Alignment by Langmuir/Schaefer monolayers of bent-core liquid crystals

Wilder Iglesias, a Timothy J. Smith, b Prem B. Basnet, c Sharon R. Stefanovic, c Carsten Tschierske, d Daniel J. Lacks, b Antal Jákli a and Elizabeth K. Mann c

Received 29th March 2011, Accepted 5th July 2011
DOI: 10.1039/c1sm05546a

Langmuir films of bent-core molecules at the air/water interface are transferred onto a solid surface by the inverse-Langmuir-Schaefer (ILS) technique. Previous work by the authors demonstrated that ILS films of a symmetric bent-core molecule can serve as effective planar alignment layers for a nematic bent-core liquid crystal cell, but the Langmuir films were unstable and formed multilayers at very low pressures. Here, films of bent-core molecules with one hydrophilic end connected to the bent core by a short aliphatic chain are tested as alignment layers. The hydrophilic group led to much more stable Langmuir films, and also to a molecular tilt at the surface which could be controlled by molecular area. This interpretation of the molecular behavior was supported by a combination of atomically accurate molecular dynamics simulations of up to 36 bent core molecules at a water surface and by the continuous variation of tilt induced by ILS films in a rod-like liquid crystal cell. The ILS films were then tested as alignment layers for a bent-core nematic: highly-compressed films induced perpendicular alignment, which provides a significant step towards their practical application.

I. Introduction

The discovery of the mesogenic properties of bent-core (BC) molecules 1 has opened up a major new and exciting dimension in the science of thermotropic liquid crystals (LCS). These mesogens have a rich phase diagram including a vast number of smectic and columnar phases denoted by B1–B7. 2–5 Seminal findings, having broad implications for the general field of soft condensed matter, include the observation of ferroelectricity and of spontaneous breaking of chiral symmetry in smectic phases composed of molecules without chiral stereo-centers. 6 These phases are candidates for devices with fast switching times. Nematic phases of BC molecules are much less common and their study lags behind that of the smectic and columnar phases, but they show a number of interesting rheological 7 and electromechanical properties. 8

Effective alignment layers, which yield controlled molecular configurations at the surface that propagate into the bulk liquid crystal, are crucial both to improve control of experiments designed to explore the behavior of bent-core molecules and to effectively exploit this behavior. Good alignment has been hard to achieve with the common methods used for rod-like (calamitic) molecules because of the symmetry breaking of the bent-core mesogens (Fig. 1). An alignment layer made up of molecules of similar shape has a major advantage: the shape and symmetry of the molecules in the alignment film and in the bulk liquid crystal are compatible.

Langmuir films, molecularly thin films self-organized on the smooth water surface, allow external control of the phase and orientation within the film through the average molecular area, as dictated by the interaction of the molecules with each other and the substrate. These films, transferred to a solid substrate by

Fig. 1 Cartoon models comparing the alignment of rod-shaped (a,b) and bent core (c,d) molecules according to two common models: (a,c): the groove model; (b,d): a hydrocarbon layer model. The symmetry arguments are similar for more accurate models.
Langmuir/Blodgett or Langmuir/Schaefer techniques, thus have a wider and more easily controlled range of properties than films self-assembled directly at the solid interface.

Previous studies showed that bent-core Langmuir films could be made and transferred to solids. We recently demonstrated that such films of symmetric bent-core molecules could be used to align bent-core nematic liquid crystal films in the plane of the surface. However, these Langmuir films were unstable, forming multilayers at near-zero pressure. The balance of hydrophobicity and hydrophilicity that governs the stability of all Langmuir films is tipped too far towards hydrophobicity. Therefore, new types of amphiphilic bent core molecules with a hydrophilic group at one end of the molecule have been designed and synthesized to improve attraction between the molecule and the water surface. In this work an amphiphilic bent-core mesogen Z2b with one hydrophilic COOH end group has been investigated with respect to its self-assembly at the air water interface. The asymmetric hydrophilicity, and the combination of amphiphilicity with a rigid bent shaped unit, also allows for striking changes in molecular alignment as the layer is compressed: the bent core molecules may transition from quite flat on the surface, as seen previously, to almost upright with only the hydrophilic end tethered to the surface. The experiments we present here suggest a gradual transition between such configurations. Realistic atomistic simulations of collections of up to 36 bent-core molecules packed together at a water surface support this interpretation.

The films transferred at different compression states were used for the alignment of rod-like and bent-core nematic phases. The alignment depends strongly on the thin film structure. With highly compressed films we succeeded here, to our knowledge for the first time, in aligning bent-core nematics perpendicular to the water interface. The asymmetric amphiphilicity, and the combination of amphiphilicity with a rigid bent shaped unit, also allows for striking changes in molecular alignment as the layer is compressed: the bent core molecules may transition from quite flat on the surface, as seen previously, to almost upright with only the hydrophilic end tethered to the surface. The experiments we present here suggest a gradual transition between such configurations. Realistic atomistic simulations of collections of up to 36 bent-core molecules packed together at a water surface support this interpretation.

The films transferred at different compression states were used for the alignment of rod-like and bent-core nematic phases. The alignment depends strongly on the thin film structure. With highly compressed films we succeeded here, to our knowledge for the first time, in aligning bent-core nematics perpendicular to the surface. This provides a significant step forward to the practical application of the rich phase behavior of bent-core molecules. Further, the comparison of the behavior of the two types of bent-core alignment layers and their very different effect on both rod-like and bent-core nematic liquid crystal cells provides insight into the general properties of alignment layers effective for bent-core nematics.

II. Materials and methods

A wide variety of techniques are used to form and characterize Langmuir and Langmuir/Schaefer bent-core films, and to test their effectiveness in aligning both rod-like and bent-core nematic liquid crystals.

A. Materials

The synthesis and purification of Z2b together with the analytical data and the investigation of the thermotropic LC behavior has been reported previously. Fig. 2 shows the chemical formula of this compound together with the structure of the previously investigated symmetric compound Be2Cl, with symmetric hydrophobic end-chains, and the two nematic liquid crystals 5CB, a conventional rod-like mesogens, and CN6, a bent-core mesogens with a cybotactic nematic phase, used for alignment studies. Table 1 summarizes the phase transition temperatures of all compound of interest for this work. 5CB was commercially available (Alfa Aesar, 99% pure); compounds CN6 and Be2Cl have been reported previously and were provided by C. Tschierske (Halle) and W. Weissflog (Halle), respectively and were used as provided.

B. Isotherms and ILS transfer

Surface tension isotherms were determined using the KSV™ (Finland) minitrough system, including control barriers, Wilhelmy plate and software. Simultaneously, we used a homemade Brewster Angle Microscope (BAM) to monitor the phase changes of the material deposited in the trough as the barriers compressed and decompressed it. Well-collimated p-polarized light from an Argon-ion laser with wavelength 488 nm was reflected off the monolayer at the Brewster Angle to a biconvex lens that focused the image on a CCD camera. A diacronic sheet analyzer was used before the final lens to check for any rotation of the polarization by the Langmuir film, which would indicate in-plane optical anisotropy.

Z2b was dissolved in chloroform (Aldrich A.C.S HPCL grade) at ~0.6 mg/ml. This solution was spread on top of the Langmuir trough filled with pure water (PureLab Plus system; obtaining a resistivity of 18.2 MΩ/cm and passing the shake test, meaning that small bubbles in solution burst as soon as they reach the surface), to an initial area/molecule of ~1.5 nm². If the initial film

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase sequence on heating (°C)</th>
<th>Phase sequence on cooling (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z2b</td>
<td>Cr 140 Iso</td>
<td>Iso 122 M 83 C21</td>
</tr>
<tr>
<td>Be2Cl</td>
<td>Cr 145 Iso</td>
<td>Iso 143 N 103 C22</td>
</tr>
<tr>
<td>CN6</td>
<td>Cr 98 NcybC 101 Iso</td>
<td>Iso 101 NcybC 53 C23</td>
</tr>
<tr>
<td>5CB</td>
<td>Cr &lt; 23 N 35 Iso</td>
<td>Ref. 24</td>
</tr>
</tbody>
</table>

a) Iso = isotropic liquid, M = unidentified mesophase, NcybC = nematic phase composed of SmC type cybotactic clusters, Cr = crystalline solid.
molecular area was less than ~1 nm², the initial configuration included multilayers.\textsuperscript{24} Barriers moved at 5 cm min\textsuperscript{-1} to both compress and decompress the Langmuir film.

Inverse Langmuir-Schaefer (ILS) deposition was used to transfer the Langmuir film to a glass plate. This technique consists of drawing the substrate upwards through the Langmuir film, almost parallel to water surface. The glass sample is kept at an angle of ~30° for 5 min to allow the water between the ILS film and the glass to flow out. Up to two samples were made at different pressures from the same Langmuir film.

\textbf{C. AFM}

The uniformity of the transferred films were tested with a NanoScope III atomic force microscope (AFM) using the tapping mode to reveal the topography of the transferred films. This translates into a measurement of the height of the features observed on top of the glass surface.

\textbf{D. Liquid crystal cells: Fabrication and characterization by polarized optical microscopy (POM) and the crystal rotation method (CRM)}

Two slides coated by ILS with Z2b at the same surface pressure were used as alignment substrates to construct liquid crystal cells with 10 µm spacers. The dipping directions of the slides were carefully aligned. These cells were filled with one of two molecules with nematic phases: 5CB was filled at room temperature, in the nematic phase and then heated up to 50 °C (isotropic phase) to avoid flow induced birefringence, while CN6 was filled at 105 °C, in the isotropic phase. All measurements on the cell were made on their nematic phase, 25 °C for 5CB and 85 °C for CN6.

Polarized optical microscopy, in which these cells were rotated parallel to and between crossed polarizers, was used to observe qualitatively any alignment parallel to the cell plane. The tilt of the director was then quantified by the crystal rotation method (CRM) proposed by Baur et al.\textsuperscript{29} This method consists in a two step process: First the liquid crystal cell is rotated between crossed polarizers azimuthally (parallel to the polarizers with the laser beam as the axis of rotation), to find a maximum in the transmitted light intensity, which determines the projection of the nematic director in the plane of the cell. The value of the pretilt angle is then determined from the light transmission as a function of angle, rotating the cell in the plane formed by the laser and the projection of the nematic director. This method is most sensitive to the pretilt angle when that angle is near either 0° or 90°.

\textbf{E. Computer simulations}

Molecular dynamics simulations are carried out for collections of up to 36 bent-core molecules packed together at a water surface. A molecular dynamics simulation tracks the movement of atoms with time, due to the forces between the atoms. The simulation proceeds by numerical integration of equations of motion, wherein at each timestep each atom moves in response to the forces on it, and the forces are then recalculated after the atom moves. All atoms are explicitly modeled in these simulations.

The simulations are carried out using the Gromacs software package,\textsuperscript{30} with simulation details as follows. The simulations are run at fixed temperature, using the velocity rescaling thermostat with a time constant of 1 ps;\textsuperscript{31} temperature control is done separately for the bent-core molecules and the water to ensure the same fixed temperature in both. The Coulombic interactions are evaluated using the Particle Mesh Ewald method,\textsuperscript{32} while the non-Coulombic interactions are directly summed up to a cut-off length of 1 nm. The boundaries of the simulation cell are periodic in all three directions; to create water surfaces, the z dimension of the simulation cell is set to a large value so that the water cannot form a continuous phase in that direction, which results in slabs of liquid water oriented perpendicular to the z dimension. The time step for the numerical integration is 1 fs.

Molecular interactions are parameterized with the OPLS force field.\textsuperscript{33} The force field parameters included with the Gromacs package cover all charge, bond angle, 1,4-interaction pairs, and dihedral interactions, with the exception of the ester oxygen bond angles and the biphenyl dihedral interactions. The ester oxygen bond angle parameters are taken from Charifson et al.\textsuperscript{34} The biphenyl dihedral parameters are obtained by fitting the Ryckaert-Bellemans function\textsuperscript{15} to electronic structure results for the energy of the biphenyl molecule as a function of the interphenyl dihedral angle.\textsuperscript{36}

The simulations are carried out with a water layer and bent-core molecules initially in the space above the water surface. A box height of 20 nm in the z-dimension ensures negligible interaction between the periodic images of the water layer. The number of water molecules in the simulation varies between 1000–3000 (depending on the surface area of desired in the simulation). Either a fixed volume or a fixed pressure is imposed in the simulations. The number of water molecules in the simulation varies between 1000–3000 (depending on the surface area of desired in the simulation).

III. Experimental results and discussion

\textbf{A. Langmuir film: Surface pressure-area isotherms and Brewster angle microscopy}

Both the surface pressure isotherms and the Brewster angle microscopy images (Fig. 3) demonstrate that the bent-core Z2b films are more stable than the symmetric Bc-2Cl molecule previously studied. This stability is seen in the isotherm in two different ways: (1) The area/molecule where the surface pressure starts rising, known as the coarea, was very small for Bc-2Cl, corresponding to film thickness ~7 nm (see Fig. 3),\textsuperscript{38} which is too thick for a single layer of molecules even standing on one end. For Z2b, the coarea is about twice as high as for the symmetric molecule, corresponding to film thicknesses ~2.5 nm, which is intermediate between the ~0.6 nm width of a single phenyl group, and the ~4.5 nm maximum length of the molecule. The ~2.5 nm thickness also corresponds well to the values seen in molecular simulations of a single molecule.\textsuperscript{39} (2) The Bc-2Cl film does not re-spread significantly on decompression; note that the pressure drops almost immediately to near zero. Bc-2Cl remains stacked in multilayers.\textsuperscript{17,18} Even when compressed above their collapse pressures as shown in Fig. 3, the Z2b films re-spread on decompression. At zero pressure after
decompression, a viscoelastic monolayer covers the surface, very unlike the Be-2Cl cases.

Note also that Z2b sustains quite high surface pressures before the film starts to collapse into the third dimension. Such collapse is clearly seen in BAM images as bright striations above ~55 mN/m.40

Brewster angle microscopy also shows a notable difference in the uniformity of the Z2b films compared to the Be-2Cl films, which show many fractures and floating islands interpreted as stiff multilayers. Again, we attribute the more uniform films to the better tethering of the hydrophilic head group to the water surface.

At low pressures, after a compression/decompression cycle, the films have an in-plane optical anisotropy, with an optical axis uniform over areas larger than the ~1 mm field of view. This uniformity makes impossible the usual test for anisotropy in a Langmuir film, by the changing contrast between domains as the analyzer is rotated: unlike for a liquid crystal cell, both the polarization direction and the sample cell are fixed by the experiment. In the previous study of Be-2Cl, we developed a method of measuring the optical anisotropy, by rotating domains of liquid crystal film with respect to the trough instead.34 The same process also revealed anisotropy in Z2b films at low surface pressures, after decompression, although the data was insufficient to deduce the tilt of the optical axis with respect to the vertical nor the optical anisotropy, because of an added difficulty: domains floated in a very viscoelastic liquid, instead of the gas-like phase seen with Be-2Cl. The data did clearly reveal such anisotropy.28,40 We can thus expect a similar anisotropy in the transferred film at low pressure, which would give a preferred direction for an alignment layer.

B. Atomic force microscopy

Atomic Force Microscope (AFM) images were taken in tapping mode to reveal the topography of the transferred films; this translates into a measurement of the height of the features observed on top of the glass surface. Films were transferred at several pressures along the isotherms. We saw that the roughness of the Z2b transferred films is ~2–5 nm (compared to ~0.5 nm over this length scale for a bare glass slide), and remains of the order of a molecular length even at the highest deposition pressures.39 Be-2Cl on the other hand showed a clear layered structure with a thickness increment ~0.6 nm, the size of a phenyl ring, implying multilayers of the molecules lying flat on the surface.

C. Liquid crystal cells: Polarized optical microscopy (POM) and crystal rotation method (CRM)

Two slides coated by ILS with Z2b at the same surface pressure were used as alignment substrates to construct liquid crystal cells, as described in Section 2.C. These cells were filled with one of two molecules with nematic phases: 5CB is a well known rod-like liquid crystal mesogen with a room-temperature nematic phase, chosen as an imaging tool to give insight into the configuration of the “alignment monolayer” by its influence on the alignment of the bulk rod-like phase in the cell.41 CN6 is a bent-core liquid crystal mesogen with a well-studied nematic phase.23

Polarized optical microscopy checks for alignment direction: cells are placed on a rotating platform between cross-polarizers under an optical microscope. The cell angle for which the light is completely extinguished (dark state) indicates the direction for which the projection onto the substrate plane of the director n is aligned with either the polarizer or the analyzer of the microscope. Turning the platform 45° away from the dark state, either clockwise or counter clockwise, yields the bright state. A greater contrast between these two states (dark and bright) implies a pretilt angle of the cell closer to 0 degrees (planar alignment) and no contrast implies approximately a 90 degree pretilt (perpendicular or homeotropic alignment.) With no well-established alignment direction, both bright and dark domains appear. These different domains change from bright to dark and vice versa within 45° rotations as before, but a nematic director n cannot be specified for the whole cell.

Aligning 5CB. Fig. 4 show the results of polarized microscopy on 5CB sandwiched between films of Z2b. The cell is close to planar alignment at low transfer pressures and to perpendicular at high transfer pressures for the alignment layers. The large-scale optical anisotropy of these films is consistent with that observed in the original Langmuir layer. Quantitative measurement of the tilt angle of the optical axis with respect to the surface plane (‘pretilt’) induced by the bent-core monolayer (Z2b) on the bulk of the cell (5CB) are shown in Fig. 5, using the crystal rotation method (CRM) as described in Section 2.D. The method is most precise when the tilt is near either the planar or perpendicular orientations. Like the qualitative POM results, CRM show high values of the director tilt at high transfer pressures for the alignment layers, and low values at low transfer pressures (Fig. 5). CRM additionally suggests a nearly continuous transition between tilt angles of 10° (nearly planar alignment) and 90° (perpendicular alignment.)
Aligning nematic bent-core molecules. Since Z2b films deposited on glass slides through ILS form a controlled Langmuir film that successfully aligned rod-like mesogens, these films were tested as alignment layers for bent-core mesogen. Liquid crystal cells were prepared using the same procedure as before, and filled with CN6\(^{23}\) (see Fig. 2). We can see in Fig. 6 that this method did not succeed in aligning CN6 mesogens parallel to the substrate (planar alignment). However, perpendicular alignment was achieved using substrates with Z2b molecules transferred at high surface pressure. Planar configuration of bent-core liquid crystals has been achieved using regular alignment methods, i.e. a polyimide film, or with our previous bent-core films, but the perpendicular alignment is particularly hard to achieve due the multiple possible configurations as suggested by Fig. 1.

D. Simulation results

The combination of experimental results, particularly the action of the transferred films on the alignment of rod-like nematic liquid crystal, suggests that the orientation of the bent-core molecules on the water surface is nearly parallel to the surface at low pressures and then gradually tilts up, strongly tethered to the surface by the hydrophilic end, as the molecular area is decreased. However, none of the experimental techniques directly probe molecular orientation at a molecular scale.

Molecular simulations were therefore carried out to determine the orientations of Z2b molecules on a water surface as a function of the surface density. The simulations were carried out both under constant volume and constant pressure conditions, with various numbers of Z2b molecules in the simulation, and from various initial conditions. The orientation of each molecule in a simulation was defined as the angle between horizontal and the vector projection from the central ring to the last ester oxygen on the end of the molecule with the aliphatic chain. This angle was calculated for each molecule individually over 400 equally spaced points in time and averaged to obtain a mean angle.
value for the entire simulation. The results are shown in Fig. 7. At low surface densities, or high molecular area, the Z2b molecules lay flat on the surface of water. As the molecular area decreases, the molecules become increasingly oriented vertically. At low molecular area, the Z2b molecules are nearly perpendicular to the water surface. Note that consistent results are obtained with the different simulation methodologies, confirming that the results are independent of these details. Snapshots of representative configurations from the simulation, shown in Fig. 8, illustrate these changes in orientation.

A description of average molecular configurations of the Z2b molecules is given in Fig. 9. This figure shows 2-dimensional projections of the average of the Z2b molecule at low and high surface densities. These projections show the positions of 11 segments of the molecule (described in the figure caption): the vertical dimension is the average z-coordinate relative to that for the water surface (defined as the position where the water’s density reaches 500 g L⁻¹, or about half its normal density), and the horizontal dimension is the average position along the molecular axis, defined as the average value of \( \frac{\bar{r}_i - \bar{r}_N}{|\bar{r}_N|} \), where \( \bar{r}_i \) is the vector from the 1st segment to the i^{th} segment, and N is the last segment. At low surface densities, the acid group is slightly below the water surface, the central part of the molecule essentially lies on the water surface, and the aliphatic end rises furthest above surface with an average height of 2.5 Å above the water. At high surface densities, the acid end lies at the water surface, and the rest of the molecule rises vertically from that surface as layer is compressed. The tilt found by the simulations and that imparted by the transferred layers to the rod-like molecules in the liquid crystal cells (Fig. 5) are directly compared in Fig. 7. Clearly the trend and the molecular area around which the tilt occurs is the same, but the transition from nearly planar to nearly perpendicular alignment is much more abrupt in the experimental case. Note however that for the simulation we measure directly the tilt of the upper half of the bent-core; the hydrocarbon chain follows this general angle, but with more fluctuations, since the average radius of a stretched hydrocarbon chain is less than that of the bent core. The experimental data on the other hand probes the tilt of the bulk rod-like liquid crystalline material, which should follow the tilt of the hydrocarbon chains on the bent-core transferred layer. To do this, the hydrocarbon chains of the 5CB plausibly interpenetrate those of the bent-core molecules (see Fig. 10). Packing constraints in the swollen hydrocarbon chain region would tend to force all those chains towards the normal. The tilt of the bulk rod-like molecules would thus transition to perpendicular alignment at higher molecular areas than does the bent-core alignment layer alone, in agreement with experimental observations.

Fig. 7 Average angle of Z2B molecules with respect to the water surface, as a function of molecular area. Open circles are simulations at fixed pressure, and filled squares are simulations at fixed volume. Pink, blue, green, gray, and black symbols represent results for 36, 25, 16, 8, and 1 Z2b molecule per simulation cell, respectively. These angles are defined by the vector from the central phenyl ring to the oxygen where the core is attached to the aliphatic chain. Dark blue diamonds represent the experimental data in Fig. 5, with the area/molecule estimated from the pressure during deposition and the compression isotherm in Fig. 3.

Fig. 8 Images of the bent-core molecules from simulations at a lower surface density (left) and a high surface density (right). For clarity, only one of the 36 Z2b molecules in the simulation is shown (the Z2b molecules are tightly packed on the surface). Note that the bent-core molecules stand more vertically at higher surface densities.

Fig. 9 Two-dimensional projections of the average structures of the Z2b molecules. (a) Molecular area of 30 nm²/molecule; (b) molecular area of 29 nm²/molecule. Green circles represent the centers of mass of the phenyl groups, red diamonds represent several of the carbon atoms in aliphatic segments, and blue triangles represent the centers of mass of the acid groups. Bars represent the standard deviations for the probability distributions (when bars are not visible, they are smaller than the symbol).
Conclusions

The experimental results and simulations together strongly suggest that these bent-core molecules are tethered to the surface by their hydrophilic end group. The relative uniformity of the films as seen in AFM and in BAM suggest that as the Langmuir film is compressed, the molecules tilt off the surface. The action of the transferred films in aligning rod-shaped molecules in a liquid crystal cell suggests a slow change in molecular tilt. Comparing these results to those on a symmetric molecule with both ends hydrophobic strongly suggests that it is the hydrophilic end group that allows this. This is supported by molecular dynamics simulations of the tilt as a function of surface density. The results also demonstrate that the ILS-transferred Langmuir films can be used to change continuously the pretilt angle on a liquid crystal cell.

Z2b monolayers transferred at varying surface pressures provided effective alignment for a rod-like liquid crystal: nearly planar (parallel to the substrate) when transferred at low pressures, and nearly perpendicular (homeotropic) when transferred at high pressures. Quantitative measurements by the crystal rotation method, supported by the molecular dynamics simulations in Fig. 7, additionally suggest a nearly continuous transition between tilt angles of 10° and 90°. Liquid crystal devices typically use either perpendicular or planar alignments. Alignment is usually achieved by rubbing, or light buffing. However, continuously varying the pre-tilt angle from near zero to 90 degrees can be very important for optical applications, such as optical gratings, or for achieving chevron-free SmC* films. There are a number of examples for doing this, including changing the temperature, dipping a perpendicular-aligning polyimide in a solvent, overcoating a perpendicular-aligning agent (silane) by a planar-aligning substrate, varying the thickness of the planar agent, rubbing perpendicular-polyimide with various pressures, and by mixtures of two polyamic acids. In contrast, our inverse Langmuir-Schaefer films deposited at different surface pressures shows that a continuous transition is possible with a single layer. Similar behavior was seen with the lipid DLPC transferred by Langmuir-Schaefer techniques directly to the 5CB/water interface.

For the nematic bent-core mesogen, CN6, planar alignment was not achieved by these Z2b Langmuir-Schaefer films. However, perpendicular alignment was achieved using substrates with Z2b films transferred at high surface pressure. Planar configuration of bent-core liquid crystals has been achieved using regular alignment methods, \textit{i.e.} a polyimide film, or with our previous symmetric bent-core films, but the perpendicular alignment is particularly hard to achieve due the multiple possible configurations as shown in Fig. 1 and discussed in more detail elsewhere.

We note that the striking contrast in how Z2b and Bc-2Cl align the rod-like \textit{vs.} bent-core nematics. For Bc-2Cl, the molecules were quite flat on the surface, leading, with compressed films, to good planar alignment for a bent core nematic, but no alignment at all for the rod-like 5CB. We suggest that this is because a planar arrangement of the symmetric Bc-2Cl gives at least two distinct preferred directions for aligning a rod like molecule, one along each leg of the bent-core. On the other hand, the tethering of the Z2b and Z1b to the surface can break the symmetry of the layer. The good, nearly planar alignment of the rod-like molecules at low deposition pressures implies a fixed direction for the un-tethered hydrocarbon chain. However, the bent core nematic is not aligned by these films. Both the rod-like and the bent-core nematics are aligned perpendicular to the surface by the more compressed films, suggesting a configuration such as that in Fig. 10.

Further, the comparison of the behavior of the two types of bent-core alignment layers and their very different affect on both rod-like and bent-core nematic liquid crystal cells provides insight into the general properties of an alignment layer effective for bent-core nematics: the alignment layer must provide a combination of molecular shape and symmetry appropriate to uniquely determine the desired alignment. Langmuir/Schaefer layers of carefully-chosen bent-core molecules provide one convenient method of constructing such a layer, but others might be designed using the same principle.

As a future application possibility we note that perpendicular alignment stabilized \textit{e.g.} by a polymer network in the nematic phase, or by cooling to the SmA phase could be used to achieve uniform gray-scale switching of bent-core molecules using in-plane electrodes.

Acknowledgements

This work was supported by NSF grants DMR-0907055 and DMR-0906852. We would like to thank the Ohio Supercomputing Center for providing computational resources for this study. We would especially like to thank W. Weissflog for very fruitful early collaborations on this project, including providing the Bc-2Cl.

Notes and references
