

State of the Art in Liquid Crystals Nanophysiochemical Properties at Surfaces and Interfaces, and Frontier for Posterity

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Abstract

Liquid crystals (LC) have been drastically protracted in recent years, due to the ferret out of novel nanophysiochemical properties at surfaces. Physiochemical characteristics, such as weak intermolecular forces manifested like odd-even effect, hydrogen bonding, and electric double layers make them ideal for variety of applications. Furthermore, the orientation of LC exploits the conventional and novel detection method for protein binding event on nanostructured surfaces and protein crystallization on lipid monolayers. These explorations include the detection of parts per billion (ppb) chemical warfare agents on surfaces as well as new mechanisms for driving the reorientation of liquid crystals. The scope of the present review attempts the recent progress on using LC to amplify a wide range of engineered surface chemistry progressed from liquid-solid and liquid-aqueous interfaces. The distinct features of LC role in imaging and biosensing have been discussed. From these studies, it is clear that the LC has the enormous potential as a promising material for the biomedical applications.

Keywords: Liquid crystals, Nanostructured surfaces, Orientation of LC, Detection, Biosensing

Introduction

LC is a substance that exhibits a phase of matter that has properties between those of a conventional liquid, and those of a solid crystal. It has been discovered about 100 years ago by plant physiologist Dr. Friedrich Reinitzer (1857-1927) and physicist Dr. Otto Lehmann (1855-1922) investigated some esters of cholesterol

(Cholesteryl benzoate)^{1,2}. LC has attracted growing interests over in the last decade. Several thousands of organic compounds are identified in the form of LC. During 1960s to 1970s Liquid-crystal technologies grew enormously, assurance for display technologies, which largely act upon the basic and applied research³. LCs are elongated organic molecules that form intermediate phases between crystalline solids (having long range order) and liquids (having only short range order). LC is polymorphic in structure, results from a partial 'breakdown' in positional and orientational order of the crystal lattice¹. At particular temperature LCs change from the crystalline solid phase to an opaque liquid, which transforms at a defined higher temperature to an optically clear liquid (Figure 1). The range of temperature for the material exists as a LC different from compound to compound. Some materials have a broad LC range; while others exhibit a narrower margin¹. LC has a greater intra and intermolecular mobility than classical solids.

There are many different types of LC phases, which can be distinguished based on their different optical properties. The significance of LCs in understanding both the liquid and the solid state are characterized by unusual physical properties. LCs can be subdivided into two classes: such as thermotropic and lyotropic LCs. Most of thermotropic liquid crystals (TLCs) have an isotropic phase at high temperature. TLCs exhibit some intriguing optical properties and it is possible to use these to characterize a liquid crystalline material further. The vast majority of thermotropic liquid crystals are composed of rod-like molecules.

LC has their own specific orientation which is categorized into two basic alignments such as homeotropic and planar. The orientation of the organic molecules dissolved in the LC has different regioselectivity and chemoselectivity⁴. The unique optical, electrical and mechanical properties influence the distinct orientation of LC. Recently LCs have been used in nanotechnologies as templates for nanomaterial fabrication. Due to its anisotropy⁵, LCs have many important technological applications. In many applications of nanotechnologies, a uniform orientation of LC is desired, which is achieved by applying an external force to change the orientation of an already established liquid crystal phase or by aligning the LC material on a nanoscale patterned surface. The ordering of molecules within

LCs makes them attractive for a variety of sensing and interfacial applications^{6,7}.

Ionic liquid crystals are a class of liquid-crystalline compounds that contain anions or cations. Ionic liquid crystals can be considered as materials that combine the properties of LCs and ionic liquids. Ionic liquids can also be used to immobilize transition metal catalysts in the liquid phase of biphasic catalytic reactions⁸. Other applications include their use as solvents for

extraction processes and as an electrolyte for batteries, fuel cells, and dye-sensitized solar cells⁹.

The liquid-crystalline state is also widely encountered in biological systems. Luk *et al.* reported that the LC materials containing a variety of functional groups are non-toxic to live mammalian cells. In particular, fluorinated liquid crystals exhibited minimal toxicity toward 3T3 fibroblasts and corneal epithelial cells¹⁰. Lockwood *et al.* has reported the use of TLC for culture of human embryonic stem cells (hESCs) at interfaces. The cells show levels of differentiation comparable to that observed for cells on Matrigel-coated glass controls. This enables direct imaging of the rearrangement of Matrigel by the hESCs through changes in the appearance of the LC when observed using polarized light microscopy¹¹.

This review gives an overview of nanophysiochemical properties distinguished by surface and interfacial phenomenon, and intends to feed the emerging researchers in the field of LC technology. This also highlights the different class of orientations, molecular recognition, protein interaction, and applications in the sensor development.

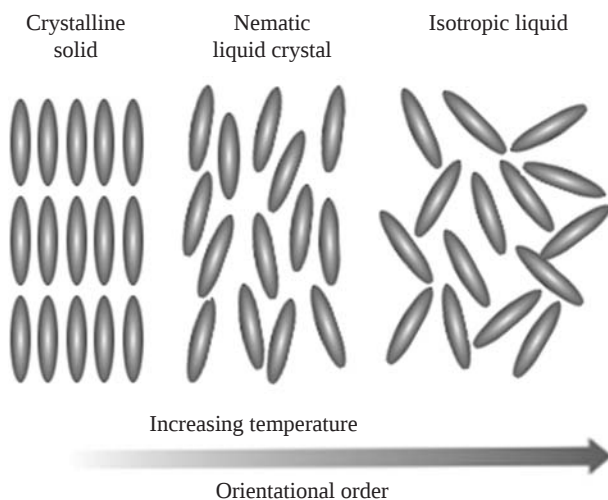


Figure 1. Schematic diagram illustrating the degree of order of LC. Nematic liquid crystals have intermediate phase property between liquid and solid.

Liquid Crystal-Solid Interface

A unique way of controlling both the chemistry and the topography of a surface is the use of self-assembled monolayers (SAMs) of alkanethiols on gold films

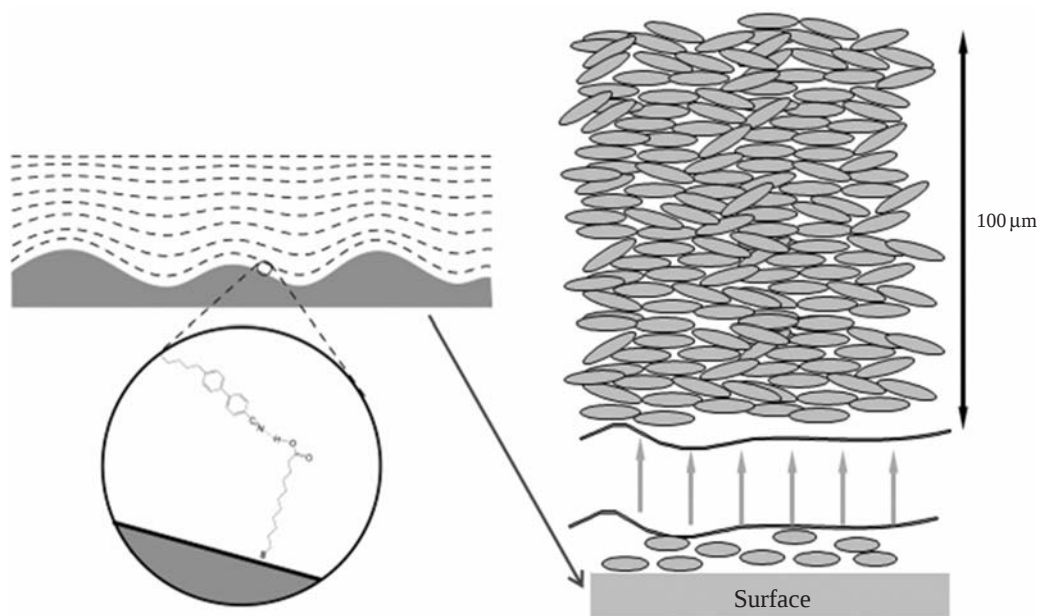


Figure 2. Orientation of LC sensitive to nanometer-scale topography and surface functionality. LCs can transduce molecular events at surfaces into optical signals through reorientation of the bulk LC.

deposited at an oblique angle from the normal to the sample substrate. While SAMs can provide surfaces with different functional groups and with more or less invariant monolayer structure, obliquely deposited gold films possess a subtle anisotropic topography on the nanometer scale. The maximum anisotropy in the topography evidently lies between the directions parallel and perpendicular to the gold deposition as the oblique deposition breaks the degeneracy in plane of the surface. This anisotropic nanotopography possesses a range of interesting characteristics that are subtle, but has a strong impact on the orientation of LCs (Figure 2)^{12,13}.

Odd-even Effects on the Anchoring of LC

When LCs are brought in contact with a SAM supported on obliquely deposited gold films, both the out-of-plane and in-plane orientation of LC become very sensitive to the molecular details of the SAM. For example, on SAMs formed from methyl-terminated alkanethiols, 5CB (4-cyano-4'-pentylbiphenyl) adopts a uniform planar alignment with the azimuthal direction perpendicular to the direction of gold deposition when there are odd number of carbons in the alkyl chain of the alkanethiols, but parallel to the direction of gold deposition when there are even number of carbons in the alkyl chain. The odd-even effects in the LC orientation are triggered off by thermodynamic (e.g., temperature, strain, and chemical potential) and structural parameters (e.g., surface roughness and thickness)^{13,14}.

Luk *et al.* have studied the dependence of LC orientation on the odd and even number of carbons in the alkanethiol¹⁰. The structural odd-even effects stimulate odd-even alterations of chemical, physical, and surface and interfacial properties such as chemical reactivity, electronic property, frictional behavior, and electrochemical properties. These characteristics were observed on various organic (highly oriented pyrolytic graphite (HOPG), molybdenum disulfide (MoS₂), metal substrates including Au (111), Ag (111), Cu, Al), and inorganic (Al₂O₃ and SiO_x/Si) self-assembled monolayer on solid surfaces¹⁵.

Researchers from the University of California reported the discontinuous azimuthal anchoring transition for nematic liquid crystals (NLCs) with parallel anchoring to the surfaces of SAM formed from alkanethiols on gold. The azimuthal orientation of 5CB and MBBA (N-(p-methoxybenzylidene)-p-butyl aniline) depends upon the odd or even number of carbons of the alkanethiols¹⁴.

Skaife *et al.* have used nanostructured gold surfaces for the determination of orientations of supported LCs; these studies supported the influence of gold film on

the orientation of LCs¹⁶. For example, different orientations were observed on SAMs formed from alkanethiols that contain even number of carbons (e.g., CH₃(CH₂)₁₁SH) and odd number of carbons (e.g., CH₃(CH₂)₁₀SH)¹⁴. Apart from this, the odd-even effects exhibiting in the aggregated or solid state were studied by sum frequency generation (SFG), low-frequency Raman, solid-state C nuclear magnetic resonance (NMR), or circular dichroism (CD) spectroscopy elsewhere¹⁷. The difference between the even and odd alkyl chains in the solid state is ascribed to the difference of the packing in crystal structure¹⁸.

Important Role of Hydrogen Bonding on Azimuthal Orientation of LC

Orientational behavior of LC is regulated by the shape and size of their molecular constituents and non-covalent intermolecular interactions¹⁹. The impact of hydrogen bonding on the generation or stabilization of LC phases has recently been appreciated. Several classes of compounds have been synthesized based on the intermolecular hydrogen bonds between similar or dissimilar molecules. The effect of intermolecular hydrogen bonding on the formation of LC phases was first studied by Gray and Jones, focusing on the dimerization of 4-alkoxybenzoic acids and trans-4-alkoxycinnamic acids²⁰. Liquid crystalline heterodimer formed by a pair of complementary hydrogen bond donor and acceptor (4-butoxybenzoic acid and trans-4-(4-ethoxybenzoyloxy)-4-stilbazole) triggered an intense and high activity in the fabrication of supramolecular hydrogen-bonded LCs¹⁴. In addition to that the intramolecular interactions such as non-covalent interactions hydrogen bonding, ionic bonding and dispersion forces play a vital role in the preparation of supramolecular assemblies of LC²¹.

Hydrogen bonding between the mesogens and acid groups on the nanostructured surface influences the azimuthal orientation of LC. The orientation can be driven by short-ranged interaction between the 5CB and COOH groups on the surfaces. Luk *et al.* have investigated 10 different LC molecules oriented on carboxylic acid or methyl-terminated SAMs supported on obliquely deposited gold films. The mesogens comprising the LCs each possess different hydrogen bond acceptors, and the azimuthal orientations of LC were found to be influenced by hydrogen bonding. From that study they have revealed the dictating efficiency of hydrogen bonding between LC and surfaces. Generally LCs constitute different types of hydrogen bond acceptor like fluoro, ether, ester, cyano, and imine groups¹⁰. Hydrogen bond strength increases with the electronegativity of the atoms in the hydrogen bond acceptor²². Some of the other factors vitalized for hyd-

rogen bond strength include degree of hybridization, charge density, steric effects, bonding geometry and the process of chelation²³. Study of hydrogen bond interaction within SAMs formed from the carboxylic acid-terminated alkanethiols by using IR and absorption spectroscopy was undertaken²⁴.

Electrostatic Interactions Driving the Orientational Transition of LC

Electrostatic interactions (Electrical double layer) are described by the reaction field model for the coupling between the molecular charge distributions, within a cavity identified with the volume occupied by the molecules²⁵. Numerous studies have reported on electrical double layers formed by the contact of the surfaces with isotropic aqueous and nonaqueous liquids²⁶. Electrical double layer generated by the ionization or the dissociation of salts that are immobilized on the near surfaces are induced by the interaction taken place at the interfaces⁷. Potential of the electrical double layer determines the transition of the LC on interacting surfaces²⁷. Some examples for the electrostatic interactions deriving LC transition are described as follows.

Shah *et al.* observed changes of LC orientation from planar to homeotropic, LCs of *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) or mixtures of MBBA and *p*-ethoxybenzylidene-*p*-*n*-butylaniline (EBBA) on chromium or indium/tin oxide surface, due to the possess of negative dielectric anisotropy⁷. The orientational transitions of LC are regulated by some important parameters such as, density of the surface, liquid crystal layer thickness, Debye length, and dielectric anisotropy²⁷. The homeotropic orientation of LC on the SAM of HOOC(CH₂)₁₀SH was triggered by the electrical double layer formed during the dissociation of sodium ions. In other study chlorodimethyloctadecyl-silane induced homeotropic transition of NLC was reported. Here the weak polar surface energy plays an important role for the homeotropic alignments of LC²⁸.

Recently Lena *et al.* have reported a theoretical approach for the statistical mechanics of ferroelectric nanoparticles in LC, which predicted the enhancements of LC properties in good agreement with experiments²⁹. Previous experiments have shown that low concentration of ferroelectric nanoparticles can greatly enhance the physical properties of NLCs. They are important for technological applications, because they provide a new opportunity to frame the potential utility of LCs without additional chemical process.

Sensing of Chemical Exposure on Environment by LC

It has been demonstrated recently that micrometer-

thick films of the both nematic 5CB and smectic 8CB supported on nanostructured surfaces decorated with metal ions can be used to detect organophosphonates (OPs) at parts-per-billion (ppb) levels in gas phases. The approach is based on four principles: (1) mesogens at interfaces can communicate their orientations deep into the bulk of a liquid crystal (up to ~100 μm from the surface), which permits amplification of chemical signals generated when analytes bind to functionalized surfaces, (2) because mesogens possess liquid-like mobilities, information about the binding of the analytes can be propagated rapidly through films of LCs, (3) the birefringence of a LC provides a means of transducing a binding event on a surface into an optical signal that can be easily visualized by the naked eye, and (4) because the orientation of LC near a surface reflects the molecular structure of the surface, it is possible to design surfaces such that orientational transitions of LCs can be triggered by the binding of small molecules (e.g., OPs) to surfaces^{7,30}. Abbott *et al.* have demonstrated the use of the 5CB and 8CB supported on copper (II) perchlorate salts to detect low concentration of dimethylmethylphosphonate (DMMP)⁷.

Liquid Crystal-Aqueous Interface

Previous studies with solid-liquid crystal interfaces has made a number of fundamental discoveries regarding the means by which LCs are anchored on surface-modified materials, and further demonstrated that LCs can be used to amplify biomolecular interactions occurring on the surfaces of solids that present covalently immobilized receptors. However, the lateral mobility of species within biological membranes is essential for many types of biological function, such as association of proteins involved in signal transduction across membranes³¹, complexation of enzymes³², and substrates within biological membranes³³. To address this issue, an experimental system that permits the use of LCs to amplify binding events occurring at fluid interfaces was developed. The simplest approach, unconfined films of liquid crystal on water surfaces, proved to be useful in the presence of surfactant molecules in solution (Figure 3). This experimental setup has been used to study surfactant adsorption phenomena, the formation of biomimetic lipid interfaces, and biomolecular interactions occurring at these interfaces.

Influence of Surfactants on Aqueous-LC Interfaces

Studies of the adsorption of surfactants at interfaces has progressed on various fronts over the past decades,

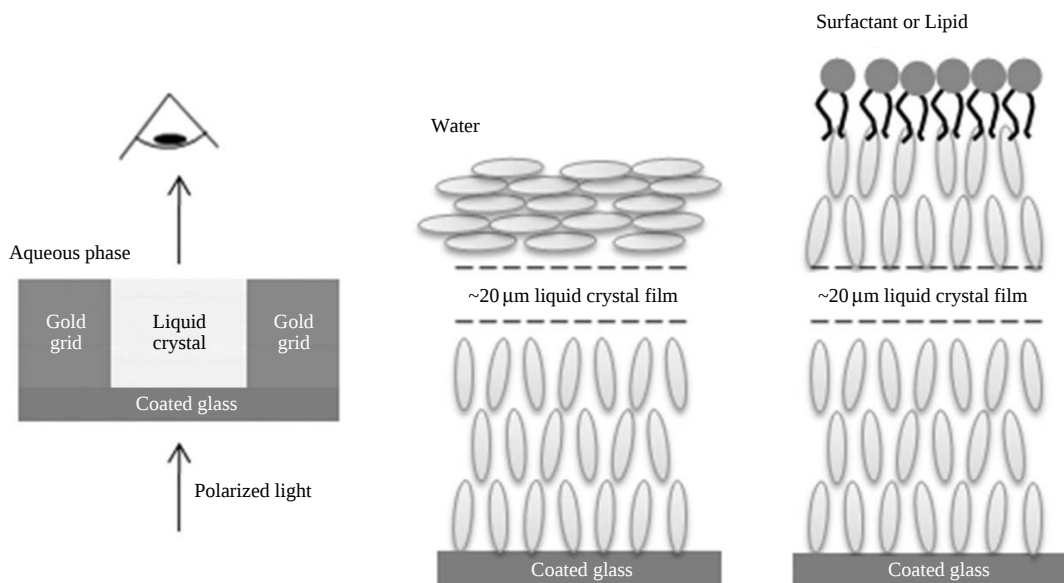


Figure 3. Schematic of the experimental set-up used to investigate aqueous-LC interfaces.

enabled in part by development of new instrumentation that permits the characterization of surfactant-decorated interfaces. LC may take homeotropic anchoring or planar anchoring depending upon the structure of interface³⁴. In aqueous-LC interface the adsorption of surfactant trigger the orientational transition of LC³⁵. Through systematic studies of the structure of surfactant head group and tail structure, researchers have discovered much about the nature of the orientations induced in LCs by surfactants.

Bolaform surfactants possess two hydrophilic moieties connected by a hydrophobic hydrocarbon chain, and typically take on looped conformations when adsorbed at air-water interfaces³⁶. In a demonstration of the influence of the orientation of the surfactant chain on the anchoring of LCs at the aqueous-LC interface, bolaform surfactants with dibromo and hydroxyl/trimethylammonium bromide head groups were observed to cause planar anchoring of the LC. This is presumably the result of a looped surfactant conformation at the aqueous-LC interface. A system of mixed bolaform and linear surfactants led to a means of visualizing competitive adsorption to the aqueous-LC interface. Active control of adsorption was achieved by mixing FTMA (11-(undecylferrocenyl)trimethylammonium bromide), a bolaform redox-active surfactant, and CTAB (cetyltrimethylammonium bromide), a classical cationic surfactant³⁷. Both reduced and oxidized FTMA led to planar anchoring of the LC at all concentrations used in the study, while CTAB caused homeotropic anchoring at concentrations of 5 μM . The anchoring

caused by mixtures of FTMA and CTAB was dependent on the oxidation state of the FTMA. CTAB mixed with reduced FTMA produced planar anchoring, whereas the same concentrations of CTAB mixed with oxidized FTMA led to homeotropic anchoring of the LC. These results are consistent with adsorption properties of the two surfactants: reduced FTMA more strongly adsorbs to the LC interface than CTAB but oxidized FTMA adsorbs more weakly than CTAB. The anchoring was observed to be reversible by alternating between reduced and oxidized states of FTMA³⁷. The transitions between homeotropic and planar anchoring were followed with time and quantified via birefringence interference colors, leading to a means of assessing kinetics of competitive adsorption in the aqueous-LC system. The observed birefringence colors are the result of variation in tilt angle of the LC and have been used to characterize the tilt present at the aqueous-LC interface in the presence of adsorbed surfactant.

The studies on the effect of head group and tail structure show that interactions of the tails of the adsorbed surfactants and the LC largely dictate the orientations of the LC. This interaction is facilitated through adsorption of surfactants to the aqueous-LC interface from the bulk solution. Support for this mechanism is found in the many parallels between the results of previous work with surfactants at the aqueous-LC interface and studies of the adsorption behavior of surfactants to air-water or oil-water interfaces. For example, the classical anionic surfactant sodium dodecylsulfate (SDS) shows concentration-dependent anchoring of the LC,

from planar at concentrations below 0.1 mM to homeotropic at concentrations greater than 1 mM. Further, the addition of electrolyte to SDS solutions leads to homeotropic anchoring even at concentrations of 0.1 mM. This is presumably due to increased adsorption of SDS to the interface facilitated by screening of electrostatic repulsions by the electrolyte. Others have also demonstrated the ability of tail-LC interactions to direct LC orientations³⁷. Barmiento & Vreken demonstrated anchoring transitions in mixed Langmuir monolayers of 8CB and pentadecanoic acid (PDA) on water. Compression of these monolayers resulted in a decrease of the tilt angle of 8CB (measured from the normal) and the formation of multilayers of 8CB, as probed by second-harmonic generation and surface pressure measurements. The change in tilt angle of the 8CB was attributed to interactions between 8CB and the tails of PDA³⁸.

Lipid Monolayer Assembled at the Aqueous-LC Interface

In an effort to create a more stable interface amenable to the study of biological interactions, films of phospholipid were formed at the aqueous-LC interface. Spontaneous formation of phospholipid monolayer at interface between NLC and aqueous phases gives rise to patterned orientations of the LC that reflect the different organization of the lipid monolayer³⁹.

Brake *et al.* have demonstrated the self-assembly of phospholipids (L- α -phosphatidylcholine- β -oleoyl- γ -palmitoyl (L-POPC), dipalmitoyl phosphatidyl choline (DPPC), and L- α -dilauroyl phosphatidyl choline (L-DLPC)) at aqueous-LC interfaces. Lipid films were produced by exposing a LC-filled grid to a solution of small unilamellar vesicles (~36 nm diameter) of L- α -dilauroyl phosphatidylcholine (DLPC)³⁹. Vesicles of this size are known to deposit at hydrophobic interface and the adsorption behavior was visible in the LC texture. The initially bright optical appearance of the LC (indicative of planar anchoring) developed black domains-corresponding to homeotropic anchoring of the LC-that nucleated and grew over time.

An alternate method of delivering lipid to the interface is to mix the appropriate lipid with a micelle-forming surfactant before contacting the LC. This method provided the same end result after exchange of the bulk solution for lipid- and surfactant-free buffer but followed a different path: the transition from planar to homeotropic did not show domain formation in the mixed micelle system but a smooth, continuous transition. Fluorescence microscopy showed that varying the ratio of surfactant to lipid produced lipid layers ranging from a full monolayer (ratio of 30 : 1) to only 70% of a full monolayer (ratio of 300 : 1)³⁹.

Biomolecular Interactions at the Lipid-laden Aqueous-LC Interface

Lipid-laden interfaces between LCs and aqueous solutions provide an environment within which the interactions of proteins and lipids can be amplified into orientational transitions in the LCs. The orientational response of the LC can report time-resolved changes in the spatial organization of the lipid layer induced by protein binding activity⁴⁰.

Both weak and strong specific protein binding events were reported at the lipid-laden aqueous-LC interfaces, represented by the binding of phospholipase A2 (PLA2) to D-DPPC ($K_d \sim 10^{-4} - 10^{-3}$ M) and Neutr Avidin to biotinylated DPPE ($K_d \sim 10^{-14}$ M). While densely-packed monolayers of lipid at the aqueous-LC interface showed no response to non-specific protein binding, lipid layers at low areal density reported the organization of non-specific protein adsorption³¹. Cytochrome c, BSA, mouse IgG1, and goat IgG caused changes from homeotropic to near planar anchoring of LCs when introduced to interfaces laden with L-DLPC at sub-monolayer coverage.

The PLA2 system was used with L-phospholipids to demonstrate the ability of LCs to report enzyme activity at the aqueous-LC interface. PLA2 binds but does not cleave D-lipids, whereas PLA2 catalyzes the hydrolysis of a fatty acid tail from L-lipids. Both specific binding and enzymatic activity (hydrolysis) of L-DLPC and L-DPPC were observed as changes in LC appearance from dark to bright (homeotropic to planar)^{41,42}. Fluorescently labeled lipids and proteins revealed that protein binding, phase separation of lipid and hydrolysis products, and desorption of hydrolysis products all led to orientational transitions in the LC³¹.

Frontier of Liquid Crystals

Although LCs have been used in a wide range of electro-optical devices, such as flat-panel displays, the use LCs to amplify biomolecular interactions into optical signals has not been investigated until recently. The surface-driven orientational behavior of LCs with the advancement in the fabrication of surfaces with specific chemical functionality and nanometer-scale topography enables a fundamentally new type of assay system to investigate a variety of bio/chemical events on surfaces. For instance, chemical transformations of surfaces, receptor-mediated binding of proteins to surfaces, and regulatory protein pathways can be analyzed by using LCs.

Printing of Oriented Proteins on Surfaces

Affinity microcontact printing (α CP) can be com-

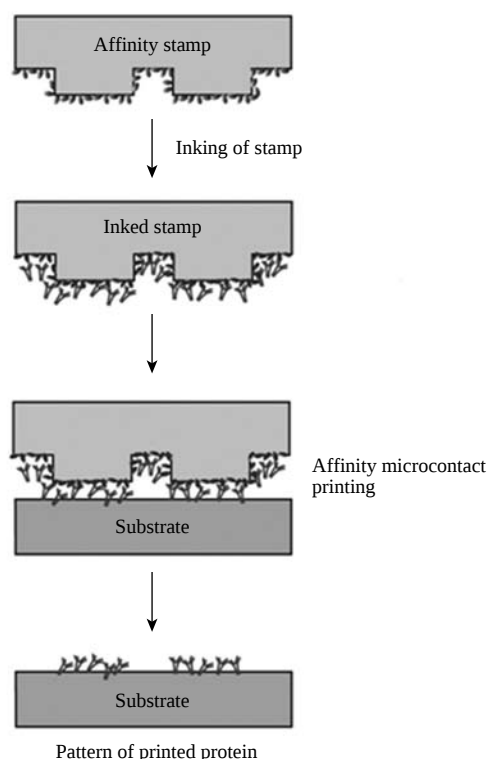


Figure 4. Experimental procedure for the imaging of affinity microcontact printed proteins using liquid crystals.

combined with LC analysis to visualize the printed proteins. α CP of proteins is new types of soft-lithographic technique that exploits functionalized elastomeric stamps with a receptor to capture a targeted analyte from a mixture of protein solution and then transfer the analyte onto solid substrates as printed patterns⁴³.

Figure 4 describes the schematic path for the study revolves around a model system in elastomeric stamps formed from superior bio-compatibility PDMS⁴⁴ which were covalently functionalized with biotinylated bovine serum albumin. The inked stamp was then contacted with a gold substrate that had been decorated with an amine-terminated SAM. After stamping the protein onto the gold substrate, the immobilized protein was imaged by placement of a micrometer-thick film LC on the surface⁴⁵. Jang *et al.* have used this method to test cancer cells, detection of epidermal growth factor receptors from crude cell membrane extracts⁴⁶. This result demonstrates that LC- α CP approach can be used to explore various receptor-mediated binding events of proteins to surfaces.

LC-based Biosensor for Molecular Diagnostics

As evidenced by the current discussion, LC sensor

technology has numerous potentially important applications on the field of medical diagnostics and public health. For example, Tercero Espinoza *et al.* characterized the alignment properties of 5CB on vesicular stomatitis virus bound to cationic surfaces. Using this result, Jang and colleagues demonstrated that the external structure of viruses could be identified and differentiated based on induced orientational response of LC⁴⁷. The application of LC sensors as rapid diagnostic methods may be especially promising in the area of biodefense and globally emerging infectious diseases as well⁴⁸⁻⁵⁰. Key factors of birefringent and surface sensitive properties of LC towards the analyte molecules are poised to play an important role in molecular diagnostics. LC molecules have the capability to transduce the optical appearance of signals from the biological process or structure. Unique electrical and optical properties of LC have a delicate response to the molecules of certain surface interactions, providing LCs as a biosensor for a wide range of biological applications. The study of LCs as biological sensors, with their potential as a sensitive, low cost, point-of-care diagnostic platform, will provide promise as a prospective future technology.

Concluding Remarks

Here we have reviewed the orientation of LCs in response to the effect of surface chemistry includes solid-LC and aqueous-LC interfaces. The various applications of these chemical phenomena in LC interactions have been reviewed. The primary factor influencing ordering of the LC in the presence of chemicals, surfactants, or phospholipids appears to be the structure and organization of the surface molecules. The use of biologically relevant LC will surely overcome the existing crisis through simplification of complex diagnostic procedures and sensitive process. The emergence of LC-based bionanotechnology will result in notable broad range of interdisciplinary research not limited to molecular biology, biochip, sensors, drug discovery, and nanophotonics. Although those studies are still at infancy level, in the near future, more detailed research will unravel the underlying innovations behind the LC science and technology.

Acknowledgements

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References

- Hussain, A., Pina, A.S. & Roque, A.C.A. Bio-recognition and detection using liquid crystals. *Biosens. Bioelectron.* **10**, 1-8 (2009).
- Madhusudana, N.V. Recent advances in thermotropic liquid crystals. *Current Science* **80**, 1018-1025 (2001).
- Woltman, S.J., Jay, G.D. & Crawford, G.P. Liquid-crystal materials find a new order in biomedical applications. *Nature Materials* **6**, 929-938 (2007).
- Reichardt, C. Solvent and Solvent effects in organic chemistry, 3rd ed; Wiley-VCH: Weinheim (2003).
- Gupta, V.K., Skaife, J.J., Dubrovsky, T.B. & Abbott, N.L. Optical amplification of ligand-receptor binding using liquid crystals. *Science* **279**, 2077-2080 (1998).
- Hwang, H. *et al.* Optoelectronic manipulation of microparticles using double photoconductive layers on a liquid crystal display. *BioChip J.* **1**, 234-240 (2007).
- Shah, R.R. & Abbott, N.L. Principles for measurement of chemical exposure based on recognition-driven anchoring transitions in liquid crystals. *Science* **293**, 1296-1299 (2001).
- Alam, M.T., Islam, M.M., Okajima, T. & Ohsaka, T. Ionic liquid structure dependent electrical double layer at the mercury interface. *J. Phys. Chem. C.* **112**, 2601-2606 (2008).
- Binnemans, K. Ionic liquid crystals. *Chem. Rev.* **105**, 4148-4204 (2005).
- Luk, Y.Y. *et al.* Using liquid crystals to amplify protein-receptor interactions: design of surfaces with nanometer-scale topography that present histidine-tagged protein receptors. *Langmuir* **19**, 1671-1680 (2003).
- Lockwood, N.A. *et al.* Thermotropic liquid crystals as substrates for imaging the reorganization of matrigel by human embryonic stem cells. *Advanced Functional Materials* **16**, 618-624 (2006).
- Gupta, V. & Abbott, N.L. Uniform anchoring of liquid crystals on SAM on obliquely deposited films of gold. *Langmuir* **12**, 2587-2593 (1996).
- Jerome, B. Surface effects and anchoring in liquid crystals. *Rep. Prog. Phys.* **54**, 391-451 (1991).
- Gupta, V.K. & Abbott, N.L. Azimuthal anchoring transition of nematic liquid crystals on self-assembled monolayers formed from odd and even alkanethiols. *Physical Review E.* **54**, 4540-4543 (1996).
- Tao, F. & Bernasek, S.L. Understanding odd-even effects in organic self-assembled monolayers. *Chem. Rev.* **107**, 1408-1453 (2007).
- Skaife, J.J. & Abbott, N.L. Quantitative interpretation of the optical textures of liquid crystal caused by specific binding of immunoglobulins to surface-bound antigens. *Langmuir* **16**, 3529-3536 (2000).
- Izumi, H., Yamagami, S., Futamura, S., Nafie, L.A. & Dukor, R.K. Direct observation of odd-even effect for chiral alkyl alcohols in solution using vibrational circular dichroism spectroscopy. *J. Am. Chem. Soc.* **126**, 194-198 (2004).
- Soutzidou, M. *et al.* Low-frequency Raman spectroscopy of n-alcohols. LAM vibration and crystal structure. *J. Phys. Chem. B.* **106**, 4405-4411 (2002).
- Stephen, M.M., Yonezawa, J., Horner, M.J., Christopher, W.M. & Michael, D.W. Structure and rheology of hydrogen bond reinforced liquid crystals. *Chem. Mater.* **16**, 3045-3055 (2004).
- Gray, G.W. & Jones, B.J. Mesomorphism and chemical constitution. The effect of halogen substitution on the mesomorphism of the p-n-alkoxybenzoic acids. *J. Chem. Soc.* 2556 (1954).
- Kato, T. Self-assembly of phase-segregated liquid crystal structures. *Science* **295**, 2414-2418 (2002).
- Brown, T.L., LeMay, H.E.J. & Bursten, B.E. Chemistry-the central science, Prentice Hall, NJ, 1993.
- Jeffrey, G.A. An introduction to hydrogen bonding, Oxford University Press, NY (1997).
- Crooks, R.M., Yang, H.C., McEllistrem, L.J., Thomas, R.C. & Ricco, A.J. Interactions between self-assembled monolayers and an organophosphate: detailed study using surface acoustic wave-based mass analysis, polarization-modulation FTIR spectroscopy and ellipsometry. *Faraday Discuss.* **107**, 285-305 (1997).
- Bottcher, C.J.F. & Bordewijk, P. Theory of electric polarization; Elsevier: Amsterdam, **1**, 1973.
- Israelachvili, J.N. Solvation forces and liquid structure-as probed by direct force measurements. *Acc. Chem. Res.* **20**, 415-421 (1987).
- Barbero, G., Chuvyrov, A.N., Kaniadakis, G., Miraldi, E. & Rastello, M.L. Surface-polarization effect in the alignment of nematic liquid crystals. *J. Phys. II*, **3**, 165-173 (1993).
- Abderrahmen, A., Romdhane, F.F., Ouada, H.B. & Gharbi, A. Investigation of the liquid crystal alignment layer: effect on electrical properties. *Sci. Technol. Adv. Mater.* **9**, 025001-025005 (2008).
- Lopatina, L.M. & Selinger, J.V. Theory of ferroelectric nanoparticles in nematic liquid crystals. *Phys. Rev.* **102**, 197802-197805 (2009).
- Yang, K.-L., Cadwell, K. & Abbott, N.L. Use of self-assembled monolayers, metal ions and smectic liquid crystals to detect organophosphonates. *Sensors and Actuators. B* **104**, 50-56 (2005).
- Brake, J.M., Daschner, M.K., Luk, Y.-Y. & Abbott, N.L. Biomolecular interactions at phospholipid-decorated surfaces of thermotropic liquid crystals. *Science* **302**, 2094-2098 (2003).
- Schutkowski, M. *et al.* High-content peptide microarrays for deciphering kinase specificity and biology. *J. Angew. Chem.-int. Edit* **43**, 2671-2674 (2004).
- Dietrich, C. *et al.* Lipid rafts reconstituted in model membranes. *Biophys. J.* **80**, 1417-1428 (2001).
- Lockwood, N.A., De Pablo, J.J. & Abbott, N.L. Influence of surfactant tail branching and organization on the orientation of liquid crystals at aqueous-liquid crystal interfaces. *Langmuir* **21**, 6805-6814 (2005).
- Poulin, P., Stark, H., Lubensky, T.C. & Weitz, D.A.

- Novel colloidal interactions in anisotropic fluids. *Science* **275**, 1770-1773 (1997).
36. Messmer, M.C., Conboy, J.C. & Richmond, G.L. Observation of molecular ordering at the liquid-liquid interface by resonant sum frequency generation. *J. Am. Chem. Soc.* **117**, 8039-8040 (1995).
 37. Brake, J.M., Mezera, A.D. & Abbott, N.L. Effect of surfactant structure on the orientation of liquid crystals at aqueous-liquid crystal interfaces. *Langmuir* **19**, 6436-6442 (2003).
 38. Barmantlo, M. & Vreken, Q.H.F. Reorientation of liquid-crystal molecules in mixed surfactant/LC Langmuir films. *Chem. Phys. Lett.* **209**, 347 (1993).
 39. Brake, J.M., Daschner, M.K. & Abbott, N.L. Formation and characterization of phospholipid monolayers spontaneously assembled at interfaces between aqueous phases and thermotropic liquid crystals. *Langmuir* **21**, 2218-2228 (2005).
 40. Brake, J.M. & Abbott, N.L. Coupling of the orientations of thermotropic liquid crystals to protein binding events at lipid-decorated interfaces. *Langmuir* **23**, 8497-8507 (2007).
 41. Park, J.S. *et al.* Formation of oligopeptide-based polymeric membranes at interfaces between aqueous phases and thermotropic liquid crystals. *Chem. Mater.* **18**, 6147-6151 (2006).
 42. Moraille, P. & Badia, A. Enzymatic lithography of phospholipid bilayer films by stereoselective hydrolysis. *J. Am. Chem. Soc.* **127**, 6546-6547 (2005).
 43. Renault, J.P. *et al.* Fabricating microarrays of functional proteins using affinity contact printing. *Angew. Chem.-int. Edit* **41**, 2320-2320 (2002).
 44. Park, B. & Song, S. Investigation on coating methods of a self-assembled monolayer on PDMS surface. *BioChip J.* **1**, 140-143 (2007).
 45. Tingey, M.L., Wilyana, S., Snodgrass, E.J. & Abbott, N.L. Imaging of affinity microcontact printed proteins by using liquid crystals. *Langmuir* **20**, 6818-6826 (2004).
 46. Jang, C.H. *et al.* Using liquid crystals to report membrane proteins captured by affinity microcontact printing from cell lysates and membrane extracts. *J. Am. Chem. Soc.* **127**, 8912-8913 (2005).
 47. Jang, C.H., Cheng, L.L., Olsen, C.W. & Abbott, N.L. Anchoring of nematic liquid crystals on viruses with different envelope structures. *Nano Lett.* **6**, 1053-1058 (2006).
 48. Singh, R.P. *et al.* Biosensor arrays for environmental pollutants detection. *BioChip J.* **2**, 223-234 (2008).
 49. Pal, S. & Song, M.J. Integrated circuit bipolar semiconductor microchip-based optical detection of biomolecules: parallel applications as a miniaturized sample platform and a two-dimensional photodetector. *BioChip J.* **1**, 124-133 (2007).
 50. Cho, H.M. *et al.* Characterization of novel self-assembled materials for surface modification of sensor chip. *BioChip J.* **2**, 206-211 (2008).