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Electrooptical dynamics of ultra-thin nematic liquid crystalline films supported on ZnSe functionalized with alkanethiol self-assembled monolayers.

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Abstract

The electrooptical properties of zinc selenide (ZnSe), a semiconductor transparent in the infrared region of the electromagnetic spectrum, have been exploited in the development of a variety of scientific technologies. Previous studies have demonstrated the facility of this substrate for the adsorption of alkanethiol self-assembled monolayers (SAMs) and the supporting of nematic liquid crystals (LCs), such as 4-cyano-4‘-pentylbiphenyl (5CB). We have investigated the influence of the ZnSe surface morphology on the electrooptical dynamics of ultra-thin 5CB liquid crystalline films supported on both the bare substrate and a surface functionalized with hexadecanethiol (HDT) SAMs. Infrared spectra indicate that the introduction of an HDT monolayer between the ZnSe surface and the liquid crystalline film reorients the average director of the film with respect to those supported on bare ZnSe. Furthermore, the attenuation of the electronic effects of the ZnSe surface by the SAM led to a notable decrease in the
threshold voltage required to induce the Fréedericksz transition in the 5CB film. This feature of the HDT functionalized ZnSe suggests the possibility of fine-tuning the dynamics of 5CB, allowing for additional applications of the substrate. In conjunction with this study, we report a new bi-layer positive resist methodology for the fabrication of a gold interdigitated electrode microarray on ZnSe—a methodology that can be readily generalized for the fabrication of other microscale structures on ZnSe.

Introduction

As their name suggests, liquid crystals (LCs) represent an intermediate phase of matter and exhibit properties of both liquids and solids. Since their discovery in the late nineteenth century, the unique properties of LCs have been exploited to develop a variety of scientific and popular technologies. The most ubiquitous such application is found in modern liquid crystal displays (LCDs). Though LCDs are no longer a novelty, there has been continued research into their improvement over the past few decades.\(^1\) Even so, display technology represents just one of the many fruitful applications of LCs, which have also been implemented in solar cells, optical communications, hyperspectral imaging, and LASER technology.\(^1,2\) More recently, LCs have also been utilized as sensitive probes to investigate the properties of a variety of chemical\(^3\) and biological\(^4-6\) analytes. The unique electrooptical properties of LCs facilitate the success of each of these applications.

As noted, LCs are an intermediate phase of matter that exhibit properties of both liquids and solids.\(^1\) Generally speaking we distinguish between a liquid and solid with reference to two parameters: positional and orientational order. Because the atoms or molecules in an ideal crystal must occupy spatially defined lattice points, crystals are said to exhibit a high degree of positional order. Similarly, the atoms or molecules in an ideal crystal must also point in a well-defined direction, and crystals are thus said to exhibit a high degree of orientational order. Ideal liquids are unlike crystals in both respects: the molecular axes of freely tumbling molecules in a liquid phase do not possess any long-range orientational order,
and individual molecules are free to diffuse throughout the container. In contrast to these traditional phases, LCs can possess varying degrees of positional and orientational order. Such curious behavior can be explained with reference to the inherent anisotropy—in shape, polarity, or both—that is present in liquid crystalline molecules. This anisotropy leads to the stabilization of a given molecular orientation without requiring individual molecules to remain fixed. Often, the anisotropy of liquid crystalline phases is further manifest in their sensitive response to a variety of environmental stimuli, such as the application of an electric field. In the absence of competing forces, the permanent dipole moment of a LC will align with the direction of the applied electric field. Furthermore, nanoscale surface topography at the interface between a substrate and a liquid crystal phase can drastically influence the orientation and dynamics of LCs, a property of particular interest to this study.

Though a variety of different liquid crystalline phases have been isolated and characterized, the so-called nematic phase is among the most widely researched. Nematic liquid crystals (NLCs) are typically rod-shaped molecules that exhibit liquid crystalline behavior over a wide variety of temperature and environmental conditions. The nematic phase possess no positional order, but maintains long-range orientational order, i.e. the individual molecules of a NLC freely translate throughout the container, but the collection of NLC molecules has a tendency to “point” along the same direction. This directionality is typically represented and as a vector quantity, aptly named the director of the LC. The director of a LC sensitive to electronic perturbation will have a tendency to align with an applied electric field. Despite the aforementioned stability of nematic phases, NLCs are still sensitive to environmental stimuli and the topographical features found at their interfaces.

Generally speaking, anisotropic materials exhibit birefringence, i.e. a liability to have distinct indices of refraction depending on the direction of polarization of light shone through the sample. Nematic liquid crystals are no exception to this trend, and we find that light polarized parallel to the LC director has a significantly different index of refraction than light polarized perpendicular to the director. By the same measure, light of different polarizations
will travel through the NLC at different velocities, such that phase-aligned incident photons will gradually grow out of phase as they pass through the NLC. Liquid crystals are therefore able to change the polarization of an incident beam of light, provided there is a “twist” in the layer of LCs. If a system with a twist is placed between crossed polarizers, light will propagate through the system, whereas a twist-free column of LCs would prevent propagation through the second polarizer. Electronic systems containing LCs can be constructed such that the equilibrium state is twisted, but the application of an electric field removes the twist from the LC column. In such systems, light can only pass through the crossed polarizers upon application (or removal) of the electric field (this is a simplified version of the system exploited in LCDs). Analysis of these electrooptical properties yields information about the orientation and dynamics of LCs supported on a given substrate.

The inherent directionality of liquid crystalline phases often proves advantageous, and nearly all applications of LCs require the orientation of the molecular axis of a LC to be well-defined and controlled. Interfacial perturbations have long been used to achieve a high degree of control of LC dynamics. Two decades ago, Nagata and coworkers\(^8\) mechanically rubbed a polyimide coating across the surface of indium tin oxide (ITO) to create directionality on the otherwise smooth ITO surface. This anisotropy was shown to impart directionality to NLCs supported on the surface, with the LC directors aligning along the direction of rubbing. Other studies have reported similar effects. While such methods effectively orient large seas of LCs, many modern applications require small, patterned regions of LCs, and such an arrangement is difficult to achieve by mechanical rubbing.\(^9\) These methods also suffer from a lack of reproducibility.\(^10\) Due to these deficiencies, researchers have continued to pursue other approaches to functionalize LC-bearing substrates.

Self-assembled monolayers (SAMs), a hallmark of modern nanotechnology, offer an appealing alternative for controlling LC behavior. Monolayers may form when molecules from either a solution or the gas phase adsorb onto the surface of a solid. Self-assembled monolayers typically, though not necessarily, consist of a homogenous mixture of organic molecules
that each contain a head group, a spacer, and a functionalized terminus that gives the surface of the SAM any of a number of desired chemical properties. The head group adsorbs—often with a preferred orientation—to a metal, metal oxide, or semi-conductor, lowering the free energy of the surface.\(^{11}\) The space region, which typically consists of straight-chain hydrocarbons, serves to attenuate the electrostatic forces of the surface and impart stability in the structure of the SAM through dispersive van der Waals interactions. As such, the length has been shown to significantly influence the stability of SAMs, and it is difficult to achieve well-defined SAMs if the space group is too small.\(^{11-13}\) Variations in the chain length of adsorbate molecules has even been shown to impact the orientation, and thereby surface properties, of SAMs on certain substrates.\(^{12}\) The breadth of research involving SAMs makes them a particularly attractive target to functionalize substrate surface properties, and a variety of reports of their use to support LCs can be found in the literature.

Much of the original effort to model the behavior of LCs on SAMs investigated systems of NLCs supported by assemblies of straight chain alkanethiols on gold (Au), silver (Ag), and copper (Cu),\(^ {9,10,14}\) as alkanethiol SAMs on coinage metals were already well-characterized.\(^ {9,10,12,14}\) As early as 1996 Gupta and Abbott\(^ {14}\) demonstrated that the composition of an alkanethiol SAM on Au exerts significant influence on the orientation of 4-cyano-5’-pentylbiphenyl (5CB), a common nematic liquid crystal. Notably, the alignment of the 5CB phase on SAMs of even-chain alkanethiols was orthogonal to the alignment on odd-chain alkanethiols. Interestingly, a similar phenomenon was not observed when the same SAMs were deposited on a Ag surface. In a subsequent study,\(^ {9}\) these authors showed that homogenous alkanethiol SAMs caused a planar (parallel to the surface) orientation of 5CB liquid crystals, while a so-called mixed SAM of long- and short-chain alkanethiols promoted a homeotropic (normal to the surface) orientation of the same phase. Given this result, it seems reasonable that varying the ratio of long to short alkanethiols in the SAM could allow for more meticulous control over the tilt angle of NLCs, a possibility that was later realized.\(^ {10}\) Though Au based systems allow for significant control over LC behavior, their
utility is somewhat limited due to the negligible light transmission through gold films. When ultra-thin (< 10 Å) layers of Au are used to combat this problem, the control over LC orientation is diminished. These difficulties have led to the investigation of the behavior of LCs on other SAM-substrate systems.

Substrates consisting of alkylsilane monolayers adsorbed to glass are one such alternative. Following the precedent of these previous studies, researchers attempted to correlate alkylsilane chain length with LC alignment, though significantly different behavior was observed. Where homogenous monolayers of alkanethiols on gold all led to a planar arrangement of LCs, an increase in the chain length of alkylsilane monolayers was found to induce an abrupt transition from planar to homeotropic orientation of LC films. Further, no odd-even alternation of the LC orientation was observed for this substrate-monolayer system. A later study showed that mixed alkylsilane monolayers of appropriate molar ratios can support the homeotropic alignment of NLCs, as was seen for the alkanethiol SAMs of gold. Despite this work, only minimal control over LC orientation can be achieved for glass-alkylsilane systems, and directionality can only be imparted on the LC field of this system through mechanical rubbing of the SAM. This severe limitation warrants the continued search for alternative substrate systems for supporting LCs.

In order to be viable, any candidate substrate must support stable and well-defined SAMs and transmit light over a large region of the electromagnetic spectrum. As noted above, SAMs will readily form only on metals, metal oxides, and semi-conductors, and we largely limited to these classes of material. One such candidate is the semi-conductor zinc selenide (ZnSe), which has already been shown to support alkanethiol SAMs in a preliminary study. It was also demonstrated that patterned monolayers can be achieved on this surface through microcontact printing, a feature that could allow the introduction of microscale features on the substrate surface. Additionally, polycrystalline thin films of ZnSe allow for continuous transmission of light in the visible and infrared regions, so these systems will not face the transmission limitations of Au. Regrettably, the alkanethiol SAMs of ZnSe are not expected
to exhibit an odd-even alternation effect.\textsuperscript{13} Even so, the success of microcontact printing and the broad transmission range of this substrate validate further investigation into the supporting of LCs on SAM-functionalized ZnSe.

Furthermore, initial studies of the behavior of 5CB liquid crystalline thin films supported on bare ZnSe have been completed.\textsuperscript{19} This work began with the fabricication of a gold inter-digitated electrode array (IDA) on the ZnSe surface. The purpose of this IDA was twofold: it created a boundary of a defined height (40 nm) for the liquid crystalline film and allowed for the application of an electric field across the film. Subtle nanoscale differences in the surface morphology of the ZnSe substrate were shown to impact LC alignment on ZnSe. When a surface with a spicular morphology was used, homeotropic alignment of the LCs was observed. Conversely, the fine grooves of a corrugated ZnSe surface enforce a planar LC alignment. This study also demonstrated that the kinetics of LC reorientation upon application of an electric field and the dynamics of relaxation upon removal of the same were markedly different for the spicular and corrugated ZnSe substrates. Overall, this study demonstrated that the surface morphology of ZnSe exerts a significant influence on both the orientation and electrooptical dynamics of 5CB thin films.

Since ZnSe has been shown to adsorb alkanethiol SAMs, and the surface features of ZnSe are known to influence 5CB alignment, it is of interest to determine the extent to which SAM-bearing ZnSe might reorient 5CB films and lead to changes in the electrooptical dynamics of the same. Herein, we report the use of hexadecanethiol (HDT) SAMs to influence the orientation and electrooptical dynamics of 5CB ultra-thin films supported on ZnSe.

**Experimental**

**Fabrication of an IDA on ZnSe**

A new bi-layer positive resist photolithography scheme was used to fabricate a gold electrode array on ZnSe (Figure 2). A slide of ZnSe (41 mm x 23 mm x 2 mm, International Crystal
Laboratories) was rinsed with Remover-PG (> 99% N-methyl pyrrolidinone, MicroChem), then deionized (DI) water, followed by three cycles of rinsing with isopropyl alcohol (IPA) and drying under nitrogen N₂. The slide was then coated with a bi-layer positive resist consisting of LOR5A adhesion promoter (MicroChem) and SPR-3012 imaging resist (MicroChem). Both chemicals were applied to the substrate with spin coating using a Brewer Science CEE X200 spin coater. Once the ZnSe slide was held firmly on the vacuum (pulling 23-25 inHg), the LOR5A promoter was dispensed around the perimeter of the slide. The promoter was dispersed across the slide at 900 rpm prior to being cast at 5000 rpm for 45 s. Once the spin cycle was complete, the substrate was baked at 200 °C for 2 min. and then cooled to room temperature. The SPR-3012 resist was then applied to the coated substrate using the same parameters, followed by a 1 min bake at 95 °C for 1 min. After the substrate had cooled to room temperature, the desired pattern was developed onto the substrate using a Karl Suss MABA6 Mask Aligner. A quartz mask with a negative of the desired pattern (2 sets of 50 pairs of interlocking electrodes 15 µm wide separated by 15 µm spaces) was placed on the substrate in hard contact mode and exposed for 8 s with 365 nm wavelength light using a mercury vapor lamp (8 mW cm⁻², 100 µm gap). The substrate was then developed in CD-26 (MicroChem) for 90 s to remove the resist from the regions of the substrate that had been exposed to ultraviolet light. The slide was then examined for defects using optical microscopy with a Nikon L200N microscope. If no defects were observed, the substrate was coated with 50 Å of chromium followed by 400 Å of gold. The remaining resist-metal layer was removed with a 30 min treatment in Remover-PG at 80 °C. A successfully patterned substrate can be seen in Figure 1.

Atomic Force Microscopy

Atomic force microscopy (AFM) was utilized to probe the surface roughness of mechanically polished polycrystalline ZnSe substrates (International Crystal Laboratories). Images were collected using a Bruker Icon AFM equipped with a Scanasyst Air probe set in tapping mode.
over a 20 µm scan size with a 2.5 nN set point and a 0.5 Hz scan rate. Similar images were collected to determine the height of the Au electrodes on the IDA (*vide supra*).

**Development of Alkanethiol SAMs on ZnSe**

The formation of 1-hexadecanethiol (HDT, Sigma Aldrich) SAMs on ZnSe was accomplished by two different methodologies: immersion and microcontact printing. In either case, the ZnSe surface must be free of surface contaminants, especially organic material, in order to support adsorption of a SAM. Thus, mechanically polished ZnSe slides (International Crystal Laboratories) were cleaned using a UVP SOG-1 ultraviolet ozone chamber (UVOC). Slides were placed in the UVOC for 20 min and rinsed with 200 proof ethanol (EtOH, Sigma Aldrich) and dried with nitrogen gas (N₂, Sigma Aldrich) at 40 psi. This cleaning process was repeated a total of three times to furnish a clean ZnSe substrate. Contact angles of 5 µL drops of UltraPur (Sigma Aldrich) water were measured using a housemade goniometer; droplets that wet the ZnSe surface were taken to indicate that the substrate was sufficiently cleaned. In subsequent manipulations, all reagents were stored in glass and polytetrafluoroethylene (PTFE) laboratory wares that had been cleaned with Piranha Solution, a 3:1 mixture of concentrated sulfuric acid (H₂SO₄, Sigma Aldrich) and hydrogen peroxide (H₂O₂, Sigma Aldrich) in the usual manner.

In order to adsorb a HDT SAM by immersion, an approximately 1 mM ethanolic solution of HDT was prepared and transferred to a PTFE developing chamber. A cleaned ZnSe substrate was then placed inside the chamber and sealed to develop for 24 h. After this time, the slide was removed from the chamber, rinsed with EtOH, and dried with N₂ as described above.

Monolayers adsorbed to substrates by microcontact printing employed a polydimethylsiloxane (PDMS) stamp, which was prepared using a standard PDMS kit (Sigma Aldrich), which was mixed and transferred into a Petri dish to obtain a flat surface. The stamp was prepared in a cleaned petri dish such that complete coverage of the surface with the mono-
layer could be obtained. Once the stamp had set, it was cleaned by rinsing with EtOH and
drying with N₂ ten times. Sufficient 10 mM HDT was then placed on the surface of the
stamp and allowed to sit for 2 min. The excess HDT solution was then removed from the
stamp under a gentle stream of N₂. The stamp was immediately pressed to the surface of a
cleaned ZnSe substrate and the SAM was adsorbed to the substrate over 2 min.

Regardless of the chosen adsorption method, contact angle goniometry was used as a
first confirmation of the presence of a SAM. More rigorous confirmations were obtained
using Fourier transform infrared (FT-IR) spectroscopy. A liquid nitrogen cooled Hyperion
3000 FT-IR microscope (100 scans, 2 cm⁻¹ resolution, 5 µm × 5 µm window) was used to
detect the presence of low intensity C–H stretches near 2850 and 2920 cm⁻¹. Spectra were
collected across multiple regions of the substrate surface in order to determined the extent
of monolayer coverage.

**Electrooptical Studies**

Successfully patterned ZnSe IDAs were used for the electrooptical studies of 4-cyano-4’-
pentylbiphenyl (5CB, Sigma Aldrich). Electrical leads for the IDA were attached to the
substrate using 26 gauge copper wire, affixed to the slide with conductive silver epoxy (World
Precision Instruments, # 4948), which was cured overnight at 70 °C. The IDA was then
cleaned using the UVOC procedure described above. Once the slide had been cleaned, 2 µL
of 5CB was applied to the electrode region of the patterned ZnSe substrate. An additional
piece of ZnSe was cleaned in the UVOC and placed on top of the IDA. This assembly was then
compressed in an electrooptical cell and baked overnight at 70 °C to homogenize the 5CB
film. The copper leads were attached to a GW Instek Laboratory DC Power Supply (Model
Number PS-1850), and the equilibrium state of the 5CB layer was achieved by repeated
application of a 15 V pulse to the system.

A visual representation of the electrooptical dynamics of 5CB was obtained by capturing
images of the assembly using a Motic Moticam 2300 3.0 MP Live Resolution microscope
camera in 1 V increments ranging from 0 to 15 V. More quantitative studies were conducted by inserting a polarizer into the Bruker FT-IR microscope and collecting spectra across the same range of voltages at polarizations both parallel and perpendicular to the electrode array system. These spectra were subtracted from a background scan of the filled electrooptical cell in order to obtain a less obscured picture of the 5CB dynamics.

Results and Discussion

Atomic Force Microscopy

Following the successful fabrication of the gold IDA on ZnSe, resistivity measurements across the electrode were taken to ensure that no shorts were present in the system. Atomic force microscopy (AFM) was used to measure the dimensions of the fingers of the electrode array (Figure 4). Though the IDA was fabricated to obtain an electrode height of 40 nm, AFM studies revealed that a height of only 20 nm was achieved. This lowered electrode height will result in a significantly thinner 5CB film.

Since both monolayer adsorption and LC alignment depend heavily on substrate morphology, it was of interest to analyze the surface of mechanically polished polycrystalline ZnSe. Measurements were taken at three locations on each of three slides of ZnSe, and a representative sample of these images can be found in Figure 3. The AFM images show that the substrate contains surface features on the order of 30 nm, and the root mean square (RMS) roughness of the slides ranged from 3.39 to 6.61 nm. Given the inherent roughness of our substrate, the prospect of monolayer adsorption might seem bleak. A variety of thermodynamic parameters contribute to the stability of a monolayer, among which the van der Waals (vdW) interaction between neighboring chains of adsorbate molecules is often the most critical. Because the features of the ZnSe surface are significantly larger than the length of an adsorbate molecule, the vdW interactions in our system will be reduced relative to a smoother sample. As a result, the surface morphology of ZnSe should render monolayer
adsorption less favorable. Regardless, the successful adsorption of alkanethiol monolayers to ZnSe has been described previously\textsuperscript{13} and is also demonstrated below.

**Adsorption of HDT Monolayers**

Once a slide had been subjected to the UVOC cleaning process described above, the contact angle of a 5 µL droplet of UltraPur water was used to evaluate substrate cleanliness. Contact angles between 20 and 25° were taken to indicate that the substrate was sufficiently clean. Upon adsorption of a HDT monolayer, the hydrophobicity of the substrate increased significantly, and water droplets were seen to dewet the monolayer-bearing substrate, such that contact angles of 98.4 ± 0.5° were measured. These latter contact angles were more consistent, suggesting that the adsorption of a monolayer mutes the irregularities on the ZnSe surface.

Following the collection of contact angles, monolayer quality was evaluated by FT-IR spectroscopy. The presence of methylene stretching modes at 2850 and 2920 cm\textsuperscript{-1} with an intensity on the order of 0.001 absorbance units indicated that a monolayer had formed. A representative IR spectrum for an HDT monolayer can be found in Figure 5. For measurements at various locations along the substrate surface, the two peaks characteristic of HDT SAMs were consistently observed with appropriate intensities. This result indicates that monolayers formed by immersion adsorbed to ZnSe in a homogenous manner. When, however, microcontact printed monolayers were analyzed, some regions of the substrate were found to contain lower intensity HDT peaks or even none at all, despite the lack of pattern on the PDMS stamp. Hence, we have definitive evidence that microcontact printed “SAMs” of ZnSe do not form a homogenous monolayer at the micrometer scale, despite indications that this technique is successful at adsorbing patterned SAMs onto ZnSe.\textsuperscript{13}

The failure of microcontact printed HDT SAMs of ZnSe can be understood in light of the mechanism of microcontact printing and the surface roughness of ZnSe. As its name implies, microcontact printing transfers a monolayer adsorbate molecules to the surface of
a substrate by direct contact between the surface and a PDMS stamp. If contact between
the stamp and the surface is not made, then there is no mechanism by which the adsorbate
molecules can transfer to the substrate. The surface features of mechanically polished ZnSe
(Figure 3) are sufficiently large that it the PDMS stamp likely does not contact the valleys
in the ZnSe topography. Thus, the uneven surface of ZnSe would lead us to anticipate the
uneven monolayer coverage that we observed in the FT-IR studies.

Electrooptical Studies

For a perfectly homogenous liquid crystalline film, the transmittance of the electrooptical
cell as visualized through polarized microscopy would be uniform. As seen for the image at
0 V in Figure 6, however, ultra-thin 5CB films supported on ZnSe are not homogenous, but
instead contain a number of microdomains. The ZnSe surface roughness likely imparts this
inhomogeneity into the 5CB film. As the voltage applied across the electrodes is steadily
increased, something of a decrease in the transmittance is observed between 3 V and 6 V,
followed by an increase in transmittance between 6 V and 10 V (Figure 6). Unexpectedly,
we then observe a drop-off in transmittance across certain wells of the electrode array such
that nearly no light is transmitted. Given the setup of the microscope and polarizers, we
would expect the transmittance to gradually increase as the 5CB molecules align themselves
to the electric field; these results are not well understood.

A semi-quantitative picture of the reorientation of the ultra-thin 5CB film can be obtained
with reference to the results of the polarized FT-IR spectra studies. Upon the application
of an electric field, the individual 5CB molecules have a tendency to rotate such that the
director of the LC, which lies along the C−N dipole, aligns itself with the electric field lines,
perpendicular to the fingers of the electrode array (see Figure 1B). Because the C−N triple
bond can only absorb light polarized along the the direction of the normal mode, the change
in the absorbance of the C−N stretch peak at 2228 cm$^{-1}$ serves as probe of the average
reorientation of the film with respect to the polarization of the incident light. An increase in
absorption upon the application of an electric field indicates the film is reorienting towards the direction of polarization on average, while a decrease indicates an average reorientation away from the direction of the polarization.

In Figure 7A we present the FT-IR difference spectra for 5CB supported on bare ZnSe with light polarized parallel to the fingers of the electrode array. As previously noted, the decrease in the C–N absorption indicates that the LCs have a tendency to rotate away from the direction of this polarization upon application of an electric field. This result is to be expected given the tendency of the average director of the 5CB film to lie perpendicular to the electrode array in the presence of a strong electric field. When light perpendicular to the electrode fingers was employed, an increase in the absorbance of the C–N triple bond is observed as expected (Figure 7B). We note, however, that the increase in absorbance in this second instance is almost twice as large as the decrease mentioned above. The discrepancy between these values provides information about the reorientation of the 5CB film about the third cardinal axis (perpendicular to the electrode fingers and polarized normal to the substrate plane), which cannot be probed directly with this experimental setup. The additional absorbance increase shown in Figure 7B is accounted for by a commensurate reorientation away from the this third axis. Hence, the electric field tends to cause the LCs to rotate from a somewhat homeotropic orientation into a plane parallel to the substrate. Assuming that the Freederickz transition causes the average director of the LCs to align perpendicular to the electrode fingers and in a plane parallel to the substrate, we can determine the average equilibrium orientation of 5CB in the ultra-thin film. At its equilibrium position in the electrooptical cell, the average 5CB molecule has something of a tilt away from the plane of the substrate and an azimuth that is partially rotated away from the electrode fingers.

We now compare the average orientation of the molecules in a 5CB ultra-thin film supported on bare ZnSe to that of 5CB supported on a HDT-bearing substrate. The polarized FT-IR study was repeated for an IDA and ZnSe cover slip that had been microcontact printed to adsorb an HDT SAM. Though this method of SAM deposition does not lead to
the same uniformity coverage of the substrate as can be obtained by immersive adsorption of HDT (*vide supra*), the immersion protocol was found to dissolve the silver epoxy and short the circuitry on the IDA. Since the individual electrodes are 20 nm in height, it remains a distinct possibility that HDT molecules did not absorb to the ZnSe on the IDA at all. Despite these difficulties, the HDT coverage on the cover slip of the electrooptical assembly and likely partial HDT coverage on the IDA-patterned ZnSe was sufficient to cause a significant change in the average orientation of the 5CB film (Figure 8). A comparison of Figures 7A and 8A, the absorption spectra for polarized light parallel to the electrode fingers for the bare and SAM-bearing assemblies, respectively, reveals an astonishing similarity between the bare and SAM-functionalized ZnSe; the spectra are all-but-indistinguishable. For polarized light perpendicular to the electrode fingers, however, a four-fold increase in the change in absorbance is observed for the HDT-bearing substrate (Figures 7B and 8B). As before, the difference between the increase in absorption for light parallel to the electrode fingers and the decrease for light perpendicular to the same is accounted for by reorientation with respect to the third cardinal axis as defined above. The aforementioned four-fold increase in the change in absorbance for the HDT-ZnSe system indicates that the reorientation of LCs toward the plane containing the substrate is much more significant for 5CB films supported on HDT than the bare substrate. Interpreting the spectra found in Figure 8 in light of those in Figure 7, we conclude that the HDT monolayer causes the average 5CB molecule to adopt a more homeotropic alignment with respect to those supported on the bare substrate. The presence of the SAM does not seem to exert any significant influence on the average azimuthal angle for the 5CB film.

Since even incomplete adsorption of an unpatterned HDT monolayer to the surface of ZnSe was shown to cause a significant change in the average orientation of molecules in a 5CB film, it is of interest to determine the extent to which a uniform HDT monolayer would exert an even greater influence of 5CB orientation. Work towards circumventing the difficulties of immersive absorption of a monolayer to both the IDA and the ZnSe coverslip is
currently underway as is the use of Physical Vapor Deposition (PVD) to generate significantly smoother ZnSe substrates. Upon successful adsorption of a homogenous film, the polarized FT-IR and microscopy studies for the improved substrate assembly will be completed and the influence of the monolayer reevaluated.

Conclusions

We have shown that the surface morphology of ZnSe prevents the uniform adsorption of a HDT monolayer by microcontact printing, though this difficulty is not encountered when a monolayer is adsorbed through more traditional immersion methodologies. The roughness of the surface of ZnSe also leads to the presence of microdomains in a 5CB film supported on the substrate. Through a combination of polarized microscopy and FT-IR studies, we have also demonstrated that a HDT monolayer adsorbed to portions of the surface of a ZnSe substrate causes a 5CB ultra-thin film to adopt a more homeotropic alignment than a film supported by the bare ZnSe substrate.
Figure 1: (A) Gold electrode patterned on ZnSe. (B) Electrode array region of the IDA.

Figure 2: Schematic of the bi-layer positive resist photolithographic fabrication of the electrode array.

Figure 3: Representative AFM images of the surface of a bare polycrystalline ZnSe substrate.
Figure 4: AFM image of the Au electrode dimensions on the ZnSe IDA; an electrode height of 20 nm was achieved.

Figure 5: Representative IR spectrum for HDT-bearing ZnSe. Low intensity peaks at 2850 and 2920 cm$^{-1}$ indicate monolayer formation.

Figure 6: Polarized microscopy images of a 5CB ultra-thin film sandwiched in the bare ZnSe electrooptical cell at different applied voltages.
Figure 7: FT-IR spectra of the bare ZnSe electrooptical cell: (A) incident light parallel to the electrode fingers and (B) incident light perpendicular to the electrode fingers.

Figure 8: FT-IR spectra of the HDT-bearing ZnSe electrooptical cell: (A) incident light parallel to the electrode fingers and (B) incident light perpendicular to the electrode fingers.
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References


