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Optical Kerr-like response of dye-doped nematics

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Abstract. When small amounts of suitable dyes are added to a pure nematic liquid crystal, its nonlinear optical response may be enhanced by over two orders of magnitude and even be reversed in sign. This feature may be interesting for applications. We measured the enhancement of the nonlinear optical Kerr coefficient of several dye–nematic mixtures, in order to gain some insight on the molecular mechanism that is supposed to be the basis of the phenomenon.

1. Introduction

Liquid crystals in the nematic phase show optical nonlinearity because of light-induced molecular reorientation [1, 2]. In simple experimental configurations, nematic liquid crystals simulate a genuine Kerr-like optical medium, having typical values of the nonlinear optical Kerr index $n_2 \simeq 10^{-5}$ cm^2 W^{-1}, of about 10^7 times the n_2 of typical organic liquids such as CS_2 [3]. Since the optical reorientation is a collective phenomenon, however, the response time is very long, ranging from 0.1 s to a few seconds. Medium power, commercial CW lasers may be used to induce exceptionally high nonlinear optical effects in liquid crystals. All effects based on the laser-induced change of refractive index have been reproduced in liquid crystals; examples are self-focusing, wave mixing [4], self-diffraction [5], etc. It should be noticed, however, that the optical reorientation in liquid crystals is a very complex phenomenon, yielding a number of nonlinear optical effects that cannot be explained through a third-order expansion of the nonlinear polarization. They include intrinsic optical bistability [6], self-induced stimulated light scattering [7], self-oscillations [8] and even the onset of deterministic chaos [9]. Such a very complex and rich phenomenology has been studied extensively in the last few years and it can be traced back to the angular momentum transferred from the optical field to the orientational degrees of freedom of the liquid crystal. On the application side, liquid crystals have been proposed as holographic storage materials and have been introduced either in the core of optical waveguides to produce nonlinear effects such as beam self-splitting [10], or in the cladding of optical fibres to realize optical switching in directional couplers [11].

Recently, it was observed that laser-induced reorientation can be enhanced by almost two orders of magnitude by adding a small quantity (less than 0.1% by weight) of a suitable dye to the pure nematic host, yielding a corresponding amplification of the optical Kerr response of the material [12]. For some dyes the sign of the optical Kerr coefficient n_2 was found to be reversed upon the addition of the dopant, changing the pure nematic from a self-focusing to a self-defocusing Kerr-like medium [13]. Other material constants such as polarizability, elastic constants, heat capacity, etc, remain the same as in the pure

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host. Since its discovery, the phenomenon of the 'dye effect' has been studied extensively [14–17]. Laser heating effects have been excluded, because different dyes yield different enhancements even for equal values of light absorbance. It is now commonly accepted that the amplification phenomenon is related to some photo-induced molecular effect producing an extra torque on the molecular director of the nematic host [18]. The reversibility of the phenomenon, when the light beam is switched off, excludes, however, the occurrence of photochemical irreversible transformations. At present, only two families of dyes have proved to be effective in enhancing the nonlinear optical response of nematics, namely anthraquinone derived dyes and azodyes. In the last case, it is probable that photo-induced conformational changes in the dye molecule may lead to the extra torque, but this must be excluded for anthraquinone dyes, as it is well known that dyes belonging to this family do not undergo conformational transformations. Although the underlying molecular mechanism is still under study, the possibility of enhancing the already huge nonlinear optical response of liquid crystals (and of changing the sign of n_2) *without reducing the response time* may be of interest for applications, especially when a moderate absorption can be tolerated. A phenomenological model to explain the dye amplification effect was proposed recently and has proved to be successful in predicting the main features and order of magnitude of the observed phenomena in the anthraquinone dye family [18]. In order to gain some insight into the dye-induced extra torque, a simplified version of this model is presented in the next section, while the rest of the paper is devoted to the experimental characterization of a set of interesting dye–liquid crystal mixtures.

2. The molecular mechanism

The laser-induced reorientation of the molecular director $\boldsymbol{n}$ is originated, in pure nematics, by the electromagnetic torque per unit volume

$$\boldsymbol{\tau}_{\mathrm{em}} = \frac{1}{8\pi}\,\mathrm{Re}(\boldsymbol{D}^* \times \boldsymbol{E}) = \frac{\epsilon_{\mathrm{a}}|E|^2}{8\pi}(\boldsymbol{n}\cdot\boldsymbol{e})(\boldsymbol{n}\times\boldsymbol{e}) \tag{1}$$

where $\epsilon_{\mathrm{a}} = \epsilon_{\parallel} - \epsilon_{\perp}$ is the dielectric anisotropy of the liquid crystal at the optical frequency, $|E|^2$ is the squared amplitude of the optical field, proportional to the laser intensity I, and $\boldsymbol{e}$ is its polarization direction. Upon the addition of dye, a further photo-induced torque τ_{ph} is induced, having the same form as $\boldsymbol{\tau}_{\mathrm{em}}$:

$$\boldsymbol{\tau}_{\mathrm{ph}} = \eta\boldsymbol{\tau}_{\mathrm{em}} \tag{2}$$

where η is a dimensionless constant (usually very large), roughly proportional to the dye concentration. The model is based on two assumptions: first, light absorption generates an anisotropic population of electronically excited dye molecules and, second, excited and ground state dye molecules have different intermolecular orientational interactions with the nematic host. In the presence of the laser radiation, linearly polarized along the direction $\boldsymbol{e}$, some of the dye molecules are maintained in their excited state. For anisotropic dye molecules, the excitation transition rate w depends on the orientation of the dye molecule, according to

$$w = |E|^2\left[\sigma_{\perp} + \sigma_{\mathrm{a}}(\boldsymbol{l}\cdot\boldsymbol{e})^2\right] \tag{3}$$

where $\sigma_{\mathrm{a}} = \sigma_{\parallel} - \sigma_{\perp}$, $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the dye absorption strength for light polarization $\boldsymbol{e}$ parallel and perpendicular to the dye molecule direction $\boldsymbol{l}$, respectively. The quantity σ_{a} is a measure of the anisotropy of the dye excitation process. Denoting by t_{e} the overall lifetime

of the dye excited state, the steady state probability of finding a dye molecule in the excited state is

$$p = \frac{wt_e}{1 + wt_e} \simeq wt_e \tag{4}$$

where the last equality holds for low light intensity I, where the dye saturation is negligible. Now, we assume that a dye molecule oriented along $\boldsymbol{l}$ exerts on the director $\boldsymbol{n}$ of the liquid crystal an average torque, having the quadrupole–quadrupole form

$$\boldsymbol{\tau}_{e,g} = Su_{e,g}(\boldsymbol{n} \cdot \boldsymbol{l})(\boldsymbol{n} \times \boldsymbol{l}) \tag{5}$$

where S is the order parameter of the nematic host, and u_e, u_g are positive coupling constants, that we take to be *different* in the ground and excited states of the dye molecule. Then, the average photo-induced torque per unit volume that the dye exerts on the molecular director is

$$\boldsymbol{\tau}_{ph} = N_d\langle p\,\boldsymbol{\tau}_e + (1 - p)\boldsymbol{\tau}_g\rangle \tag{6}$$

where N_d is the number concentration of dye molecules. In the limit of negligible dye saturation, we may assume that the orientational distribution function of the dye molecules is weakly affected by the presence of light, so that the average in equation (6) can be made using the initial (no light) dye distribution function f_0. In the absence of light, no average torque is exerted on $\boldsymbol{n}$, so that $\langle\boldsymbol{\tau}_g\rangle = 0$, when the average is performed by using f_0. Then equation (6) is simplified to

$$\boldsymbol{\tau}_{ph} = N_d\langle p(\boldsymbol{\tau}_e - \boldsymbol{\tau}_g)\rangle. \tag{7}$$

This average is not zero, in general, because of the dependence of the transition probability p on the azimuthal angle ϕ of $\boldsymbol{l}$. Using equations (3)–(5), we obtain, in the dye no saturation limit,

$$\boldsymbol{\tau}_{ph} = N_d\sigma_a t_e|E|^2 S(u_e - u_g)\big\langle(\boldsymbol{l} \cdot \boldsymbol{e})^2(\boldsymbol{n} \cdot \boldsymbol{l})(\boldsymbol{n} \times \boldsymbol{l})\big\rangle. \tag{8}$$

Now, a direct calculation shows that

$$\big\langle(\boldsymbol{l} \cdot \boldsymbol{e})^2(\boldsymbol{n} \cdot \boldsymbol{l})(\boldsymbol{n} \times \boldsymbol{l})\big\rangle = \big\langle \sin^2\theta\cos^2\theta\big\rangle(\boldsymbol{n} \cdot \boldsymbol{e})(\boldsymbol{n} \times \boldsymbol{e}) \tag{9}$$

where θ is the angle between $\boldsymbol{l}$ and $\boldsymbol{n}$. Inserting this equation into equation (8), we see that the photo-induced torque $\boldsymbol{\tau}_{ph}$ is indeed proportional to the optical torque $\boldsymbol{\tau}_{em}$, as anticipated in equation (2), the factor η being

$$\eta = \frac{8\pi N_d\sigma_a t_e S(u_e - u_g)}{\epsilon_a}\big\langle \sin^2\theta\cos^2\theta\big\rangle. \tag{10}$$

Using the orientational distribution function of the dye molecules in the absence of light (Z is the normalization factor)

$$f_0(\theta) = \frac{1}{4\pi Z}e^{m\cos^2\theta} \tag{11}$$

it can be shown that $\big\langle \sin^2\theta\cos^2\theta\big\rangle = S_d/m$, where S_d is the order parameter of the dye (in the ground state) and $m = Su_g/2kT$. Then the amplification factor η is given by

$$\eta = \frac{2kT\lambda(n_e\alpha_e + 2n_o\alpha_o)t_e S_d(u_e - u_g)}{h\epsilon_a u_g} \tag{12}$$

where we used the following relationship among the absorption strength σ_a and the absorption coefficients α_o and α_e of the ordinary and extraordinary waves [19]

$$\sigma_a N_d = \frac{\lambda(n_e\alpha_e + 2n_o\alpha_o)}{8\pi h}. \tag{13}$$

In this expression, n_o and n_e are the refractive indices of the two waves, λ is the optical wavelength and h is Planck's constant. Equation (13) is derived by integrating equation (4) over the whole solid angle and equating the result to the average number of photons absorbed by one dye molecule, as obtained from the beam Poynting vector. In order to compare the overall efficiencies of different dyes on a molecular basis, it is expedient to introduce a molecular merit figure μ, defined as

$$\mu = \frac{2kTt_e S_d(u_e - u_g)}{hSu_g} = \frac{\eta\epsilon_a}{\lambda S(n_e\alpha_e + 2n_o\alpha_o)}. \tag{14}$$

We notice that all quantities in the last term on the right-hand side of equation (14) are measurable experimentally, while all quantities in the middle term depend on molecular parameters. In particular, μ is normalized with respect to the dye concentration and absorption strength. Division by S is included to have a finite limit when the host order parameter $S \to 0$, as happens going into the isotropic phase, and in the limit $Su_g \ll kT$, when the dye order parameter is very small. In both cases, $2kTS_d/Su_g = S_d/m \to \frac{2}{15}$, and we get

$$\mu \simeq \frac{2t_e(u_e - u_g)}{15h}. \tag{15}$$

This expression of μ remains valid even in the isotropic phase. The figure of merit μ measures the average angular momentum transferred to the host per dye molecule, in units of h. The angular momentum transfer can be interrupted by spontaneous decay of the excited dye molecule to the ground state or by rotational diffusion, tending to restore the cylindrical symmetry of the dye distribution function around $\boldsymbol{n}$. The effective lifetime t_e is therefore given by

$$t_e = \frac{t_f}{1 + Dt_f} \tag{16}$$

where D is the rotational diffusion coefficient of the dye molecules and t_f is the lifetime of the dye excited state. A more complete approach, based on the diffusion equations for the angular distribution functions f_g and f_e of the dye molecules in the ground and excited state, is reported in [18, 20].

3. Experiment

We measured the nonlinear optical response of several dye–liquid crystal mixtures in the nematic mesophase. Because of the large enhancement produced by the dye, a 10 mW He–Ne laser focused to a spot $w_0 \simeq 40$ μm was enough to induce a nonlinear phase shift $\Delta\phi \simeq 2\pi$. A second, unfocused, He–Ne beam was made to pass through the sample as a probe. The probe beam was split into the two arms of a Mach–Zehnder interferometer, as described in [21]. The two beams of the interferometer were recombined at a small angle, in order to obtain, for a homogeneous sample, an interference pattern of parallel straight line fringes. The image of the fringes was magnified by a lens system, projected onto a screen and then recorded by a CCD camera. The nonlinear transverse phase shift $\Delta\phi$ was measured from the fringe shape deformation, produced by the pump beam. In the experiments where the optical wavelength λ was changed, the pump beam was an argon-pumped dye laser. Pump and probe incidence angles were 37° and 43°, respectively, and both beams were TM polarized. Oblique incidence and TM polarization of the pump beam guarantee that the nonlinear optical response of the nematic film simulates a genuine Kerr-like medium. The nonlinear phase shift of pure liquid crystal samples was also measured and used as

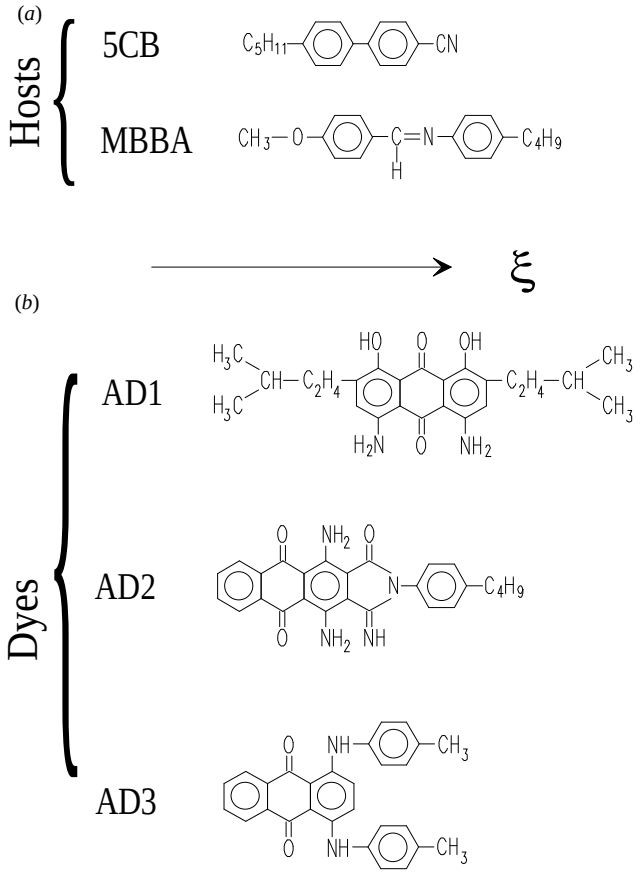

Figure 1. (*a*) Structure formulae of the employed nematic hosts; (*b*) structure formulae of the employed dyes.

a reference. All samples were 50 μm thick and planarly aligned by rubbing a polyvinyl alcohol coating deposited on the glass walls. This coating is known to provide strong planar alignment at the walls, after rubbing. All samples were oriented with the rubbing direction along the beam incidence plane so that only the extraordinary wave propagated in the liquid crystal.

In separate experiments, we studied a number of mixtures with various dyes and different liquid crystal hosts. In this large set we selected a subset of nine 'representative' mixtures, on which we focused our attention. The mixtures of this subset were obtained by mixing three dyes and three liquid crystal hosts, with a weight-to-weight ratio of about 0.1%. The dye molecular structures are reported in figure 1(*b*). All dyes were anthraquinone derivatives. Dye AD1 (anthraquinone derivative 1) was chosen because it is the most effective positive-η dye discovered so far; AD2 was also positive, but with a lower η value, and AD3 was the strongest dye having a negative η. The three liquid crystal hosts were 5CB, MBBA and E63, the latter being a cyanophenyl mixture. All chemicals were provided by BDH company. The two pure host molecules are reported in figure 1(*a*). The composition of the E63 mixture is reported in [22]. We included E63 because it was employed in many

Table 1. Measured properties of dye–nematic mixtures for $\lambda = 633$ nm and $T = 24\,^{\circ}$C.

Dye–LC	α_o (cm^{-1})	α_e (cm^{-1})	$\Delta\phi/P_0$ (rad mW^{-1})	η	μ
AD1–5CB	42	190	6.6	99	3400
AD1–E63	68	700	5.7	237	2500
AD1–MBBA	94	190	2.5	25	740
AD2–5CB	82	370	0.92	19	340
AD2–E63	50	480	0.59	15	240
AD2–MBBA	82	350	<0.2	<1.4	<40
AD3–5CB	98	210	-1.6	-27	-650
AD3–E63	117	360	-1.3	-31	-470
AD3–MBBA	17	38	-0.36	-3.5	-550

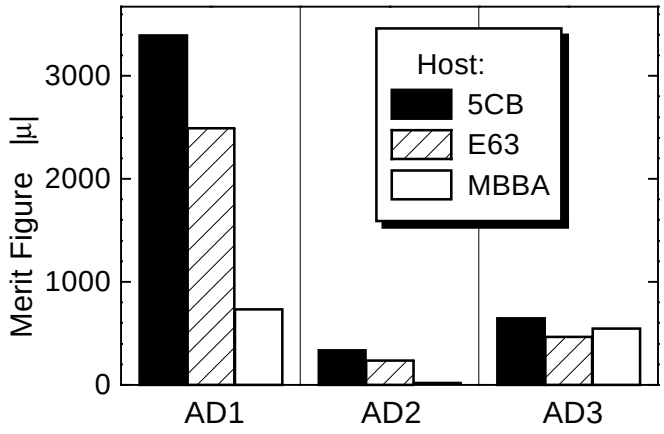

Figure 2. Merit figure $|\mu|$ (absolute value) at $\lambda = 633$ nm and $T = 24\,^{\circ}$C.

previous works on the subject and, therefore, it can be used for comparison; moreover, E63 has a much larger order parameter than 5CB and MBBA, at the working temperature, and, therefore, it allows us to investigate the effects of higher dye order.

The measured properties of the nine guest–host combinations are reported in table 1. The merit figure is shown in figure 2. The incident intensity I_0 at the beam centre is related to the laser power P_0 by $I_0 = 2P_0/g\pi w_0^2$, where g is a geometric factor taking into account the transverse elastic effects [23]. In our experimental conditions $g \simeq 4$. It is evident that the hosts E63 and 5CB enhance the dye-induced torque effect of AD1 and AD2. No appreciable enhancement was observed for the negative-η AD3. We see, therefore, that specific intermolecular guest–host interactions may play a fundamental role. We suggest, in particular, that polar interactions may be important, because E63 and 5CB are made of molecules having the strong polar cyano group CN, while MBBA has no strong polar groups in its molecule. This hypothesis is also supported by measurements of the dye order parameter S_d in polar and nonpolar hosts. A somewhat indirect proof that guest–host intermolecular forces may change when the dye goes into its electronic excited state, is provided by the solvent-induced shift of the dye absorption spectrum. We found a redshift of the absorption peak of about 5 nm in the polar hosts E63 and 5CB, with respect to MBBA (see figure 3). This shift corresponds to an interaction energy difference of about 1.5 kJ mole^{-1}, which has the proper order of magnitude. The fact that the shift is

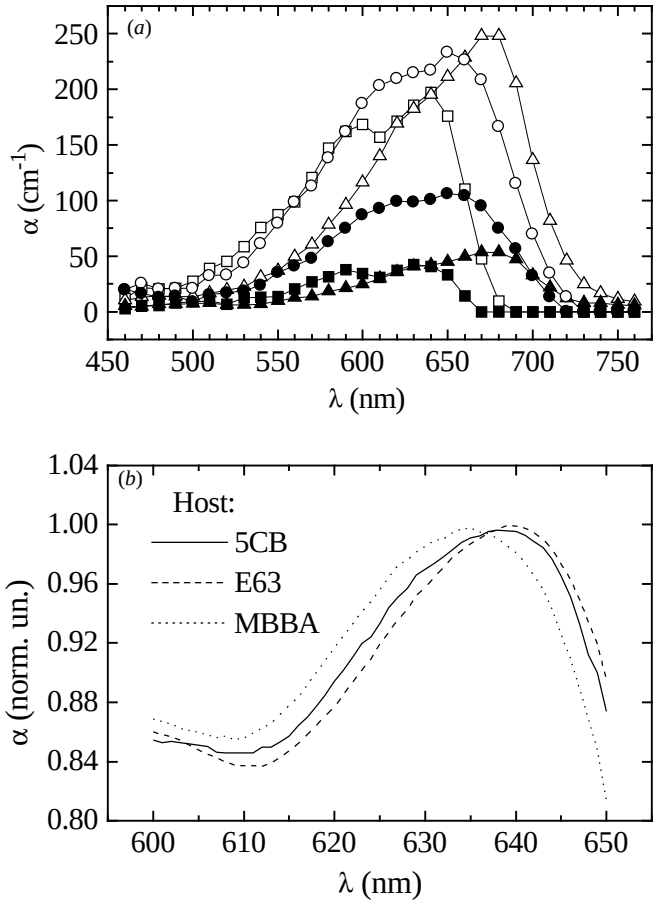

Figure 3. (*a*) Absorption spectra. Open symbols, α_e; full symbols, α_o. Squares, AD1; triangles, AD2; circles, AD3. The absorption spectrum of AD2 (triangles) is divided by a factor of two. Nematic solvent, 5CB. (*b*) Detail of absorption peak of AD1 in 5CB, E63 and MBBA, showing the solvent-induced redshift.

towards the red indicates that the interaction with the host is stronger when the dye is in its excited state. We also checked the wavelength dependence of the merit figure μ. Our results are reported in figure 4. In the E63–AD3 mixture, μ was found almost wavelength independent, as expected from the model. A more complex wavelength dependence was observed in E63–AD1. We ascribed this discrepancy to the fact that AD1, unlike AD3, has a double-peaked absorption spectrum. A good fit with the experimental data can be obtained by assuming that each absorption band has its own merit figure. The overall merit figure is then obtained as

$$\mu(\lambda) = \frac{p_0(\lambda)\,\mu_0 + p_1(\lambda)\,\mu_1}{p_0(\lambda) + p_1(\lambda)} \tag{17}$$

where $\mu_{0,1}$ are the merit figures of the two bands and $p_{0,1}(\lambda)$ are the probabilities that, on absorbing a photon, the dye molecules end up in the excited state corresponding to the band 0 or 1, respectively. To fit the data, we used equation (17), assuming $p_{0,1}(\lambda)$ having typical Gaussian + Lorentzian shape and using $\mu_{0,1}$ as fitting parameters. The result of the fitting

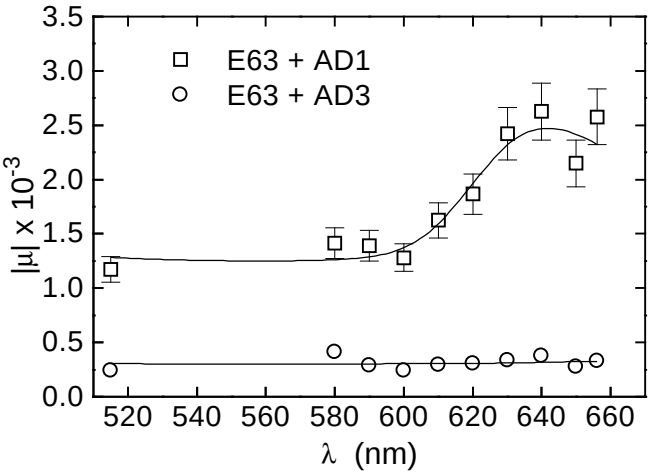

Figure 4. Experimental and theoretical merit figure μ versus wavelength λ for AD1 and AD3 in E63 at $T = 24\,^{\circ}$C.

is shown in figure 4 as a full curve. The best-fit values of μ_0 and μ_1 were $\mu_0 = 2200$ and $\mu_1 = 1300$.

4. Conclusions

Our experiments provide evidence that the dye-induced amplification of the nonlinear optical response of liquid crystals may depend dramatically on the specific intermolecular forces between the guest and the host. For some anthraquinone dyes, the presence of strong dipolar groups in the host molecule seems to enhance the effect. In these same mixtures, an appreciable solvent-induced redshift of the dye absorption spectrum is present, supporting the idea that the guest–host interaction may change upon excitation of the dye molecule. This change, together with the angular anisotropy of the distribution function of the dye molecules excited by the incoming laser beam, produces a corresponding change in the mean field seen by the liquid crystal molecules, yielding the observed photo-induced extra torque. Although the experimental data are in good agreement with the theory, some aspects of the phenomenon are not clear yet. For example, it is still impossible to predict, for a given guest–host combination, whether the resulting medium will be self-focusing ($\mu > 0$) or self-defocusing ($\mu < 0$). The merit figure μ is strongly dependent on molecular parameters (dipole moment, lifetime, etc) of the dye molecule in its ground and excited states. Having measured these parameters, an interpretation of the data should be more feasible. Conformational photo-transformations may also play a role in the dye-induced torque for some dyes, but they must be excluded in the case of anthraquinone derivatives. The molecular model presented here does not apply to the case of photo-induced conformational changes, although the generalization seems to be straightforward. However, a recent experiment [24] made with azo-dyes (which can suffer conformational changes), was interpreted as a change of the sign of the merit figure μ as a function of the laser incidence angle, which is in disagreement with the predictions of the molecular model outlined here. Further experimental and theoretical work is evidently desirable.

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