodgett films of a simple amphiphile with an electroactive head group (Table 3, c)

To shed light on the local structural properties of a representative sample of the first generation of prototype functionalized surfactants (Tables 1 and 2) a detailed structural study of 2-octadecylsulfanyl-*p*-benzoquinone was performed. This was done by elucidating the structure both of the compressed monolayer on water using synchrotron X-rays[7,31,34,54] and of

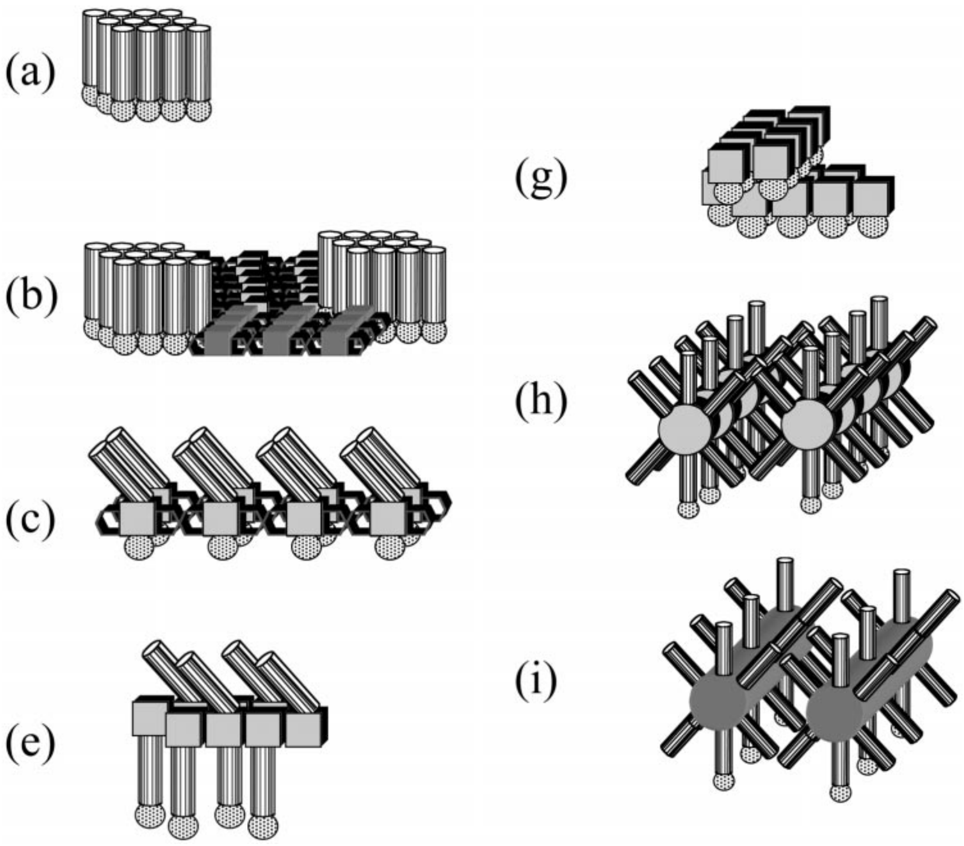


Fig. 6 Typical in-plane packing motifs in monolayer films of prototype molecules shown in Table 3. Letters in parentheses refer to Table 3. (a) Simple amphiphiles form hexagonal structures.[7,82] (b) Segregation of electroactive molecules and long-chain fatty acids.[38,52] (c) Simple amphiphiles with an electroactive head group pack with tilted alkyl chains.[34,54] Amphiphilic hairy board polymers (e) stack perpendicular to the conjugation length, in a 'lock and key' arrangement, determined by the alkyl side chains.[59,63] LB films of non-hairy ionic polymers are shown to form fibrillar structures (g).[37] Hairy disks (h) arrange in π-stacked lamellae, separated by alkyl chains.[35,36,81,83,84] The hairy rigid rod polymers (i) organize in lamellae separated by the alkyl side chains.[68,70]

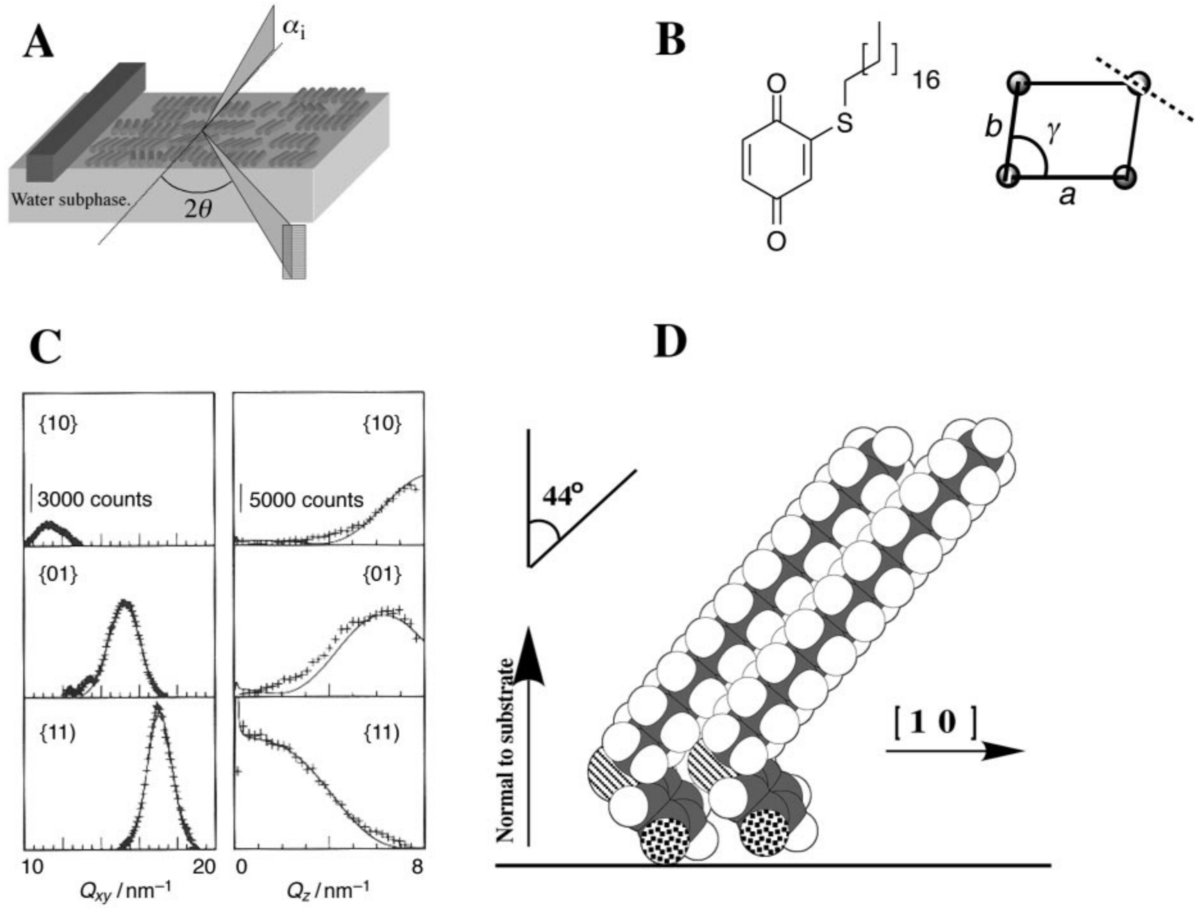


Fig. 7 A: Schematic illustration of diffraction experiment on a Langmuir film.[7,31] B: Chemical structure of 2-octadecylsulfanyl-*p*-benzoquinone and unit cell and tilt direction of alkyl chains (dotted line).[34] C: Observed Bragg reflections from monolayer of the quinone.[34] D: Model of two adjacent molecules in Langmuir–Blodgett film inferred from fits to the observed Bragg peaks and Bragg rods.[34]

a Langmuir–Blodgett film transferred to a solid support by atomic force microscopy.[34]

The X-ray scattering observed from a densely packed monolayer, compressed roughly to the collapse pressure of the film, reveals 3 distinct diffraction peaks corresponding to an oblique unit cell with an area of 23.1 Å^2 (Fig. 7B, Table 4). This area is very close to the projected area of the head group provided it is standing upright on the surface with the long axis of the quinone parallel to the surface normal.[54] In other words, the diffraction data show that the head groups are forced into a close-packed arrangement providing good intermolecular overlaps and hence possibly good conduction as found for $(TMTSF)_2PF_6$ for example.[54] The alkyl chain only needs ≈ 19 Å^2 in its upright position on the surface. Since the available projected area per molecule is larger than this value, a tilting of the alkyl chain is possible and indeed observed.[34,54,55] From the widths of the diffraction peaks the size of the individual scattering domains can be estimated to be relatively small (about 30 Å in diameter).[34]

Transfer of the monolayer to a solid support under constant surface pressure proceeds smoothly.[34,55] Due to the roughness of the solid support the resulting Langmuir–Blodgett film is not sufficiently planar to allow detection of the in-plane X-ray scattering. Instead a variety of other techniques have been employed to characterize the film.[34,54–56] Among these atomic force microscopy (AFM) has been an extremely powerful tool as seen from the AFM image of the surface of the film shown in Fig. 8. The AFM provides direct images of the crystalline domains in the film as evidenced by the contact mode imaging of the methyl end-groups of the alkyl chains protruding towards the AFM cantilever shown in Fig. 8A.[34] Between the ordered domains, domain boundaries extending over several nanometres are observed as indicated in Fig. 8B.[34]

Table 4 Lattice parameters for Langmuir and Langmuir–Blodgett films of 2-octadecylsulfanyl-*p*-benzoquinone

Parameter	Pressurized film on water	Transferred film on solid support
a/Å	5.60	5.87
b/Å	4.19	4.56
γ/°	80	82.3
Area/Å^2	23.1	26.5

Fourier analysis of the crystalline domains provide very accurate unit cell parameters, which are compared to the values found for the compressed monolayer on water in Table 4.[34,54] One sees that the area per molecule has expanded by 17% during transfer of the monolayer to the solid support, loosening, in other words, the contact between the quinone head groups. This expansion presumably leads to multilayer defects created during transfer. In addition the diameter of the domains has grown from ≈ 30 to ≈ 150 Å.[34] These changes may be understood by observing that the packing of the alkyl chains in the transferred film corresponds to a local energy minimum packing motif of alkanes[54] contrary to the packing motif found in the compressed monolayer on water (see below). The transfer process thus seems to stimulate a kind of annealing, where the energetically most favored arrangement becomes predominant once the pressure exerted by the barriers is relieved.

For the first time these data provided direct evidence of the local packing motifs and nanoscale morphology of the Langmuir and Langmuir–Blodgett films of functionalized sur-

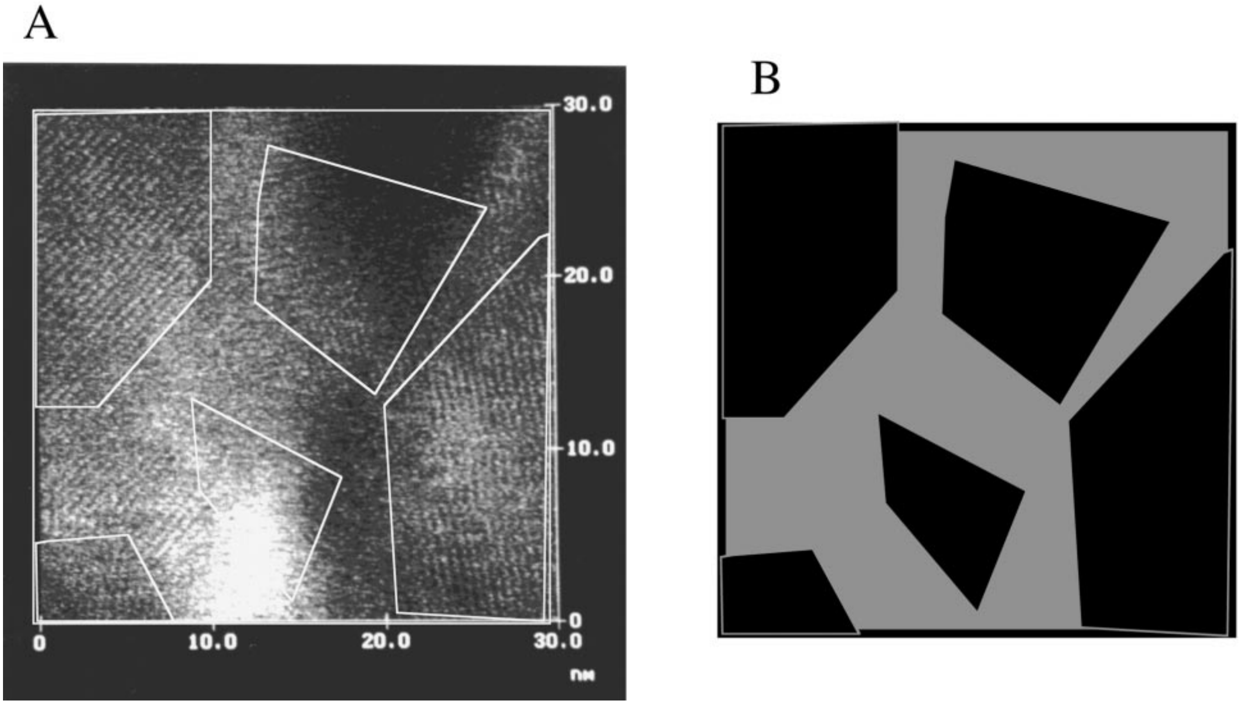


Fig. 8 A: AFM micrograph (31 × 31 nm) of a double layer of the electron acceptor 2-octadecylsulfanyl-*p*-benzoquinone on top of a double layer of cadmium behenate ($CH_3(CH_2)_{20}COOCd$).[34] B: Schematic illustration of the highly ordered domains (black) connected through less ordered regions (gray).

factants such as those exemplified in Tables 1 and 2. The observed expansion of the unit cell strongly indicates that the molecules relax towards a structure allowing the alkyl chains to pack more favorably once transferred to the solid support.[34,54] The situation is illustrated schematically in Fig. 9 showing how the barrier on the Langmuir trough can easily push the soft alkyl chains together in the lateral direction. The head groups hence become close-packed resulting in good intermolecular contacts. This is, as mentioned earlier, the first prerequisite for obtaining good conductivity. The alkyl chains, on the other hand, are pushed into non-equilibrium positions in the pressurized film. This imposes a stress in the film, kept at bay by the barrier, which leads to the formation of rather small crystalline domains. Once transferred to a solid support, the alkyl chains relax resulting in an expansion of the area per molecule in the film.

Since a major part of the cohesive energy in the monolayer is associated with the alkyl chains it is not surprising that this structural sub-unit is able to win the packing competition between head and tail once the pressure on the film is released. In return the head group interactions are sacrificed.

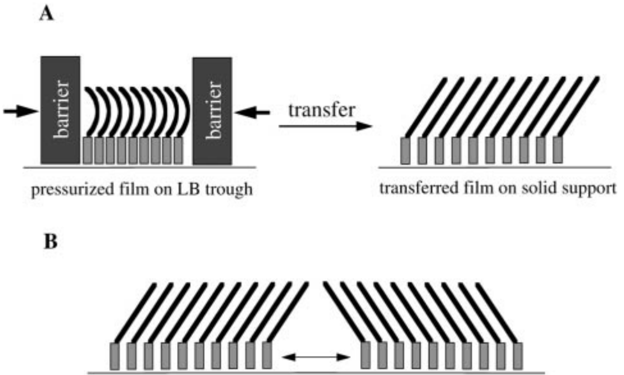


Fig. 9 A: Schematic illustration of the packing in a pressurized Langmuir film on water and in a Langmuir–Blodgett film transferred to a solid support. B: Illustration of domain boundary between domains with different tilt of the alkyl chains.

As proposed in 1992[53] based on general arguments, these observations provide direct structural evidence showing that two serious problems are associated with the realization of highly conducting LB films from this molecule: (i) the head groups are not necessarily closely packed (rather the alkyl chains are) and (ii) the domain boundaries are very broad (see below). To overcome the first problem stable local structures transferred to solid supports are essential. These can apparently best be realized if there is no strong competition between the packing motifs of the head group and the alkyl chain. To avoid this competition one could in principle use Kitaigorodskii's packing tables for alkanes[54,57] and try to design a head group that would fit perfectly to one of the preferred packing motifs of alkanes. In practice this is not easy. In fact it is likely to be as risky as trying to predict crystal structures in general, because of the very flexible nature of the surfactant molecule.

Viewed on the nanometre scale the pronounced domain boundaries (Figs. 8 and 9) are also unfavorable for conducting electrons which have to pass the boundaries during the conduction process. As discussed earlier in this section, the wider the domain boundaries are the smaller the macroscopic conductivity will be due to the limiting conductivity of the grain boundaries. Comparisons with Langmuir–Blodgett films of simple fatty acids[32,33] indicate that wide domain boundaries, which are not present in fatty acid films of non-tilted molecules, are due to the special packing problems encountered with the functionalized surfactant. In particular, the tilt of the alkyl chain must pose a problem at the boundaries of crystallites of different orientation (see Fig. 9). To overcome this, one should aim at non-tilting alkyl chains in the design of the functionalized surfactants in order to achieve high conductivity. Since the projection of the functionalized head group will always be larger than the projection of one alkyl chain, this requirement can only be fulfilled by grafting more than one alkyl chain to each head group. Designing such molecules, requiring close packing of two or more alkyl chains together with the head groups, will not be an easy task. Work following

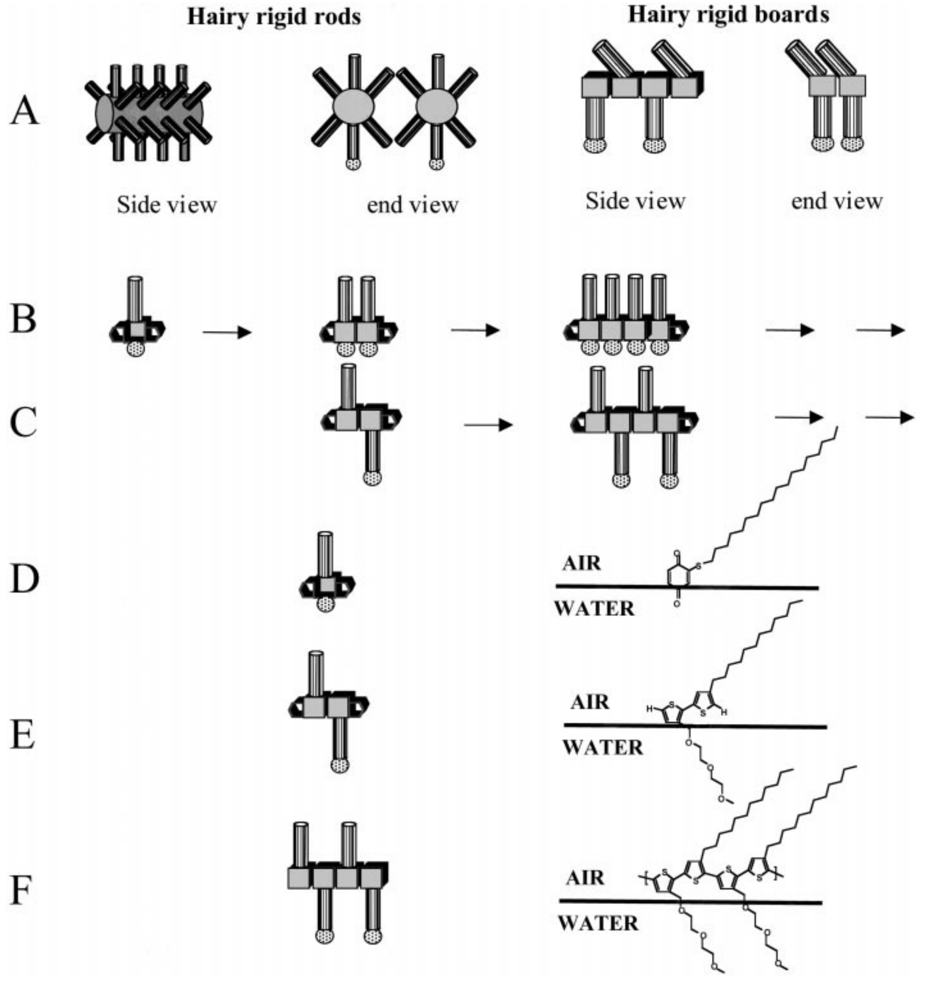


Fig. 10 A: Schematic illustration of hairy rods and hairy boards. B, C: Two possibilities of hinging molecular surfactants into hairy boards. D–F: Examples of selected prototype structures (see text).

this general strategy[39,53] has accordingly not led to highly conducting LB films so far.

In addition to these fundamental packing problems, it is also a problem that some Langmuir–Blodgett films tend to be unstable over time.[56,58] In the case of the surfactant described above, films simply crystallize into their original 3-dimensional crystal forms when kept under ambient conditions.[56] Again this is evidence in favor of the hypothesis that there is no strong cohesive energy keeping the local structure together.

Owing to problems with doping of LB films of 2-octadecylsulfanyl-*p*-benzoquinone, attempts to make measurements of the conductivity were never made.

2.3.1 Summary of structural studies of Langmuir–Blodgett films of simple amphiphiles with electroactive head groups (Table 3, c). In conclusion, investigations of the first generation of functionalized surfactants launched in the late '80s and early '90s (Tables 1 and 2) have shown that the Langmuir–Blodgett technique can indeed be used to direct the molecules into desired supramolecular structures. This can be useful when the target physical property of the films is derived from the molecular properties by simply adding these up. Preparation of second order non-linear optical Langmuir–Blodgett films and rectifying films are examples in this category. Collective properties as for example electrical conductivity can also be achieved in Langmuir–Blodgett films. However, the control of the detailed molecular structures is difficult because of the flexibility of the molecules and because of the competition between different packing motifs preferred by the individual molecular sub-units. In addition, the molecular surfactants are quite mobile, and, with time, they have a tendency to diffuse into thermodynamically more stable and functionally less interesting structures. Taken together these data indicate that design of *molecular* surfactants is not the most promising way towards highly conducting, stable and yet processable thin films.

2.4 Structural studies of Langmuir–Blodgett films of amphiphilic hairy board polymers (Table 3, d)

In an effort to merge the design of rigid rods, providing highly stable films, with the attractive intramolecular electronic properties found in the functionalized molecular surfactants, the concept of hinging the molecular surfactants into amphiphilic polymer boards was recently proposed.[59] Clearly, if the roughly circular hairy rods could be replaced by flat boards standing edge-up on the water surface the contact between the electroactive parts would be decisively improved. This type of structure could encompass conduction from both the conjugated π electrons lengthwise and the π-stacked orbitals sidewise (Fig. 10A, F) and one could hope to come close to more 2-dimensionally coupled conductors as it is known from for example bulk poly(3-alkylthiophene)s.[60–62]

From a molecular design point of view, the hinging strategy opens a number of new possibilities as illustrated schematically in Fig. 10B. First of all, covalent bonds between the functional head groups ensure a much better edge-on electronic contact between neighboring head groups allowing an extended π-conjugated system to develop. Energetically, the change is very dramatic and this should improve stability of the films in addition to providing a highly conducting system along the polymer 'board'. Secondly, the hinging opens up the possibility

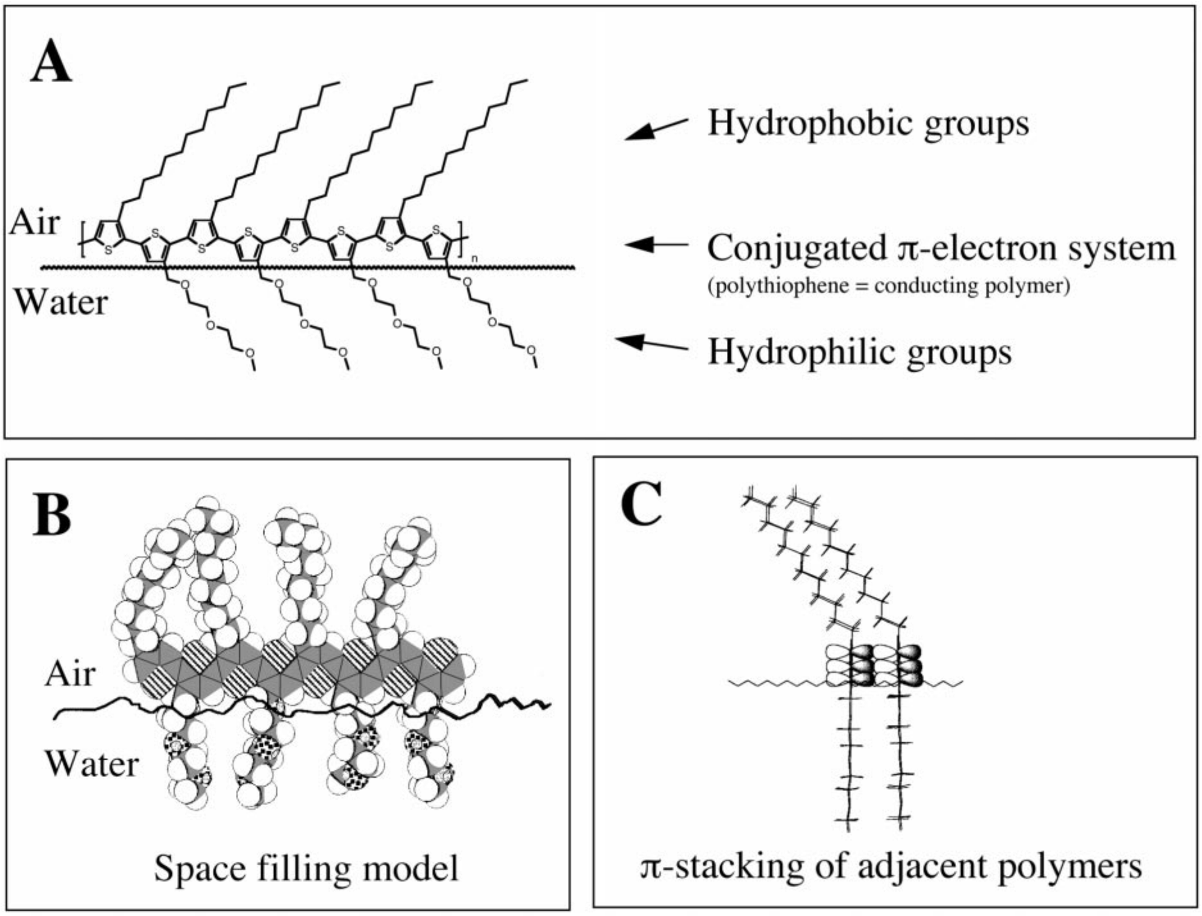


Fig. 11 A: Orientation of an amphiphilic polythiophene derivative on a water surface (poly(3′-dodecyl-4′-(2,5,8-trioxanonyl)-2,2′-bithiophene)). B: Space filling model of a polymer segment on water showing the void space between the alkyl substituents. C: Side view of π-stacked dimer on the water surface showing efficient overlap between π electrons on adjacent sites.

to place the polar and non-polar substituents on adjacent functional moieties as illustrated in Fig. 10C, thereby expanding the range of possible geometrical shapes of the polymers considerably. This separation turns out to be of particular importance for the packing of the individual surfactants once pre-organized on the water surface (see below). The separation of the polar and non-polar groups in combination with the hinging of the functional head groups has led to a new type of amphiphilic polymeric surfactant illustrated in Fig. 10F which has been characterized recently by X-ray diffraction[63–65] as described in detail in section 2.4.1.

Composites of surfactants and non-amphiphilic conjugated 'boards' (*e.g.* poly(3-alkylthiophene)) have also been extensively studied.[66,67] Conductivities ranging between 10 and 100 $\mathrm{S\,cm^{-1}}$ are typically measured for such systems in the most favorable cases (Table 3, f). The in-plane structure of these systems has not been studied so far.

Multilayer LB films of non-amphiphilic polyphenylene derivatives possessing large dichroic ratios have been studied in relation to light emitting diodes and other applications.[68–70] The in-plane structure of these films is suggested to be similar to that of hairy rods, *i.e.* stacked lamellae of the polymer molecules. The resemblance to hairy rods rather than hairy boards is presumably due to the twisted backbone in the polyphenylene polymer causing poor electronic interactions both along the polymer and between adjacent chains. High electrical conductivity can therefore not be expected from these systems.

2.4.1 Langmuir–Blodgett films of amphiphilic regioregular polythiophenes. In this section we will discuss briefly a concrete realization of the above ideas of hinging functional sub-units together. As recently demonstrated[63,64] this strategy makes it possible to use the Langmuir–Blodgett technique to promote the self-assembly of π-stacked conjugated polymer chains into a stable monomolecular layer with a local structure that is optimal for electrical conductivity.

The results are achieved by synthesizing regioregular amphiphilic polythiophene copolymers with alternating hydrophobic and hydrophilic side groups (Fig. 11).[63] These polymers can form a rigid board-like structure that has a hydrophobic side and a hydrophilic side with the highly conjugated polythiophene core as the functional element (Fig. 11).

By choosing this particular substitution pattern, the preferred transoid conformation of adjacent thiophene units will allow all the hydrophilic groups to interact with water if these molecules are spread on a water surface. Conversely, the hydrophobic substituents will all point away from the water surface resulting in a molecular structure that is highly conjugated and amphiphilic. Owing to the relatively large spacing between the alkyl chains, which is imposed by the polymer backbone, there is room for an adjacent polymer floating on the water surface to dock to the first polymer leading to a close-packed π-stacked structure in which adjacent pre-organized polymers are displaced along the polymer direction by one thiophene unit (Figs. 11 and 12). The self-assembly process on the water surface eventually results in the formation of highly ordered (crystalline) domains. These are shown by X-ray diffraction (XRD) to have a local structure similar to structures known from studies of thick films of regioregular poly(3-alkylthiophene) where electrical conductivities as high as 1000 $\mathrm{S\,cm^{-1}}$ are found for doped samples.[60,62,71,72]

The structure of the Langmuir monolayer of poly(3′-

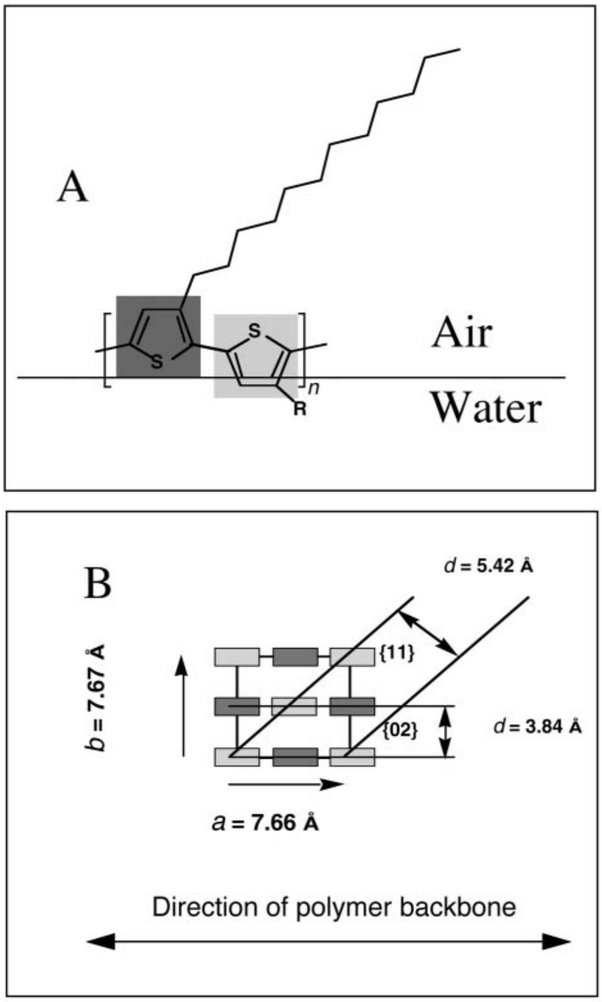


Fig. 12 A: Side view of repeat unit of amphiphilic polythiophene organized on a water surface. B: Top view of the thiophene units (boxes) in a centered rectangular unit cell with $a = 7.66$ and $b = 7.67$ Å representative of the monolayer packing. The gray scales designate the two different orientations of the thiophene units in the cell as indicated in A.

dodecyl-4′-(2,5,8-trioxanonyl)-2,2′-bithiophene) compressed to 30 mN m^{-1} pressure has very recently been studied by grazing incidence diffraction (GID) of synchrotron X-rays[63,65,73] as described for 2-octadecylsulfanyl-*p*-benzoquinone in section 2.3.[7,31,34] A superposition of three peaks, corresponding to interplanar spacings of 3.84 and 5.42 Å for the narrow peaks and ≈4.6 Å for the broad peak, is observed.[63] The resulting unit cell is shown in Fig. 12.

The width of the domains giving rise to coherent scattering, inferred from the diffraction peak widths,[65] corresponds roughly to 13 parallel polythiophene chains forming a bundle of highly structured molecular (semi)conductors. The size of the domain along the direction of the polymers is presumably not less than the average polymer length amounting to about 400 Å ($M \approx 21\ 000$).[63,74] Hence, the self-assembly process at the water surface has led to an organization of more than 100 efficiently conjugated thiophene units along the polymer backbone stacked in bundles of 10–15 units. This is illustrated in Fig. 13 which summarizes the monolayer data. The domains can be packed on the surface so that the entire surface is covered by an organic equivalent of a polycrystalline semiconductor wafer. The amphiphilic nature of the film allows nanoscale manipulations through the hydrophobic effect as described briefly below.

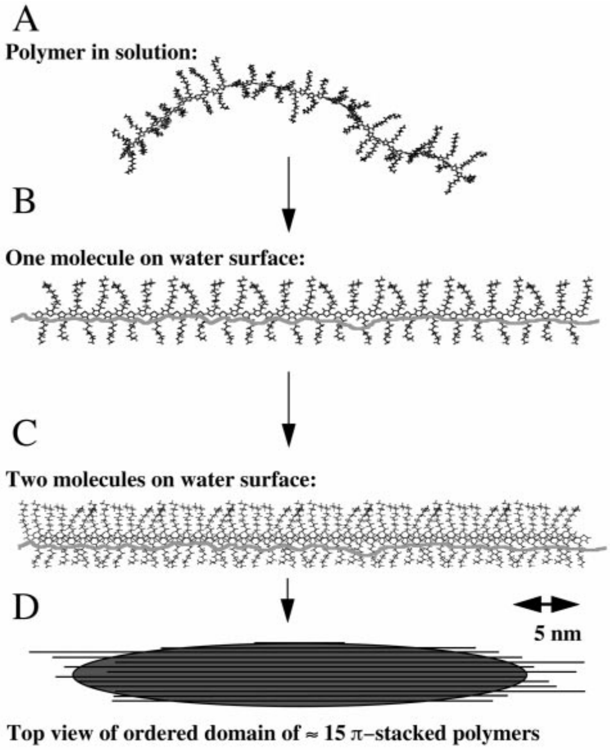


Fig. 13 Summary of the self-assembly process of the amphiphilic polythiophene derivatives on the water surface.

2.4.2 Self-assembly of electronic circuit structures of polythiophene. Transfer of monolayers of poly(3-dodecyl-4′-(2,5,8-trioxanonyl)-2,2′-bithiophene) by LB deposition to a substrate that has been patterned into hydrophilic and hydrophobic areas results in the replication of the pattern with polythiophene domains covering the hydrophilic areas only. This has been demonstrated by patterning a gold coated silicon wafer by microcontact printing[75] with a pattern taken from an electronic chip (Fig. 14A).[63,64] When transfer occurs at the up stroke, the monolayer only sticks to the hydrophilic areas of the substrate and selective transfer of the monolayer results. After transfer, imaging by atomic force microscopy shows the micro chip pattern now with conducting parts represented as 2.5 nm high lanes of π-stacked polythiophene (Fig. 14B). This result demonstrates that the 'hydrophobic effect' known to play a central role in biology in defining the structure of biomolecules can also be exploited to structure molecular electronic systems on solid supports.

2.4.3 Conductivity of polythiophene monolayers. In the characterization of conducting monolayers the size of the sample area under investigation can be a key factor for the outcome of the measurement because of the polycrystalline nature of the sample. Pseudo 2-dimensional monolayers are furthermore highly sensitive to disorder and impurities, so macroscopic measurements of conductivity may not reveal a true picture of the intrinsic local conductivity. To relate the supramolecular structure to the conductivity it is therefore necessary to develop methods for probing the electronic transport properties also on the nanoscale. AFM microscopes equipped with Kelvin Force capabilities[76] represent one of the few examples of such possibilities. In particular this technique allows the doping state of a thin film to be characterized because the technique maps out the electrochemical potential of the surface with nanometre resolution. This is illustrated in Fig. 15 showing a Kelvin Force AFM scan of an $AuCl_3$ doped monolayer of poly(3-dodecyl-4′-(2,5,8-trioxanonyl)-2,2′-bithiophene) on a SiO_2 wafer. The monolayer is deposited by horizontal dipping rendering the polar groups outwards as indicated in Fig. 15A. Fig. 15B shows a height scan of the

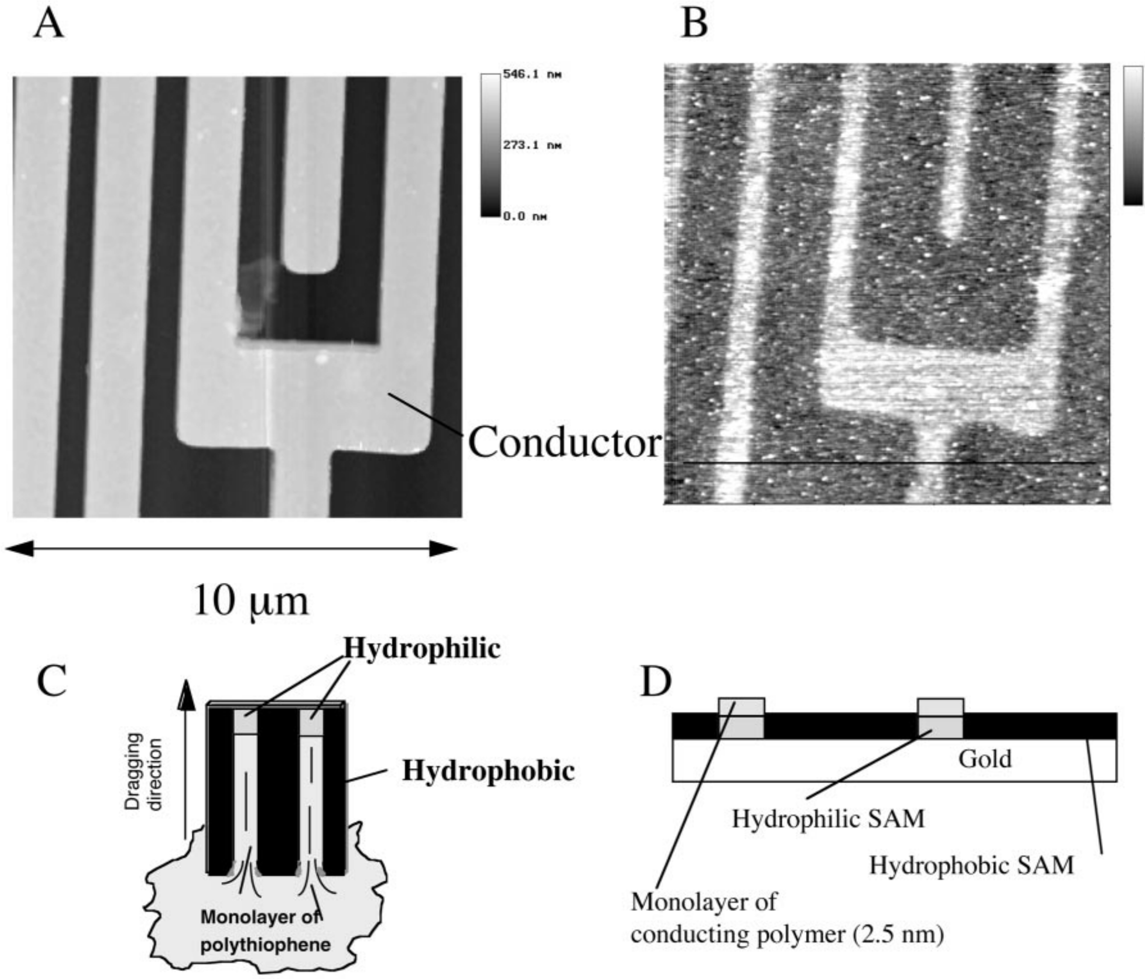


Fig. 14 A: Atomic force microscopy image of the 'master' electronic chip used as model for preparation of a polydimethylsiloxane (PDMS) stamp for microcontact printing of alkylthioles on gold. B: Replica of the chip now as 2.5 nm high polythiophene 'wires'. The picture is a contact mode AFM image of a gold coated silicon wafer patterned into hydrophobic and hydrophilic areas by micro contact printing with hydrophobic and hydrophilically terminated alkylthioles. Subsequently, the wafer has been drawn out of a Langmuir trough with a monolayer of amphiphilic polythiophenes on the surface by the Langmuir–Blodgett technique as illustrated in C.[63,64] The amphiphilic polythiophene only sticks to the hydrophilic areas resulting in a replication of the original electronic chip pattern. D: Schematic illustration of cross section of the AFM micrograph, B, along the depicted solid line.

doped film and the black dots on the micrograph correspond to the location of gold clusters, which are formed during the oxidation of the film. Since the cantilever used in the experiment is covered with gold, these clusters turn up as dark spots with 0 V potential difference to the gold on the cantilever which serves as a reference for the potential measurement. The screening of the clusters by the monolayer is clearly visible as shadows around each cluster (Fig. 15C). In between the gold clusters a uniformly doped monolayer of polythiophene is revealed. The conductivity of such monolayers is measured to range between 50 and 100 S cm^{-1} as discussed in detail in forthcoming publications.[71,77]

2.4.4 Summary of structural studies of Langmuir–Blodgett films of amphiphilic hairy board polymers (Table 3, d). In section 2.3 a number of problems that are inherent to functionalized molecular surfactants with spatial mismatch between head and tail (Table 3, c) were described. In essence, the competition between the optimum packing of either head or tail, combined with a substantial flexibility of the molecules, appear as a hindrance to efficient crystal engineering at the 2-dimensional air–water interface. It is simply not enough to reduce the dimensionality of the desired assembly process by one dimension as long as the molecules are still allowed total rotational and orientational freedom as well as access to numerous intramolecular configurations. The process has to be further simplified; and one possibility for doing this seems to be exemplified by designing amphiphilic hairy boards by hinging molecular surfactants together. The assembly process of these macromolecules can be described as a stepwise process as illustrated in Fig. 13. (i) The individual macromolecules are pre-organized as floating boards on the water surface by proper design of the hydrophilic/hydrophobic substituents on the polymeric core. The long axis of these pre-organized objects is confined to the plane of the water surface (Fig. 13A, B). (ii) The further assembly of the boards is now effectively a problem similar to ordering matches floating on water. Since the individual boards can attract each other through π stacking they will cluster on the surface. The intermolecular interactions between alkyl chains grafted onto the boards control the relative orientation of adjacent π-stacked boards in the direction perpendicular to the π stack. In the case of amphiphilic regioregular polythiophene derivatives the void space between alkyl chains on one board will simply be filled by the similarly spaced alkyl chains on the adjacent board by displacing the board by one thiophene unit relative to its neighbor (Fig. 13C, D).

3 Discussion

Spin cast films of poly(3-alkylthiophene)s are presently being developed as the organic constituents in field effect transis-

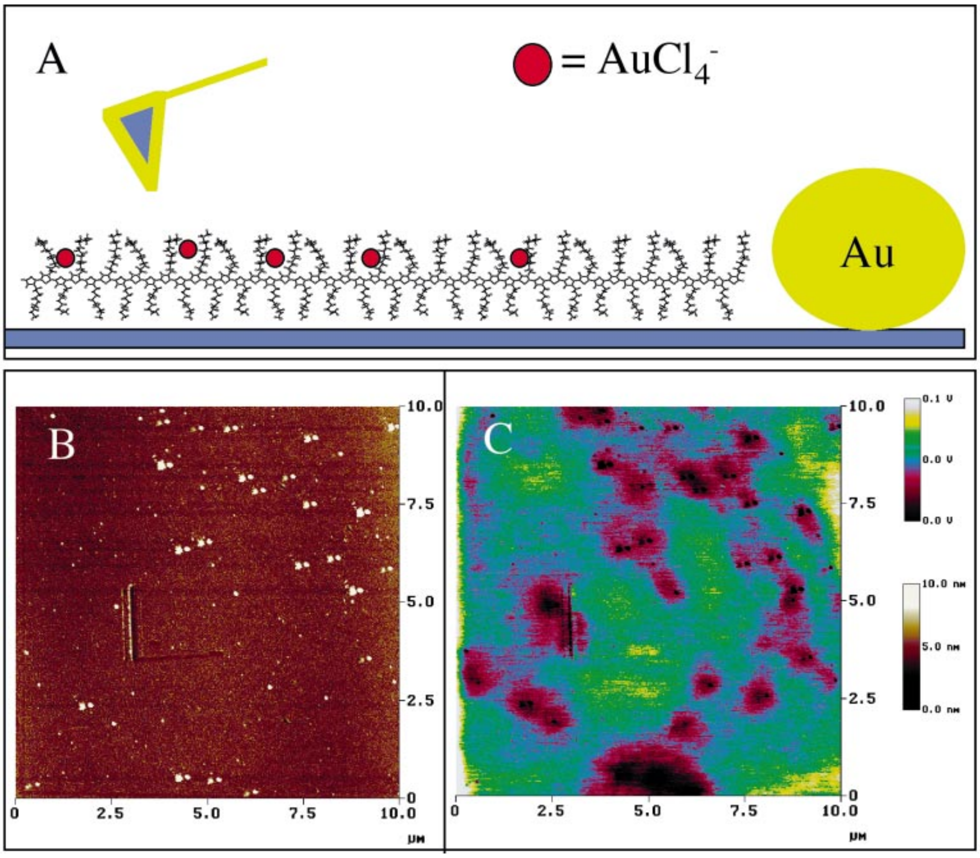


Fig. 15 A: Schematic representation of Kelvin Force Microscopy: gold coated tapping mode tip is used both to determine the topography and probe the local potential in the film which consists of polythiophene doped with $AuCl_3$ (red circles), and gold clusters (yellow circle). B: The topography micrograph of the film surface recorded simultaneously with (C) the Kelvin Force micrograph revealing the surface potential relative to gold. Protrusions appear double due to tip artifact (double tip).

tors.[78–80] For this application the carrier mobility is one of the essential parameters to optimize. The work with field effect transistors therefore has many analogies to that on optimization of the conductivity in the doped polythiophene films. In both cases the successful optimization will rely on improved understanding and control of the structure of the sample on all scales. Langmuir–Blodgett films will probably not find their way to mass produced organic field effect transistors because they are too complicated to make. However, from the assembly point of view they are interesting 'two dimensional' analogues to the three dimensional films. One advantage is that unique structural characterization, both using X-rays and scanning probes, is possible. Furthermore, the morphology of the monomolecular layers is easier to characterize because they are confined to an interface. It is therefore interesting that systems in which the assembly is directed by π stacking organize in the same type of structure both on the water surface and as bulk films.[62,63] The polythiophene samples described above provide one example of this (Table 3, d). Very recent studies[81] show that this analogy also holds for π-stacked hairy disks (Table 3, h). Contrary to these systems, the π stacking is not sufficiently strong for the simple amphiphiles with electroactive head groups (Table 3, c) to direct the formation of stable local structures in which the electroactive groups are efficiently stacked.

On the nano- and micro-metre scale interesting lessons may also be learned by studying LB films. The effect of tilted alkyl chains, resulting in wide domain boundaries, is one example of this which gives an important pointer to new molecular designs: to minimize domain boundaries tilted alkyl chains should simply be avoided. In spite of this type of information, there is still a long way to go before the boundary formation is fully understood and brought under control even in LB films. Control of domain boundaries and the nano- and micro-scale morphology in general is therefore very likely to become the main challenge in the future.

For use as good conductors, a substantial number of dopants need to be incorporated in the preorganized films. With regard to the distribution of dopants the Kelvin Force microscopy method offers new and intriguing possibilities which are likely to contribute to our further understanding of this crucial step. The successfully doped film, in which a highly conjugated and highly structured polymer is organized, will certainly be an excellent conductor. The possibilities of obtaining superconductivity in such structures should also not be neglected.

Finally the successful preparation of highly conducting multi-layer LB films of conjugated polymers remains an intriguing scientific goal. This not the least due to the resemblance of such structures to quantum well systems known from semiconductors to produce a wealth of new electronic phenomena.

4 Conclusions and outlook

Since 1995, when conducting LB films were last reviewed, a number of new studies have provided significantly higher values of the in-plane conductivity which now approaches 100 S cm^{-1}. This value has been reached for appropriately doped amphiphilic conjugated polymers (Table 3, d), and for mixed films of simple surfactants with conjugated polymers or charge transfer systems (Table 3 b, f). The success of using conjugated polymers for conducting LB films hence represents one of the major steps forward since 1995.

New structural techniques comprising scattering from Langmuir films using synchrotron radiation, and atomic force microscopy to characterize molecular and nanoscale structure of Langmuir–Blodgett films, have opened a new window for studies of the assembly process of monomolecular films. Structural studies of this type, reported so far for a member of the family of simple molecular surfactants with an electroactive head group and an amphiphilic derivative of polythiophene, reveal how the competition between the packing of the electroactive part and the alkyl part of the molecules results in different local structures. It is argued that control of a stepwise assembly process of surfactants on the water surface can be achieved by designing surfactants in which π stacking drives the assembly in one direction while the packing of the alkyl chain determines the structure in the perpendicular direction.

Appropriate doping of the films, allowing a large number of charge carriers to enter the sample producing doped films which are stable over time, still seems to provide a major stumbling block towards practical application of conducting LB films. Further work on amphiphilic systems may provide a useful way to guide counter ions into thin films in a non-destructive way and in this way help improve stability and conductivity also for spin cast films.

In summary, the preparation of conducting or semiconducting thin films of high electronic quality (*i.e.* high conductivity or carrier mobility respectively) from solution provides a tremendous challenge for the supramolecular chemist. This is because molecules need to be taken fast and efficiently from a disordered state in solution to highly ordered structures in the thin films. As part of this puzzle, the pseudo 2-dimensional self-assembly process at the air–water interface can provide interesting keys to how the supramolecular structure can be controlled. Considerable insight is now available about the local (Ångström scale) organization of molecules on the surface in particular about factors controlling the competition between π stacking and alkyl chain packing.

Rules allowing efficient control over the nanoscale and microscale morphology of solution cast thin films are yet to be revealed, and this will presumably constitute one of the major challenges for the future both for LB films and spin cast films.

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