The development of self-assembled liquid crystal display alignment layers


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From simple pocket calculators to mobile telephones and liquid crystal display (LCD)-TV, over the past few decades, devices based on LCD technology have proliferated and can now be found in all conceivable aspects of everyday life. Although used in cutting-edge technology, it is surprising that a vital part in the construction of such displays, namely the alignment layer, relies essentially on a mechanical rubbing process, invented almost 100 years ago.

In this paper efforts to develop alignment layers (also called command layers) by processes other than rubbing, namely self-assembly of molecular and macromolecular components will be discussed. Two topics will be presented: (i) tuneable command layers formed by stepwise assembling of siloxane oligomers and phthalocyanine dyes on indium tin oxide surfaces and (ii) command layers formed by self-assembly of porphyrin trimers. The potential use of these layers in sensor devices will also be mentioned.

Keywords: supramolecular chemistry; self-assembly; liquid crystals; devices; surfaces; sensors

1. Liquid crystals

The first observations of liquid crystalline behaviour were made in the 1850s, by biologists Virchow, Mettenheimer and Valentin. They found that a compound from the nerve core exhibited strange behaviour when viewed with polarizing light. Unfortunately, they did not immediately recognize the full potential of their discovery and simply labelled the substance a ‘living crystal’. The official discovery of liquid crystals is credited to Otto Lehmann and Friedrich Reinitzer (figure 1). In 1888, Reinitzer discovered that cholesteryl benzoate changed from a clear to cloudy liquid before crystallizing. Together with the German physicist Otto Lehmann, who noted that the cloudy fluid was actually a new phase of matter, he published a landmark paper in 1889 entitled ‘Über fliessende Krystalle’ (Lehmann 1889).

The idea of a fourth state of matter was fiercely disputed by the scientific community, and it was only some 30 years later, when the reports of liquid crystalline states and molecules forming liquid crystalline phases became too numerous to be ignored, that the concept of liquid crystals was finally accepted.

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Liquid crystal phases, almost without exception, appear in a class of molecules called mesogens, which is derived from the Greek phrase ‘species in between’. These molecules possess an anisotropic shape, i.e. either their molecular axes have differing lengths or the properties of the constituent parts of the molecules vary (e.g. hydrophobic–hydrophilic or rigid–flexible parts). In addition, in order to display mesogenic properties, the molecules have to interact with each other through non-covalent interactions. These intermolecular interactions are mainly responsible for the liquid crystalline properties exhibited by mesogenic materials and for their interactions with the surface (vide infra), which are critical for device applications. In order to fully appreciate how a liquid crystalline device can be modified or manipulated by these interactions, it is worthwhile to highlight the basic principles of liquid crystals, from the molecules involved through to the phases they form; all of which are a result of intermolecular forces.

Liquid crystalline molecules are commonly subdivided into the following categories: thermotropes; lyotropes; liquid crystalline polymers; and polymer solutions (Collings & Hird 1997). The former liquid crystals possess a temperature interval in which the compound is in a liquid crystalline state, which can consist of several different liquid crystal phases. Above or below this interval, the compound is in an isotropic or solid phase, respectively (figure 2).

These thermotropes can themselves be subdivided into two general classes of molecules, viz. calamitic and discotic. The first category comprises all rod-like molecules (figure 2), which possess an elongated shape; they usually consist of a rigid part containing two or more rings (usually phenyl or cyclohexyl rings), which are substituted with more flexible hydrocarbon moieties (Collings & Hird 1997). Probably, the most common class of calamitic liquid crystals involves simple substituted cyanobiphenyl compounds (chart 1). A special class is formed by the calamitic liquid crystalline compounds comprising metal-containing molecules, dubbed ‘metallo-mesogens’. Although these compounds have been known since the beginning of the last century, they spurred serious interest only about a decade ago showing promise as advanced functional materials (Serrano 1996). Recently, a new series of thermotropic liquid crystals, the bent-core mesogens, which show much promise for electro-optical applications, was discovered (Pelzl et al. 1999).
The second class of thermotropes, discotics, consists of disc-shaped molecules. Discovered by Chandrasekhar et al. (1977), in this type of molecule the core is usually based on aromatic moieties, e.g. triphenylene or phthalocyanine (chart 1; Chandrasekhar & Ranganath 1990; Chandrasekhar 1993; Collings & Hird 1997; Demus et al. 1998). The rigidity of the core enables the stacking of the mesogens into columns, while the peripheral substituents provide enough disorder and freedom of movement to prevent crystallization. This leads to the formation of a liquid crystalline phase with a columnar structure (figure 3).

In contrast to the thermotropic systems, lyotropic compounds form a liquid crystalline phase when dissolved in the proper solvent (Bahadur 1991). A generic structure for lyotropic compounds is an amphiphilic one, which combines a polar head group with an apolar tail, e.g. as found in soap molecules. When dissolved in water, the hydrophobic effect leads to the aggregation of the apolar tails,
which underpins the formation of structures such as vesicles, micelles and lamellar phases. In these phases, only the polar head groups are exposed to the water, shielding the apolar tails.

The third class of liquid crystals is formed by liquid crystal polymers: main- and side-chain polymers (Ober et al. 1984; Shibaev & Platé 1984, 1985; Collings & Hird 1997; Wang & Zhou 2004). In the former class, the mesogenic unit is incorporated directly into the main chain of the polymer. In most cases, the monomer unit comprised a rigid aromatic part, capped by flexible chains. In a polymer, this configuration allows the rigid parts to form a semi-crystalline lattice, while the aliphatic connector parts provide sufficient freedom of movement to induce a liquid crystalline phase (figure 4a). The second class of liquid crystalline polymers has the mesogenic units attached as side chains to the polymer backbone, via flexible spacers. This allows the formation of a layered, rigid lattice, in which the polymer backbone now provides the disorder (figure 4b). In contrast to main-chain liquid crystalline polymers, these compounds show liquid crystalline properties over much wider temperature ranges. This is often attributed to the independent movement of the mesogenic units with respect to the (often entangled) polymer.
backbone, allowed by the spacer. Therefore, the choice of spacer and mesogenic unit is crucial to the liquid crystalline properties of this class.

A special type of polymer liquid crystal, which can be expected to play an increasingly important role in the future, is the one that consists of biological molecules. They form only liquid crystalline phases when they are dissolved in high concentration, an example being the tobacco mosaic virus (Stanley 1935). This virus is a helical rod-like biopolymer comprising an RNA chain surrounded by 49 protein subunits for every three turns of the RNA helix (figure 5a). The assembly displays a repeat length of 69 Å. Complete viruses are rod-shaped (figure 5b), which gives the virus its mesogenic properties. Colloidal suspensions of the virus exhibit several liquid crystalline phases, such as nematic (figure 5b) and smectic phases.

2. Liquid crystal phases

In addition to a variety of liquid crystalline building blocks, there is also a wide variety of liquid crystal phases. The system used to classify liquid crystalline phases was developed by the French scientist Freidel (1922) and is based on the different molecular orientations the liquid crystal molecules have in the different phases. In this system, the simplest liquid crystal phase is the nematic phase of calamitic molecules. When viewed with a polarizing microscope, this phase exhibits long threads (figure 6a), hence its name after the Greek word for thread. The molecules in this phase tend to orient themselves parallel to a common director and remain in this conformation while diffusing throughout the phase (figure 6b). Their lack of positional order, however, gives rise to the occurrence of disclination lines, which are defects in the order and are responsible for the threads seen with the polarizing microscope.

Discotic liquid crystals also form nematic phases in which the short axis of the molecule aligns along a single direction, which is dubbed the director. If the discotic mesogens exhibit a tendency to stack, liquid crystal phases consisting of columns can be formed, which possess rectangular or hexagonal patterns.
Another common calamitic liquid crystal phase is the smectic phase, in which the centre of mass of the constituent molecules is arranged in layered structures (figure 7). The smectic phase is subdivided into two major classes. If the director of the liquid crystal molecule is at an angle of 90° to the layers, then the phase is called smectic A (figure 7a). If this angle has any other value than 90°, the corresponding phase is called smectic C (figure 7b).

If the molecules of the liquid crystalline phase are chiral, or mixed with a chiral molecule, the entire phase becomes chiral. In this phase, which is called the cholesteric phase, the directors of the liquid crystal molecules describe a helical path as they traverse a liquid crystal domain. The occurrence of a cholesteric phase is indicated by adding an asterisk to the phase, e.g. smectic C*.

Given the huge variety of mesogens available and the array of liquid crystal phases that can be formed, it can be readily foreseen that numerous new phases still remained undiscovered. It is therefore somewhat surprising that already before World War II, most scientists thought that liquid crystal research had been completed. This conclusion was arrived at when a mathematical basis for
the study of mesogenic systems was provided by Oseen (1933) and Zöcher (1933). In addition, liquid crystals seemed to have little industrial applicability. All this changed, however, when the liquid crystal display (LCD) was invented.

3. Liquid crystal displays

A display based on liquid crystals was first suggested by Richard Williams of the Radio Company of America in 1963 and developed into a device several years later (Williams 1963a,b). Since his device required operating temperatures well above 100°C, its power consumption was too high and its display quality too low. The company, however, soon developed mixtures that operated at room temperatures and continued research well into the 1970s. A much-improved version of the LCD, dubbed the twisted nematic LCD, was developed by James Fergason of Kent State University, Ohio. It was patented in 1969 by his company ILIXCO, with the patent being applied for in 1971 (Fergason 1969). Its basic principles had already been described by Schadt & Helfrich (1971), who applied their subsequent patent (Helfrich & Schadt 1971) several months earlier than Fergason (Castellano 2005).

Two independent observations on liquid crystalline behaviour, deemed mere curiosities at the time, now form the basis of all LCD technology. The first observation was reported by Mauguin (1911a,b,c), who noted that liquid crystal domains could be aligned by placing them in contact with a crystal surface (Mauguin 1911a, 1913). He further observed that when a mesogenic compound was placed between two aligning surfaces of different orientations, the average direction of the molecular axis of the mesogenic molecules in a domain (the director) smoothly followed the transition, rotating from one surface to the other, inducing a partial helical turn (Mauguin 1911a,b, 1913).

The second essential discovery that forms the basis of all LCD technology in the 1930s was reported by Freedericksz. He observed that it is possible to use an electric field to control the orientation of liquid crystal molecules (Freedericksz & Zolina 1933). If the field strength exceeded a threshold value, the dipoles of the liquid crystal molecules would orient parallel to the field, abandoning any previous orientation. In honour of its discoverer, such a transition is now called a Freedericksz transition.

At that time, no immediate applications of these discoveries were foreseen. This abruptly changed with the combination of the two observations to construct the twisted nematic LCD (Fergason 1969; Helfrich & Schadt 1971; Schadt & Helfrich 1971; Castellano 2005). Its operating principle is as brilliant as simple (figure 8). A liquid crystalline compound, usually a calamitic nematic liquid crystal, is sandwiched between two conductive surfaces—mostly indium tin oxide (ITO)—covered with an alignment layer, which induces uniform planar alignment of the liquid crystal near the surface (vide infra). By orienting the alignment directions of the two surfaces in a perpendicular fashion, the director of the liquid crystal between the surfaces rotates over 90° going from one boundary to the other in a partial helical turn, as shown by Mauguin (figure 8a). If the distance between the two plates is much larger than the wavelength of incident light, the photons will have their polarization direction rotated by 90°, while traversing the cell by the interaction with the chiral helical liquid
crystalline structure between the plates (Mauguin 1911c). By incorporating crossed polarizers into the device scheme, a twisted nematic liquid crystal cell is constructed which is capable of allowing light to pass through these crossed polarizers (off-state; figure 8a). This property can be turned off by applying an electric field between the two conductive alignment layers. Once the field strength exceeds the Freedericksz transition, the liquid crystal molecules will align parallel to the field direction (figure 8b).

As the partial helical turn is no longer present, any incident light will not have its polarization direction altered and, consequently, is no longer able to exit the cell through the second polarizer, which causes the cell to appear dark (on-state, figure 8b). When the electric field is switched off, the liquid crystal reverts back to its original chiral structure and the cell is once again capable of transmitting light.

4. Inducing liquid crystal alignment

A crucial element of the twisted nematic LCD is the alignment layer, which is used to induce uniform and planar alignment of the liquid crystal molecules near the surface. Surprisingly, the process first applied in the late 1960s to achieve this is very similar to the process commercially used today. Simply called ‘rubbing’, it had already been developed in the 1920s (Zöcher 1925). The method entails the unidirectional rubbing of a spin-coated polymer surface with a piece of cloth, e.g. velvet (figure 9a). The contact between the cloth and polymer layer creates microscopic grooves on the surface of the polymer (figure 9b) and aligns
(substituents of) individual polymer chains. When a liquid crystalline compound is interacted with such a surface, the mesogen adopts a macroscopic alignment (figure 9b, inset).

The alignment mechanism associated with rubbing has been debated for decades, but for polymer-coated surfaces, the current consensus is that the predominant alignment mechanism can be ascribed to the generation of a statistically important number of similarly oriented bonds in the top layer of the polymer (Rasing & Musevic 2004; Takatoh et al. 2005), i.e. the alignment of individual polymer chains and their substituents by the rubbing process. The precise intermolecular interactions between the liquid crystal and the molecules of the alignment layer still remain unclear.

The rubbing technique has the advantage of being relatively straightforward, easy and cheap, and generates very stable alignment layers. As it is already a widely applied process in industry, no large investments are required (Rasing & Musevic 2004; Takatoh et al. 2005). However, there are also some serious drawbacks associated with the method, which all arise as a result of the physical contact between the alignment layer and the velvet cloth during the rubbing process (van Haaren 2001; Rasing & Musevic 2004). These drawbacks result in the creation of faulty pixels, which can make an entire display line economically unviable. The contact between the alignment layer and the rubbing cloth creates debris, which remains on the alignment layer and interferes with uniform liquid crystal alignment. The lower local surface concentration of the alignment layer also creates a contrast ratio that differs from site to site. Furthermore, the rubbing of the two materials creates electrostatic charges, which interfere with the electric field switching of the display and can even destroy electronic circuits used to switch the pixels in unison. In order to minimize the harmful effects of these drawbacks, the entire process is performed in a clean room, devoid of dust and charges, making it a very labour-intensive process. In addition, as the need for larger and larger displays increases, e.g. with the onset of large LCD-TVs, the process requires ever more scaling up. Although factories are currently capable of processing plates of more than 4 m², building a rubbing machine for even larger substrates, as demanded by market pressure, would be ‘a nightmare for engineers to build and operate’ (van Haaren 2001). As a consequence, research into other ways of aligning liquid crystals has been revived and has become increasingly more important in the past decades.
5. Alternatives: non-contact alignment

Non-contact techniques are the most promising in replacing the rubbing process, photo-alignment being one of the most investigated approaches. This method, without exception, relies on the isomerization of double bonds to induce ordering. The most commonly used compounds include derivatives of azobenzene and cinnamic acid (scheme 1), which undergo cis–trans isomerizations upon irradiation with (polarized) light. It is the alignment of the double bonds and their subsequent reaction to form cyclobutanes that results in an ordered surface (scheme 1). A more comprehensive review of these methods was recently published (Hoogboom et al. 2006a).

Recently, we reported another alternative to rubbing, which is based solely on hierarchical self-assembly processes from solution (Hoogboom et al. 2003). When an ITO plate was immersed into a solution of the naphthalene-functionalized siloxane 1 (chart 2), an alignment surface was generated without the use of external stimuli (e.g. rubbing or photo-alignment).

This ordering effect could be attributed to two competing processes, which occur simultaneously. The first process is related to the creation of stronger intermolecular interactions between the large π-surfaces of 1, when compared with the aforementioned cinnamic acid derivatives. A consequence of this increased interaction is that 1 oligomerizes in solution, forming rigid cyclic and linear oligosiloxanes (figure 10a). As the oligomer grows, it becomes increasingly less soluble, resulting in its precipitation on the ITO surface. The second process involves the covalent grafting of these precipitating oligosiloxanes onto the ITO surface (figure 10b). By very carefully tuning the rates of both processes, i.e. by ensuring that oligomers with the right size precipitate and graft at the right time during layer formation, a highly ordered surface was formed by self-assembly, which was shown to be capable of inducing uniform surface alignment of liquid crystalline molecules (figure 10c). These self-assembled alignment surfaces were readily incorporated into standard twisted nematic LCDs (figure 10d) and

\[ \text{Scheme 1. Photochemical isomerization of (a) azobenzenes and (b) cinnamoyl derivatives.} \]
rivalled industrially manufactured displays in terms of interaction energy between the alignment layer and the liquid crystalline matrix.

Surprisingly, the overall direction of the surface ordering—and hence the liquid crystal alignment—was determined by the underlying ITO plate (Figure 11). If an ITO plate was cut in half before layer formation, and the two halves were placed in the same solution of 1, but in different orientations, the direction of the self-assembled alignment layer was found to depend on the orientation of the surface in the solution. This observation was attributed to the morphology of the ITO plate, which was shown to contain parallel groove-like
structures of nano-sized dimensions. This directional ordering arises from the manufacturing procedure of the ITO plate itself. During the formation of the self-assembled command layer, the size and ordering of these nano-grooves was amplified by several orders of magnitude. It should be noted that this whole process could be performed under standard laboratory conditions, eliminating the need for clean room facilities in alignment layer construction.

More recently, we demonstrated that the hierarchical rubbing process described previously can also be applied to other siloxane derivatives, and we have developed a supramolecular approach that enables not only rational control, but also fine-tuning of the properties and alignment of nematic domains (Hoogboom et al. 2005). An alignment surface containing metal-binding sites was constructed by incorporating pyridine-functionalized siloxane 2 (chart 3) into the deposition process. The resulting alignment surface could be used to template the epitaxial growth of highly ordered columnar aggregates of the metallated dye zinc-phthalocyanine (ZnPc) from solution (figure 12a).

By varying the time of immersion of the pyridine-functionalized surface into a zinc-phthalocyanine solution, the aggregate height could be controlled, i.e. from 25 nm after 30 min to 50 nm after 3 h.

These ZnPc-functionalized command layers were capable of inducing stable alignment of the common nematic liquid crystal 5CB, with domain sizes of the order of hundreds of micrometres. Fine-tuning of the non-covalent interactions between the surface and the liquid crystal, and hence the degree of alignment, can be achieved by further ordering of the alkyl tails of the ZnPc aggregates, viz. by applying a shear force (figures 12c, inset and 13). Polarized Fourier transform infrared experiments showed
that the absorption intensity of the stretch vibrations of the alkyl tails of the phthalocyanine was dependent on the polarization angle of the incident light, indicating that these tails were ordered within domains (figure 13a). In addition, this orientation could be controlled by applying a shear flow (figure 13b,c). The anchoring energy, which is a quantitative measure of the strength of the intermolecular interactions between the alignment layer and the mesogen (Rasing & Musevic 2004), was found to be strongly dependent on the immersion time of the ITO plate into the ZnPc solution, and hence the stack height (figure 13d). As such, this technique offers considerable possibilities for the direct control over the interactions between the alignment layer and the mesogen.

The alignment properties of these layers could be further influenced by the addition of molecules to the liquid crystalline matrix of the display, which are capable of coordinating to and, subsequently, dissolving the aggregates. Introducing micro- or nano-molar amounts of amines (e.g. amino acids such as alanine and glycine, and several aliphatic amines) into the cell resulted in the loss of alignment (figure 12d). A wavefront was seen traversing the cell (figure 12d), leaving a non-aligning layer devoid of ZnPc (figure 12a). By using nanomolar concentrations of pyridine, which coordinates more weakly than aliphatic amines, the alignment capability of the system was retained; but the anchoring energy was reduced by a factor of 2.5 (figure 13d). In addition, when a chiral amine was used in the experiments, a cholesteric phase, embedded inside a normal nematic one, was observed in the cells (figure 14). These combined results clearly demonstrate the potential of supramolecular command layers to tune the nematic domain properties.

It is also possible to use supramolecular alignment layers to detect and monitor the presence of large proteins (viz. 5 nm sized lipase, CALB) on a surface (Hoogboom et al. 2006b). As described previously, the molecules in liquid crystalline compounds possess numerous strong interactions between neighbouring mesogens; hence, any change in the orientation of these molecules at an alignment surface is transmitted into the liquid crystal bulk. Thus, small changes at a surface are effectively amplified in size by several orders of magnitude. Consequently, liquid crystals can be considered as molecular magnifying glasses, bringing surface changes at the nanoscale into the realm of the naked eye, without the need for additional processing.
By incorporating an ester-containing substrate into a self-assembled siloxane alignment layer for liquid crystal cells (figure 15a), it was shown that the presence of a lipase (CALB) could be directly detected through its enzymatic action on the alignment layer, without the need for fluorescent labelling or enzyme assays. Upon hydrolysis of the surface by the enzyme, the alignment layer undergoes a dramatic local change in polarity, passing from a benzyl group to an acid group wherever the enzyme is active. The mesogens near the surface, especially near the boundary of enzymatic activity, adopt a different orientation (figure 15a), disrupting uniform alignment. This in turn alters the ordering of the liquid crystal matrix near the surface, which is transferred into the mesogenic bulk and amplified up to levels that can be easily detected by the human eye (figure 15b).

6. Alignment layers by self-assembly of molecules at a surface

The creation of uniformly patterned surfaces by controlled self-assembly of molecules in an anisotropic fashion can be foreseen to become the ultimate bottom-up approach to the construction of alignment layers for liquid crystals. However, complete control over the specific adsorption of molecules on a surface, a prerequisite for the generation of predictable and well-defined assemblies, is difficult to achieve. One route towards well-defined arrays of molecules is to use self-assembly in tandem with physical phenomena, such as...
surface dewetting. For such an approach, disc-like chromophoric molecules, e.g. phthalocyanines or porphyrins (Elemans et al. 2006), have been shown to be ideal building blocks. Supramolecular approaches, in general, are synthetically less demanding than covalent approaches; however, the precise control over the positioning of the constituting components into a desired
assembly is not trivial. In this context, the study of self-assembly processes at solid–liquid interfaces is of great interest.

Following this route, we have synthesized large, disc-shaped compounds, in which six porphyrin molecules are arranged in three overlapping pairs around a central benzene core, giving them the overall structure of a propeller (figure 16a; Biemans et al. 1998). Monolayers of these porphyrin hexamers could be imaged with submolecular resolution at a liquid–solid interface of 1-phenyloctane and highly oriented pyrolytic graphite (HOPG), using STM (Elemans et al. 2003). The free base hexamer \( \text{H}_2\text{3} \) was found to adsorb onto the surface in a kinetic ‘face-on’ structure, in which the molecules are positioned flat with their large aromatic surfaces directed towards the HOPG surface. After a few hours, the molecules gradually changed their orientation into an ‘edge-on’ fashion, orthogonal to the surface in the form of stacks, which appeared to be thermodynamically the most stable arrangement. The face-on or edge-on orientation of the zinc analogue \( \text{Zn3} \) could be precisely controlled by the addition of bidentate ligands to the solution containing the porphyrin hexamers. In the presence of an excess of the bidentate ligand 1,4-diaza[2,2,2]bicyclooctane (DABCO), the molecules of \( \text{Zn3} \) oriented themselves exclusively into an edge-on orientation (figure 16b), whereas the addition of 4,4′-bipyridine forced them to

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Figure 15. (a) Schematic of the effect of the hydrolysis of a substrate-containing alignment layer by CALB on the orientation of mesogens. (b) Polarizing micrographs of the corresponding changes in liquid crystal texture. Images, 400×600 µm.
assume a face-on orientation all over the surface (figure 16c). The relatively small DABCO molecules fit exactly into voids between the molecules of $\text{Zn}_3$, thereby coordinating to the zinc ions and interconnecting the hexamers to form extended stacks of metal-coordinated polymers on the surface. In contrast, the 4,4'-bipyridine ligand is too large to fit into the voids between the molecules of $\text{Zn}_3$, preventing a stable edge-on orientation of the hexamers, leading to a face-on arrangement on the surface.

As an extension of this work, even larger porphyrin disc-like molecules were designed and synthesized, viz. porphyrin dodecamers $\text{H}_4\text{4}$ and $\text{Zn}_4$, consisting of an extended benzene core to which 12 porphyrins are attached (figure 17a; Lensen et al. 2004a). In contrast to the hexamers, these molecules have a more disc-like shape, with two sets of six porphyrins stacking on top of each other to form a ‘yo-yo’-like architecture (figure 17b,c). As a result of strong intermolecular

Figure 16. (a) Structure and side and front views of a model of porphyrin hexamer 3. (b) STM image of $\text{Zn}_3$ with a 10-fold excess of DABCO at the solid–liquid interface of 1-phenyloctane and HOPG; $U_t = -220 \text{ mV}$ and $I_t = 1 \text{ pA}$. (c) STM image of $\text{Zn}_3$ with a 10-fold excess of 4,4'-bipyridine; $U_t = -180 \text{ mV}$ and $I_t = 1 \text{ pA}$. (Adapted with permission from Elemans et al. (2003). Copyright Wiley-VCH 2003.)
π–π stacking interactions, this compound H24 arranges itself at a liquid–solid interface of 1-phenyl octane and HOPG in huge domains of exclusively edge-on oriented discs with an intermolecular distance of 12 Å (figure 17d). Surprisingly, Zn4 did not form stable monolayers at this interface, but upon the addition of DABCO, again extended stacks of metal-coordinated polymers were observed by STM (figure 17e). As a result of the presence of the ligand molecules, the intermolecular distance between the zinc dodecamers increased from 12 to 18 Å.

Both porphyrins 3 and 4 were found to form unique mesoscopic architectures at a surface upon drop casting a chloroform solution of these compounds on mica or glass. After evaporation of the solvent, micrometre-sized rings were observed, of which the size and size distribution were found to be strongly dependent on the wettability of the surface (figure 18a; Lensen et al. 2004b). The formation of these well-defined rings is proposed to occur according to the so-called ‘pinhole’ mechanism, which is a combined process of molecular self-assembly and physical wetting/dewetting phenomena (figure 19; Schenning et al. 1996). Upon evaporation of the thin chloroform film, at a certain stage, pinholes, in which the surface is in contact with air, are formed. At the edges of these pinholes, the rate of solvent evaporation is higher than in other places of the film, leading to a flow of porphyrin molecules in the direction of the pinholes, where their concentration locally increases. After further evaporation of the solvent, the porphyrin material is deposited in the form of ring-like architectures, which have an empty interior.

To get more information about the orientation of the deposited molecules within the rings, their optical properties were investigated with the help of polarized fluorescence spectroscopy and near-field scanning optical microscopy (NSOM; figure 20b,c; Jeukens et al. 2004; Lensen et al. 2004b). Upon excitation of the rings with polarized light in a vertical direction, emission was mainly observed at the sides of the rings (figure 18b). Analogously, emission was observed at the top and bottom positions in the rings upon excitation with polarized light in a horizontal direction. Taking into account the direction of the transition dipoles in the molecules, it was concluded from these observations that the porphyrins are organized in edge-on columnar stacks, which are oriented radially within the rings (figure 18d).

Although the ring-shaped architectures formed by 3 and 4 are interesting and provide important information with regard to the self-assembly behaviour of these compounds, they are not suitable for use as alignment layers for liquid crystalline molecules. Instead, larger line-shaped patterns are required. With this in mind, we designed a new disc-shaped porphyrin compound, viz. 5, consisting of three porphyrin moieties, which are attached to a central benzene core via amide bonds (figure 20a; van Hameren et al. 2006). It was reasoned that the presence of these hydrogen bonding units would enhance the stacking between the discs, resulting in the formation of longer one-dimensional aggregates instead of rings. Indeed, when a dilute solution of 5 in chloroform was drop cast onto a mica surface, highly uniform patterns of linear aggregates were formed upon evaporation, consisting of bundles of stacks of 5. Both the periodicity (13 µm) and the height (55 nm) of the lines were highly defined, and the lengths of the lines extended up to almost 1 mm (figure 20b).
In contrast to the ring-shaped architectures formed by 3 and 4, the lines generated by 5 are believed to be deposited by a solvent evaporation process, which is denoted by the ‘coffee-stain mechanism’ (figure 20c; Deegan 1998). According to this mechanism, the contact line of an evaporating solution is pinned one or more times, often caused by the presence of aggregates of solute within the droplet. In this case, the solvent evaporation rate is highest at these contact lines, and dissolved material is now transported to the outside of the droplet in the direction of the contact line. In the case of 5, small columnar stacks (approx. 10–15 molecules) of the compound are already formed in solution, as was demonstrated by small angle neutron scattering (SANS). These aggregates are believed to be responsible for the pinning of the contact line, and after their

Figure 17. (a) Structure of porphyrin dodecamer 4. (b) Top view and (c) side view of a molecular model of 4. (d) STM image of H$_2$4 at the solid–liquid interface of 1-phenyloctane and HOPG; $U_t = -225$ mV and $I_t = 1$ pA. (e) STM image of Zn3 with a 10-fold excess of DABCO; $U_t = -225$ mV and $I_t = 1$ pA.
deposition act as nucleation sites for further growth of extended stacks. The highly defined periodicity between the lines is believed to be the result of spinodal dewetting phenomena (Higgins & Jones 2000).

Figure 18. (a) Typical AFM image of rings formed by hexamer 3 and dodecamer 4 on a hydrophilic surface. (b) Polarized fluorescence microscopy image of the rings of 3 on hydrophilic carbon-coated glass, with vertical excitation and detection; inset: vertical excitation and horizontal detection. (c) The same as of (b), but with horizontal excitation and detection; inset: horizontal excitation and vertical detection. (d) Proposed internal structure of the rings formed by 4; for 3, a similar structure is valid. (Adapted with permission from Lensen et al. (2004b) and Jeukens et al. (2004). Copyright Wiley–VCH 2004 and American Chemical Society.)

Figure 19. Schematic of ring formation according to the ‘pinhole’ mechanism. (Reproduced with permission from Lensen et al. (2004b). Copyright Wiley–VCH 2004.)

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It was investigated whether similar patterned surfaces on glass (with patterned areas up to 3 mm^2) could be used as alignment layers for the liquid crystalline compound 4-n-pentyl-4′-cyanobiphenyl (5CB) (van Hameren et al. 2006). Liquid crystal cells, consisting of one glass plate covered with the aggregates and a non-rubbed counter plate spin-coated with a commercially available polyimide, were prepared and filled with 5CB. Polarizing microscopy showed that the cells contained aligned liquid crystal domains of several square millimetres (figure 21) in the regions where the linear aggregates were present on the surface and no alignment in other areas. The alignment was interrupted by concentric circles, which were the contact pinning lines that were still present after evaporation of the droplet. Second harmonic generation (SHG) measurements revealed that the orientation of the long axis of the 5CB molecules was parallel to the linear aggregates on the surface (figure 21). By using such an approach, it can be envisaged that an ordered alignment layer could be constructed by the flow of a thin molecular solution over a large surface.

7. Conclusions

The results presented in this paper show that LCD cells can be constructed using alignment layers that are formed by self-assembly processes. Although, at present, the technology has not yet reached the level of sophistication that is needed for the large-scale production of LCDs, the first steps have been made, which hold great promise. Apart from LCD production, self-assembled alignment layers may find future application in sensor systems, as was shown in the first part of this paper. This opens the way to a facile, naked-eye detection of analytes, e.g. amino acids, peptides and, perhaps, proteins.

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Figure 21. Application of the patterns formed by 5 on a glass substrate as alignment layers for 5CB; polarizing microscopy images of a liquid crystal cell between crossed polarizers (denoted by ‘P’ and ‘A’). (a) LC ordering parallel to the analyser. (b) The texture after the rotation of the sample over 45°. The local orientation of the 5CB molecules, deduced from the SHG rotational anisotropy patterns (insets), is depicted schematically in both the images. Scale bars, 200 μm. (Adapted with permission from van Hameren et al. (2006). Copyright AAAS 2006.)
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