International School of Liquid Crystals
18th Course

"Liquid crystal nanostructures and self-assembling: from organic electronics to metamaterials"

2nd School of the Italian Liquid Crystal Society

***E. Majorana* Centre for Scientific Culture, Erice (Italy)**
Erice, 3 -10 July 2011

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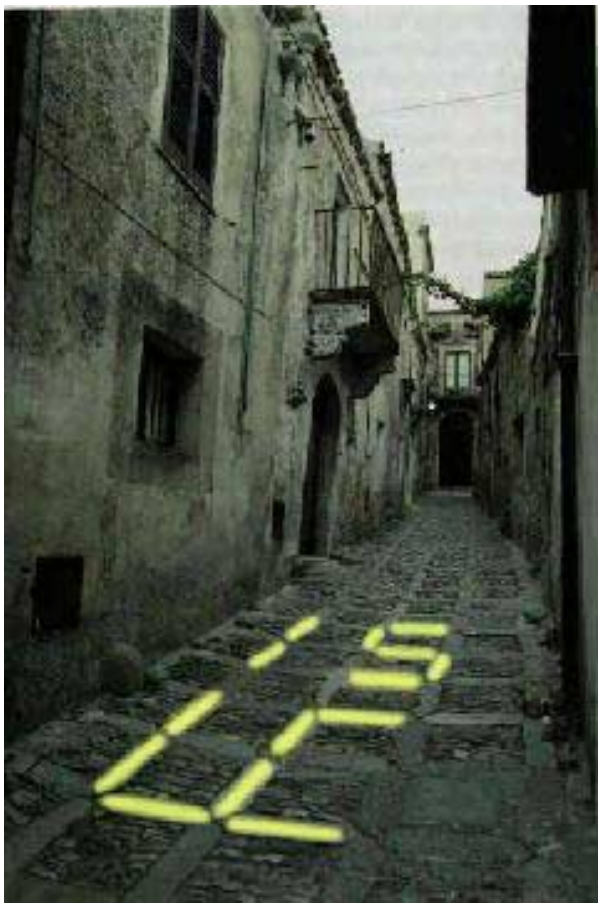

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All-optical devices based on photosensitive liquid crystals

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We present our recent experimental and simulation results on guided wave devices which can be switched and tuned by light driving signals. We will show different waveguide structures both on glass and silicon substrates [1] using liquid crystals as core using light signals whose power in the order of few mW to control propagation. Preliminary results using azo-dye doped liquid crystals demonstrate a further reduction of driving power. Silicon and glass based devices will be discussed and compared. All-optical tunable filters can also be obtained by using photosensitive composite materials. Recent experimental findings will be presented on an integrated optic filter, which combines the simple and low cost ion-exchange waveguide technology with a composite LC methyl red (MR) azo-dye photosensitive compound to obtain full optical tuneability. The structure of the integrated optical filter recalls a previous POLICRYPS based electro-optic tuneable filter [2]. The prototype showed a pass-band with more than 20 dB signal suppression at the Bragg wavelength with a bandwidth of the transmitted notch of about 3 nm. A tuning range of 6.6 nm was observed by applying a pump signal of 45 mW. Full consistency between experiment and simulation results was found. The measured shift is nearly double from previous results achieved in electro-optically tunable POLICRYPS based filters, because of the nematic liquid crystals methyl red properties. These devices can trigger the development of a new generation of low power, compact and low cost all-optical components for next generation fiber optic telecom and sensor systems.

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Acknowledgment: Effort sponsored by the Air Force Office of Scientific Research, Air Force Material Command, USAF, under grant number FA8655-10-1-3070.

Planar Steering of Light-Induced Waveguides via Voltage Controlled Interface

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We propose a novel device for the electro-optical steering of light-induced waveguides realized in nematic liquid crystals (NLC). The light-induced waveguides are formed via optical spatial solitons, self-confined waves at mW powers thanks to the reorientational nonlinearity.[1-4] Using both the large electro-optic response and the high anisotropy of NLC [4-5], we can induce discontinuities as large as 0.2 in the refractive index distribution by means of modest voltage biases, permitting beam steering as large as 70°. In particular, we employ comb electrodes with fingers parallel to the light propagation direction (Figure 1). [2] The low-frequency electric field acts directly on the molecular director in proximity of the NLC-glass interface, with perturbation propagating across the whole NLC thickness owing to intermolecular forces: the cell effectively behaves as a planar cell with rubbing (anchoring) angle determined by the applied bias. [2] If two series of comb-electrodes with different applied voltages are combined with a common ground contact (Figure 1), it is possible to create an interface in the cell mid-plane, with width ruled by the cell thickness *L* and with an overall jump on the dielectric properties (index) ruled by voltages. The symmetry in the electrode configuration allows the in-plane rotation of the NLC molecules in the vicinity of the mid-plane, thus reducing the detrimental effects of out-of-plane beam dynamics and maximizing the available step in refractive index. The span of the output angle can be maximized by designing the device (beam incidence angle, rubbing angle, cell thickness *L* large enough to get adiabatic changes at the interface) as to encompass both total internal reflection and refraction when the two biases are applied. The results discussed hereby are an important step forward in the design and realization of all-optical communication systems.

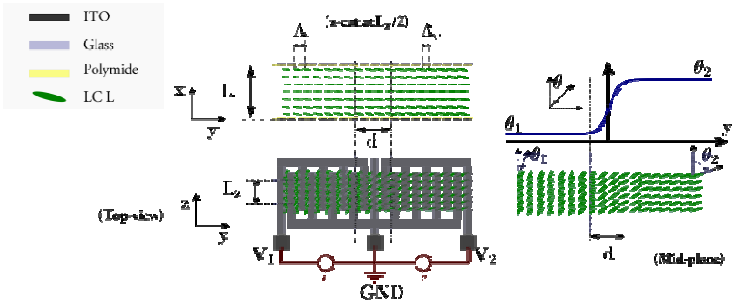

Figure 1: Sketch of the signal steering device.

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On the effects of uniaxial and biaxial nanoparticles on the molecular organization of nematic fluids

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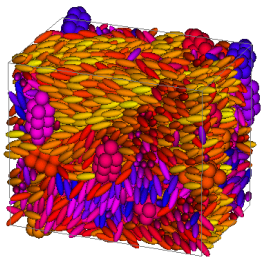
Recent studies of liquid crystals doped with nanoparticles have given rise to a number of novel practical applications [1-3] and pointed the way towards the possibility of improving the physical and electro-optical properties of liquid crystals. Enhancement in the electro-optical properties of liquid crystals is dependent on the size, type, concentration and intrinsic characteristic of the nanoparticles. For example, due to the large permanent dipole moments, ferroelectric nanoparticles could induce realignment of neighbouring liquid crystal molecules, thereby increasing the order parameter and lowering the threshold voltage [1-3].

Here we present a simple molecular level modeling of nanoparticles and a Monte Carlo simulation study of their effect on the order and the molecular organization of a nematic liquid crystal they are suspended in (see figure).



More specifically, nanoparticles, either of uniaxial or biaxial shape, have been modeled as a collection of spherical Lennard-Jones sites, while the mesogens are represented as Gay-Berne ellipsoids [4].

Simulations have been performed at different concentration of nanoparticles, anchoring strength and temperatures in order to monitor the changes induced on the equilibrium phases of the systems [5].

Support to this work from EU-STREP project "Biaxial Nematic Devices "(BIND) FP7-216025 is gratefully acknowledged.

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LC orientation control inside capillaries

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Abstract

Photonic crystal fibers (PCFs) have attracted considerable interest in the last decade and their combination with liquid crystals enables an improved control of PCF optical properties. Thermal, electrical and optical tuning of photonic liquid crystal fiber properties can find various potential applications in optical devices [1, 2].

In this paper we present photo and thermally-induced liquid crystal (LC) orientation methods, applying an extra orienting layer which can be adapted for PCFs [3-7]. These methods enable an induced planar or homeotropic boundary conditions for LC material in the capillaries. The experimental results of different orientations of a nematic liquid crystal in capillaries are shown.

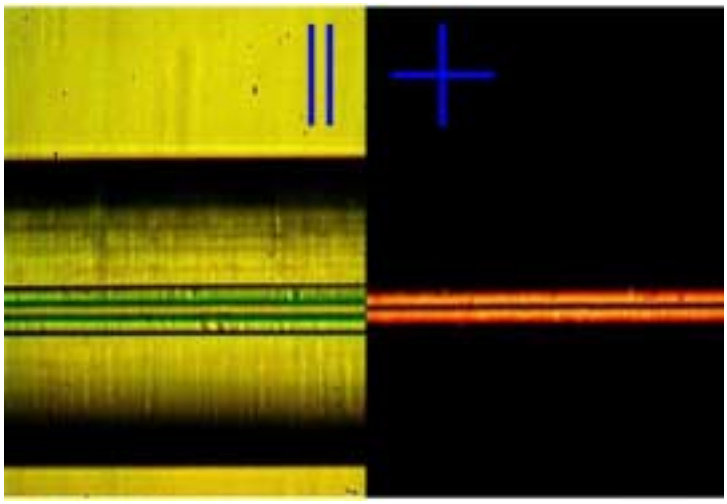

Fig. 1 Escaped radial orientation of nematic LC under polarizing microscope

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Effect of lateral substitution on properties of azobenzene-based photosensitive chiral liquid crystals

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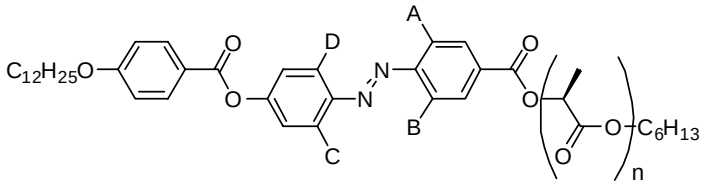
Photosensitive liquid crystals are intensively studied due to their high application potential in photonics. One of the most important types of these materials are based on azobenzene moiety. Its very pure photochemistry is quite crucial for the stability of such photosensitive materials. The principle of their functionality is the photoinduced reversible $E \leftrightarrow Z$ isomerisation of the –N=N– bond, which causes changes in the mesomorphic properties of liquid crystalline materials. The reverse Z → E isomerisation can proceed both photochemically and thermally (relaxation). The relaxation rate is one of the main limiting factors for practical applications of these materials [1, 2]. For the last few years, we have intensively studied some azobenzene-based materials [3, 4]. In this work, we present the effect of lateral substitution of the azobenzene moiety on the relaxation rate, UV spectra and mesomorphic properties.



A, B, C, D = H, Cl, Br, CH_3, n = 1, 2

Non-substituted compound possesses the SmC* - SmA* - TGB_A - N* - BP mesophase sequence. In general, broadening the molecular core by lateral substitution results in disappearance of the blue phase and reduction of the polymorphism and decrease of the phase transition temperatures.
Kinetic measurements showed that the lateral substitution by chlorine, bromine and methyl group, resp., exerts a large effect on relaxation rates and activation parameters. Depending on the molecular structure, *Z*-isomers were stable enough to be separated by column chromatography. In that case the properties of the pure *E*- and *Z*-isomers can be studied separately.

Acknowledgements:
This work was supported by the Czech Science Foundation (projects P204/11/0723 and IAA100100911 and Ministery of School, Youth and Sports of the Czech Republic (from specific university research MSMT No 21/2011).

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Nematic braids: classification of knotted and linked disclination lines

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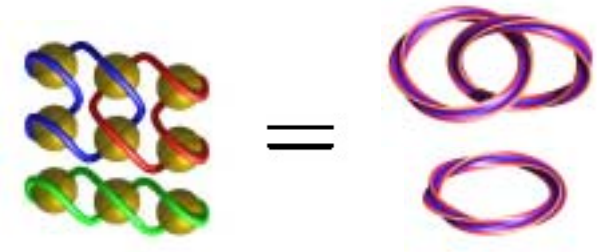
Experiments with nematic braids show rich variety of knotted and linked disclination lines that can be rewired by optical manipulation [1,2,3]. These structures also exhibit symmetry, ordering and topological diversity, allowing us to combine different classification tools and create a unified description for entire classes of different structures.

We demonstrate the use of tetrahedral rewirings for classification of entangled states in different geometries. We use the self-linking number [4,5], a topological invariant which counts the number of turns of the director field profile for a single loop. This invariant can be extended to the linking matrix (L) which summarizes self-linking numbers of multiple loops, together with their pairwise linking numbers. Combining this with mathematical classification of knots and links [6], we obtain complete topological information for all possible -1/2 disclination loop structures in a chosen geometry.

We focus on entangled structures that occur in rectangular 2D colloidal lattices in twisted nematic cell [2]. With the use of geometric description given by the formalism of tetrahedral rotations [4], we generate idealized zero-twist parametrizations of the structures. Using their uniform periodic structure, we automate the classification by calculating the linking matrix and Jones polynomial. We present different topological structures found on the same colloidal lattice in diagrams that reflect hierarchical structure of the configuration space.



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Structural and conformational investigation of stilbene derivatives as solutes in nematic liquid crystalline solvents

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Molecules with internal bond rotational possibilities usually adopt a single conformation in the solid state, but have a conformational distribution in liquids and gases. The structure in solid state can be obtained with high precision by x-ray or neutron diffraction, while in gaseous state several experimental methods and theoretical approaches are commonly used. For the liquid state, which chemically and biologically is generally the most interesting phase, the available experimental methods are of limited applicability. In this context, NMR spectroscopy in liquid-crystalline solvents (LXNMR) has proved to be a particularly effective and elegant technique to study the conformational distribution of solutes. Analysis of the NMR spectra of flexible molecules in liquid crystalline samples yields many different observables and in particular the partially averaged dipolar couplings, D_{ij}, which are directly related to the structure, orientational order and conformational distribution of the molecules [1].

In this contribution we focus our attention to a molecular determination and conformational equilibrium investigation of stilbene derivatives by LXNMR method. A conformational study of stilbene is important because it is the simplest case of linkage of two aromatic rings through a double bond. Stilbene linkage exists in several compounds that show mesogenic properties; trans-stilbene is the smallest member of diphenylpolyenes, a class of compounds with peculiar photophysical and photochemical properties; finally, some stilbene derivatives have estrogenic activity and are commonly employed in hormonal and anticancer therapies.

The proton NMR spectra of two stilbene derivatives, the *trans*-stilbene (12 spin-system) and the (E)-1,2-bis(4-chlorophenyl)ethene (10 spin system), dissolved in the nematic liquid crystal ZLI1132, have been obtained and analyzed to yield two sets of 19 and 12 D_{ij}, respectively. These couplings have been used to investigate the structure of the rings and the ene fragments of the two molecules and the rotational potential about the bonds between the phenyl rings and the central double bond. The AP method combined with direct probability description of the torsional curve has been used to obtain the conformational distribution of the torsional angle ϕ [2]. Preliminary results on both molecules indicate that the NMR data are consistent with a non planar structure, and this evidence is in agreement with several theoretical calculations [3].

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Novel Mesophases Formed by X-Shaped Bolaamphiphiles with Oligo(Phenyleneethinylene) Central Core

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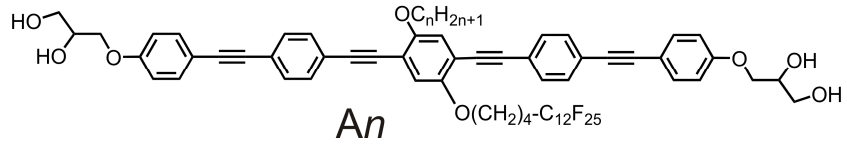
In several studies, the mesophase morphologies of T-shaped bolaamphiphiles with one lateral substituent have been investigated [1]. Such compounds exhibit different types of lamellar and columnar phases. The columnar mesophases represent honeycomb-like arrays of polygonal cylinders. More complex mesophases will be formed, if an additional substituent (R_2), incompatible with the first one (R_1), is attached in lateral position at opposite sides of the rod-like core to give X-shaped bolaamphiphiles [2]. In the recent work, one class of X-shaped bolaamphiphiles have been synthesized (**A*n***). The structure of them is shown below.



One serie of oligo(phenyleneethinylene) derived bolaamphiphiles are reported, where the length of the lateral alkyl chain has been variated, which lead to LC phases with rhombic, square and triangular shape of the cylinder cross section. In addition, continuous phase transitions between different cylinder structures were observed in some cases. The mesophase behaviour of the synthesized compounds was investigated by means of polarization microscopy, differential scanning calorimetry and X-ray scattering and was confirmed by electron density maps calculated from X-ray data and was compared with analogous compounds.

Acknowledgement

This work, as a part of the ESF EUROCORES Programme SONS, project SCALES, was supported by funds from the DFG and the FP6 under contract No. ERAS-CT-2003-989409 and was also supported by funds from the DFG as part of the Forschergruppe FOR 1145.

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Optical manipulation exploiting liquid crystalline systems with holographic tweezers

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We report an investigation of manipulation and trapping capabilities of polarization holographic tweezers, exploiting liquid crystal (LC) droplets in water. LCs represent an interesting challenge in the context of optical trapping, being characterized by anisotropy, viscoelasticity, aggregation and supramolecular configuration flexibility, richness of phenomena related to confined geometries (droplets, thin films). The polarization holography [1], in combination with LC's emulsions demonstrates how polarization gradient offers new capabilities for optical trapping and manipulation. An optical force related to light's polarization can influence optically isotropic particles, while in the case of birefringent particles, this polarization pattern is able to simultaneously exert forces and torques in opposite directions depending on the particle's position. Experiments with LC's emulsions allow verify the expected scenario and make evidence of an unconventional trapping of spinning birefringent particles in circularly polarized fringes [2]. This unusual trapping observed for rotating bipolar nematic droplets has suggested the involvement of the hydrodynamic force, originating from the peculiar optical force field.

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Mesogenic Ni(II) complexes of C_{1h} symmetry forming columnar Col_{hd} phase by dipol-dipol interaction.

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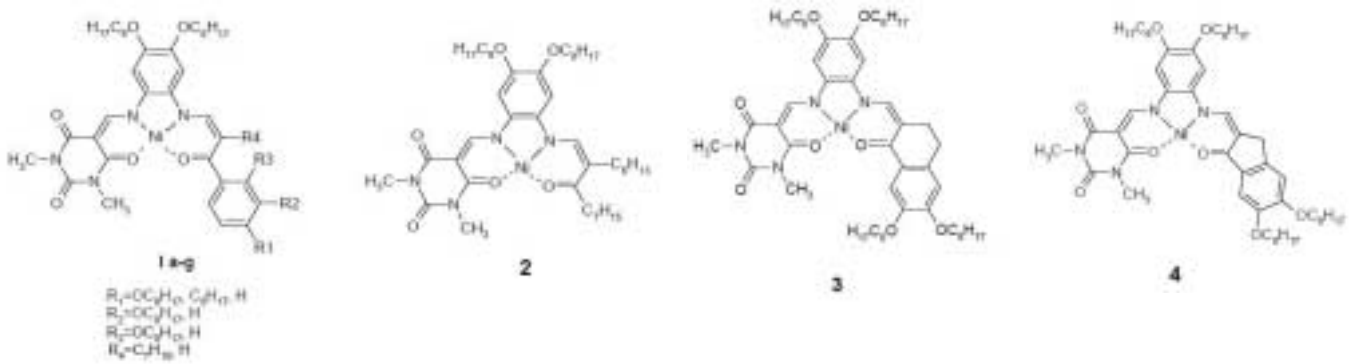
The synthesis and mesogenic properties of tetradental Ni(II) complexes are presented. The described compounds have C_{1h} molecular symmetry as their mesogenic core is constructed from two non-identical chelating fragments: enaminoketone and barbiturylidenomethylenoamine rings. At barbituric ring two short substituents, methyl groups, are attached. In the complexes of **series I** the carbonyl carbon of the enaminoketone group is connected with the phenyl ring, that can have octyloxy chains substituted at *para*, *meta* or *orto* positions (R_1, R_2 or R_3). In the compound **2** the phenyl ring is replaced by heptyl chain and hexyl group is attached at the vinyl carbon (position 2) of the enaminoketone moiety. Compounds **3** and **4** posses in their mesogenic cores rigid indanone or tetralone fragments. All the synthesized complexes exhibit liquid crystalline hexagonal columnar disordered phase (Col_{hd}). The mesophases were identified under polarising microscope examination of liquid crystalline textures and were confirmed by the X-ray studies. Phase transition temperatures and enthalpy changes were determined by calorimetric measurements. The similar complexes having symmetric enaminoketone mesogenic core have much higher clearing temperature and very frequently do not exhibit LC phases or even do form lamellar phases.



Scheme 1 Molecular structure of studied compounds.

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Acknowledgment: Effort sponsored by the Foundation for Polish Science, TEAM/2010-5/4

Cyclopalladated Nile Red metallomesogens: synthesis and properties

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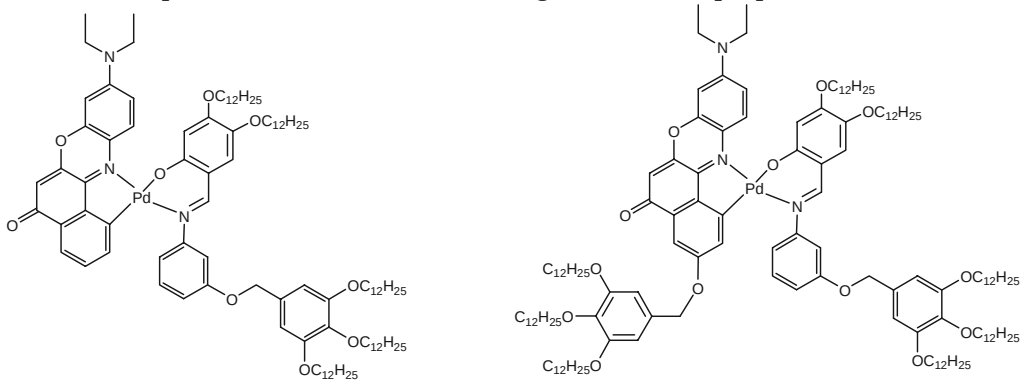
We present the synthesis and the properties of two new cyclopalladated Nile Red discotic complexes embedded to complete the coordination sphere of the Palladium (II) metal centre of an ancillary Schiff Base polysubstituted ligand (see Figure 1) in order to obtain an hemi-disk-like (complex **1**) or a full-disk like (complex **2**) geometries. Cyclopalladated complexes have already been reported for their remarkable properties as photorefractive materials[1] and recently polysubstituted azobenzene based cyclopalladated discotic complexes have been investigated showing photoconduction properties throughout their absorption spectrum range (UV/Vis to NIR).[2] Upon thermal annealing of their discotic mesofase, although limited homeotropic alignment has been observed, an increase of their photoconductivity by one or two order of magnitude has been registered. Using Nile Red dye as a cyclometallated ligand should have several advantages. First, resulting complexes should present higher absorption properties all over the UV-Vis spectrum due to the intrinsic properties of the dye. Moreover, due to the higher rigidity of the aromatic core of Nile Red and its possibility to form intermolecular hydrogen bondings, the mesophase of the resulting complexes should be more stabilized increasing both their temperature range as well as their predisposition to homeotropically self annealed. Prelimiray results obtained for this new class of photoconductive cyclometallated liquid crystals will be presented and discussed through a structure-properties correlation study.



1 **2**

Figure 1: Structure of the synthesized complexes **1** and **2**

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Interaction of Near Field Standing Wave with Metamaterials

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Abstract. Negative Refractive-Index Metamaterials (NRIMs) are exotic composite materials that display properties beyond those available in naturally occurring substances. These materials are artificially structured composites that have the potential to fill the critical voids in the electromagnetic spectrum, where material response is limited and enable the construction of novel devices. They are also called Left-Handed Material (LHM) with simultaneous negative permittivity and negative permeability exhibit reverse electromagnetic properties. Emergence of this new paradigm leading to some very interesting consequences is the subject of this study. It is to prove that the amplitude of evanescent wave on transmission in the forward direction of electromagnetic wave decays exponentially while in the backward direction, it may grow in the LHM having negative refractive index. The Fresnel formulas have been used for the calculation of transmission and reflection coefficient and the amplitude of evanescent wave has been determined. The physical reasoning for negative light refraction is given. It is suggested that the fabrication of left handed materials with the use of nanophotonics may be fruitful for manipulating the light in the nanoscale and fabricating the optical devices on the lines of photonics crystals

Keywords: Left handed materials; metamaterials; negative permittivity and negative permeability.

Order parameter–based entropic sampling to study low probable microstates in liquid crystal systems

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Lattice based Monte Carlo (MC) simulations on liquid crystal (LC) films in the nematic phase have revealed stable existence of qualitatively distinct director structures with essentially the same energy, under otherwise identical macroscopic constraining conditions. Interestingly usual Markov chain MC dynamics guided by energy based Metropolis transition matrix could not connect the microstates of the different director structures, leading to the belief that these sets of microstates could have been separated in the configuration space by non-ergodic regions (within the accepted limitations of such simulations). This aspect was further probed by developing a sampling method which performs a random walk in the configuration space which is uniform with respect to the order parameter, while the system is essentially kept at the same energy. It is quite similar to the so-called entropic sampling performed for uniform energy walks [1], with the difference that the walk is now along the order parameter space (say, S-sampling). This led to the detection of microstates which are at once at the (same) low energy and very low order [2], and these correspond to extremely rare states which are practically inaccessible by the usual canonical sampling methods. The S-sampling thus yields a representative distribution of microstates with respect to the order parameter within the canonical ensemble. In this work we carry out a similar study on a bulk sample in the presence of an external field (based on Lebwohl-Lasher model) with a view to obtaining the spatial functions of orientational correlations of different (very rare) director distributions, within the given equilibrium ensemble.

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A New Method to Compute Chemical Potential

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Abstract

We present a new simulation method to calculate the free energy and the chemical potential of a hard particle system and investigate the isotropic-nematic phase transition. The method relies on the introduction of a parameter dependent potential to smoothly transform between the hard particle system and the corresponding ideal gas. We applied the method to study the phase transition behavior of a square monodispersed platelet system. The equilibrium state was found with an isobaric Monte Carlo (MC) technique. We introduce the parametrized potential to interpolate the system between the ideal gas and the hard particles. After selecting the potential, we performed MC runs, ranging from the ideal gas to the hard particle limit. Through an iterative procedure, we compute the free energy and chemical potential of the square platelet system by evaluating the volume of the phase space attributed to the hard particles. From the obtained normalized pressure-chemical potential plot, we find a sharp coexistence pressure for the system. A comparison of the result obtained by the method with that done by a traditional method will be presented. Our method provides an intuitive approach to investigate the phase transitions of hard particle systems.

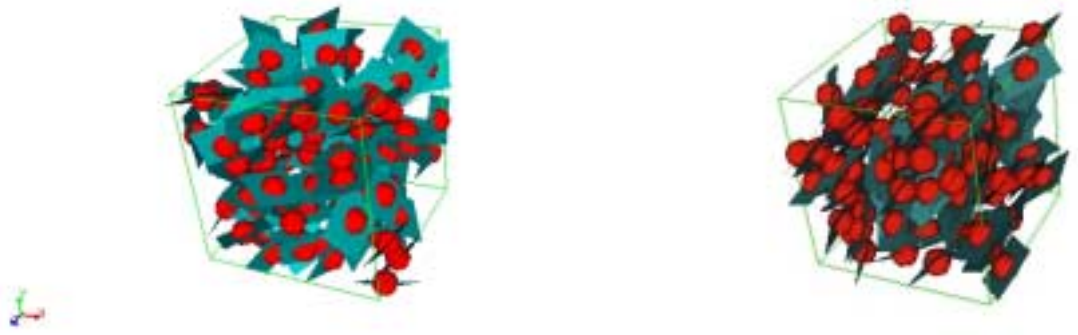

Figure 1: (left) Isotropic phase and (right) Nematic phase of the system of 120 square platelets. Each red ball indicates the center of mass.

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Polarization gratings for real time circular dichroism measurements

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Circular dichroism (CD) spectroscopy is a special technique that provides unique information on chiral molecular structures by measuring their differential absorption with respect to the left and right circular polarization states of light.
We present an original and simple diffractive spectrographic method for CD measurements, which enables real-time acquisition and suppress the artifacts of the conventional CD spectrometers, introduced by anisotropic samples and nonideal optical elements. The method exploits a single liquid crystal based cycloidal optical axis grating, recorded via polarization holography, whose first orders of diffraction have amplitudes that are proportional to the right and left circular polarization components of the light impinging on it. We demonstrate that, using unpolarized white light and the intrinsic spectral selectivity of the grating, the true CD spectrum is evaluated in parallel in the spectral range of interest from the intensities of the two diffraction orders.

Physical properties of TiO_2 nanotubes from DC sputtered Ti films

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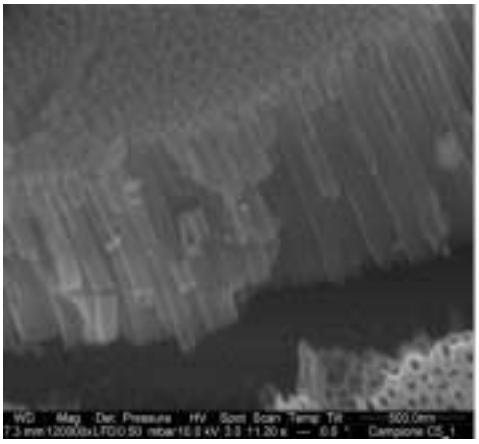
***Abstract*:**
Anodically fabricated TiO_2 nanotube arrays[1] have attracted significant attention in the scientific community because they have proven to be a robust and cost-effective functional material widely investigated in many applications especially those related to energy conversion such as photoelectrochemical water splitting and solar cells. The poster deals with TiO_2 nanotube synthesis from DC sputtered Ti films. In particular, we refer about: 1) anodization process for their growth both on conducting glass and on ITO-coated glass; 2) control over their physical dimensions (pore diameter; tube wall; tube length) by means of anodization parameters such as time, voltage, temperature and electrolyte concentration; 3) measure on their optical properties.



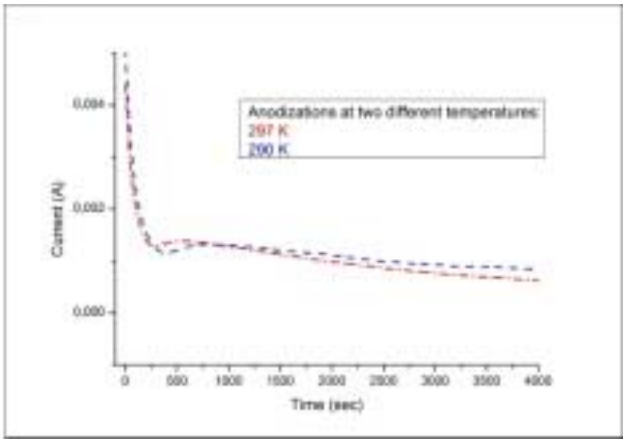


Figure 1 TiO_2 nanotubes from a 500nm Ti sputtered film. Figure 2 Anodization current vs time plots at different temperatures.

Anodization was carried out in a cell with a two electrode setup using a Pt counter electrode. The surface of the Ti sputtered film exposed to the process was about 490 mm^2. An ethylene glycol bath with different ammonium fluoride concentrations was used. Samples were anodized at different temperatures, with different anodization voltages and for different time span. TiO_2 nanotubes with pore diameter in the range 40-80 nm were obtained; Figure n.1 shows 80 nm pore diameter sample. The control about TiO_2 nanotube physical dimensions is a key element to develop applications. Our measures on pore diameter, tube wall and tube length show dependence of these geometric properties on the anodization parameters. Information about the anodization progress can be obtained from the current vs time plots as shown in Figure n. 2. A detailed discussion about the linear[2] dependence on the anodization voltage is given. The electrical properties of the TiO_2 structures were measured by Agilent 4294A Impedence Analyser in the range 40 Hz-110 MHz.

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The smectic phase of 8CB revisited at atomistic resolution

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The n-alkyl cyano biphenyl (nCB) mesogens are probably the most studied and characterized liquid crystalline compounds ever, as well as the paradigmatic case of the nematics employed in displays. The first few mesogenic homologues of the nCB series (n=5-8) possess a nematic phase, while 8CB is the first to show also a smectic phase. The nCB are particularly interesting as test beds for theoretical investigations, given the availability of an enormous number of experimental data with a variety of techniques [1] and have been studied with quantum chemistry [2] and simulation [3-6] methods. In particular, we have recently derived a united atoms force field for nCB homologues, showing that the experimental isotropic-nematic transition temperatures can be reproduced within 4 K thus allowing for a molecular level interpretation of the small odd-even effect along the series [6]. Other properties, like density, orientational order parameters, NMR residual dipolar couplings and static dielectric constants were also reproduced, demonstrating the feasibility of predictive *in silico* modeling of nematics from the molecular structure.
In this work we have extended our Molecular Dynamics (MD) computer simulations to the smectic phase of 8CB. Starting from an isotropic sample made of 750 8CB molecules and gradually cooling it, we have observed the spontaneous onset of the ordered nematic and smectic phases. A comparison between the properties of the simulated system and experimental data, in particular the transition temperatures and the smectic layer spacing [7] as well as orientational order parameters [8], confirmed the reliability of the force field. Moreover, simulations allowed us to identify unambiguously the type of antiparallel arrangement of molecules in the smectic double layer phase.

Support to this work from EU-STREP project "Biaxial Nematic Devices" (BIND) FP7-216025 is gratefully acknowledged.

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Liquid crystal elastomers laser writing for application in microfluidics

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Nowadays, Liquid Crystal Elastomers (LCEs) constitute an interesting approach to their applications in microfluidics. LCEs can include azobenzene units: in the main chain, as cross-linker or disperse in the polymer. Azo dyes have the advantage that are non-toxic and, at less in principle, you can slightly tune their absorption spectrum by adding different functions on the aromatic rings using simple chemical reactions. Usually LCEs are made by polymerization of methylsiloxane monomer backbone with mesogenic biphenyl side-chain units and a cross-linker forming side-chain LCE [1-2]. The same mesogenic biphenyl side-chain units was used in photopolymerization by Sungur et al. without using the siloxane backbone producing a main-chain LCE [3]. We used photopolymerization to obtain LCE and studied it for their application on microfluidics.
A Direct Laser Writing System, using two photon absorption at a wavelength of 780nm is used to polymerize the mixture in the nematic phase. By controlling the focus position with a piezo translation stage, this setup allows the design of microsized structures in 3D like micro channels or tiny actuators.

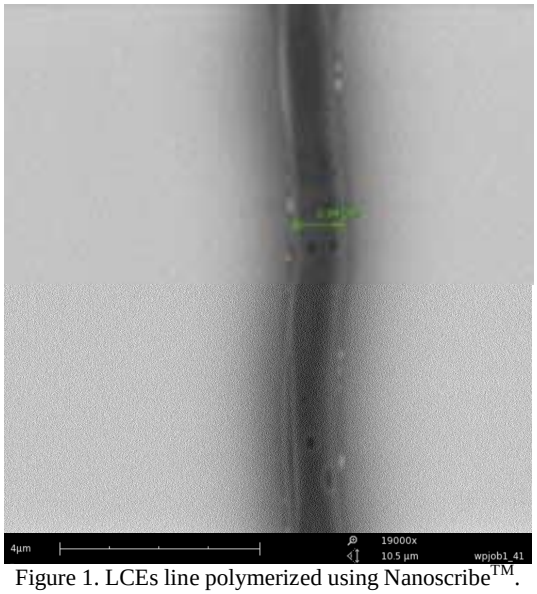

Figure 1. LCEs line polymerized using Nanoscribe™.

Using finite element modeling (FEM) we tried to reproduce some experiment that has been done so far. We studied the light propagation in the material and the induced bending. This movement of the LCE could be used in a microfluidics environment to design a small actuator.

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Freely Suspended Smectic Films in Aqueous Environment

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Smectic liquid crystals easily form thin films which are freely suspended on a solid frame in air. These systems have been thoroughly studied for various purposes such as structural studies of smectic phases, investigating phase transitions in two-dimensional systems, and studying various physical properties of liquid crystals [1].

In the present study, we explore the preparation of freely suspended smectic films in water [2]. A prerequisite is the presence of a surfactant which accumulates at the liquid-crystal/water interface and induces a homeotropic anchoring of the director, so that the smectic layers align parallel to the two film surfaces. The presence of the surfactant might also serve as a handle to tune properties such as the surface tension of the films (which is hardly possible for freely suspended films in air). We study the formation of films in water using different frames and different surfactants, and we focus especially on the thinning behaviour which occurs when the temperature is increased towards the smectic - nematic or smectic - isotropic transition.

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Colloidal entanglement in chiral nematic colloids

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We have experimentally and theoretically studied topological disclination lines around the colloidal particles in π, 2π and 3π twisted chiral doped nematic liquid crystals. By using the laser tweezers, the liquid crystal around the particles was quenched from the isotropic into the nematic phase. We observed the formation of various conformations of entangled defect loops, which form around particles to compensate the distortion in the molecular orientation caused by particle surfaces. In π cell the disclination line is entangled around the single colloidal particle like the figure of eight. In addition to this, more than 17 different entangled colloidal dimers were observed in π cell, which is much richer than in planar and π/2 twisted cells [1] [2]. Propagation of defect loop along the chiral plane and wrapping around the colloidal particle was observed with increasing chirality. Furthermore, most of these structures have been theoretically confirmed by using numerical modelling based on Landau-de Gennes free energy minimisation. The colloidal structures in chiral nematics offer exciting routes for optical applications [3].

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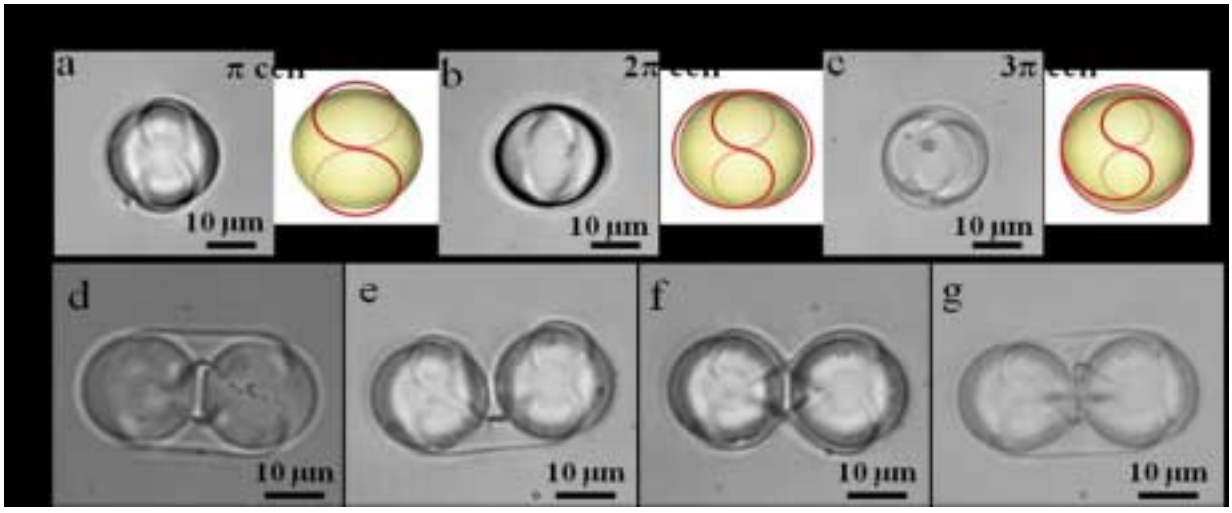

Figure 1. (a-c) Entangled defect loop around the single colloidal particle in a π, 2π and 3π cell and comparison with theoretically calculated structures, (d-g) Entangled colloidal dimers in π cell among many possible structures.

Design of Tunable Apodized linearly Chirped Fiber Bragg Gratings for Broadband Dispersion Compensation

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***Abstract*:**

Nowadays, optical communication systems have very important role in data transferring. In particular, multichannel systems such as Wavelength Division Multiplexing (WDM) and Optical Time Division Multiplexing (OTDM), can send more than one hundred channels simultaneously on the same optical fiber with high bit rates. A commonly used figure of merit for communication systems is the bit rate–distance product, (BL). This BL product and consequently the performance of optical systems can be limited dramatically by dispersion-induced pulse broadening. Because when a broadened pulse arrives to receiver, it is not possible to recognize whether it was 1 or 0. For this reason, some dispersion management schemes have been developed, but most of them have special economical or practical application limitations and problems [1]. For this reason, finding an all optical, fiber based, effective and also economic solution is really important. There are two popular methods to eliminate the dispersion: one is by using a Dispersion Compensating Fiber (DCF), which is better suited to compensate over a wide range of wavelengths. However, it introduces higher loss and additional penalties due to increased non-linearities[2]. Another solution is the insertion of Fiber Bragg grating (FBG) as a dispersion compensator. FBGs are periodic structures that can offer very effective dispersion management solutions because of their low loss insertion properties and also flexible design possibilities [3]. Among different structures of FBGs, chirped fiber Bragg gratings can be used to compress temporally broadened pulses in WDM and Long-Haul systems. In this kind of grating, the resonant frequency is a linear function of the axial position z along the grating and it effectively introduces different delays at different spectral components of the pulse to cause arrive them simultaneously at the fiber output. Figure1 shows how chirped fiber Bragg gratings can be used to remove dispersion effect in WDM systems [4]. However, these structures suffer from ripples in both reflection spectra and time delay. To remove these ripples, apodization technique can be really useful, in which the induced perturbation at reflective index is made non uniform across the grating, resulting in z-dependent reflective index [5]. In addition, applying Liquid Crystal in the structure of grating can help us to design a tunable apodized compensator to achieve the most efficient results.

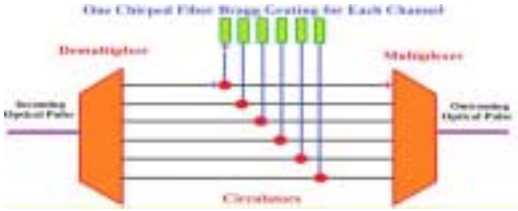

Figure1: Application of Chirped Fiber Bragg Gratins as dispersion Compensator in one WDM system

Here we show how one linear chirped apodized fiber Bragg grating can act as an efficient all optical solution to compensate dispersion of broadband wavelengths. To achieve this goal, we study the effect of variation on different parameters of chirped fiber Bragg grating like length of the grating, modulation depth and chirp variable. In addition, we try to find the appropriate parameters for apodization profiles like Gaussian, Sinc, Raised Cosine, Kaiyser to design a most perfect dispersion compensator. Also, the effect of Liquid Crystal as an additional parameter to control the reflective index of fiber Bragg grating to achieve a more tunable compensator is discussed. Finally, we offer an acceptable tunable structure to compensate dispersion of tens of kilometers of single mode fiber that can be applicable on WDM systems.

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A Computer Simulation of dipolar biaxial nematics

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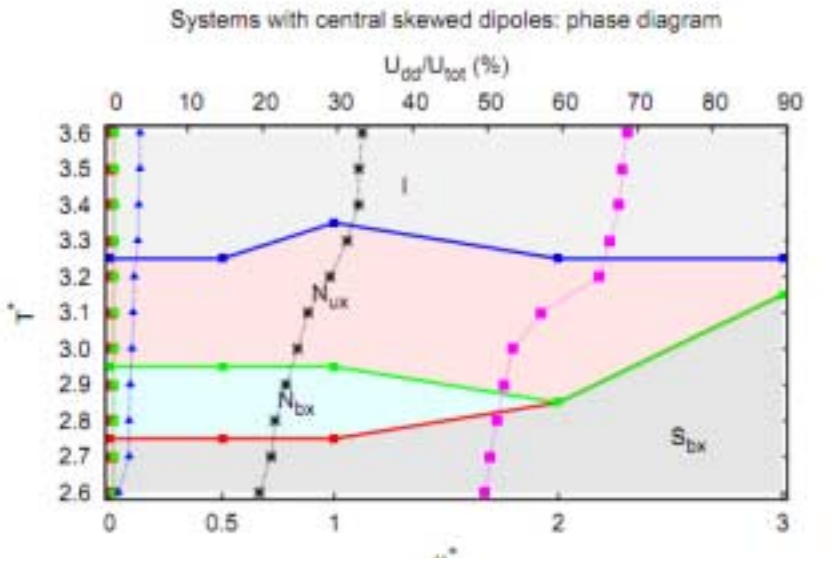
Molecules in biaxial nematic (N_b) liquid crystals (LC) organize along two orthogonal preferred directions (directors). The study of such systems is now of great interest, also in view of their potential applications in a new generation of faster displays [1], where the secondary director is switched.
The aim of our study was to understand properties and phase behaviour of systems of dipolar biaxial Gay-Berne ellipsoids [2] as a function of dipole intensity and orientation. We have simulated various systems composed of 1024 particles with an embedded electric dipole represented by two point charges, always placed in the center of the ellipsoid but with different orientations for each system. We have considered systems characterized by a longitudinal, a transversal, or by a skewed dipole with two different orientations. The dimensionless dipole strength (μ*) was varied increasing from 0.5 up to 3.0, while the temperature ranged from T* = 2.6 to 3.6. We compare the observed behavior with that of a reference system devoid of charges and discuss the effect of dipole strength on phase stability. To assign the correct phase type (see Figure) to every temperature, we have computed the order parameters characteristic of uniaxial and biaxial phases [3], along with other thermodynamical values such as the contribution of the dipolar term to the total energy.
In general, increasing the dipole strength destabilizes the nematic biaxial phase, while stabilizing smectic biaxial phases.



Phase diagram for systems having central skewed dipoles. Dipolar contribution to total energy is also shown: red square are referred to neutral system, green star to system with μ = 0.5,blue circle to system with μ* = 1.0, black triangle to system with μ * =2.0, purple filled circle to system with μ* = 3.0.*

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Modeling of nonlinear beam propagation in chiral nematic liquid crystals

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Chiral nematic liquid crystals are unique materials in nonlinear optics due to their vast reorientational nonlinearity and anisotropy. As the director orientation changes along the structure, modeling of molecules reorientation and light propagation requires vectorial methods. Many work have been already done in this field in linear [1,2] and nonlinear cases [3]. In this work we present three dimensional full-vector beam propagation method derived directly from Maxwell equations combined with exact equations describing director reorientation based on the Frank-Oseen equation with two reorientational angles (tilt and azimuthal). We show light propagation solutions in chiral nematic liquid crystals for different input beam polarization and width. We analyze formation of a soliton-like beam which have been already observed in many experiments [4,5]. Comparison between a single and two reorientational angles solutions is also provided.

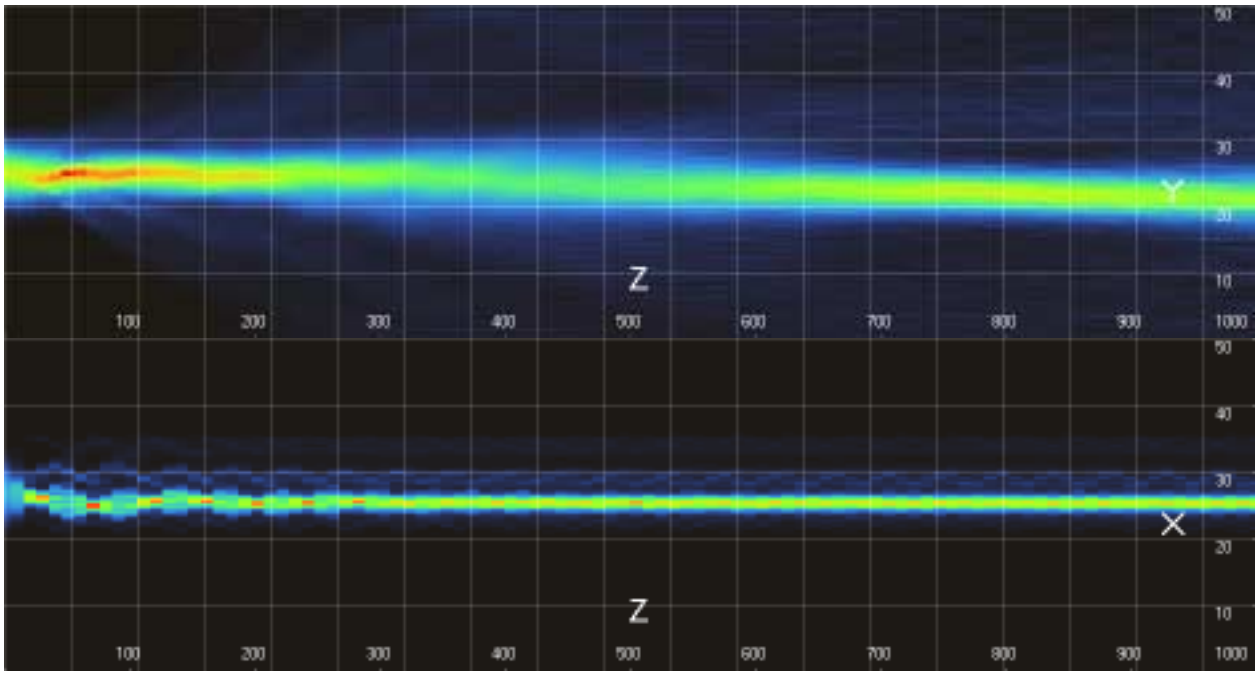

Fig.1 Light propagation solution in chiral nematic liquid crystal cell. Soliton-like beam formation is observed.

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Organic Dyes with Nanorods and Nanoparticles TiO_2 for Solar Cells

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The surface modified titanium oxide nonoparticles of different morphology (spheres and rods) were synthesised. The synthesis of TiO_2 rods (diameter 20 nm, length 1 μm) was conducted by hydrothermal method applying microwaves and using powder TiO_2 as starting material [1]. The TiO_2 spheres (diameter 3.5 nm) are obtained by organic synthesis [2]. Further, TiO_2 nanoparticles surface was modified with organic days: porphyrins and metallomesogens or liquid crystals. Their solubility in liquids and liquid crystals were tested. Improved solubility is important in view of future applications e.g. to build solar cells. The properties of obtained materials were tested by TEM, x-ray and optical measurements (Raman, absorption, fluorescence).

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Acknowledgment: The research was in part supported by the Foundation for Polish Science (TEAM/2010-5/4) and by Polish Ministry of Science and Higher Education (IP2010-036570).

Defect structures in cholesteric droplets

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Liquid crystals possess interesting optical properties that are attractive for applications in optics and photonics. Novel applications focus on fabricating all-photonic circuits from soft matter which requires designing novel optical elements. Indeed, recent advances demonstrate broadband tunable lasers from thin cholesteric films [1], optically creating and switching between different (meta)stable defect structures in cholesterics [2], and tunable microlasers from nematic and cholesteric microdroplets [3].

Director profile is known to be bipolar or concentric in nematic droplets and onion-like in cholesteric droplets with planar anchoring [4]. Theoretical approaches applied to understand these structures in the literature use calculations based on director order parameter and topological theory [5]. Even though these models give reasonable agreement to experimental data, the structure, especially in the proximity of defects, is not fully known. Here, we present stable and metastable structures in cholesteric droplets calculated with the phenomenological Landaue – de Gennes tensorial approach. We show that several defect conformations can form in the diametrical and radial spherical structure to compensate for the surface-imposed bending of the cholesteric layers (Fig. 1). Specifically, we address the role of the cholesteric pitch and anchoring conditions on the structure type. Finally, we analyze the stability of possible structures.

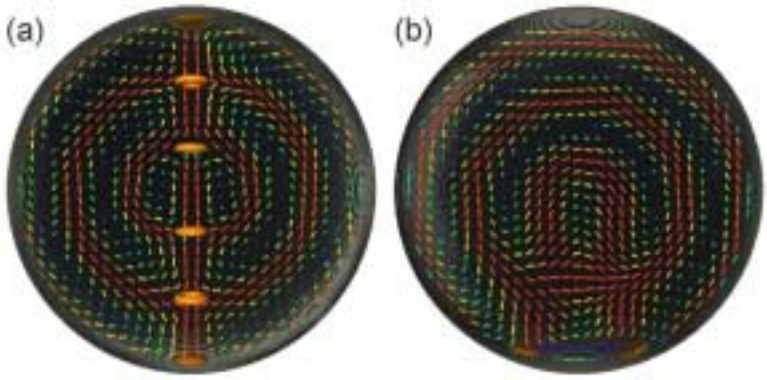

Figure 1 Two structures in cholesteric droplets: (a) diametrical spherical structure with ring defects (instead of expected disclination line [5]), (b) radial spherical structure with two surface defects (instead of expected disclination line [4]). The defects are visualized as isosurfaces with constant nematic order parameter *S=0.48*.

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Control of anchoring of discotic liquid crystals for understanding of organic solar cells

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Discotic Liquid Crystals (DLCs) are generally built of a flat rigid polyaromatic core that is surrounded by flexible alkyl or alkoxy tails. One of their features is the ability to form a special type of self-assemblies, called columnar mesophases. Some of columnar mesophases are considered as high-quality one-dimensional semiconductors for prospective use in organic electronics [1]. One of the crucial aspects in the design of the efficient device is the proper arrangement of the two-dimensional crystal of organic material on the electrodes surface, so that the charges guided from the bulk of the active layer to the contact do not exhibit the detrimental mismatch in the geometry.

Scanning Tunelling Microscopy (STM) in constant-current mode at a solid/liquid interface has been used as a technique for determining the supramolecular structure of the first adsorbed monolayer of various 2,3,6,7,10,11-hexaalkoxytriphenylenes on Highly Oriented Pyrolytic Graphite (HOPG) and gold Au (111). Information gained by this comparative studies should further reflect in the assembly of columns on top of these structures since the first monolayer often defines the organization of molecules in the bulk [3]. A competition between two geometries of hexagonally-packed self-assemblies has been observed in the case of hexapentyloxytriphenylene (H5T) on (111) facets of flame annealed gold.

Complementary technique involved so-called Time-of-Flight measurements, which probe the charge transport properties in the bulk by analysis of photocurrent decays in the home-made and commercially available liquid crystalline cells.

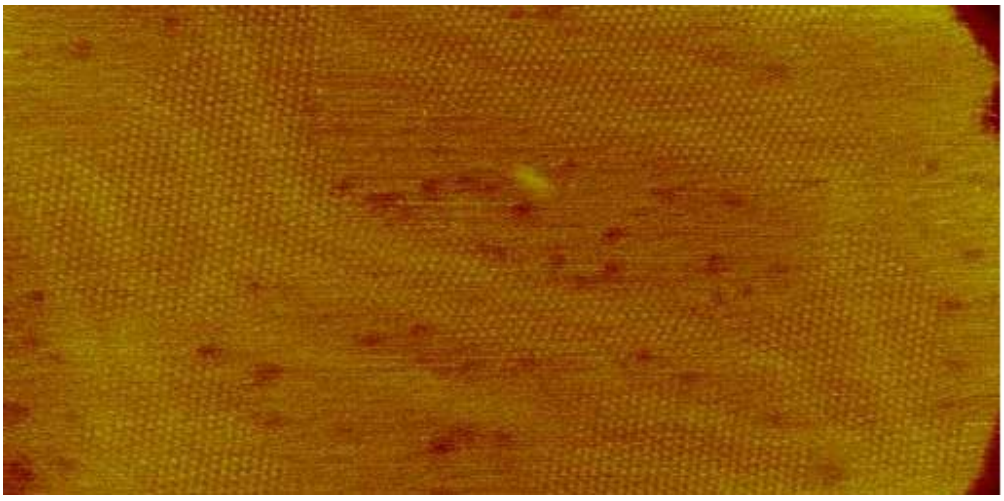

Figure 1. STM image of self-assemblies of 2,3,6,7,10,11-hexaalkoxytriphenylene on Au(111)/n-tetradecane interface. Size: 90 x 180 nm, parameters: current set point = 10 pA; sample bias = 100 mV.

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Photonic band gap fibers with novel chiral nematic and low-birefringence nematic liquid crystals

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Over the past decade, photonic crystal fibers have become the subject of an increasing research interest. Particular attention has been focused on the possibility of filling the air holes of the photonic crystal fibers with liquid crystals [1] due to their high sensitivity to temperature and external physical fields. Thermally, electrically and optically tunable micro-structured fibers filled with liquid crystals have been recently reported [2-5]. Chiral nematic liquid crystals (ChNLCs) seem to be novel and interesting materials to infiltrate PCFs [6].
In this paper experimental results of a novel PW600 chiral nematic liquid crystal (LC) (Fig.1) with significantly reduced temperature sensitivity of the selective Bragg reflection are presented. The PW600 LC as a new material was used to fill prototype PCFs with 3, 5, 6 and 8 rings of the holes manufactured by MCSU, Lublin and temperature – induced photonic band gap shifts have been observed. Additionally, experimental results with a new low-birefringence NLC 1800B are presented. The results obtained suggest great potential of the LC filled photonic crystal fibers for optical fiber attenuators and modulators.

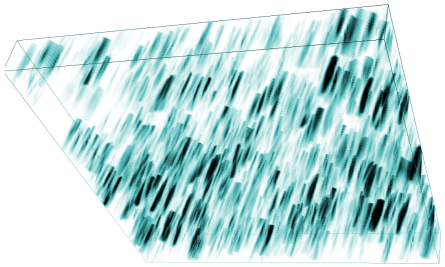

Figure 1. Liquid crystal cell with chiral nematic PW600, after electric field was applied.

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Acknowledgment: The work was supported by the Polish National Science Centre under the grant N507 303040 and by the MISTRZ Programme of the Polish Science Foundation.

AFM Study of self assembled molecules on surfaces

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We present our recent atomic force microscopy (AFM) studies on a curcumin based Zn(II) complex as a possible candidate as anticancer agent[1]. We have investigated the morphology of the molecule on a nanoscale level to test the effect of different substrates and solvents on the shape and the aggregation properties of the molecule. The obtained results will help in understanding the interaction of the studied molecule with DNA or chromonic systems .
The molecules have been studied on different substrates (silicon, mica), chosen for their atomically flat surface, and dissolved in different solvents: chloroform, ethanol and water. To check the aggregation properties, self assembled films were produced by Langmuir technique [2] at different surface pressures (5, 12, 18 mN/m) and by spin coating.
Measurements performed in chloroform have shown that the molecule has a discotic shape with a height of 0,5 nm. The wetting properties of the substrate play a role in the aggregation properties and the film formation.

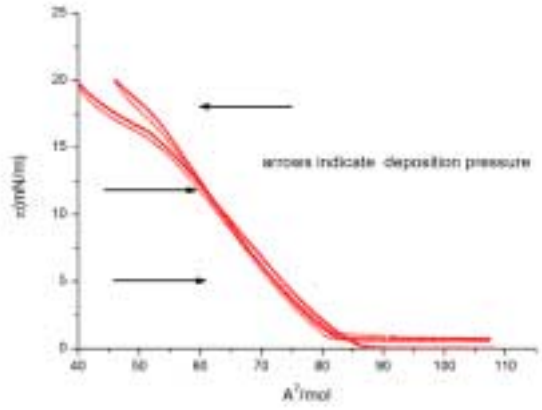

Figure 1. π-A hysteresis curve of the molecule (D7)
during compression and decompression of the film

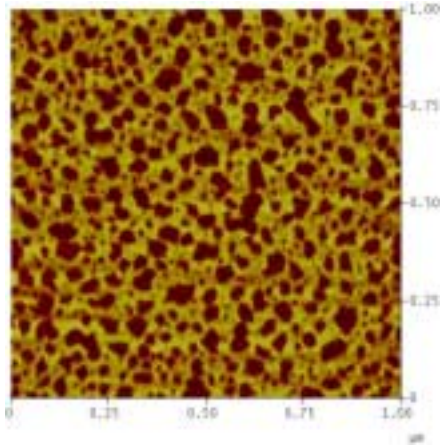

Figure 2 A monolayer of D7 deposited on mica

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Acknowledgment:
The financial support by MIUR (PRIN2008) “Self-assembly of nucleic acids: a molecular toolbox for soft matter science” is gratefully acknowledged.

All-optical rectangular liquid crystal waveguide

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In this paper the study of a nematic LC (NLC) waveguide (LCW) in a novel rectangular geometry is reported where a low power optical pump in C band (1530-1565 nm) causes an effective reorientation of the NLC molecules [1,2].
The waveguide, schematically illustrated in Fig.1, is based on a NLC E7 (Merck) infiltrated in a rectangular SU8 hollow on glass substrate. The NLC is the core material of the waveguide, whereas the cladding is represented by the glass and SU8 photoresist. The rectangular gap of SU8 to be filled with the NLC (width and height of 15 μm) is obtained by a photolithographic step. The substrate glass is a 500 μm borosilicate glass D263 (Schott) with a refractive index slightly bigger than LC ordinary refractive index (see Table 1). A polymer (Nylon 6) is deposited by spin coating on the surfaces in contact with NLC to permit, after a rubbing process, to align the NLC molecules along a desired direction. The NLC is infiltrated by capillarity in the gap and next sealed by a UV adhesive NOA61 (Norland) at both input and output of the waveguide. The use of these polymer stoppers prevents formation of droplets which cause large input and output scattering.
A rectangular hollow waveguide permits a better fiber coupling with less coupling losses and better polarization maintaining during propagation than a V-waveguide previously reported [2].

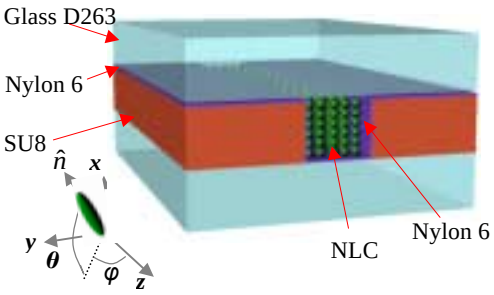

Fig. 1. Schematic of the rectangular LC waveguide with a representation of the molecular director $\hat{n}$

Materials	Refractive index @ 1.55 μm
E7	$n_{//}$ = 1.689 $n_{\perp}$ = 1.502
SU8	n = 1.575
Glass D263	n = 1.516

Table 1. Refractive indexes of device materials.

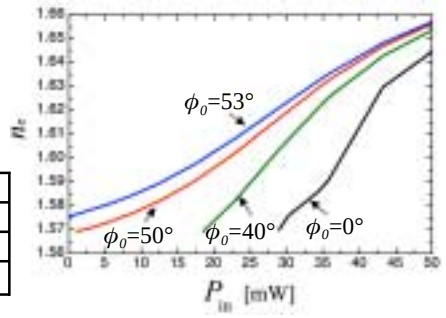

Fig. 2. Refractive index of the fundamental mode varying the input optical power for different alignment conditions.

The LC molecular director $\hat{n}$, represents the average unit vector of the molecular orientation. Its reorientation depends on an applying an external field, on the NLC characteristics and on the anchoring conditions. In this case the external field is provided by an optical laser pump (@ 1.550 μm) with a TE polarization. The molecular director distribution was obtained by coupling the solution of the Poisson equation describing the electrostatic problem with the minimization of the free energy written in its integral form given by the Oseen–Frank equation [3].
The effective refractive index of the waveguide can be modified by changing the twist angle with the alignment conditions (φ_0) and the laser beam itself. Only when the effective refractive index of the LCW is larger than the SU8 one, light can propagate. In Fig. 2 the effect of the optical beam on the effective refractive index of the fundamental mode is shown for different alignment conditions. The larger φ_0 the less power is needed to obtain a guiding mode. With a power of 1 mW and φ_0=50° is possible to split by a cut-off condition to a guided mode.

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Spatial solitons carrying optical vortices in nematic liquid crystals

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A link between fundamental optical spatial solitons [1,2] and doughnut-shaped vortices [3] is provided by the existence of the dynamic bound states of solitons in the form of azimuthally modulated vortex solitons, or azimuthons [4]. Here we report on the first experimental studies of spatial solitons carrying optical vortices in nematic liquid crystals (NLCs). Our experiments are carried out in a planar cell, filled with 6CHBT NLC. A single-charged vortex beam is generated with a fork-type amplitude diffraction hologram from extraordinarily polarized cw laser beam. We show that in nonlinear regime (P > 2 mW), the initial radially symmetric vortex intensity undergoes drastic transformation: the vortex "doughnut" breaks up into two beams with a dark core transformed into a tilted stripe. Such symmetry-breaking can be understood in the context of *vortex astigmatic transformations* [5]. Further increasing the input vortex power (P > 2.3 mW) leads to greater narrowing of the output beam and the formation of self-trapped rotating *dipole azimuthon* [4] [Fig.1]. We show that the two-lobe beam is spatially twisted inside the cell, the direction of the twist is defined by topological charge of the input vortex beam, and the rate of twist depends on the excitation level. Moreover, we observe nonlinearity-induced charge-flipping of the central phase dislocation. In these topological reactions the central phase dislocation (vortex line) splits into three lines with alternating topological charges, similar to a pitchfork bifurcation. We argue that these transformations can be explained by self-induced astigmatic deformations of the vortex beam [5], which do not require external anisotropy stemming from the boundary conditions. We believe that our results provide the first experimental observation that nonlocal nonlinear media can become an efficient mode self-converter.

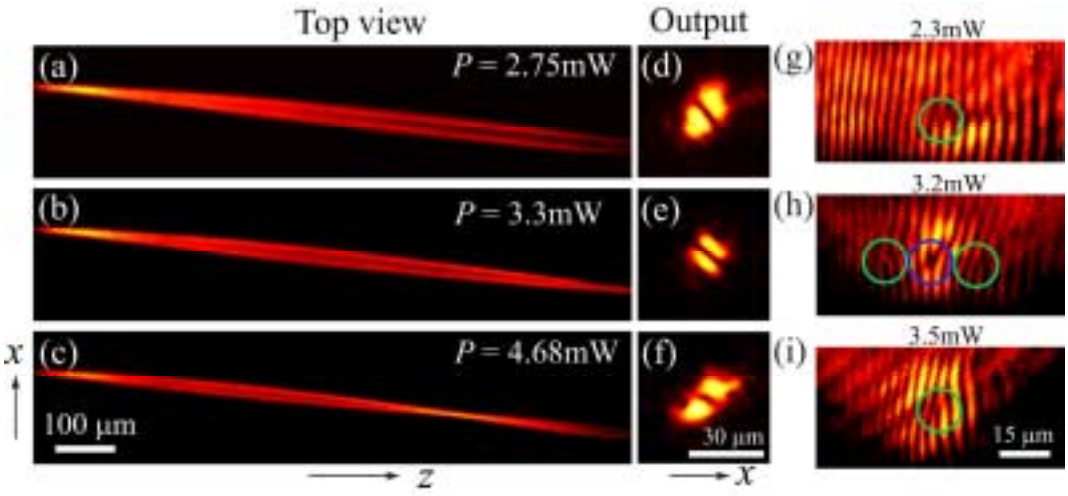

Figure 1 (a-f) Generation of a dipole azimuthon demonstrating the power-controlled twist and breathing of the beam. (a-c) Top view in the plane (x, z) for three different input powers. The walk-off angle of about 4.5^0 is defined by the molecular anchoring at the cell boundaries. The transverse intensity patterns at the cell output are shown in (d-f). (g-i) Experimental interferograms with topological reactions of nonlocal dipole azimuthon. The circles indicate positions of phase singularities with charges +1 (green) and −1 (blue).

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Tuning the Surface Wettability of Liquid Crystal Cellulosic Films

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The ability that a molecule presents to perform conformational switching upon the action of specific external stimuli has been an active topic of investigation (i.e., [1]). Along with engineering of the surface morphology, the control of surface wetability is one of the most important interfacial features due to its application in industry. This can be obtained, for instance, with the *cis*-to-*trans* isomerization using light irradiation. Azobenzene cellulose derivatives can be reversibly switched between *trans* and *cis* forms using light irradiation and have been studied. [i.e., 2]
In previous work the azoacetoxypropylcellulose (AzoAPC) was obtained by the esterification of acetoxypropylcellulose (APC) with the activation of the carboxyl group of the Azo moiety using a carbodiimide as decoupling agent and 4-dimethylaminopyridine as catalyst. However this synthetic route leads to urea derivatives as sub-products, which are difficult to remove from the polymer network. This type of synthesis was chosen in order to prevent the presence of HCl in the reaction means and consequent polymer's depolymerization. [3]
We report here a different synthetic route to produce AzoAPC via azobenzene acid chloride derivatives (AzoCl). The AzoCl was obtained from the reaction of azobenzene carboxylic acid derivative and oxalyl chloride using dimethylformamide as catalyst. The AzoCl formed reacted with APC to afford AzoAPC. The compounds were characterized by means of FTIR, NMR and DSC and the polymer was found to have a degree of substitution of 0.06.
Polarized optical microscopy was used to investigate the texture of thin flexible films obtained by casting from very diluted acetone solutions (see Figure 1). The effect of UV radiation upon the polymer wettability was performed.

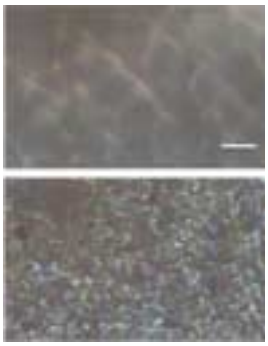

Figure 1. Cross-polarized images of an AzoAPC film before UV irradiation casted from an acetone solution. As the microscope focal plane is lowered an upper "network" structure (top picture) and a lower texture (down picture) characteristic of a cholesteric phase with polygonal fields can be identified. In the "network" image it seems that a periodical distance (in average equal to 3 μm) can be seen. Those black and white lines can be associated to the cholesteric pitch. Bar represents 15 μm.

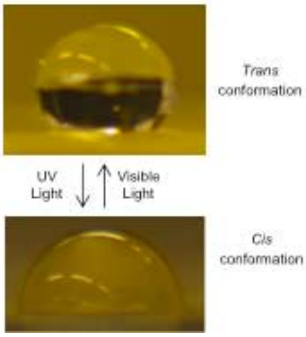

Figure 2. Water droplet on the initial more hydrophobic (*trans* conformation) AzoAPC film surface before UV radiation and on the less hydrophobic surface (*cis* conformation) after UV radiation.

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Acknowledgment: This work was partially supported by Portuguese Science and Technology Foundation- FCT- through contract number PTDC/CTM/099595/2008. S. Kundu and L.F.V. Pinto acknowledge FCT grant no. SFRH/BDP/34096/2006 and SFRH/BDP/65133/2009, respectively. Other support includes the Air Force Office of Scientific Research, Air Force Material Command, USAF, under grant number FA8655-10-1-3020. The US Government is authorized to reproduce and distribute reprints for Governmental purpose notwithstanding any copyright notation thereon.

Tunable Self-focusing and Self-steering of Nematicons

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Nematicons, i.e., optical spatial solitons in nematic liquid crystals (NLC), have been attracting a great deal of attention due to their unique properties such as, for example, excitability at powers of a few hundred μW and the possibility to be electrically and/or optically (by other light beams) bent.[1] In this work we investigate, both experimentally and theoretically, the nematicon behavior for different degrees of nonlinearity, discussing how the latter affects the beam width (self-focusing) and trajectory (self-steering). Having defined the angle between the molecular director $\hat{n}$ (i.e., the local optic axis) and the beam wavevector $\boldsymbol{k} = n_0 k_0 \hat{z}$ (k_0 is the vacuum wavenumber, n_0 the linear refractive index), the propagation of the extraordinary wave in the plane yz in a homogeneous NLC cell of thickness L across x is ruled by the equivalent 2D model [2,3]

$$2ik_0 n_0 \left(\frac{\partial \Phi}{\partial z} + \tan\delta \frac{\partial \Phi}{\partial y} \right) + D_y \frac{\partial^2 \Phi}{\partial y^2} + k_0^2 \Delta n_e^2 \Phi = 0 \tag{1}$$

$$\frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} - \left(\frac{\pi}{L} \right)^2 \psi + \gamma \sin\left[2\left(\psi + \theta_0 - \delta \right) \right] |\Phi|^2 = 0 \tag{2}$$

where Φ is the beam magnetic field and ψ is the all-optical perturbation on θ, with θ_0 being the unperturbed θ, i.e., $\theta_0 = \theta(\Phi = 0)$. In Eqs. (1-2), D_y is the diffraction coefficient along y, $\delta^{(b)}$ the walk-off of the soliton, $\gamma = [\varepsilon_0/(4K)] \left(n_\parallel^2 - n_\perp^2 \right) \left[Z_0 / (n_0 \cos\delta) \right]^2$, and Δn_e^2 is the nonlinear change in the extraordinary refractive index n_e. Eq. (2) is a reorientational equation which allows to compute the dielectric properties of the medium (δ and n_e) once it is known the torque exerted by light on the NLC molecules, whereas (1) determines the beam profile once the $\hat{n}$-distribution is known. It is clear from Eq. (2) that the nonlinear response, determined by the optical torque, depends on the initial angle θ_0: hence, by changing θ_0 it is possible to easily modify the nonlinear response of the sample, the latter feasible via an applied bias in a planar cell with interdigitated comb-like electrodes. [3] In the limit $\psi \ll \theta_0$, using Eqs. (1-2) it is possible to define two scalar parameters to investigate self-focusing (ruled by Δn_e^2) and self-steering (determined by δ) versus θ_0: a nonlocal Kerr coefficient n_2, given by $n_2(\theta_0) = 2\gamma \sin\left[2(\theta_0 - \delta)\right] n_e^2(\theta_0) \tan\delta$, and $c_\delta(\theta_0) = \frac{d\delta}{d\theta_0}$, proportional to the sensitivity of δ to the light intensity (Fig. 1), respectively. Numerical simulations of Eqs. (1-2) via BPM confirm the soliton behavior versus θ_0 (Fig. 1). Figure 1 also shows the corresponding experimental results, with an excellent agreement with the theoretical predictions.

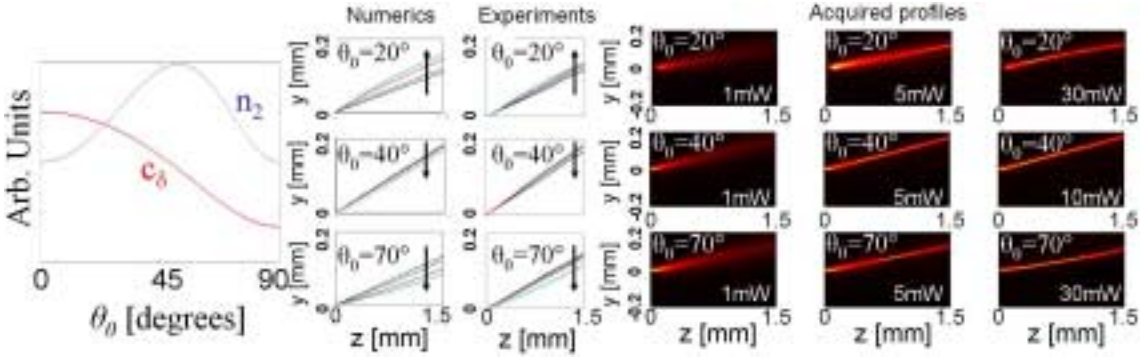

Fig. 1. First column: plot of n_2 and c_δ versus θ_0. Second (third) column: numerical (experimental) trajectories; the arrows indicate increasing power. In the last three columns the acquired beam evolutions in yz are displayed.

Our findings can find interesting applications in the design and realization of all-optical networks with topology controlled by the signal itself.

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Micro/nano structures with plasmonic properties utilizing PDMS and gold nanoparticles.

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Abstract

Fabrication of samples showing plasmonic properties is a fundamental step towards the realization of devices, which can exhibit peculiar electromagnetic properties. Theoretical studies demonstrate that assemblies of Gold or Silver nanoparticles can be considered as building blocks (or meta-atoms) of a metamaterial[1]. In this work we illustrate some fabrication techniques that can reveal useful for the realization of this kind of sample. We used PDMS materials[2] (and other photo-patternable polymers) in combination with Gold nanoparticles for realizing micro/nano structures. Field of application of such devices can include novel solar applications[3].

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Acknowledgements

The research leading to these results has received funding from the European Union's Seven Framework Programme (FP7/2007-2013) under grant agreement n°228455.

The present communication is co-funded by the European Commission, European Social Fund and Calabria Region. Authors are the only responsible of this communication and the European Commission and Calabria region decline every responsibility on the use that will be done with the contained information.

Dielectric characterisation of a ferroelectric and antiferroelectric liquid crystal

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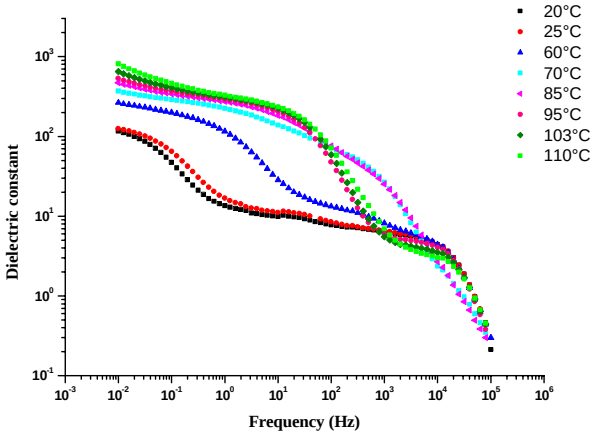
Liquid crystals exhibiting both a ferroelectric and an antiferroelectric phase are interesting for a great number of applications in electro-optical devices. In particular, for their fast response time they can be employed in visual display applications [1].
We present our recent investigations on the electric properties of W129, an orthoconic smectic liquid crystal which presents both ferroelectric and antiferroelectric smectic C phases. In particular, W129 is a very interesting material since it is able to exhibit an high spontaneous polarization (> 300 nC/cm^2 at room temperature) in virtue of its tilted chiral structure. This liquid crystal has been synthesised by professor Dabrowski at the Military University of Technology, Warsaw, Poland.
In the present study, dielectric relaxation of W129 has been studied as a function of the frequency of an applied electric field through Dielectric Spectroscopy technique. For this purpose the Cole-Cole function [2] has been used to determine the distribution parameter, the dielectric strength and the relaxation frequency as a function of temperature.
Finally, we present a first attempt to study the morphological and ferroelectric properties of a thin layer of W129 deposited on ITO using Atomic Force Microscopy techniques.



Frequency dependence of the real part of the dielectric constant at different fixed temperatures.

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Dark solitons in nematic liquid crystals

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In this work we present the first experimental observation of a dark soliton in nematic liquid crystals [1,2]. While the latter are known to support stable (2+1)D bright optical solitons arising from the focusing reorientational nonlinearity [3], using a homeotropic cell filled with a mixture of 5CB commercial liquid crystal and an azo-dye, we induce a defocusing nonlinearity via the lowering of the order parameter due to the dye-mediated interaction between the liquid crystal molecules and an extraordinarily polarized beam [4,5]. We present a suitable model encompassing the negative nonlinearity and the absorption due to the dye presence, showing linear and saturable nonlinear regimes of propagation of a bell-shaped beam with a π-phase jump across its transverse profile. We confirm our numerical findings by launching a Gaussian beam with the suitable phase step and observing the "notch" self-confinement as a function of the initial power. Further, we checked the guiding properties of the optical structures, launching a low power beam collinear with the notch: when in the ordinary polarization, the probe "feels" a negative refractive index well, thus defocusing, while in extraordinary polarization it is guided within the notch, demonstrating the propagation of a dark nematicon.

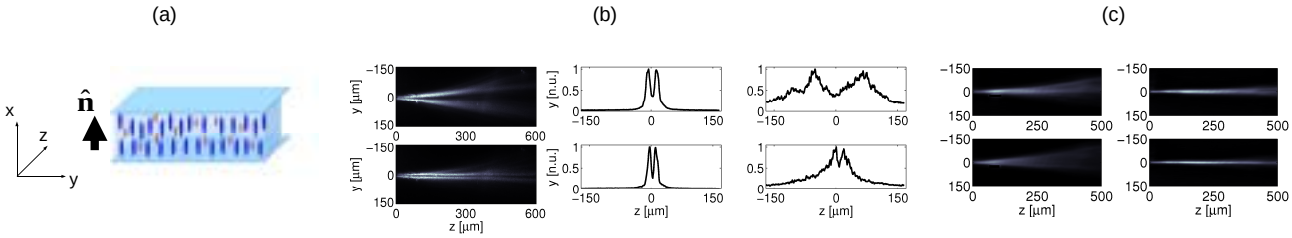

Figure 1. (a) Sketch of the sample used in the experiments. (b) Propagation of the Gaussian beam with a π-phase jump. Acquired photo (first column) at low (up) and high (bottom) input power and corresponding input (middle column) and output (last column) profile. (c) Propagation of the probe beam for the same powers as in (b), for ordinary (left column) and extraordinary (right column) polarization.

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Rehological and ^{1}H-NMR Spin-Spin relaxation time for the evaluation of the effects of PPA addition on bitumen.

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Abstract. Bitumen is the typical binder adopted for road pavementsconstruction (asphalts) and it is the main responsible for pavement performance.Essentially bitumen can be described as a colloidal dispersion of asphaltene particles, coated with layers of stabilizing polar resins, in a continuous oil phase [1]. Although you can write a very simple definition of bitumen, its chemical composition is very complex and still not completely known.It has been largely studied and analyzed in the last years, and several types of additives are used to improve their properties and achieve better applicative performances [2]. Indeed rutting and cracking are the two major failure modes that affect road pavements. Different types of cracks, like those caused by car traffic load, temperature cycling and cold climates, indicates the road deterioration. Chemical composition and the resultant rheological properties, influence the behaviour of asphalt mixtures. However, the properties of binders are currently characterized using standardized and/or modified standardized empirical test methods. Here we present a laboratory evaluation of the rheological properties of bitumen which has been doped by different percentage of Polyphosphoric acid (PPA) by using a Stress Controlled Rheometer. In addition measurement of proton relaxation times (T2) were exploited in order to corroborate the rheological data. We studied modified bitumen with a PPA content at 0,9% and 1,9%.

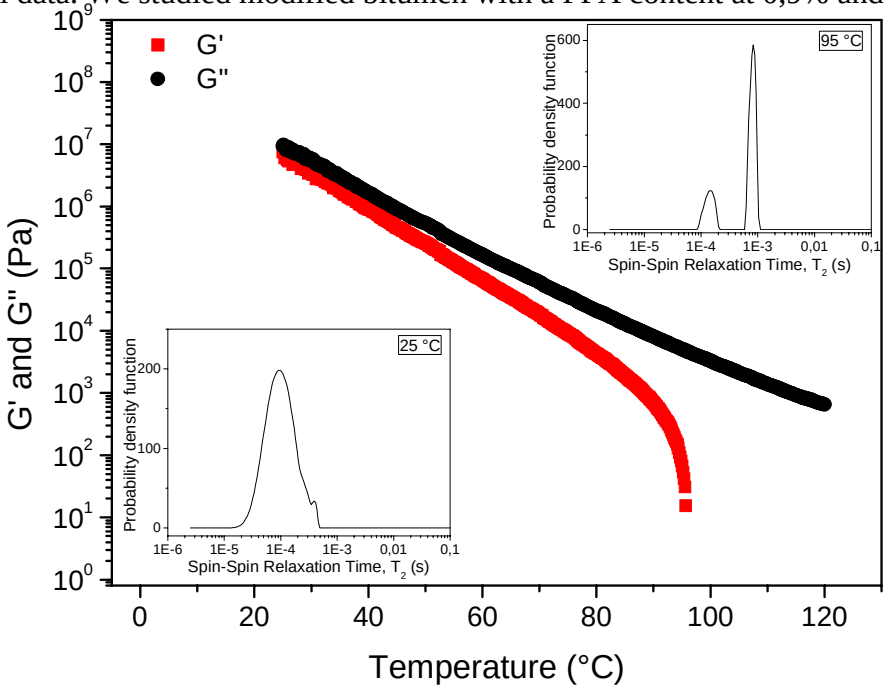

Figure 1: Temperature scan of G' and G" moduli obtained by a time-cure test at 1 Hz. Inverse Laplace transform of the spin-spin relaxation decay obtained by NMR.

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An ESR characterization of α,ω-bis(4'-cyanobiphenyl-4-yl)nonane symmetric dimer mesophases

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Liquid crystal (LC) dimers formed by covalently linking two mesogenic groups, show peculiar properties with respect to the constituting monomers. A combination of retention of the basic structural components of liquid crystalline main-chain polymers (e.g. the flexible spacer) and their easy synthesis and study, makes these mesogens unrivalled model compounds for their high molar mass counterparts [1,2]. Besides, due to the rich variety of mesomorphism (nematic N, smectic A SmA, etc.) and properties these dimeric systems are of great interest as building blocks in the design of novel materials. One example is provided by the class of symmetric dimers nBCB consisting of two cyanobiphenyl mesogens connected by a flexible $(CH_2)_n$ alkyl chain spacer [3]. These dimeric LCs show pronounced odd-even effect in the nematic-isotropic transition temperature and entropy. Moreover the possibility that a biaxial nematic phase could occur has been suggested [3].

Here we study the highly flexible odd-spacer dimer α,ω-bis(4'-cyanobiphenyl-4-yl)nonane (9BCB) by means of the Electron Spin Resonance (ESR) spin probe technique, already successfully employed in similar [4] and other complex systems [5] for its high sensitivity. We present results of different ESR experiments performed on 9BCB (here a cholestane-type nitroxide spin probe, 3β-doxyl-5α-cholestane (CSL) is used), with the aim of elucidating its order and molecular organization, as well as its dynamics, issues which are still matter of scientific discussion. The possibility that this system, which in view of its odd alkyl and flexible spacer should contain both bent and straight conformers, exhibits a biaxial phase has also been investigated.

As for the symmetric endecane dimer (11BCB), which has been investigated resorting to the same technique, the experimental results show that below the N phase 9BCB undergoes another transition before entering the crystalline state Cr, as also detected by differential scanning calorimetry (DSC) measurements. This intermediate phase, named N_X, possesses different features whether it is obtained by heating the sample from the Cr state, or rather by annealing it from its isotropic form. In the first case, the dimer ESR spectrum shows the typical characteristics of a three-dimensional nematic polydomain (3DP), whose local orientational order parameter $\langle P_2 \rangle$ value corresponds to that calculated by means of atomistic Molecular Dynamics simulations performed on the same system [6]. In the annealed sample the LC molecules arrange instead in a structure which shares properties of a two-dimensional polydomain (2DP) and of a smectic phase (most probably SmA), as supported by the dimer inability to reorient along the magnetic field B, once this is rotated.

Acknowledgments: This work was supported by the EU-STREP project "Biaxial Nematic Devices" (BIND)FP7-216025.

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New symmetric azomethinic dimer: the influence of structural heterogeneity on the liquid crystalline behaviour

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Thermotropic liquid crystals (TLCs) have been of great technological importance throughout the years due to their practical applications. Polymers with thermotropic behaviour can be used as advanced materials for many industrial applications, such as matrices for advanced composites, electronic packaging materials, high-strength fibres and electronic devices, organic light-emitting devices, and organic field-effect transistors [1–3].

The symmetric dimeric liquid crystalline compounds formed by two identical mesogenic units linked via a single flexible spacer are interesting compounds, investigated as models for liquid crystalline polymers or for their unusual mesomorphism, different to that of the corresponding monomers [5–7].

Taking into account these facts, we thought interesting to create a model for the studying the influence of polymer polydispersity on their liquid crystalline properties. For this, a new azomethinic dimer and its structural heterogenic mixtures with diamine reagent were prepared and their thermotropic properties analyzed. The pure azomethinic dimer has a monotropic nematic mesophase and crystalline polymorphism, while its structural heterogenic mixtures present a plastic mesophase in the first heating scan, similarly to many polydisperse semicrystalline or rigid polymers. The occurrence of the monotropic mesophase is suppressed for 15% diamine content, while its stability range is suppressed for 10% diamine content. The crystalline polymorphism is affected by structural heterogeneity, too. [8].

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