Light-induced effects in liquid crystals: recent developments

F.Simoni*, L.Lucchetti
Dipartimento di Scienze e Ingegneria della Materia, SIMAU
Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona, ITALY

ABSTRACT

In this paper we outline that light-induced effects in liquid crystals are still able to provide scientific and technological novelty in spite of a long time investigation started more than thirty years ago. Here we review some recent achievements related to new phenomena that have been studied in the past few years. In the first part of our report we discuss optical trapping of nematic colloids whose origin relies on the elastic properties of liquid crystals rather than on the field gradient that is on the basis of conventional optical tweezing. In the second part we present some recent results obtained in studying the self-phase modulation in bent core nematic liquid crystals, pointing out a peculiar two regimes behavior.

Keywords: liquid crystals, optical reorientation, nonlinear optics

1. INTRODUCTION

Light induced reorientation and the consequent giant nonlinear optical response has been discovered in 1980 and deeply investigated for more than three decades [1]. Molecular reorientation occurs in any fluid however it gives rise to a huge effect in liquid crystals (LC) due to the long range correlation of anisotropic molecules that leads to the well known collective behavior of these materials. During more than three decades many effects originated by light induced optical torque on LC molecules, have been discovered and investigated. On the other hand effects due to light absorption leading to local order parameter variations, photo-chemical transformation or modification of the surface conditions have also been demonstrated. Many different phenomena have been discovered linking optical propagation to the peculiar properties of liquid crystals, among them the colossal optical nonlinear response showing a nonlinear refractive index up to 10^3 cm^2/W must be mentioned [2]. Due to this huge amount of work already carried out, that covers a broad range of phenomena and materials, it seems that most of the relevant light induced effects have already been studied.
However, in spite of all this work, in the past few years new perspectives in this field have been given by investigations along the following directions: (i) the optoelastic trapping effects in LC driven by light induced molecular reorientation; (ii) the observation of nonlinear optical properties in newly developed LC such as Blue Phase LC and Bent Core Nematics (BCN) showing non conventional response.
Within this frame we will discuss here: (i) our recent results pointing out the original characteristics of light driven trapping and manipulation of microparticles dispersed in LC (nematic colloids) opening a new horizon of applications for these materials [3-5]; (ii) the peculiar aspects of nonlinear optical response of a BCN material [6], whose interest lies in the possibility of obtaining the still elusive biaxial and ferroelectric nematic phases starting from these kind of LC.

2. OPTOELASTIC TRAPPING IN LIQUID CRYSTALS

The long-range orientational correlation of molecules in LC has been exploited to study self-assembling of microparticles thus realizing two-dimensional structures of various type based on the strong anisotropic potential felt by nematic colloids. In particular topological defects occurring near the dispersed microparticles become very important in determining the type of interaction and the final self-assembled structure [7-10]. Of course, the extension to the third dimension in such structures may have a great application potential for realization of photonic crystals and metamaterials in the visible range of wavelengths.
Based on this motivation the research on optical manipulation of colloidal particles dispersed in nematic LC started more than a decade ago leading to the observation of unconventional optical trapping, unexpected since one of the basic

*f.simoni@univpm.it.

Liquid Crystals XX, edited by Iam Choon Khoo, Proc. of SPIE Vol. 9940, 994006
 · doi: 10.1117/12.2235912

conditions for optical trapping based on tight focusing was not fulfilled: in fact in this case the refractive index of the LC was higher than the one of the particle, while the opposite must hold to get attractive forces originated by optical field gradient [11,12].
While this first observation was explained considering two regimes: below and above the light-induced optical reorientation (Optical Freedericksz Transition, OFT) in homeotropic nematics (i.e. provided with perpendicular alignment boundary conditions). A following investigation pointed out that optical trapping in LCs is induced even with moderate focusing conditions [3].
In other words trapping of nematic colloids is possible even if : (i) $n_P < n_{LC}$ and (ii) N.A. < $(N.A)_{min}$. These are opposite conditions with respect to the ones required for gradient field trapping used in optical tweezers. In fact in this case the refractive index of the particle n_P must higher than the one of the surrounding medium (in this case n_{LC}) otherwise a repulsive force is originated. The second condition to realize optical tweezers is to provide high numerical aperture (N.A.) focusing necessary to realize the required field gradient, therefore there is a minimum value [$(N.A)_{min} \approx 0.7$] below which trapping is not possible. On the contrary with particle dispersed in LC this condition can be dropped.
Experiments were performed using 50 μm thick samples of 5CB (pentyl-cyanobiphenil) including a dispersion of spherical particles with average radius R = 2.5 μm and refractive index n_P =1.37. The refractive indices of 5CB at λ = 532 nm are n_o =1.54 and n_e = 1.71. The particles were coated by N,Ndimethyl-noctadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP) in order to obtain vertical (hometotropic) anchoring of LC molecules on the colloid surface. The same treatment was applied to the cell glass substrate to get homeotropic alignment of the LC sample.
The used light source was a frequency-doubled Nd:YVO_4 laser (Coherent,VerdiV2) at λ= 532 nm focused on the sample through a conventional inverted microscope apparatus. The focusing optics had a numerical aperture N.A. ranging from 0.45 to 0.25, depending on the used objective, however always lower than the minimum value necessary to get gradient filed optical trapping calculated for our system. Additionally the experiments were performed in underfilling conditions that is with the laser beam waist smaller than the radius of the back aperture of the objective, to further reduce the actual numerical aperture. The laser beam was linearly polarized and had a Gaussian distribution on the sample with power ranging from few milliwatts to about 200 mW.
Under these experimental conditions stable optical trapping was always observed above an optical power dependent on the distance between the particle and the focal spot. As the laser beam was switched on, the particle was attracted towards the focus and the movement was video recorded by means of a CCD camera at a rate of 25 frames/s.

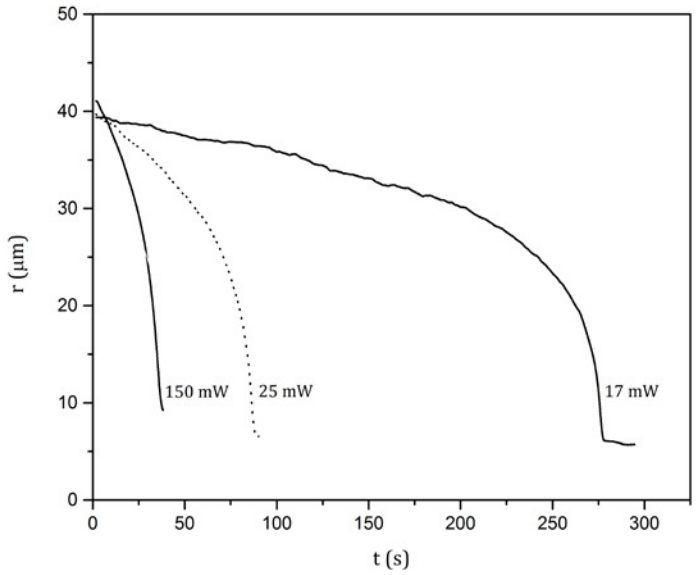

Figure 1. Plot of the particle position vs time during optical trapping. The colloid stops at an equilibrium distance $r_{eq} \neq 0$ from the center of the trap.

A typical variation of the distance r(t) between the particle and the center of the laser spot is shown in fig. 1, for different laser power. Time t = 0 s corresponds to laser switch on that is controlled by an electronic shutter. This plot is obtained by the analysis of the video recorded tracking of the particle.
Following a conventional approach, data reported in fig. 1 allow to work out the force acting on the nematic colloid, whose typical behavior is given in fig. 2.

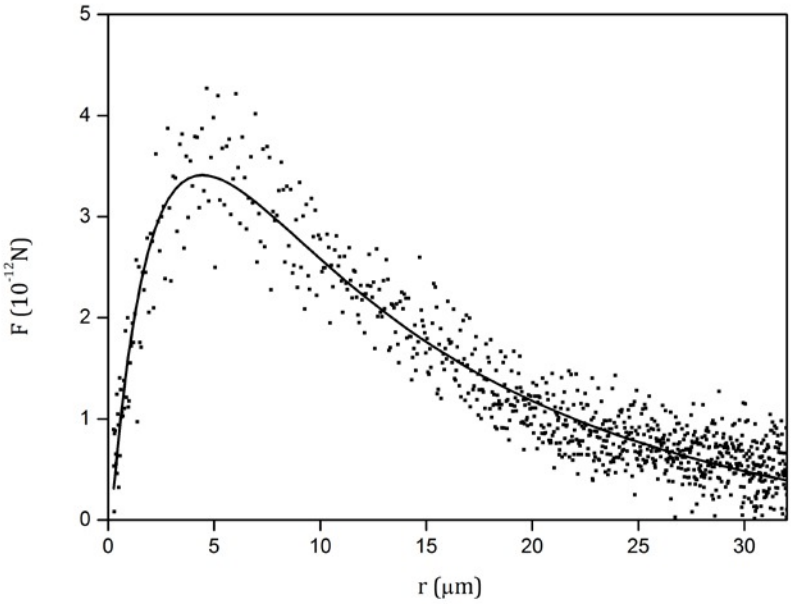

Figure 2. Typical behavior of the modulus of the trapping force vs the distance from the center of the laser spot. The solid line is the best fit using Eq. (1).

The attractive force increases as the particle approaches the trap, reaches a maximum then decreases and eventually vanishes. The curve can be described fairly well by the function:

$$F = -\frac{A}{r^2} + \frac{B}{r^3} \qquad (1)$$

A and B are constants whose values to be found through the fitting procedure. Eq. (1) shows a Coulomb-like dependence of the attractive force (in the high r region) in agreement with other authors [12].
Even if the interaction between a laser induced reoriented nematic and a colloid cannot be considered as the interaction between two colloids some conceptual similarities are possible. In fact the interaction between two colloids dispersed in LC has been demonstrated to be induced by the orientational defects around the colloids and by the consequent minimization of the elastic energy of the system that is achieved when the colloids are close to each other. In a similar way we should consider the optical trapping phenomenon, in this case having nothing to do with the field gradient trapping typical of optical tweezers. In our case the similarity is due to the light-induced reorientation in the focal area in a way that such a distorted area acts as a "ghost colloid" interacting with the real colloid via minimization of the elastic energy. For this reason we can denominate this effect *optoelastic trapping*. Actually it is remarkable that attraction in optoelastic trapping is usually stronger than the one between two colloids. In fact while the former exhibits a Coulomb-like dependence on r^{-2}, the latter depends on r^{-4} in case of defects with dipolar symmetry.
Light focusing on LC may also induce heating thus producing a local decrease of the order parameter. The consequent gradient of the order parameter occurring between the nematic colloid and the light spot can induce trapping under appropriate experimental conditions. Also in this case the origin is the minimization of the elastic energy of the system.

However when light-induced reorientation prevails an additional parameter becomes available for this trapping effect. In fact low frequency electric field can also reorient LC molecules either towards or outwards the electric field direction depending on the dielectric anisotropy $\Delta\varepsilon$ of the material.
The optical trapping experiments described above have been repeated by using conductive glass substrates (with ITO coating) in order to apply a low frequency electric field (1KHz) normal to the sample boundaries. The application of such a field stabilizes the homeotropic alignment, in case of positive dielectric anisotropy of the LC, therefore exerts a torque opposite to the one given by the optical field on the LC molecules. In this way we expect a reduction of the attractive force and possibly a quenching of trapping. The effect is clear looking at fig. 3, where the particle position vs time is reported at a fixed laser power of 10 mW for different values of the applied voltage.

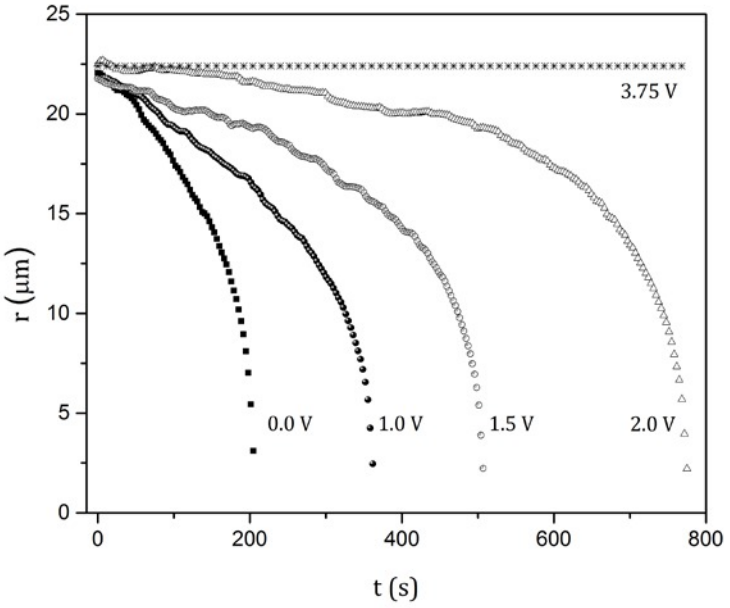

Figure 3. Plot of the particle position vs time during optical trapping for different values of the voltage applied to the sample for nematic LC with dielectric anisotrpy $\Delta\varepsilon>0$.

Fig. 3 shows a motion slower and slower as the voltage is increased up to a condition where trapping quenching is achieved and the attraction force is cancelled. It can be shown that the effect is due to a progressive reduction of the constant A in eq.(1), that measures the strength of the attractive force.
In contrast, in the case of liquid crystals with negative dielectric anisotropy, we expect an opposite effect: by increasing the applied voltage a torque in the same direction of the optical torque is applied therefore a broadening of the elastic reorientation around both the ghost and the real colloid is induced. In this way enhancement of the attractive interaction is obtained. This is shown in fig. 4, reporting the same parameters as in fig. 3, but related to the experiment performed using the nematic LC ZLI-4788 (from Merck) with a negative dielectric anisotropy $\Delta\varepsilon=-5.7$.
Summarizing, light-induced reorientation can be used for optical manipulation getting trapping forces in the range of 10^{-12}N, of the same order of magnitude as the ones typical for optical tweezers, but with a wider interaction range of tens of micrometers. This optoelastic interaction occurring between the nematic colloid and the orientational distorted area can be tuned by using an external electric field that controls the distance above which the interaction is screened by thermal orientational fluctuation of the nematic host. That is reduction and quenching of the interaction can be induced in LC with positive dielectric anisotropy while enhancement of the attracting force and broadening of the interaction range can be induced by a low frequency voltage applied to LC with negative dielectric anisotropy. Enhancement can lead to an interaction range on a submillimetric scale.

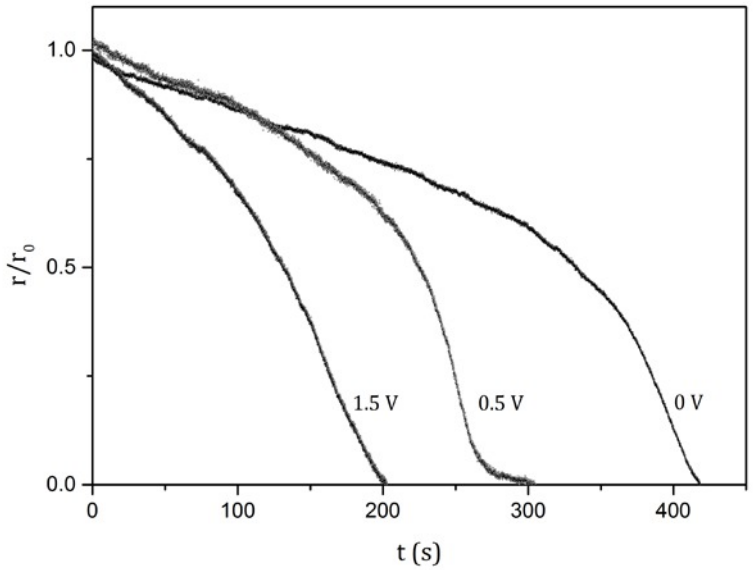

Figure 4. Plot of the particle position (normalized to the initial position r_0) vs time during optical trapping for different values of the voltage applied to the sample for nematic LC with dielectric anisotropy $\Delta\varepsilon<0$.

3. NONLINEAR OPTICAL RESPONSE OF BENT CORE NEMATICS

A considerable interest has been devoted in recent years to the study of the nematic phase of bent-core nematics (BCN) due to its unconventional properties. These nematogens have been considered as prime candidates in the search for the biaxial and the ferroelectric nematic phases, that still await undisputable experimental verification in low molecular-weight thermotropic mesogens. From an applicative point of view, BCN could give rise to a new generation of faster liquid crystal devices [13-18].

The enhanced sensitivity to external (magnetic and electric) fields and the giant flexoelectricity stimulate the interest in investigating the nonlinear optical response of BCN, that is almost unexplored [19]. Here we discuss the recently reported results concerning the self-phase-modulation (SPM) [6].

The investigated BCN, named OC4-2MePh (mono2MeODBP), is a molecule based on a 2,5-bis(phydroxyphenil)-1,3,4-oxidiazole (ODBP) mesogenic core with three lateral methyl groups. The interest in this particular molecule is motivated by the recently observed enhancement of the local biaxiality, highlighted by small angle X-ray reflection measurements [20-23]. The sample was sandwiched between two ITO-coated glass substrates treated with a rubbed polyimide layer to induce planar anchoring of the primary molecular director **n**. Mylar spacers were used to control the thickness, fixed at 100 μm. The obtained cell was placed in a controlled temperature chamber fixed at 100 °C, corresponding to the nematic phase, well below the clearing point (T_c=124°C). The linearly polarized light beam of a frequency-doubled Nd:YVO_4 with λ=532 nm was focused on the sample at normal incidence by a 20-cm plano-convex lens, leading to a focal spot diameter of about 66 μm, so that the incident intensity was varied in the range 10^2 - 10^4 W/cm^2 . Measurements were performed with polarization parallel and perpendicular to the rubbing direction. A low power He– Ne laser (λ=632 nm), focused on the sample at quasi-normal incidence by a 10 cm plano-convex lens was used as probe beam.

Both pump polarizations gave rise to two different sets of ring patterns by increasing the impinging intensity. Rings appear for intensity below $I = 10^3$ W/cm^2 showing a response in the range of GON (Giant Optical Nonlinearity), however below 10^3 W/cm^2 the ring pattern is unstable, time dependent (set #1) and collapses to a stable pattern above 10^3 W/cm^2 where the number of rings N is lower (set #2).

The plot of the ring number N vs intensity is reported in fig.5 and fig.6 for set#1 and set#2 respectively.

Some of the characteristics of the set#1 of rings may suggest a thermal origin. In particular: they can be observed with both pump polarizations, the sign of δn is negative for parallel polarization and positive for orthogonal polarization, the value of δn is bigger for parallel polarization and the decay time of $\tau = (25 \pm 1)$ ms is consistent with a thermal effect, thought being quite long.

However, a deeper analysis highlights that: SPM onset depends on the cell's history, the number of rings *N* increases not only with pump intensity but also with exposure time, ring pattern is not stable with time and the delay between rings stabilization and collapse depends on *I* (higher *I* leads to shorter delay).
Noteworthy the resulting optical nonlinearity is in the range of GON, in fact by calculating the induced optical anisotropy by the number of rings, by means of the usual relations, one gets $\delta n = 0.074$ for parallel polarization, which leads to $n_2 = 2.1 \cdot 10^{-5}$ cm^2/W, and $\delta n = 0.053$ for perpendicular polarization leading to $n_2 = 1.5 \cdot 10^{-5}$ cm^2/W.

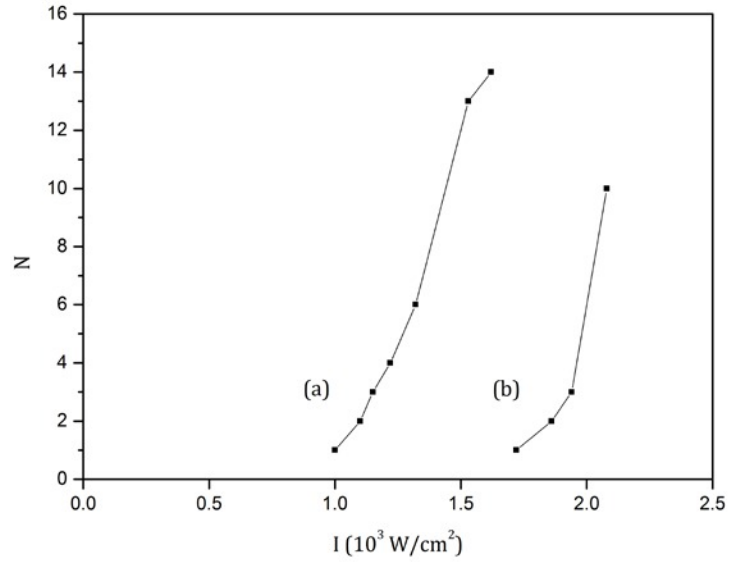

Figure 5. Plot of ring number *N* vs intensity *I* for polarization parallel (a) and perpendicular to the molecular director for set#1.

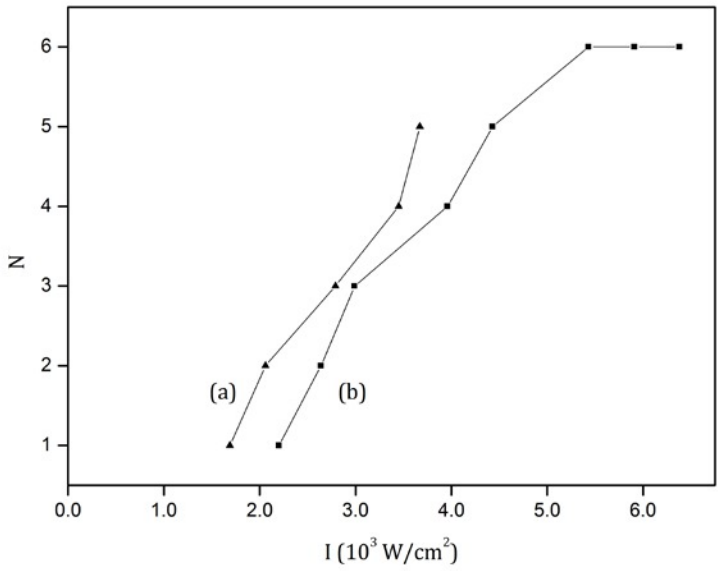

Figure 6. Plot of ring number *N* vs intensity *I* for polarization parallel (a) and perpendicular to the molecular director for set#2.

On the contrary the set#2 is fully consistent with thermal indexing, since it is observed with both pump polarizations, the sign of δn is negative for parallel polarization and positive for orthogonal polarization, the modulus of δn is bigger for parallel polarization, the decay time is $\tau = (5 \pm 1)$ ms, the pattern shows symmetric ring shape, N depends on I and is stable with time and rings disappear at light-induced isotropization ($I > 10^4$ W/cm^2).
Surprisingly, optical nonlinearity is lower than in the former case, $\delta n = 0.032$ and $n_2 = 0.9 \cdot 10^{-5}$ cm^2/W, although correspondent to higher intensity.
The peculiar behavior of the observed SPM effect can be summarized as follows:

1. high intensity pattern corresponds to a lower nonlinearity;
2. for set#1 N depends both on I and on time, that is on the irradiation dose;
3. the intensity threshold for set#1 decreases for prolonged exposure.

The characteristics of set#1 could be related to a light-induced change of the anchoring conditions at the cell surfaces dependent on the impinging light dose, which consequently affects the bulk director configuration. In particular, the Gaussian distribution of the light beam may be responsible for the non uniform modulation of the surface conditions and, as a consequence, of the refractive index change. A combination of this effect with thermal indexing could give rise to the observed behavior for the low-intensity regime. This can also explain the observed changes between the two ring sets: the different behavior due to thermal indexing may be indicative of a light-induced order transition occurring at a dose $E > E_{th}$, with E_{th} of the order of 10^5 J/cm^2 . Such a phenomenology looks promising for further investigation necessary to check the validity of the mentioned hypothesis.
Although the anchoring orientation of BCN materials is currently not fully understood and the achievement of a complete picture of this phenomenon requires further investigation, our observations demonstrate the interest of extending to these materials the study of light-induced effects. These LCs give rise to a variety of effects quite different from those observed in calamitics; on the other hand, these studies can provide further insight on physical properties of BCN not yet fully understood.

4. CONCLUSIONS

In this report we have pointed out that light-induced effects in LC are still providing interesting subjects of investigation both for what concerns phenomena occurring as consequence of the peculiar collective molecular response of LC and for what concerns the novelty of the phenomenology shown by exotic LC phases.
We described the main features of the effects leading to optoelastic trapping of nematic colloids that is important to compare to the “conventional” optical trapping used in optical tweezers. In this case the minimization of the elastic energy of LC is the physical reason of the trapping phenomenon while in conventional optical trapping it is due to high gradient of the optical field. As a consequence optoelastic trapping acts on a much broader range, that is one-two orders of magnitude higher than in field-gradient trapping (tens-hundreds of micrometers compared to few micrometers). Additionally the optoelastic trapping can be tuned by application of a low frequency electric field that can lead to quenching or enhancing of the trapping effect depending on the elastic anisotropy of the LC material. It is remarkable that in case of negative dielectric anisotropy the interaction range can be extended to submillimetric scale.
Considering the nonlinear optical response of novel LC materials we have shown the peculiar phenomenology of self-phase modulation in BCN. Experimental data point out a giant nonlinear optical response, but show a two regimes behavior that is the evidence of a light-induced order transition. It is foreseen that further investigations on this effect should provide new information of the orientational properties of BCN.

REFERENCES

[1] Simoni, F. [Nonlinear Optical Properties of Liquid Crystals and Polymer Dispersed Liquid Crystals], World Scientific, Singapore, 1997.
[2] Lucchetti, L., Di Fabrizio, M., Francescangeli, O. and Simoni F., Optics Comm. 233, 417 (2004).
[3] Lucchetti, L., Criante, L., Bracalente, F., Aieta, F. and Simoni F., Phys. Rev. E 84, 021702 (2011).
[4] Criante, L., Bracalente, F., Lucchetti, L., Simoni F. and Brasselet, E., Soft Matter 9, 5459 (2013).
[5] Simoni F., Lalli, S., Lucchetti, L., Criante, L. and Brasselet, E., Appl.Phys.Lett. 104, 011112 (2014).
[6] Lucchetti, L., Vita, F., Scharrer, E., Francescangeli, O. and Simoni F., Opt.Lett. E 40, 2953 (2015).
[7] Poulin, P., Stark,H., Lubensky, T. C. and Weitz, D. A., Science, 275, 1770 (1997).

[8] Yada, M., Yamamoto, J. and Yokoyama, H., Phys. Rev. Lett., 92, 185501 (2004).
[9] Ravnik, M., Skarabot, M., Zumer, S., Tkalec, U., Poberaj, I., Babic, D., Osterman, N. and Musevic, I., Phys. Rev. Lett., 99, 247801 (2007).
[10] Musevic, I., Skarabot, M., Tkalec, U., Ravnik, M. and Zumer, S., Science, 313, 954 (2006).
[11] Musevic, I., Skarabot, M., Babic, D., Osterman, N., Poberaj, I., Nazarenko, V. and Nych, A.,Phys. Rev. Lett. 93, 187801 (2004).
[12] Skarabot, M., Ravnik, M., Babic, D., Osterman, N., Poberaj, I., Zumer, S. and Musevic, I., Phys. Rev. E 73, 021705 (2006).
[13] Jákli, A., Liq. Cryst. Rev. 1, 65 (2013).
[14] Vanakaras, A. G. and Photinos, D. J., J. Chem. Phys. 128, 154512 (2008).
[15] Tschierske, C. and Photinos, D. J., J. Mater. Chem. 20, 4263 (2010).
[16] Dingemans, T. J., Madsen, L. A., Francescangeli, O., Vita, F., Photinos, D. J., Poone, C.-D. and Samulski, E. T., Liq. Cryst. 40, 1655 (2013).
[17] Francescangeli, O., Stanic, V., Torgova, S. I., Strigazzi, A., Scaramuzza, N., Ferrero, C., Dolbnya, I. P., Weiss, T. M., Berardi, R., Muccioli, L., Orlandi, S. and Zannoni, C., Adv. Funct. Mater. 19, 2592 (2009).
[18] Berardi, R., Muccioli, L. and Zannoni, C., J. Chem. Phys. 128, 024905 (2008).
[19] Hong, S. H., Williams, J. C., Twieg, R. J., Jákli, A., Gleeson, J., Sprunt, S. and Ellman, B., Phys. Rev. E 82, 041710 (2010).
[20] Francescangeli, O. and Samulski, E.T., Soft Matter 6, 2413 (2010).
[21] Keith, C., Lehmann, A., Baumeister, U., Prehm, M. and Tschierske, C., Soft Matter 6, 1704 (2010).
[22] Francescangeli, O., Vita,F., Ferrero, C., Dingemans, T. J. and Samulski, E.T., Soft Matter 7, 895 (2011).
[23] Francescangeli, O., Vita,F. and Samulski, E.T., Soft Matter 10, 7685 (2014).