



Giant optical nonlinearity in DNA lyotropic liquid crystals

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Abstract: We report the experimental evidence of nonlinear optical response in DNA lyotropic nematic liquid crystals. Pump-probe experiments indicate that the non-linearity is remarkably large. Quantitative assessment of the non-linear optical coefficient by transient optical grating demonstrates that the response is of the same order of the well-known Giant Optical Nonlinearity (GON) of thermotropic nematics. These results represent a further incentive to the current investigation of potential applications of DNA in biophotonics.

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1. Introduction

Since the early 2000s there was an intensive effort to develop photonic devices based on organic materials. Among the several organic materials, biomaterials are a source of continuous inspiration because of their rich architecture, hardly achieved in artificial materials. Indeed, there is a constant discovery of the variety of structural motifs and self-assembly modes adopted by basically all biological structures. One stand-out example is DNA, whose hierarchical packing in cells, bacteria and viruses has been the topic of many studies [1–4]. The self-assembly capability of DNA has also allowed the development of the so-called DNA nanotechnology, a set of strategies to induce the spontaneous formation of amazingly complex multi-strands nanostructures [5]. In parallel, concentrated DNA, both in the form of long double helices [6,7] and in oligomeric fragments [8–11], has been found to easily develop liquid crystal (LC) ordering, a condition of potential interest because of the long-ranged spontaneous ordering and resulting anisotropy of mechanical and optical properties.

Biomaterials based on DNA molecules are clearly very attractive because they might allow combining a variety of functions (e.g. mechanical and optical) and at the same time enable coupling with biological systems. It is thus not surprising that the search for new materials with photonic properties is being extended to 'the molecule of life'. A critical element in using DNA as a material is undoubtedly its cost of production by synthesis or purification. Natural DNA, mostly from salmon sperm, which is a waste product of the salmon-fishing industry is in general more accessible, even though massive synthesis technologies of DNA oligomers are being developed for some pharmaceutical industry purposes. Because of this barrier, research on DNA photonics has mainly explored natural DNA, mainly in form of thin solid films [12–14]. In this case, DNA is functionalized with a cationic surfactant, the cetyltrimethyl ammonium (CTMA), thus obtaining a DNA–lipid complex that is highly stable in temperature, insoluble in water but soluble in alcohols. In all these cases, the electro-optic and optical properties of DNA have been explored within the limits of the linear regime only.

The nonlinear optical response of DNA has been reported more than a decade ago [15] showing that a nonlinear refractive index n_2 in the range $10^{-15} \sim 10^{-14} \text{ cm}^2/\text{W}$ could be achieved, that is the same order of magnitude as the one of pure water. Recently, a much higher response has been found in thin solid films of DNA and DNA-CTMA in femtosecond regime [16]. A nonlinear refractive index up to $1.8 \times 10^{-11} \text{ cm}^2/\text{W}$ has been measured and the application of the DNA thin solid films as saturable absorbers was proposed.

Mechanism leading to stronger non-linear effects of DNA can be found when slower kinetics are considered. Light-induced collective molecular reorientation can lead to large non-linear response. This is the case of nematic liquid crystals, whose nonlinear optical coefficient easily reaches $10^{-5} \text{ cm}^2/\text{W}$ or even higher values under proper experimental conditions [18–20]. In this vein, we have recently explored the non-linear optical response of cholesteric LCs formed by concentrated solutions of DNA oligomers [21]. We found that the coupling of DNA LCs to optical fields is sufficient to produce measurable molecular reorientation. In that case, though, the amplitude of the effect was limited by the continuous twist of the optical axis, a condition that we exploited to measure the twist elastic coefficient of the phase. Here we explore DNA nematic LCs, obtained by minimizing the chirality of the phase by racemic compensation [22]. In this case, the optical torque acts coherently on the whole phase, yielding a non-linear response that we can more easily quantify and compare with the well-studied case of thermotropic LCs. We indeed find a nonlinear refractive index of the same order of those of thermotropic nematics, that is several orders of magnitude higher than the one reported in [16]. We remark that nor DNA in aqueous solution neither DNA-CTMA in an organic solvent investigated in [15] and [16], formed liquid crystalline phases. The one here reported is, to the best of our knowledge, the first evaluation of the nonlinear refractive index of DNA lyotropic liquid crystals.

2. Experimental details

The lyotropic LC phases, originally observed in long duplexed DNA polymers [6,7,23], have been more recently found to be a general motif of supramolecular organization in concentrated solutions of oligomeric duplexed DNA, although in this case the molecules lack the shape anisotropy necessary to induce Onsager-type orientational ordering [8–11]. LC ordering of DNA oligomers is the result of a more complex process of self-assembly by which duplexes aggregate end-to-end forming physically continuous longer molecular structures that are effectively analogous to long DNA, although chemically discontinuous. Indeed, oligomeric and long DNA are found to order in the same LC phases. To investigate the non-linear optical response of this class of LC materials, we chose to focus on solutions of a specific DNA oligomer because of several advantages it offers. Differently from long DNA, it readily develops LC ordering with good local uniformity and it responds on easily explored time scales. Moreover, we could access racemic mixtures, in which chiral effects are isuppressed, simplifying the understanding of the phenomena at play.

In the frame of this work we have used a DNA 12-bases-long oligomer (12mer) having base sequence 5'-AATGAATTCATT-3', here referred as "AAT". When AAT molecules are dispersed in water at a concentration above 500 mg/ml, chiral LC phases are formed [9]. Since the AAT base sequence is self-complementary, two AAT strands can pair in anti-parallel direction according to the canonical DNA double strand (dsDNA) helical structure. AAT duplexes are stable at room temperature, where our measurements are performed. Because of their large concentration in solutions, duplexes tend to assemble into linear aggregate due to the attractive stacking interaction between their terminal paired bases. As the transition concentration is reached, the end-to-end aggregation of the duplexes is stabilized and typical lyotropic LC phases are displayed.

Natural DNA duplexes adopt the notorious right-handed helical structure (R-DNA), because of the chirality of their constituent deoxyribose group. Chirality of duplexes propagates to the whole LC phase: as nematic (N) order develops, the system spontaneously

twist into a chiral nematic, or cholesteric, N^* phase. While the intrinsic chirality of DNA duplexes cannot be removed, its effect on the phase can be minimized by considering enantiomeric mixtures. In previous investigations, the chiral properties of binary mixtures of DNA oligomers and their enantiomers were considered [22]. These mixtures were obtained by solubilizing LC forming natural R-DNA oligomers with their mirror symmetric (“L-DNA”) molecules having identical sequence but synthesized using a deoxyribose with opposite chirality. L-DNA AAT chains arrange in a left-handed double helix. Since stacking interactions are not selective for handedness, even in mixtures of R-DNA and L-DNA the mechanism leading to LC formation remains, with the only difference that linear aggregates are not necessarily homo-chiral [22]. When racemic solutions, i.e. equimolar mixtures of enantiomers, are produced, the chirality of the nematic phase is suppressed. This is the condition in which the experiments here reported are performed.

Racemic AAT solutions were produced by mixing an equal volume of R-AAT and L-AAT stock aqueous solution, previously prepared at $c_{\text{DNA}} = 3$ mg/ml. Flat cells were obtained by serial deposition and evaporation of 1 μl drops of the racemic solution on a microscope glass (25 x 12 x 0.9 mm) until the needed concentration for LC ordering is achieved, $c_{\text{DNA}} = 500$ mg/ml. Cells were then covered by a second glass (20 x 10 x 0.9 mm), sealed by fluorinated oil and epoxy glue. Sample thickness is guaranteed by 20 μm diameter silica rods, used as spacers.

The resulting concentration in the cells considered in this study is $c_{\text{DNA}} \approx 500$ mg/ml and their intrinsic optical birefringence is $\Delta n = 0.02$, as obtained from c_{DNA} as described elsewhere [8]. Both birefringence and dielectric anisotropy are negative due to the molecular arrangement of DNA LC, in which the direction of largest polarizability, in the plane of the nucleobases, is perpendicular to the nematic director.

Lytotropic LCs are notoriously difficult to align since their coupling with the surface is weakened by the presence of the solvent. This is true for DNA LCs as well, which cannot be aligned with ordinary surface treatments, resulting in cells in which the director is planar but free to rotate. An example of such cells is in Fig. 1, where we show two pictures of the same cell in optical transmission microscopy through crossed polarizers with two different orientations of polarizers. As it can be easily noticed, regions appearing bright in the first picture are instead extinguished in the second and vice versa, indicating disordered achiral nematic ordering. The local director orientation is determined by uncontrolled accidental factors such as impurities or surface undulations.

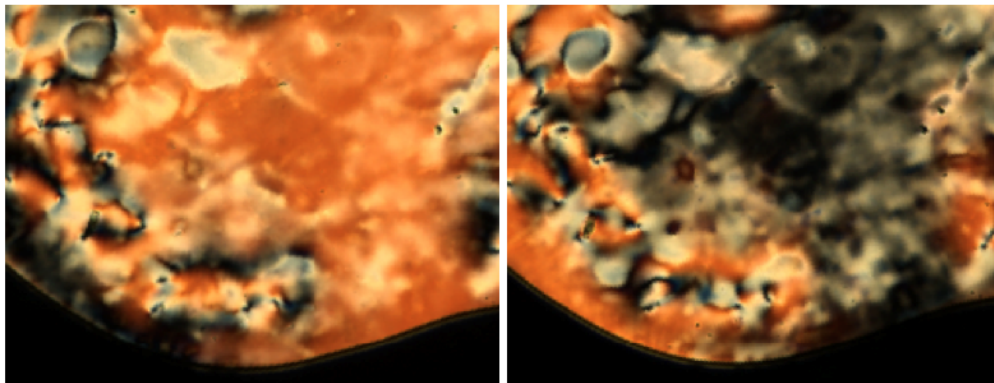


Fig. 1. Polarized optical transmission microscopy picture of the racemic L-R AAT mixture. The two images are taken from the same cell upon rotating polarizer and analyzer by 45° . Typical textures of LC nematic phase are clearly recognizable. Non-homogeneous director orientation is due to the lack of an efficient planar surface treatment for DNA aqueous solutions.

Both pump-probe and dynamic gratings experiments have been performed with a cw Argon ion laser as pump beam ($\lambda = 514 \text{ nm}$) and a low power He-Ne laser as probe beam ($\lambda = 633 \text{ nm}$). In pump-probe experiments, the two beams counter-propagate, both entering the cell at normal incidence. Gratings are produced with a standard configuration in non-tilted geometry (i.e. the writing beams bisector is parallel to the cell normal).

In pump-probe measurements the incident light is linearly polarized either along x or y and pump power ranges from 100 to 400 mW. The beam is focused by a 10 cm plano convex lens which gives a beam diameter on the sample of $50 \mu\text{m}$. The probe beam is linearly polarized at 45° with respect to the polarization of the pump and a crossed polarizer is placed behind the sample. In this geometry, the light transmitted by this analyzer before pump irradiation is due to the depolarization originated by the disordered nature of the sample. Pump irradiation produces variations of the depolarization state of the probe beam, which indicates that the LC molecules undergo reorientation under its action. A mechanical shutter enables performing irradiation cycles, which in the experiments here reported have 10 s duration and 2 s dark time separation.

In dynamic grating experiments, both pump and probe are linearly polarized parallel or perpendicular to the incidence plane. The beams diameter on the cell is 2 mm for the exciting beams and 1.5 mm for the probe beam. The grating spacing is $20 \mu\text{m}$. The irradiation time is again determined by a beam shutter allowing cycles of 10 s irradiation each, followed by 2 s of dark. This procedure avoids the onset of memory effects, which have been observed for longer irradiation time and/or higher incident intensity. A sketch of the experimental set-up is shown in Fig. 2 for both pump-probe (a) and dynamic grating recording (b).

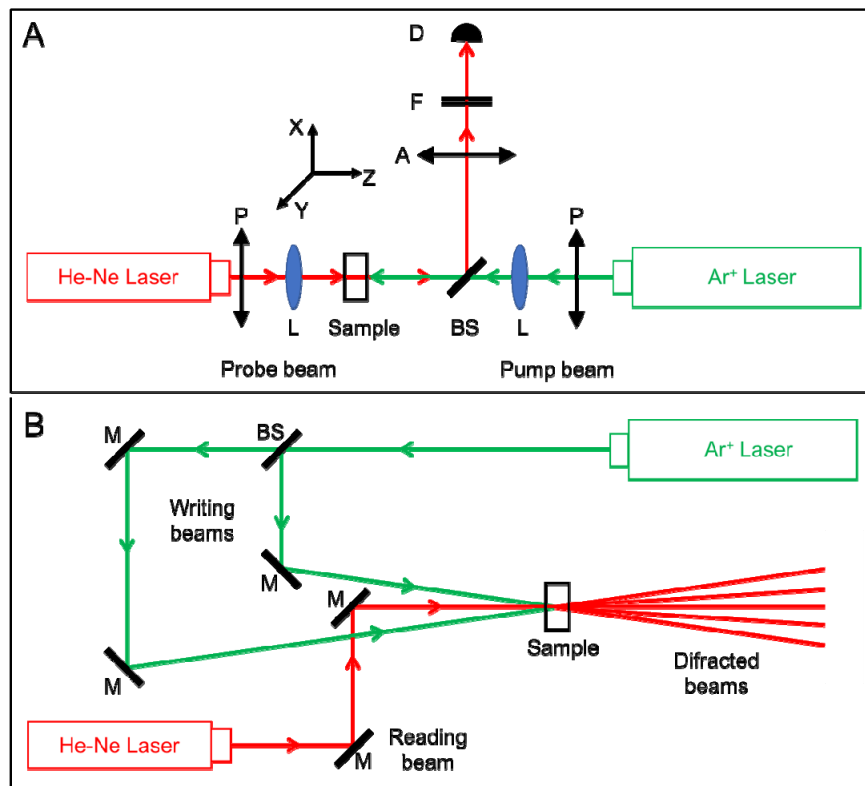


Fig. 2. Sketch of the experimental set ups. Pump probe measurements (a) and grating recording (b). The different optical components are indicated: P = polarizers, L = lens, S = sample, B.S. = beam splitter, A = analyzer, D = detector, F = filter, M = mirror.

Non-linear optical response is readily measured by the appearance of diffracted spots in the probe light. The diffraction efficiency defined as $\eta = I_{+1}/I_0$ was measured as a function of the pump intensity I_p . Here I_{+1} is the intensity of the first order diffracted beam and I_0 the one of the zero-order transmitted beam.

3. Results and discussion

Pump-probe measurements clearly show the appearance of a light-induced molecular reorientation giving rise to a change in the amount of probe light transmitted by the analyzer, as reported in Fig. 3, where the transmitted signal T is shown for different values of the pump power as a function of time. In principle, these data allow to estimate the light-induced phase shift produced by the liquid crystal reorientation [24]. However, due to the disordered configuration of the sample, the induced birefringence, which is directly connected to the optical nonlinear response, cannot in practice be easily extracted. Moreover, by inspecting the two curves in Fig. 3 corresponding to 300 and 400 mW, it is evident that the signals detected after the pump is turned off are slightly larger than those measured for lower power, indicating the onset of some sort of memory effect.

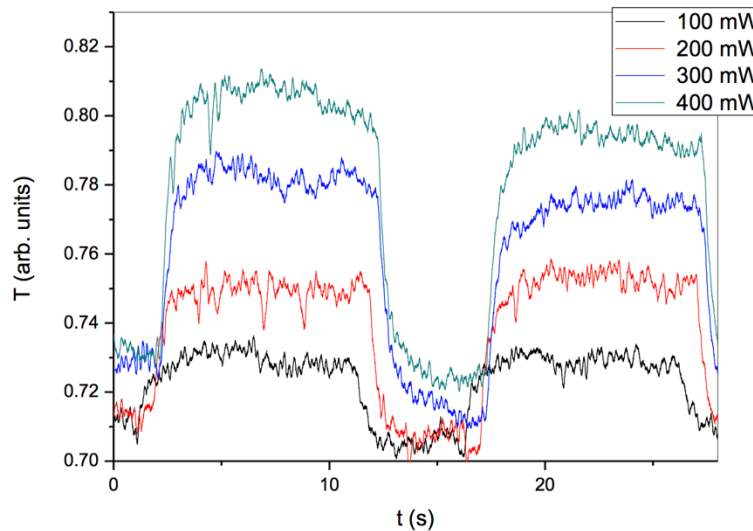


Fig. 3. Transmitted probe signal for different values of the pump power as a function of time. The pump beam polarization is parallel to the incidence plane.

On the contrary, the diffraction efficiency measured in dynamic grating experiments is suitable for the direct determination of the optical nonlinearity. Since the cell thickness d and grating spacing Λ (as determined by the crossing angle between the interfering pump beams), are equal we have

$$\lambda d / \Lambda^2 \ll 1 \quad (1)$$

being λ the wavelength of the pump beam; therefore we are in the thin grating regime [24]. In this case the first order diffraction efficiency can be calculated as:

$$\eta = |J_1(\xi)|^2 \quad (2)$$

where $J_1(\xi)$ is the Bessel function of the first order and $\xi = 2\pi d n_2 I_p / \lambda$ that includes light-induced modulation of the refractive index giving rise to light diffraction. In this expression d is the cell thickness, λ the pump wavelength, I_p the pump intensity and n_2 the optical nonlinear coefficient. If ξ is small, condition fulfilled in our case, the diffraction efficiency can be approximated as:

$$\eta \equiv \left(\pi d n_2 I_p / \lambda \right)^2 \quad (3)$$

that is $\eta \propto I_p^2$, therefore a parabolic fit of the experimental data allows the determination of n_2 , which is the parameter characterizing the nonlinear optical response of the sample. Worthy of note, Eq. (3) relating the diffraction efficiency to the nonlinear optical response does not depend on the structure of the material therefore can be applied to perfect samples as well as to randomly aligned samples, as in the case here reported.

Data showing the diffraction efficiency as a function of the writing intensity are reported in Fig. 4, in the case of both pump and probe polarized parallel to the incidence plane. The dependence of η on I_p is the one expected and the parabolic fit with the function $\eta = C I_p^2$, gives $C = (1.8 \pm 0.1) \times 10^{-5} \text{ cm}^4/\text{W}^2$, which means $(\pi d n_2 / \lambda)^2 = (1.8 \pm 0.1) \times 10^{-5} \text{ cm}^4/\text{W}^2$ and $n_2 \equiv (3 \pm 0.5) \times 10^{-5} \text{ cm}^2/\text{W}$, considering an error of 10% on the cell thickness. The dependence of η on the square of the incident intensity, is reported in the inset with a linear fit of the experimental data. The value of the nonlinear refractive index is comparable to the one obtained from the parabolic fit. By averaging the values extracted from different measurements, we find an average nonlinear refractive index $n_2 = (1.5 \pm 0.5) \times 10^{-5} \text{ cm}^2/\text{W}$. The described procedure applied to data obtained with different combinations of the pump and probe polarizations, gave values of n_2 of the same order.

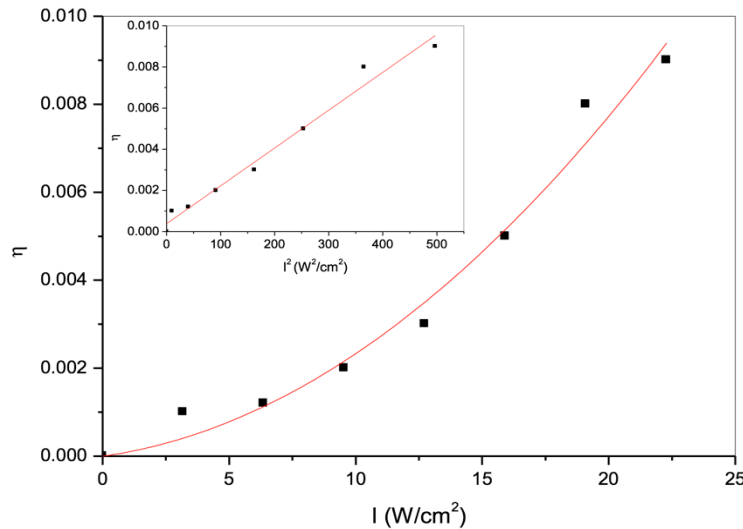


Fig. 4. Diffraction efficiency as a function of the total incident intensity. In the case here reported both pump and probe are polarized parallel to the incidence plane. Similar results have been obtained with different combinations of the polarizations of probe and pump beams. Inset: diffraction efficiency vs I^2 . A linear fit of the data is shown.

The value found for n_2 is six orders of magnitude higher than the maximum value reported so far for DNA samples [16] and is of the order of the Giant Optical Nonlinearity usually observed in thermotropic nematic cells [17]. The absence of a specific coupling of the LC axis with the surfaces is likely to affect the phenomenon producing an increase of the sensitivity, since no competition with prealignment conditions is present.

Within the range in which the system is nematic, we expect n_2 , proportional on the ratio $\Delta n^2/K$ [25], to depend on c_{DNA} only weakly due to the approximate compensation of the concentration dependence of elasticity and optical coupling. Indeed, the elasticity of the LC phase of DNA oligomers is roughly proportional to c_{DNA}^2 [26], while the birefringence of the nematic phase is approximately proportional to c_{DNA} , the nematic order parameter of DNA LC being almost constant over the entire phase.

The decay time τ_{off} can be determined by an exponential fit of the relaxation curves both in pump-probe and in dynamic grating experiments. An example of such fitting is shown in Fig. 5, where the intensity of the first order diffracted beam is plotted as a function of time, $t = 0$ marking the time when the pump is switched off. The fitting yields a decay time $\tau_{\text{off}} = (0.48 \pm 0.04)$ s. Such a slow relaxation confirms the orientational origin of the nonlinear response. Indeed, similar relaxation times are found in thermotropic nematic cells having comparable thickness [25].

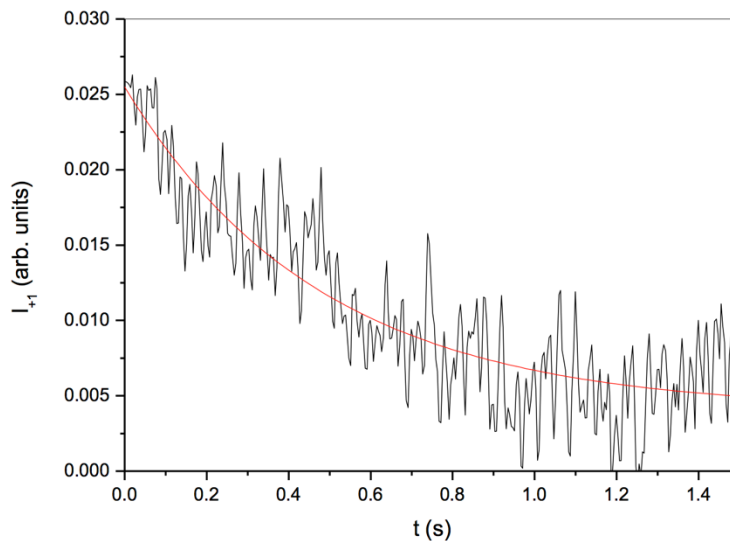


Fig. 5. Intensity of the first order diffracted beam as a function of time. $t = 0$ corresponds to the switching off of the writing beams.

Since the intrinsic birefringence of liquid crystalline DNA is one order of magnitude lower than that of 5CB, the strong nonlinear optical response that we observe indicates that the elastic constants of liquid crystalline DNA must also be significantly smaller than those of conventional thermotropic liquid crystals. This is also suggested by recent measurements on the twist elastic constant of DNA chiral nematics [21]. Moreover, the similarity of the response time of DNA nematics to that of thermotropic nematics indicates similar viscoelastic ratios. Based on this observation, we expect the viscosity of DNA nematics to be significantly lower than that of thermotropics. Overall, DNA nematics appear to have a peculiar combination of dielectric anisotropy, elasticity and viscosity, yielding non-linear optical susceptibility and kinetics similar to those of thermotropic nematics. In other words, despite their much softer structure, DNA nematics could hardly be distinguished from thermotropic nematics through their non-linear optical response alone. This intriguing combination of large response and “ultrasoft” structure makes DNA nematics a rather unique material and indicates that the study of their non-linear optical properties could turn into a powerful tool to investigate the weak DNA-DNA molecular interactions and how these are affected by DNA-binding molecules. Moreover, because of their response similar to thermotropics, it appears conceivable to use DNA liquid crystals for photonic applications based on optical nonlinear properties such as liquid crystal light valves, optical switches or liquid crystal lenses. In particular, in the context of the growing capacities of DNA nanotechnology and of the integration of multiple functions in miniaturized DNA-based devices, the non-linear response could be an important add-on. Indeed, one could envision conjugating optical switches with mechanical or structural functions in DNA-based biocompatible technologies for cell manipulation or drug delivery. Moreover, since a wealth of DNA binding molecules are known and characterized, and since it is known that the DNA LC matrix can act as an

alignment-providing scaffold for such molecules [27], it appears possible to exploit doping to enhance the non-linear effect.

Another potentially interesting feature of the samples under study is the observation of stable gratings under proper experimental conditions. For irradiation times longer than those used for data of Figs. 4 and 5 we observe diffraction gratings stable for several hours. In particular, by exposing the cell to the pump beams for 2 minutes at $I_p = 3 \text{ W/cm}^2$ the observed relaxation time was at least three hours and the diffraction efficiency was $\eta = 0.4\%$.

The origin of the observed memory effect is not clear yet. In thermotropic nematics, analogous long lasting memory effect can be obtained by doping the liquid crystals with a small amount of Methyl Red, an azo dye able to form charge complexes [28]. These charges undergo photo-assisted adsorption and desorption on the cell's substrates and this produces a light-induced change of the anchoring conditions giving rise to the occurrence of a new easy axis.

DNA is negatively charged because of the dissociation of the phosphate groups. This means that each AAT duplex carries up to 24 negative charges, making it very sensitive to surface adsorption of cations. Should an effect like the one in dye-doped thermotropics be present in this case also, memory could be explained in terms of space charge field reminiscent of surface photorefractive effect. This could be of relevance because it would indicate the possibility of optically manipulating the surface coupling of DNA. Further studies in this direction are under consideration.

4. Conclusions

We show for the first time that the ultrasoft DNA lyotropic liquid crystals in the nematic phase exhibit a nonlinear optical response of the same order as the one of conventional thermotropic liquid crystals. This is due to a peculiar balance of a weaker dielectric anisotropy, elasticity and viscosity.

The high nonlinear optical response of the liquid crystalline phase of DNA could interestingly combine with the structural potential of this polymers, to open new possibilities in devising new responsive self-assembled nanostructured fluids. At the same time the non-linear response could emerge as a tool for studying DNA-DNA interactions in concentrated solutions such as those leading to LC phases.