7th Italian-Japanese Workshop on Liquid Crystals

and

10th National meeting of the Italian Liquid Crystal Society

Book of ABSTRACTS

Istituto Biblioteca Classense- Ravenna (Italy)

7-10 July 2014
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SICL-JLCS WORKSHOP

TALKS
Predicting the chiral behavior of cholesteric phase on the basis of the molecular properties is notoriously a very difficult task. This problem was recently tackled by a combination of experiments and theory for the case of the chiral nematic ordering that develops in concentrated solutions of DNA oligomers [1-4]. In these systems the formation of liquid crystal phases is mediated by the end-to-end aggregation of DNA duplexes into columns of chemically distinct but physically continuous duplexes. The chirality of the DNA double strands gives rise to a macroscopic helical precession of molecular orientation, whose handedness and dependence on concentration and temperature follows a complex pattern difficult to unravel [2-4].

DNA cholesterics are a particularly convenient system to study the propagation of chirality. The molecular structure of the B-DNA helices is symmetric and very well known, and its chirality is very explicit. Moreover, while in typical lyotropic and thermotropic cholesterics the monomers have a fixed chirality given by the molecular or colloidal structure, the self-assembly of DNA can be exploited to modify the structure of the aggregated columns, tuning the chirality of the columnar aggregates and study its effect on the collective ordering.

Experimental results [3] indicate that once the pair interactions between helices is given, the propagation of chirality follows simple rules that take into account column length distribution and the continuity of the helix within each column. All difficulties in interpreting the nematic ordering of chiral molecules are actually nested in the determination of the torque resulting from pair interactions, as indicated by theoretical investigation performed via molecular theory and coarse grained model of the torque between helices [4]. Indeed, the sign of the torque experienced by neighboring DNA helices depends on the balance on their average distances, in turn depending on the overall concentration at which the nematic phase can be found. These facts enable interpreting a large quantity of otherwise bizarre chiral behavior observed in DNA liquid crystals.

References

Acknowledgment: Effort sponsored by the Italian Ministry of Education, Universities and Research, PRIN project
Non-peripheral Substituted Phthalocyanine with High Carrier Mobility and Its Solar Cell Application

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Liquid crystal is one of the promising materials as an organic semiconductor because of the potentially high carrier mobility comparable to that of a-Si (0.1 cm²/Vs). We have demonstrated a high carrier mobility in excess of 1 cm²/Vs in non-peripheral substituted phthalocyanine, 1,4,8,11,15,18,22,25-octaoctylphthalocyanines (C6PcH₂) [1]. C6PcH₂ shows a unique temperature dependence characteristics of the carrier mobility which must be related to the phase structure of this material. We have also demonstrated a high-efficient bulk-heterojunction solar cell based on C6PcH₂ [2]. The device can be fabricated through a spin-coating process from the blend solution of C6PcH₂ and 1-(3-methoxy-carbonyl)-propyl-1-1-phenyl-(6,6) C₆₁ (PCBM). For the formation of the optimally phase-separated nano-structure for efficient carrier generation and transportation, the mesogenic properties should play an important role. Solar cells have demonstrated a high external quantum efficiency above 60% in the Q-band absorption region of C6PcH₂ and a high energy conversion efficiency of 3.1%. By inserting appropriate buffer layers between the electrodes and active layer and by incorporating additives such as 1,8-diodooctane (DIO) into active layer for morphorogy optimization, the fill factor FF and energy conversion efficiency were improved to be 0.55 and 4.2%, respectively [3, 4]. As a donor material in the BHJ solar cell, we used a binary blend of CnPcH₂ derivatives and investigated a device performance upon changing a ratio of components in the blend. The highest power conversion efficiency was demonstrated for a C5PcH₂ concentration of 25mol% in C5PcH₂/C6PcH₂ blend, which exceeded those of solar cells utilizing pure Pc of C5PcH₂ or C6PcH₂ as a donor material. This result indicates a possibility of the device performance optimization of the solar cell upon using a blend of liquid-crystalline semiconductors as a material of active layer, as the same manner as the LC blends for the optimization of LCD performance [5]. We also investigated blend effect of C6PcH₂ and polymer semiconductor for the improvement of long-wavelength sensitivity in the bulk hetero-junction solar cells. The effective broadening of the wavelength range of the solar cell has been achieved by the use of the polymer/C6PcH₂ blend as a p-type semiconductor [6].

References

Acknowledgment: This work was partly supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by Advanced Low Carbon Technology Research and Development Program from the Japan Science and Technology Agency (JST-ALCA)
Advanced Multifunctional Materials Based on Liquid Crystal Thienoviologens

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The research in the field of electronic and photonic devices based on ordered organic semiconducting materials has been boosted by the development of new multifunctional materials [1-3]. The order characterizing liquid crystals has been exploited for improving charge mobility performances [2]. However, while in the last decade much effort has been addressed to the synthesis of hole-conducting materials (p-type), less attention has been paid on the development of electron-conducting ones (n-type). Here we show the bulk multifunctional properties of π-conjugated thienoviologen ionic liquid crystals [4] which have strong electron acceptor character and exhibit high fluorescence in the bulk state (Φ up to 68%). Notably, the combination of their optical properties with high ionic conductivity [5] and fast intermolecular electron transport, leads to their unique electrochromic and electrofluorochromic functions (Fig. 1) [6]. In addition to the above properties, these materials show photoconduction in glassy LC state at room temperature. The photoconductivity can be related to the reduction of the ionic liquid crystals, opening the way to the use in wider range of advanced optoelectronic devices [7]. Furthermore, phase separation processes in mixtures of these new semiconductor liquid crystals with other liquid crystals are under study in order to ascertain the possibility of their application in organic photovoltaic devices [8].

Fig. 1. Electrochromism in SmA phase (a) and electrofluorescence switching in the Colr phase (b).

References
Highly ordered smectic liquid crystals for organic field effect transistors
Jun-ichi Hanna, Hiroaki Iino, and Takayuki Usui

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Liquid crystals are a self-organizing molecular semiconductor, which has a π-conjugate system for a hopping site of charges and side chains along with the long molecular axis that help self-organization of molecules, and exhibit charge carrier transport properties superior to those of conventional materials, e.g., amorphous organic semiconductors. Since the discovery of electronic conduction in liquid crystals, various device applications have been proposed, including photosensors, photoreceptors for copiers, light emitting diodes, solar cells, field effect transistors, and so on. However, the device performances in these devices proposed are not as good as those fabricated with conventional amorphous and crystalline organic semiconductors, which come from a fact that basic elemental technologies have not been established to make the best use of the properties of liquid crystals yet, leading to little attention to the liquid crystals in their industrial applications of the devices.

We proposed application of polycrystalline thin films of highly ordered smectic liquid crystals solution-processed for field effect transistors, in which we can utilize unique properties of liquid crystals for overcoming the problems that cannot be solved in non-liquidcrystalline materials, e.g., inhomogeneity and poor surface morphology in solution-processed polycrystalline thin films and poor thermal durability of the films in crystalline thin films. [1,2]. In fact, a FET fabricated with polycrystallinetin film of 2-phenyl-7-decylbenzothienobenzothiophene (Ph-BTBT-10) exhibited high thermal durability up to 200°C thanks to highly ordered smectic mesophase, in addition to a small variation of FET performance thanks to uniform and molecularly flat surface morphology of the films [3].

Recently we found that the FET mobility was enhanced by about one-order of magnitude, up to 21.2 cm²/Vs by thermal annealing at 120°C for 5 min. This high mobility is comparable to these in FET fabricated with an amorphous oxide semiconductor of InGaZnO, which indicates a high potential of liquid crystals in printed electronics.

We discuss why organic transistor materials have to be a liquid crystal.

References
New composites based on liquid crystalline elastomers for micro-actuators and energy storage systems

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Liquid Crystalline Elastomers (LCEs), also known as “artificial muscles” or “shape memory” actuators can undergo controlled shape changes in response to external stimuli. Some well-known examples include nematic polysiloxane-based LCE thin films, which contracts with increasing temperature. This seminar will focus on recent advances on the preparation of new composite materials in which LCE films change shape in response to the application of an external voltage or controlled current.[1-4]

In particular, the chemical-physical characterization of these bilayer [1-4] and bi-components [5] LCE-based systems will be reported and discussed, centering the discussion on new potential applications as energy conversion and storage micro-systems and micro-actuators.

Figure 1. Optical microscopy images of gold-LCE bilayer system before (a,b,c) and after (d,e) actuation.
(f) SEM image of the same sample of image (e). Arrow indicates the nematic director orientation. [3]

References

Acknowledgment: This research was partially supported by Centre of Excellence “Namaste” (Ljubljana – Slovenia).
Structural Analyses of Liquid Crystal Blue Phases

Ying Wen¹, Yasushi Okumura², Hiroki Higuchi² and Hirotsugu Kikuchi²

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Cholesteric blue phases (BPs) occur generally in a narrow temperature range between isotropic phase and chiral nematic one. They have a self-assembled three-dimensional (3D) cubic lattice consisting of double-twisted cylinders[1], and their lattice constant is a couple of hundred nanometers. Physical properties of BPs such as the selective Bragg reflection in visible wavelength region and fast electro-optical response are attributed to the unique cubic structure. Hence, a detailed verification of the BP lattice models is worthwhile in the field of BP science. Here we present a relationship between the lattice structure and the Bragg reflection wavelength of BP studied by microspectroscope and confocal laser scanning microscopy (CLSM), which is a novel imaging technique for obtaining high-resolution optical images in 3D scale.

A stripe pattern consisting of alternating bright and dark lines were found in a domain of multi-orientation cell of BP with CLSM observation as shown in Figure 1(a). In addition to the periodicity between the lines of the stripe, another periodicity along the stripe line was found through FFT of the striped pattern. The length ratio of these two periodicities in the FFT image showed good agreement with aspect ratio of periods in (211) plane in the BP model.

Considering the resolution of CLSM in the depth direction, the overlaid images of (211) sections (Figure 1(b)) in different depths are expected to coincide with the observed stripe pattern. Series of CLSM images of (211) plane with different depths, reflecting the internal structure of the sample, were obtained by shifting the focal plane in every 25 nm in the direction of Z-axis. As a result, relative brightness on the stripes with different brightness alternately changed as a function of the depth. Through fitting with sine curves, the lattice constant was calculated to be about 330 nm according to the Z profile cycle of stripes. This result is identical with the lattice constants obtained from 2D CLSM image of (211) and (111) plane and the reflection spectrum by microspectroscope. Thus, the structure of (211) plane in 3D scale has been successfully confirmed.

Figure 1 (a) Stripe pattern image of BP I (211) plane observed by CLSM, (b) a corresponding overlapped image of cross-sections of double-twisted cylinders on (211) plane in BP I lattice model.

References
Active Plasmonics: Systems Design and Characterization

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The design and fabrication of samples showing plasmonic properties is fundamental for the realization of devices exhibiting peculiar electromagnetic properties (e.g. Metamaterials) [1]. Much curiosity is actually devoted to reconfigurable systems showing tunable plasmonic functionalities (Fig. 1) [2-4]. Here we depict the scenario of actual and future possibilities offered by such systems where the spectral position of the localized surface plasmon resonance (typical of metallic nanoparticles) can be shifted through the application of external stimuli (e.g. electric field or mechanical perturbation).

Figure 1. Basic principle of smart tapes (a) Sketch of the experimental setup. By stretching a PDMS sample coated with a single layer of gold nanoparticles the average distance between them becomes larger in the stretching direction and shorter in the perpendicular one. Stretching of the sample is accompanied by a remarkable change of colour from purple-red (b) to blue-violet (c). Images were acquired with a polarizer, mounted to a camera, with direction of polarization perpendicular to the applied strain.

References
Induction of Birefringence in Optically Isotropic Liquid Phase of Chiral Mesogenic Compound

Isa Nishiyama and Takahiro Yamamoto

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For common liquid crystal displays (LCDs), the precise control of the initial alignment of LC molecules is needed so that a good dark state, thus a high contrast ratio, can be obtained. If the optically isotropic LC phase is utilized, there is no need for concern about the initial alignment, which is great advantage for the LCD production. Representative examples of such kinds of LC phases are blue phases, which are optically isotropic without the application of electric field [1,2]. Another optically isotropic phase is a liquid phase which intrinsically shows no birefringence. Therefore, if the birefringence can be induced in the liquid phase by the application of electric field [3], it is of great use as a material for the LCD application. So far, one of our interests has been focused on the evaluation of physical properties of dichiral azobenzene mesogenic compounds, in which following interesting results have been obtained:

(a) Emergence of stable smectic Q (SmQ) phases [4],
(b) Photo-control of 3D structure of LC phases [5], and
(c) Chirality-driven cubic-tetragonal structural change [6].

In addition to those findings, the induction of the birefringence in the liquid phase has recently been observed in a dichiral azobenzene ((S, S)-AZO-PB, Figure 1). The electrically-assisted increase in the phase transition temperature is discussed in detail in terms of clinicity, and is compared with the previously reported similar behaviours, including the shift of the ferroelectric-paraelectric phase transition temperature by the application electric field observed in a ferroelectric LC [7].

![Chemical structure and phase-transition temperatures of dichiral azobenzene liquid crystal used in this study.](image)

**Figure 1.** Chemical structure and phase-transition temperatures of dichiral azobenzene liquid crystal used in this study.

References
Mesoscale models, based on the drastic simplification of representing molecules as simple rigid objects such as spherocylinders or ellipsoids or even spins on a lattice have been the cornerstone of the first generation of liquid crystal (LC) computer simulations (see, e.g. [1]). While these approaches are still very valuable in obtaining the general properties of complex LC, like LC Elastomers [2] one of the most important current challenges is to relate a realistic molecular structure to physical observables and predict properties such as morphologies, order parameters, and phase-transition temperatures. This is essential, e.g. for applications in organic electronics, like organic solar cells [3] and in interpreting detailed spectroscopic data. Atomic scale molecular dynamics simulations can now start to meet the challenge and we present some recent applications to nematic and smectic liquid crystal systems [4,5] as well as to solutes in LC where we compare with detailed NMR data [6]. We also tackle the problem of predicting alignment and anchoring strength of LC close to a solid interface, considering in detail thin films of 5CB on crystalline (cristobalite) and amorphous silica surfaces of increasing roughness [7].

Heat-driven unidirectional rotation of cholesteric LC droplets

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When a chiral liquid crystal is given a transport current, a unidirectional molecular rotation is known to take place[1,2], which is called Lehmann effect. In this report, we study the heat-current driven molecular dynamics in two-types of hemispherical cholesteric droplets by means of optical microscopies[3]. Both the droplets, coexisting with the isotropic phase and contacting on a glass substrate, are characterized by the convex-concave modulated surface and the inside orientational helix. The difference between them is the helical axis direction, i.e., one is perpendicular and the other is parallel to the substrate. Under the temperature gradient perpendicular to the substrate, the droplet whose helical axis is parallel to the heat current exhibited the pure director rotation, while the one with the axis perpendicular to the heat flow rotated by themselves as a rigid body. In the two droplets, the rotational conversion efficiency from the temperature gradient into the angular velocity showed very different dependence on the chirality strength and on the droplets size, suggesting that the rotations of the two droplets may be driven by the independent torques with different origins. This is the first observation that the cholesteric droplets under the temperature gradient exhibit the two rotational modes, the pure director rotation and the molecular barycentric motion, which can be switched to each other by changing the heat-current direction between parallel and perpendicular to the helical axis.

References

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Halogen-bonded Liquid Crystals, Gels, and Polymers

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According to the IUPAC, a halogen bond (XB) occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.$^1$

Similarities between halogen and hydrogen bonds have been emphasized in several contexts. However, it is the differences between these interactions that provide with an extra value for the design and construction of XB-based supramolecular materials.$^2$ For example, the directionality of XB has provided with unique design tools for preparing photoresponsive, liquid-crystalline complexes from non-liquid-crystalline constituents, with truly unique optical performances.$^3$ Moreover, we have employed the tunable interaction strength of halogen bonding to gain fundamental understanding of light-induced mass migration in photoswitchable polymer-azobenzene complexes; namely not many other noncovalent interactions allow controlling the polymer-chromophore interaction strength without altering the electronic properties of the chromophore.$^4$ The use of halogen-bonded mesogens to control hierarchical polymer self-assembly over the mm length scale,$^5$ together with our recent work on halogen-bond-triggered supramolecular gelation,$^6$ open up new avenues in the design of supramolecular systems.

Figure 1. Halogen-bonded dimer between a pyridyl derivative (right) and a halogen bond-donor molecule (left) containing a photoswitchable azo group.

References
Second Order Phase Transition in Hyper Swollen Lyotropic Liquid Crystals

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We have investigated the phase transition behavior by DLS measurement in the hyper-swollen lyotropic nematic (LN) phase, formed by a combination of anionic and cationic surfactants (sodium dodecyl sulfate; SDS and dodecyl trimethyl ammonium bromide; C12TAB, respectively) at a total surfactant concentration $\phi \leq 8\text{wt}\%$. The mole fraction $\alpha$ between SDS and C12TAB is varied between 2.3 and 2.7. We have found an interesting type of continuous 2nd order isotropic-nematic (I-N) phase transition for some surfactant ratios, and investigating the driving mechanism. Director fluctuations observed in depolarized (vertical-to-horizontal polarization rotation; VH) signal, clearly shows critical slowing down on both sides of the phase transition as shown in Figure. It should be noted that in all samples which show the 2nd order I-N phase transition, the size of micelles is drastically reduced above the phase transition. In addition, all have the same radius of the micelle, almost equivalent to the length of the surfactant molecules, which can be estimated from translational diffusion constant observed in polarized (vertical-to-vertical polarization rotation; VV) scattering with Einstein-Stokes’s law. It is quite reasonable that the micelle shape becomes spherical in the isotropic phase. We concluded that the 2nd order transition is driven by the decrease in the anisotropy of “building blocks” of the nematic, namely the rod to sphere transition of micelles. The birefringence continuously weakens near the 2nd order I-N phase transition due to the decrease in order parameter as well as in the simultaneous decrease in anisotropy of the building blocks. The latter also strongly affects the excluded volume interaction between micelles and thus the origin of orientational order. We have found a 2nd order I-N phase transition driven by the shape transformation of the building blocks for the first time.

Figure 1 Temperature dependence of relaxation time for two types of fluctuations with the prediction of their respective dispersion relations ($\phi=8\text{wt}\%, \alpha=2.55$).
Photopyroelectric calorimetry for the thermal and optical evaluations of light induced transitions in liquid crystals.

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In this study, the photopyroelectric calorimetry has been employed for the simultaneous determination of thermal conductivity $k$, and the specific heat $c$ over a temperature range including both the Smectic-Nematic and Nematic-Isotropic phase transitions temperature, before, during and after the UV light exposure. As expected, the UV light causes both the transition temperatures to shift to larger values due to the photochromic molecules switching to their more ordered open configuration. This reduces their disordering power on the LC mean molecular field with respect to that caused when they are in their closed configuration. As reported in fig. 1, as the UV light is turned off, the transition temperatures do not return down to the corresponding values obtained before the light had been switched on. This indicates that the prolonged (several hours) exposure of the photochromic molecules to the UV light, causes the switching to their open form to become irreversible, unlike the previously reported reversible switching effects following short exposure (several seconds) to UV light. The thermal conductivity studies revealed that, upon entering the smectic phase when cooling the sample with the UV light on, the homeotropic alignment of the LC molecules in the nematic phase may get disrupted, giving rise to multi-domain focal conics textures.

![Figure 1](image_url)

Figure 1. Specific heat over smectic - nematic and nematic - isotropic phase transitions in 8CB liquid crystals with 2% mass fraction of naphtopyran photochromic molecules molecules: before (dark gray), during (black) and after (light gray) UV light illumination.
Dynamic Amplification of Optical Signals in Photorefractive Ferroelectric Liquid Crystals

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1. Introduction
The photorefractive effect is a phenomenon wherein a change in the refractive index is induced by a combined mechanism of photovoltaic and electro-optic effects. The interference of two laser beams in a photorefractive material establishes a refractive index grating (holograms). The photorefractive effect in surface-stabilized ferroelectric liquid crystals (SS-FLCs) doped with a photoconductive compound has been reported [1]. When laser beams are interfered in a photoconductive SS-FLC, an electric field is induced within the LC phase and the direction of the spontaneous polarization is changed giving rise to a change in refractive index of the corresponding area. In this study, chiral compounds that also show photoconductivity were synthesized and mixed with the base LC compounds (Fig. 1). The properties of the obtained photoconductive FLC mixtures were examined and the relationship between the photorefractive effect and properties of the FLC mixtures were investigated.

2. Results and discussions
The photorefractive effect of FLC was evaluated by two-beam coupling experiment. A gain coefficient higher than 1200 cm\(^{-1}\) was obtained with the application of only 1 V/µm. This value is seven times larger than the gain coefficients reported in other photorefractive FLCs. The grating formation time decreased with increasing electric field strength due to the increased efficiency of charge generation. The shortest formation time was obtained to be 1 ms at 1 V/µm external electric field. Optical image amplification was demonstrated. A computer-generated animation was displayed on the SLM. The frame rate was 30 fps. A 473 nm beam was irradiated on the SLM and the reflected beam was incident on the FLC sample. A pump beam interfered with the beam from the SLM in the FLC sample. A laser beam containing the moving image of the animation was amplified by the incident pump beam (Fig. 2). This result shows that the response of the photorefractive FLC was fast enough to amplify the optical image in real time.

Reference
High-HTP macrocyclized pheynyl cinnamate dimer utilizable as photo-responsive chiral dopant for nematic liquid crystals

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Twin dimers forming liquid crystals (LCs) are composed of two mesogenic units linked by a flexible alkyl spacer. These linear dimers having two alkyl tails can be cyclized by ring-closing metathesis under high dilation in the presence of the first Grubbs catalyst. Macrocyclization of twin dimers forces the spacer to fold and the two mesogens to face to each other at a short distance and restricts the conformations.[1] When the spacer has a chiral carbon, two mesogens are fixed in a skewed overlapping alignment with the handedness determined by the spacer’s chirality. Such a cyclic chiral dimer exhibited the helical twisting power in the nematic LC solvent four times higher than that of the precursor linear dimmer and twenty times higher than that of monomeric compound.[2]

Here, macrocyclized phenyl cinnamate dimer with a chiral spacer was prepared and its photochemistry was compared with that of the precursor linear dimer and basic monomer. Irradiation of cyclic and linear dimers induced intra-molecular [2+2] photodimerization of cinnamate groups though that of monomer resulted merely in cis-trans isomerization of cinnamate. [3–9] The rate of photodimerization in the cyclic dimer was 20 times larger than that in linear one. With this photodimerization, the cyclic dimer decreased helical twisting power (HTP) from 27.5 \( \mu m^{-1} \) to 6.7 \( \mu m^{-1} \). We demonstrated that such a macro-cyclized dimer can be a photo-responsive chiral dopant of chiral nematic liquid crystals which will be applied for some interesting fields.

Molecular geometry, elastic constants and twist-bend nematic phase

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Recently, the observation of a number of unusual features in the second nematic phase formed by bent-shaped liquid crystal dimers, lead to the identification of a novel nematic organization, which following a prediction by Dozov was called a Twist-Bend Nematic (N\textsubscript{TB}).\cite{1,2} This is characterized by a periodically distorted director forming a conical helix with a doubly degenerate handedness.\cite{2} Such a picture was confirmed by a variety of experimental techniques, but agreement on this phase structure is not universal. However, valuable insights have been reached by transmission electron and optical microscopy\cite{3,4} as well as electro-optical measurements.\cite{5} From these and the analysis of NMR experiments,\cite{6,7} a remarkably short periodicity, of the order of a few molecular lengths, could be identified.

Although the structural features of the N\textsubscript{TB} phase are becoming clear, the mechanism of the N\textsubscript{TB}-N transition, the role of the dimer structure and the connection with the elastic properties\cite{8,9} remain open questions. However, low values of the bend elastic constant seem to be important. Here, using a molecular field approach, we can provide a consistent picture of the phase transition and the elastic behaviour, in relation to the molecular geometry. In particular, theory allows us to analyse the results of different experiments, focussing on those features that have been taken as a signature of the N\textsubscript{TB} organization.

References
Structure-sensitive bend elastic constants between pN and sub-nN


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Elasticity is an important factor for the performance of liquid crystal (LC) devices. It is known that the curvature elastic constants in calamitic nematic (N) LC molecules, $K_{22}$, $K_{11}$, and $K_{33}$ are usually in the range of pN in ascending order of magnitude. In this study, we synthesized diphenylacetylene-core-based compounds and found that $K_{33}$ varies sensitively depending on the chemical structure (Fig. 1); one of the compounds (p-oxyAzo5) has surprisingly high elastic constants against bend deformation, a sub-nN, over a wide temperature range; about 100 times larger than that in general liquid crystals [1]. In contrast, p-oxyEster5 has $K_{33}$ of normal values (pN) and $K_{33}$ of p-oxyTolane5 is in between.

To clarify the origin of the unusually huge $K_{33}$ values, we measured x-ray diffraction in their N phase and found a cybotactic smectic cluster formation in whole the N range only in p-oxyAzo5 [1]. Then, why can p-oxyAzo(n) homologues stabilize cybotactic clusters exceptionally? To address this, we performed ab initio molecular orbital theory calculations for core structures of molecules used, by which we search single molecular most-stable structure. The relative potential energy of the core part of studied molecules was calculated as a function of dihedral angle of a phenyl ring, as shown in Fig.2. In the figure, angles 0 and 180 degrees correspond to parallel orientation of two phenyls. We found remarkable differences in four analogous compounds; Only the azo group imposes their molecules into flat geometry with a high potential barrier. We may expect p-oxyAzo5 can pack quite well into smectic-like structure as we confirmed in the experimental results.

References
within the present contribution LCDiXRay,[1] our newly developed standard computerized procedure for the indexation of X-Ray Powder Diffraction (PXRD) patterns of columnar liquid crystals, will be described. This user-friendly software implemented in an objected-oriented framework has been included in a Java GUI program. LCDiXRay allows the straightforward identification of the columnar liquid-crystal mesophase symmetry - Hexagonal (Colh), Rectangular (Colr), or Oblique (Colo) as well as the determination of all structural information extracted from a properly indexed PXRD spectrum. In particular, the proposed program notably accelerates the identification of columnar mesophases together with the in situ determination of their structural parameters such as: mesophase type, cell dimension, cross section area, intermolecular stacking distance between consecutive discoids, and in the case of ordered mesophases, the estimation of the number of molecules constituting each discoid. Through chosen examples, the performances of LCDiXRay will be illustrated.

References

Note: LCDiXRay is freely available upon request (nicolas.godbert@unical.it)

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Comparison of Molecular Orientation Structure of Photoalignable Liquid Crystalline Polymer Films at the Near-surface and in Bulk

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Photoalignment of liquid crystals (LCs) has received considerable attention in display industries due to its cleanliness and patternability. [1] We have been carrying out systematic studies on photoresponsive liquid crystalline polymeric materials that show photoinduced molecular reorientation (Fig. 1a), and demonstrated their application to birefringent films, polarization holography and LC photoalignment layers. [2] One of the features of our materials is that the LC photoalignment can be achieved with large azimuthal anchoring, which is important for in-plane switching LC displays. For example, a LC polymer film with photo-crosslinkable mesogenic side groups exhibits significant molecular orientation parallel to the polarization of linearly polarized (LP) UV light and reveals large azimuthal LC anchoring when the film is exposed to LP UV light and subsequently annealed. [3]

For the LC alignment, evaluation of the near-surface structure of the alignment layer is important to investigate the interaction between LC molecules and the film. In this paper, thermally stimulated photoinduced molecular reorientation structures of photoreactive liquid crystalline polymer films at the near-surface and in bulk are clarified using near-edge X-ray absorption fine structure (NEXAFS) and polarization UV absorption spectroscopies, respectively [4]. NEXAFS shows an effective uniaxial in-plane orientation at the near-surface in films thicker than 40 nm, but the orientation performance in bulk decreases when film thickness decreases. Additionally, oblique molecular reorientation behavior both at the near-surface and in bulk is presented as functions of film thickness and exposure angles.

![Figure 1](image_url)

Figure 1. (a) Schematic illustration of photoinduced orientation mechanism and (b) detailed molecular orientation structure of photoalignable LCP film.

References
Liquid crystal channel waveguides for optofluidic applications

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The research on the integration of optics and microfluidics, better known as optofluidics, in combination with the optical properties of liquid crystals (LC) can be used to make both electrically and optically controlled cores for switchable and reconfigurable waveguides [1-2]. Several different devices were designed, simulated, developed and characterized, achieving routing capabilities in LC waveguides with electro-optical [3-6] and all-optical [7] control, and through nematicon propagation [8].

In this paper we present our recent results on light propagation in polydimethylsiloxane (PDMS) channels with LC infiltrated core. Polarization independent light transmission was observed, despite the typical LC optical anisotropy, and we measured a transmission variation due to the orientation of the LC molecules of only 0.3 dB. The experimental results were found to be consistent with both the orientation observed under a polarizing microscope and the simulations. Polarization insensitive behavior is an interesting feature which makes the proposed LC waveguides a basic structure for low cost devices, which can be used for optical interconnections or integrated with microfluidic circuits for lab on chip and sensing applications.

References
Phase Structure and Transition Mechanism in Azobenzene-Containing Bicontinuous Cubic Liquid Crystalline Systems.

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Liquid crystals (LCs) are a kind of liquid the structure of which can easily respond to external stimuli such as electric field or deformation. Bicontinuous cubic (Cub\textsubscript{bi}) phases are such LCs but possess much complicated molecular organizations, 3D network structures with cubic symmetry, which was first reported by Luzzati more than 30 years ago \cite{1}. Based on the characteristic structures, many applications have been proposed such as catalytic bases, separation membranes, 3D conductors, etc. \cite{2}. In thermotropic systems, the Cub\textsubscript{bi} LCs are in temperature scale neighbored by other LCs, mostly 1D smectic C (SmC) LC. Reflecting the different dimensionality of ordering (3D vs 1D), the two show quite different physical properties (e.g., optically isotropic and viscous in Cub\textsubscript{bi} vs optically anisotropic and relatively fluid in SmC). Our research group focused on the dynamic nature of those structures as LCs and selected UV light as external stimulus. By means of photoisomerization of a doped azobenzene derivative, we have achieved the light-driven SmC to Cub\textsubscript{bi} phase transition \cite{3}.

The systems constructed were binary mixtures of 4'-n-docosyloxy-3'-nitrobiphenyl-4-carboxylic acid (ANBC-22, in which “22” indicates the number of carbon atoms in the alkyl tail) and ethyl 4-(4'-n-docosyloxyphenylazo)benzoate (AZO-22). A mixture containing 20 mol\% AZO-22 shows an enantiotropic transition behavior of crystal–SmC–I\textalpha 3d–Cub\textsuperscript{bi}–Im\textsuperscript{3m}–Cub\textsubscript{bi}–Isotropic liquid. When the SmC phase is irradiated with UV light (\(\lambda=365\) nm) at a temperature far below the SmC–I\textalpha 3d–Cub\textsubscript{bi} phase transition temperature, the Cub\textsubscript{bi} phase appears very quickly in 10 s. After turning off the irradiation, the original SmC phase is quickly recovered. To elucidate the mechanism at the molecular level, we monitored the transition by grazing-incidence X-ray diffraction and Fourier transform infrared spectroscopy. An important conclusion derived is that the trans–cis photoisomerization of the doped molecules in the mixture do not directly cause the Cub\textsubscript{bi} phase formation, but rather gives rise to destabilization of the SmC phase with layered structure, indirectly favoring the formation of the Cub\textsubscript{bi} phase with a twisted molecular arrangement \cite{4}. The details are given on the day of presentation.

References

Electric field tuning of optoelastic trapping in nematic liquid crystals

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We report the effects of electric field on the optoelastic interaction occurring between a colloidal particle dispersed in a nematic liquid crystal (nematic colloid) and a “ghost” colloid which results from the local distortion of the nematic induced by a laser beam. The optoelastic interaction is induced by minimization of the elastic free energy of the system leading to particle trapping by the ghost colloid, as is the case occurring between two real colloidal particles. The effect has been investigated under experimental conditions which prevents the occurrence of conventional optical trapping induced by high gradient optical fields.

We show that application of a low frequency (1 KHz) electric field to a homeotropic sample of a nematic liquid crystal is able to control the strength and the range of the force acting on the nematic colloid. In case of liquid crystal with positive dielectric anisotropy the existence of a quenching voltage is demonstrated above which no interaction takes place, while in case of negative dielectric anisotropy an extremely large interaction range is demonstrated. Interaction range of few hundred microns has been observed.

The experimental observations are well described by a conceptually intuitive analytical model that accounts for the electrical realignment of the liquid crystal along the electric field direction and the overlap between the long-range orientation distortion around both colloids.

References

Photoalignment of liquid crystalline polymers commanded from the free surface

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To date, the surface alignment of liquid crystal (LC) materials has been achieved on solid surfaces [1]. Here, we propose approaches to control the orientation of LCs from the free (air) surface side: a photoresponsive skin layer at the free surface is prepared on a non-photoresponsive LC polymer film by surface segregation or inkjet printing an azobenzene (Az)-containing liquid crystalline block copolymer. In general, rodlike mesogens tend to orient vertically with the free surface (substrate) plane. However, we found that, in films of a block copolymer comprising of PBMA (amorphous polymer) and Az-containing LC polymer (PBMA-b-PAz), the Az mesogen is preferentially oriented parallel to the substrate [2]. This is attributed to the segregation of the PBMA block at the topmost (free) surface. The lower surface tension with high flexibility of the PBMA block results in the segregation to the free surface.

When a small amount of PBMA-b-PAz is mixed with non-photoresponsive LC polymers (for example, PPBz in Figure 1), this block copolymer segregates at the free surface by annealing. This process leads to an orientational transition from a homeotropic to a planar mode. Once a pre-planar orientation is obtained, the Az mesogens are readily aligned homogeneously by linearly polarized light (LPL) irradiation. This process can be applied to birefringence photopatterning. LPL is first irradiated in the entire film area, and successively patterned irradiation is made with orthogonal LPL. These procedures provide birefringence patterning of the PPBz film. Rotation of the crossed polarizers leads to alternations of the bright or dark tones. This two-step process indicates that the mesogens can be re-aligned by another LPL. The non-photoresponsive mesogens up to 10 μm thickness can be achieved by the photoresponsive PBMA-b-PAz skin layer of ca. 20 nm thickness existing at the free surface. Another type of patterning can be achieved by inkjet printing of PBMA-b-PAz on the surface of LC polymer films. Details will be discussed in the workshop. This polymer works as “command surface ink” [3].

References
Lasing in Liquid Crystals driven to Chaos: Plasmon-Exciton Coupling Enables Scattering and Gain

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The scientific interest for disordered multiply scattering systems find its basis on the gigantic resonance effects experienced by light-waves travelling along random trajectories in complex and rapidly changing structures. These effects originate by localization processes that take place when the Motte-Ioffe-Regel criterion is satisfied. In recent years, optical localization phenomena have been invoked as responsible of feedback mechanisms in laser action[1-2].

In this work, we report chaotic laser action in complex fluids (liquid crystals doped with gain functionalized plasmonic nanostructures), driven towards states of increasing stochasticity generated by electro-convective turbulence. We will discuss how the fractal fragmentation of dynamic domains in different turbulent regimes leads to excitation of low-threshold lasing modes that exhibit spectral and temporal characteristics of a chaotic laser oscillator. Another striking aspect of this work is related to the the gain-plasmon interplay in nanoparticle dispersed liquid crystalline materials, where a resonant energy transfer process occur during optical excitation [3-5]. These results shed some new light about the plasmonic control of the modes selection mechanism, since only some of the modes coupled to the plasmon states survive the lasing modes competition effect. Hence, plasmonic resonances and light localization processes owing to intense recurrent dynamical scattering are behind a reconfigurable dynamic laser, characterized by external control of turbulent processes occurring in dynamic scattering regimes.

References:

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Photomobile Polymer Materials: Structures and Functions

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Crosslinked liquid-crystalline polymers (CLCPs) are a class of materials that show macroscopic deformation in response to actinic light [1]. These materials contain aligned mesogenic units as well as photochromic moieties with a crosslinked structure, and deform reversibly upon exposure to actinic light, resulting from reversible photochromic reactions of the photoresponsive group. This photochemical reaction results in photoinduced phase transition or reduction in order parameters of mesogens [2], leading to a subsequent anisotropic deformation thanks to a strong coupling between the molecular order and the crosslinked polymer structures [3,4]. CLCPs as photomobile polymer materials have been intensively investigated due to their large photomechanical effects, which have enabled the fabrication of unique devices such as rotors [5], cilia [6], lenses [7], inch worm [8] and robotic arms [9].

Crosslinking in CLCPs is usually formed by covalent bonds, which produces insoluble samples. Crosslinking with non-covalent bonds may lead to a better processing of CLCPs. We used low-molecular-weight crosslinkers with hydrogen-bond acceptors to form crosslinking among polymers bearing hydrogen-bond donors by hydrogen bonding [10]. The film showed bending upon exposure to UV light and the bent film reverted to the initial state by irradiation with visible light just as the covalently crosslinked CLCPs. The LCP film crosslinked by hydrogen bonding was soluble in THF, enabling recovery, reuse and recycle of the starting materials. However, they are not mechanically stable enough for various applications. We prepared azobenzene LC polymer fibers, crosslinked by hydrogen bonding, containing chemically modified single-walled carbon nanotubes (SWNTs) as a filler (Figure 1), which exhibit reversible bending upon exposure to actinic light. The tensile stress and mechanical force generated by irradiation with UV light much increased by incorporation of a small amount of SWNTs, which is quite advantageous in various applications of these materials [11].

References


Figure 1. CLCP with chemically modified SWNTs
Orientational order parameters for low-symmetry liquid crystals

Stefano Turzi


Nematic liquid crystals are usually assumed to have uniaxial symmetry. However, many real mesogens do not possess such symmetry. It is therefore natural, and possibly important for applications, to extend the theories of liquid crystals to lower molecular and phase symmetries.

Since 1970, when Marvin Freiser of IBM predicted that molecules possessing D_{2h} symmetry could form a biaxial nematic phase [1], chemists have been attempting to synthesize such a liquid crystal. While lyotropic biaxial phases were found, a thermotropic phase proved more difficult to create. In 2004 there has been the experimental claim that bent-core molecules may form the elusive biaxial nematic phase. Since then, interest in biaxial phases has increased significantly.

However, the extensions of the existing theories to lower symmetries are far from trivial as we try to show during the presentation. In particular, we only explore some recent developments in the theory of low-symmetry nematics [2]. Namely, we discuss the abstract definition of orientational order parameters in a general setting. These are the building blocks for the construction of molecular-field and Landau theories to describe the phase behaviour of biaxial nematics (D_{2h}) and C_{2h}-nematics.

Figure 1. A sketch of the idealized molecule with D_{2h} point group symmetry. The unit vectors \( \mathbf{l}_x \), \( \mathbf{l}_y \), and \( \mathbf{l}_z \) represent the laboratory axes; \( \mathbf{m}_x \), \( \mathbf{m}_y \), and \( \mathbf{m}_z \) represent the molecular axes. The Euler angles \( \alpha \), \( \beta \), and \( \gamma \) are also shown.

SICL-JLCS WORKSHOP
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POSTERS
Macroscopic Order in a Nematic Liquid Crystal: Perturbation by Spontaneous Director Fluctuations

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The anisotropic nature of liquid crystalline materials is commonly defined by the presence of a single director. This can be manipulated by external factors including homogeneous electric and magnetic as well as inhomogeneous surface fields. It is therefore of prime importance to understand the alignment of the nematic director by either a magnetic and/or an electric field by careful evaluation of the hydrodynamic processes under both equilibrium and non-equilibrium conditions [1]. Deuterium nuclear magnetic resonance (DNMR) spectroscopy has been used to investigate the static [2,3] and dynamic [4] phenomena. Here the director is aligned by the magnetic field of the spectrometer and the application of an electric field produces a non-equilibrium state resulting in rotation of the director. This powerful technique has proved to be especially important for the investigation of director alignment in liquid crystals.

We report on the study of the anomalous director distribution, observed and predicted, during the director reorientation in a nematic liquid crystal film subject to near orthogonal magnetic and electric fields. Time-resolved DNMR spectroscopy has been employed to investigate the homogeneous field-induced director dynamics. This technique has the advantage of being able to explore the director distribution during the electric field-induced rotation of the director. Our time-resolved NMR experiments have revealed a surprising result that the alignment of the director can pass through a series of non-uniform states. This is especially true when the angle between the two fields approaches 90°. The macroscopic order has been perturbed, although the initial and final states of the director appear to be essentially uniform. However, the initial state does have a profound influence on the uniformity of the director in the intermediate states.

The spectra observed in such experiments can be accounted for with the simple assumption that at the end of the magnetic preparation time the director is not uniformly aligned. As a consequence when the two fields are almost orthogonal the different regions associated with the initial director distribution move at significantly different rates thus enhancing the non-uniformity in the director distribution. Those regions are initiated by the thermal director fluctuation.

References

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ESR characterization of BaTiO₃ ferroelectric nanoparticles suspended in a nematic liquid crystal

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The effects of suspending ferroelectric nanoparticles in a highly ordered, commercial nematic liquid crystal (LC) have been studied using the EPR spin probe technique.

Dilute suspensions of ferroelectric nanosized particles in a nematic liquid crystal (LC) have been reported to display interesting properties that can be used to improve the LC technology [1-4]. On the one hand, the presence of a well dispersed, small amount (0.1 – 1 %) of these nanoparticles does not induce any considerable LC director deformation so that the LC colloid behaves optically as a pure LC [1]. On the other, the dispersion can modify the nematic-isotropic transition temperature, increase the degree of nematic order, enhance, due to the permanent spontaneous polarization of the particle's material, the local dielectric anisotropy, and the sensitivity to an applied electric field, consequently improving the rate of the field-induced director reorientation. Practically, these dispersions are a way to combine the advantages of nematics (such as the ease of alignment) and the electro-optical response, typical of ferroelectric LCs [2,3,5,6].

Here, the ESR spin probe technique, which has already been successfully applied to characterize other complex liquid crystalline systems [7,8], was employed to determine nematic-isotropic transition temperatures, modifications in the nematic director configuration and local molecular order and dynamics of a 0.5% and a 1% dispersion of BaTiO₃ ferroelectric nanoparticles in the BL038 nematic LC. Differently from what is reported in literature, at increasing nanoparticle concentration the transition shifts to lower temperatures by a few kelvin, and the nematic order shows a small decrease accompanied by no substantial alteration of the reorientational dynamics.

References:

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Molecular Organization of Nematic Liquid Crystals Between Concentric Cylinders: Role of the Elastic Anisotropy

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Lattice simulations where a small cluster of neighbouring molecules is represented simply by a head-less vector (“spin”) have been employed in investigating orientational properties of liquid crystals (LC) since the pioneering work of Lebwohl and Lasher [1]. Simple lattice models are particularly useful for the investigation of confined systems [2] and complex geometries, where the analytical treatment with the elastic theory may be prohibitive and sometimes has to be restricted to a few approximate situations [3]. In these cases, potentially relevant from the applicative point of view, lattice simulations employing suitable chosen potentials are helpful and can be implemented in a very efficient way [4]. Likewise, the study of defects is particularly suitable to being attacked by computer simulations [5].

The aim of the present paper is to use Monte Carlo simulations to investigate the role of the elastic anisotropy on the spontaneous deformations of nematic liquid crystals trapped between concentric cylinders [6-9]. Strong anchoring and homeotropic orientation, parallel to the radial direction, are implemented at the confining surfaces. The elastic anisotropy is taken into account in the bulk interactions by using the pair potential introduced by Grunh and Hess [10] and parametrized by Romano and Luckhurst, the so-called GHRL potential [11]. In the case of equal elastic constants, a small, but appreciable, deformation in the Z direction is observed, while when the values of $K_{11}/K_{33}$ if $K_{22}=K_{33}$ are low enough all the spins in the bulk follow the orientation imposed by the surfaces. For larger values of $K_{11}/K_{33}$ spontaneous deformations, perpendicular to the polar plane, increase significantly. Our findings indicate that the onset of these deformations also depends on the ratio $K_{22}/K_{33}$ and on the radius of the cylindrical surfaces. Although expected from the elastic theory, no tangential component of the deformations was observed in the simulations for the set of parameters analyzed.

References:
Molecular dynamics simulations of 8CB smectic thin films

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Atomistic computer simulations have been recently shown to be able to predict realistic values for observables such as transition temperatures, orientational order parameters, etc, particularly for cyanobiphenyls [1]. In a recent work [2] we have extended this investigation to the study of bulk smectics like 4-n-octyl-4′cyanobiphenyl (8CB), showing that layer spacing and positional order parameters can be obtained. Here we wish to show the first application to free standing smectic thin films that have been recently studied in literature [3]. These systems have a high degree of uniformity: the alignment of smectic layers is almost perfect, allowing to build single-domain samples of various thicknesses. This makes them an ideal model for studying low-dimensional fluctuation behaviour and phase transitions. We report the results of atomistic molecular dynamics (MD) simulations of 8CB thin films of 1’500 and 12’000 molecules, with a number of smectic layers ranging from 1 to 10. The MD technique also allowed us to build and characterize films with a non integer number of layers, which are experimentally known to be unstable. The influence of the two vacuum interfaces and the extent of its propagation along the films have been studied in terms of orientational, positional order parameters and layer spacing, and results were compared with theoretical models. We have also characterized the trend of surface tension as a function of the number of layers and determined possible changes in the phase transition sequence with respect to the one of bulk systems.

References

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Thermodynamic and chemical-physical characterization of a binary mixture made of photosensitive and liquid crystalline molecules

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In this study, we have prepared binary mixtures of two rod-like molecule: a photosensitive azobenzene derivative (called J7) and a mesogen forming nematic and smectic A phases (called M11). The interest in these two compounds is related to their use to prepare photo-active liquid crystalline elastomers (LCEs), for optical applications.[1-3] In these LCEs, the relative concentration of these two molecules, used as co-monomers, is crucial to have the desired thermomechanical and optical properties.

Our goal was to build the phase diagram of the binary system J7-M1. Differential calorimetry (DSC) and polarized optical microscopy (POM) were used to characterize the mesophase behavior, and the stability of the mesophases of several J7-M1 mixtures at different molar ratios.

Moreover, ²H NMR spectroscopy of the selectively labelled M11, as it is and in different mixtures of J7-M11, was applied to study the orientational order (Szz) and its trend with the temperature.

References

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Conformational Properties and Orientational Order of a de Vries Liquid Crystal by NMR Spectroscopy

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Solid-state and liquid-state NMR spectroscopic techniques are used to describe at molecular level the behaviour of a de Vries liquid crystal (9HL) at the SmA–SmC* transition, which is characterized by the absence of the layer shrinkage, typical of non-de Vries smectogens. Previous 2H NMR studies [1] on the same smectogen, performed at a different magnetic field provided evidence of the occurrence of a tilt of one of the three phenyl rings, constituting the aromatic core of 9HL, at the SmA–SmC* phase transition. In this work, the study is extended to the whole rigid aromatic core of the 9HL. In particular, the variable temperature behavior of the mesogen studied by 1D 13C NMR cross-polarization (CP) and 2D 1H–13C PDLF (proton-encoded 13C-detected, local field) NMR experiments made possible the characterization of the conformational and orientational properties in the two smectic phases [2].

Figure 1. Simple sketch of the conformational change of the de Vries mesogen 9HL at the SmA-SmC* transition according to NMR investigations. [2]

References

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Spin-spin ILT colloidal morphology analysis and mechanical properties of ultrasound cumb rubber modified bitumen

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Approximately 9 to 10 kg of rubber from tyres per inhabitant and year are currently discarded in the industrialized societies. In addition rutting and fatigue cracking are the major distresses for road pavement performances [1-2]. Therefore, the addition of crumb rubber (CR) in the production of asphalt rubber (AR) mixes for road pavements should be considered as a sustainable technology to transform an unwanted residue into a new bituminous mixture highly resistant to fatigue and fracture [3]. In this process, the wasted rubber needs to be devulcanized (UCRM). In the present work base bitumens interacted with neat crumb and ultrasound devulcanized crumb rubber to produce AR mixes. Nuclear magnetic resonance and Rheology dynamic experiments were functional to investigate the influence of ultrasound treated crumb rubber modifier on the morpho-structure and rheological properties of bitumen binder. The partial devulcanization of the CR by ultrasounds, resulted into enhanced mechanical properties in a wide range of temperatures.

![Figure 1. Time cure tests for neat bitumen (NB), not devulcanized bitumen (NVRB), partially devulcanized rubberized bitumens.](image)

**References**


SICL MEETING

TALKS
We will review our recent work on guided optics plasmonic devices tuneable by means of liquid crystals. Optical attenuators and switches in the Long Range Surface Plasmon Polariton (LRSPP) configurations will be discussed. Then, LRSPP directional couplers in both coplanar and vertical configuration will be presented. The combination of these couplers allows to design multilevel couplers for complex plasmonic circuits and routing.

Figure 1. Schematic illustration of coplanar and vertical directional couplers.

References

Lightwave circuits based on organic materials for optical signal filtering and switching in WDM communication systems

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Periodic structures are suitable to make wavelength selective photonic devices for a large variety of applications ranging from fiber optic communications, biosensors, and lasers. We present our experimental and simulation results on guided wave devices, which can be switched and tuned electrically and optically by light driving signals in micro-and nanostructured device geometries.

Wavelength selectivity is obtained by using either the phenomenon known as whispering gallery modes in microsphere resonator or Bragg diffraction. In both cases we consider organic materials as medium to tune spectral response of the proposed devices.

Figure 1 (Left) shows a tunable electro-optic filter that combines the high Q-factor WGMs of the spherical resonators and the large electro-optic effect of the LCs into a simple filter [1]. The value of the FSR and the quality factor remains unchanged for the various values of the applied voltage. An increase of the applied voltage increases the power coupled with the sphere and increases the on–off ratio of the filter’s insertion loss. Figure 1 (Right) shows a polarization independent all-optical Bragg filter integrated on glass made of ion-exchanged channel waveguides and composite holographic gratings. The filter exhibits a power suppression of more than 20 dB at the Bragg’s wavelength. A tuning range of 6.6 nm is observed by applying an optical pump with a density power of about 1.43W/cm² [2].

NMR in different partially ordered media: a route for structure, order and conformation of small flexible organic compounds

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Over the years NMR spectroscopy in partially ordered media has proved to be a flexible and meaningful tool for dealing with orientational, positional, structural and conformational problems of a variety of small rigid and flexible organic molecules in solution [1]. The methodology is applied here to investigate different flexible bioactive or biomimetic molecules dissolved in both highly and weakly ordering phases. For the first time the strategy is used to probe the conformational distribution of some single- and two-rotor nonsteroidal anti-inflammatory drugs, belonging to the families of salicylates and profens, dissolved in weakly orienting chiral nematic PBLG phases [2]. Starting from homo- and heteronuclear dipolar couplings, difficult to extract in thermotropic solvents for systems of more than 10 spins, the torsional distributions of such molecules can be satisfactorily described by the Additive Potential model combined with the Direct Probability Description of the torsional distribution in terms of Gaussian functions (AP-DPD approach [3]). Moreover, the conformational and orientational study of two stilbenoids displaying cooperative torsions is presented in both a highly and weakly ordering liquid crystalline solvent [4]. This comparative study allows to draw some conclusions on reliability, accuracy and accessibility of desired data in the two phases.

References

Inducing topological defects by curvature and edges for tunable colloidal assembly in nematic liquid crystals.

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Topological defects in nematic liquid crystals can be used attract and trap colloids, both in bulk and at the air-nematic interface [1], and they thus constitute a powerful tool to drive reconfigurable self-assembly. Geometrical cues can be created to control the defects, which are attracted to edges, corners and regions where high-curvature features are present.

Soft and stretchable membranes with arrays of holes are a promising tool to manipulate the liquid crystal defects. The pores, initially round, can be either stretched uniaxially or swollen and deformed during a pattern transformation, similar to that observed in hydrogels [2]. In the pores deforming from round to oval, the creation of high curvature regions changes the nature and the position of the topological defects, also inducing a richer variety of defect structures.

This change in the defects, in turn, can be exploited to tune the trapping of colloidal particles, which are attracted to the poles of the elongated pores. The relative size of pores and particles is another key parameter that determines the trapping efficiency, thus paving the way to a possible method for particle sorting.

Figure 1. a-b) Defect structure in a round (a) and elongated pore (b). c) Colloids trapped near the poles of the elongated pores. Scale-bar is 10 microns.

References
Electrical response of a confined isotropic liquid sample: biological systems and liquid crystals applications


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In a liquid, among the several origins the macroscopic polarization related to an applied field may have, the ionic one stands out, which has special importance for living cells [1]. Monitoring the effective concentration of ions in a living cell is informative about transporters and the actions of the channels in a cell membrane [2]. The interplay between the existence of electrochemical forces, such as the adsorption phenomena involved in the molecular trapping and transport at biomembranes (or at the interface electrode-electrolyte), and external electric fields is responsible for several effects on the ionic distribution in a liquid medium. In biology, this interplay is used in physiological studies of ion-selectivity microelectrodes [2] or even for DNA separation by electrophoresis [3]. These ions diffuse around the cell and an internal electric field distribution across the sample arises. Interestingly, due to the structural resemblance with liquid crystals, studying the diffusion of ions in biological materials and its electrochemical effects has direct application in electro-optical devices made with liquid crystal materials. The asymmetry in the electric field distribution that results when an applied field is combined with the internal field in the charge layer has been used as the mechanism to explain the DC switching of a liquid crystal display [3], many times related to low VHR and image sticking issues. In this work, the dynamical behavior of ions in electrolytic solutions subjected to time dependent external voltage of arbitrary shape is analytically investigated in the framework of the continuum Poisson-Nernst-Planck (PNP) diffusional model. Two different continuity equations have to be solved, assuming there are positive and negative mobile ions in the medium, coupled to the Poisson’s equation governing the electrical potential across the sample. The PNP diffusion model is usually employed for the analysis of the structure and charging kinetics of electrical double layers at interfaces of electrochemical cells under conditions relevant to typical engineering applications. Moreover, these calculations are specially important for recreating the behavior of living cells where, for example, voltage-gated calcium channels respond to membrane depolarization causing potential changes, which means the electrical potential is altered with time depending on the cell’s needs [4,5].

References:

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Azo-dendrimer for Manipulating Microparticles

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Liquid crystal (LC) orientation is specified by interfaces giving an anchoring condition, and is varied by external stimuli such as electric, magnetic, and optical fields. Here, we introduce azo-dendrimer molecules, which spontaneously attach to the interfaces and act as a command surface. Momoi et al. [1] showed that the polyimide-free vertical alignment (VA) for display application can be achieved just by dissolving poly(propyleneimine)-based LC dendrimers [2] in a nematic LC (NLC) mixture. Dendritic azobenzene derivatives (azo-dendrimer) [3] are more interesting, since optical surface manipulation (command surface) is possible through photo-induced $trans$-$to$-$cis$ isomerization. Actually, some of the present authors have already reported the usefulness of the azo-dendrimer for optical devices [4,5]. In the last decades much attention has been devoted to the study of micro-/nano-sized particles, particularly for optically controlling or manipulating the structures for new applications. Here, we report two new systems for azo-dendrimer application; (1) microspheres in nematic matrix and (2) microrods in nematic matrix. In both systems, the azo-dendrimers are spontaneously adsorbed at the interfaces between the particles and the matrix just by dissolving a small amount of dendrimer (0.1-0.3 wt%) into NLC materials.

It is well known that many kinds of topological defects, such as hyperbolic hedgehog defects, Saturn rings, and boojums, emerge around a microparticle situated in an oriented NLC field. The manipulation of such defect structures is possible by applying an electric or magnetic fields. However, the surface molecular manipulation cannot be made using such field application. In our present system, the surface molecular orientation can be changed between perpendicular and parallel with respect to the interface by on and off of the UV irradiation. In our system (1), we originally observed a hedgehog defect or a Saturn ring perpendicular to the rubbing direction. Upon UV irradiation, the defect structure changes to a boojum because of the anchoring condition change in the particle surface by UV light irradiation. Our system (2) is more interesting. Depending on the angle of rod with respect to the nematic director field, the local director fields around the rod are mirror symmetric or inversion symmetric, which induce the preferential reorientation of surface LC molecules upon $trans$ to $cis$ photoisomerization. This triggers dynamic motion of rods such as rotation and translation. We will show real-time movies of such dynamic motions.

References
Molecular organisation in nematic liquid crystals close to a solid surface

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Many phenomena take place at the interface between two or more materials. For instance, in organic field-effect transistors, the first few molecular layers of the semiconductor supported on a dielectric substrate account almost entirely for the macroscopic drain-source current of the resulting device [1]. In addition to that, the charge transport is also affected by the morphology and the molecular packing of the active layer. In Liquid Crystal Displays (LCD) surface alignment of the mesogens and anchoring is a key property, still treated in an empirical way that has not, until very recently, been predicted by modelling and computer simulations [2].

Given the importance that surfaces have in affecting the properties of an overlying material, we present here a detailed characterisation of the morphology and structural properties of a common nematic liquid crystal (LC), 5CB, supported over various substrates of technological significance [2,3]. We modelled the LC/substrate interface with atomistic molecular dynamics simulations, and found that the surface ordering of the LC is influenced by the magnitude of the anchoring energy and the morphology of the substrate. We found that the molecular organisation of the LC changes in response to the chemical composition of the surface, its morphology and roughness. The predicting power of the present methodology allows us to determine the molecular organisation of a given material without any a priori knowledge, as it is based only on the accurate representation of its components.

Figure 1. Lateral view of two films of 2000 5CB molecules supported on crystal and amorphous SiO2 at 300K. Molecules are colour coded according to their orientation with respect to the surface, ranging from blue (perpendicular) to white (parallel).

References


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Visual micro-thermometers for nanoparticles photo-thermal conversion

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We present a novel method to calibrate the light to heat conversion in an aqueous fluid containing nanoparticles. Accurate control of light and heat is of dramatic importance in many fields of science and metal nanoparticles have acquired an increased importance as means to address heat in very small areas when irradiated with an intense light\textsuperscript{[1,2]}. The proposed method enables to measure the temperature in the environment surrounding nanoparticles, as a function of the exposure time to laser radiation, exploiting the properties of thermochromic cholesteric liquid crystals\textsuperscript{[3]}. This method overcomes the problems of miscibility of nanoparticles in liquid crystals, provides temperature reading at the microscale, since the cholesteric liquid crystal is confined in microdroplets, and it is sensitive to a temperature variation, 28°C-49°C, suitable for biological applications. 

In the figure below the colored trace left in the material after switching off the laser beam is shown.

References
Optical trapping of chiral microresonator

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We perform experimental and theoretical investigations of the simultaneous optical trapping and rotation of spherulite-like chiral microparticles [1,2]. The coupling of linear and angular momentum, mediated by the light spin and the microparticles chiral reflective properties, allows for fine tuning of chirality-induced optical forces and torques. The outcomes offer novel tools for optomechanics, optical sorting and sensing, and optofluidics.

Figure 1. Chiral microresonators. (a) Reflection R from a chiral layer with pitch p and variable thickness, d. (b) Transmission spectrum of a CLC film between two glass substrates with planar texture for linearly polarized light. (c) Sketch of a polymeric particle with spherulite-like configuration of the helical structure. (d) Optical microscope image of the particle between crossed polarizers. (e) SEM image of a half particle showing the “onion-like” structure.

References

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Ellipsometric study of nematic alignment on Silicon Oxides for displays

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Vertical Alignment Nematics (VANs) displays are a form of LCDs in which the liquid crystals naturally align vertically to the glass substrates. In spite of their name, the liquid crystal (LC) director is never exactly vertical, rather it always show a small angle with the normal to the sample plane called tilt that may vary throughout the cell bulk. Its values are ultimately determined by the pretilt, defined as the tilt angle on the surfaces in the absence of voltage. The control of tilt angle distribution inside VAN LC thin films is essential for many applications [1]. Higher pretilts lead to faster displays, because the delay time of the dynamic response decreases. However, increasing the pretilt the quality of the dark state is reduced, for birefringence of the off state increases accordingly. Thus a delicate balance between delay time and contrast has to be sought in the manufacturing of VAN displays. A fine control of the pretilt is crucial for VAN displays performance optimization.

With this aim, we have investigated, by means of variable angle spectroscopic ellipsometry, the pretilt angle in silicon oxides alignment surfaces, focusing on SiOx and SiO2. Those vertical alignment layers had been realized by thermal evaporation. Changing the deposition angle it is possible to control the pretilt angle. The director profile inside the sample was inferred by reflection and transmission ellipsometric measurements.

Pretilt measurements were made using an ellipsometric technique, based on recording changes in the state of polarization when a beam light impinges the surface [2]. This technique allowed measuring pretilt angle of the liquid crystal molecules placed next to the SiOx or SiO2 surfaces with more accuracy than on typical methods (especially for very low pretilt angles). The full comparative study of VANs pretilt angles on SiOx and SiO2 layers and their influence over electrooptic response will be presented.

References
Localized plasmon resonance (LPR) of noble metal nanoparticles (MNPs) opens up a new horizon for nanoscale conversion of light into heat. Due to the electron-electron scattering and the electron-phonon coupling associated with the LPR effect, the strong electric field generated around the MNPs is converted into heat and the MNPs behave as nanosources of heat. An important challenge is represented by the ability of measuring temperature variation at the surface of the MNPs under optical illumination, since the nano-localized the temperature variation is the most important parameter for applications ranging from nanomedicine to photonics. Investigation of the heat transport mechanism, from the heated MNPs to their surrounding medium, is a fundamental step in realizing nano-localized sources of heat for applications in nanotechnology and thermal-based therapies. In this framework, we have advanced a breakthrough in monitoring nanoscale temperature variations by combining capabilities of short pitch liquid crystalline compounds and MNPs. In particular, we have shown that a very interesting class of NPs is represented by gold nanorods (GNRs) which have two LPRs, namely transverse and longitudinal, which can be promptly tuned from visible to NIR, by changing the particle geometry [1]. By exploiting the selective reflection of the cholesteric liquid crystal, we have developed [2, 3, 4] a nanoscale thermometer suitable for real time and high sensitivity measurement of the localized temperature around GNRs under a suitable (resonant) and water transparent (NIR) optical illumination.

References


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Alignment of chromonic molecules

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We report our latest studies on the alignment of chromonic liquid crystals, a special class of molecules which recently attracted the attention of researchers especially for their biocompatibility. Lyotropic Chromonic Liquid Crystals (LCLCs) are water-based systems consisting of planar molecules, that present either a nematic phase and a two-dimensional crystalline order (columnar phase) increasing the concentration.

We focused our attention on the alignment of the liquid crystals phases of two chromonic compounds: disodium cromoglycate (DSCG) and guanosine derivatives.

Nematic phase of the first compound was aligned in both planar and hometropic configurations exploiting the surface properties of the alignment layers. We tested hydrophilic and hydrophobic amorphous surfaces obtaining stable-in-time alignments.

For guanosine derivatives LC phases, the planar alignment was generally hindered by surface morphology (for amorphous substrates) or by the formation of superstructures in solution, that were partially aligned on a scale of 20 microns.

A stable in time homeotropic alignment of guanosine LC phases has been obtained using the surface properties of the alignment layer, without the application of an external field. However, according to the concentration and/or the addition of salts to guanosine LC solution, the homeotropic alignment coexisted with the presence of metastable guanosine vesicles.

In both cases, the alignment behaviour was influenced by the addition of salts and concentration of guanosine in solution.

References


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Order reconstruction in turbulent nematics

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Calamitic nematics are usually described in terms of uniaxial order. Experiencing strong frustrations, they undergo a uniaxial to biaxial order transition known as order reconstruction, which has been largely investigated for quasi-static systems [1,2]. We present two experimental evidences that order reconstruction is the process responsible for defect generation at the transition occurring in the turbulent electro-hydrodynamics of nematics. In contrast to isotropic fluids, highly forced turbulent nematics present a transition between two regimes, known as Dynamic Scattering Mode 1 (DSM1) and Dynamic Scattering Mode 2 (DSM2) because they strongly scatters light [3]. DSM2 is characterized by high density of topological defects. First, we show how to control the transition threshold by varying the material biaxial coherence length. Second, we report observations of changes of textural topology due to the transition, which we visualize through the orientation of Kapustin-Williams stripes [fig.1]. Finally, we show a novel transition obtained in an analogous system leading to the suppression of turbulence. The transition occurs as an asymmetric nucleation, where nuclei expand through the propagation of a defect line. As in the DSM1-DSM2 one, this transition leads to changes of textural topology that we show using again the stripe orientation technique.

Figure 1. Two different topologies observed as a result of the DSM1-DSM2 transition. (a, b) Relaxation of a region in which DSM2 was developed (crossed polarizers). (c) Kapustin-Williams stripes perpendicular to each other showing the existence of a \(\pi\)-twisted configuration. Cell thickness \(d=100\mu\text{m}\). Voltage switched-off at \(t=0\)s. (d) Strip of paper stuck at its ends as an analogue of order reconstruction. If the strip is cut in two parts, then one part is twisted and reconnected to the other, the whole strip will be twisted. The strip will never recover the initial configuration by simple elastic deformations. Order reconstruction plays the role of cutting and reconnecting the strip, while a disclination can be thought as the part of the strip at which the order reconstruction occurs.

References
Translational Self-Diffusion in Liquid Crystals by means of NMR Diffusometry: Recent advancements

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NMR diffusometry[1] is nowadays a well established technique to investigate translational diffusion processes in thermotropic liquid crystalline phases[2] and recently, the diffusional behaviour of chiral smectic phases with different clinicity, such as the ferroelectric and antiferroelectric has been successfully measured[3,4]. In this presentation we report novel investigations of translational self-diffusion in smectic phases formed by ionic liquid mesogens based on 1-dodecyl-3-methyl-imidazolium cation (C12-MIM) with two different counter ions (C12-MIMCl and C12-MIMBF4) and nematic phases of a 1,3,4 oxadiazole-based bent-core nematogen [5].

References


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