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Hypothesis of Dye Aggregation in a Nematic Liquid Crystal: From Experiment to a Model of the Enhanced Light-Director Interaction

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We report experimental and theoretical arguments showing that the effect of strong enhancement of the light-induced director reorientation in a nematic liquid crystal doped with anthraquinone dye molecules (Jánossy effect) can be related to their aggregation. The torque on the director is due to dependence of the entropy of the aggregate subsystem on the electric field vector relative to the director.

Keywords: dye aggregation; Jánossy effect; nematic director

INTRODUCTION

Electromagnetic fields produce a mechanical torque on the nematic director and can cause a director reorientation (DR) [1]. About fifteen years ago Jánossy with his collaborators discovered that just one percent of light-absorbing dye dopands dissolved in a nematic liquid crystal (NLC) enhances this DR by a factor of hundred [2,3]. The intrigue of this discovery was that the polarizability, size, and other parameters of the

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dye molecule are rather similar to those of the LC molecule and thus could not explain the huge effect. The proposed models of this effect have assumed the dye to be present in the NLC in the form of individual molecules that do not correlate with each other [1,4–7]. It is known, however, that correlations between dye molecules can be strong and result in their aggregation in various solvents [8–11]. The best known example is aqueous solutions where molecules of many dyes aggregate into supramolecular units of different shape (J, H, I aggregates, and so on) [8]. In particular, the J and H aggregates are columns whose length can reportedly be as large as several tens or even a few hundred molecules [8]. The aggregation is driven by the energy gain due to the chemical bonding when the two plank-like dye molecules come sufficiently close and/or by the hydrophobic interaction that makes contact between the dye and solvent molecules unfavorable. Here we present experimental data and theoretical arguments showing that dye aggregation can cause a strong enhancement of DR in dye-doped NLCs. We propose an entropy-related mechanism of the DR in highly anisotropic suspensions. Our model of a suspension of columnar aggregates in a NLC is in a qualitative agreement with the experiment.

EXPERIMENT

We study a typical NLC pentylcyanobiphenyl (5CB, Merck) doped with an anthraquenone dye *N,N′-(methylphenyl)*-1,4 *diamino-anthraquenone* (D4) known to induce the Janossy effect [2,3]. The interactions between the dye molecules are evidenced by a strongly nonlinear dependence of the polarizability $a = a_L + a'\mathrm{E}^2$ on the dye concentration c defined as $c =$ (number density of dye molecules)$/n_0$ where $n_0 \approx 10^{21}\,\mathrm{cm}^{-3}$ is the number density of the 5CB molecules ($c = 0.56$ of wt.%). Here a_L and a' are constants independent of the field amplitude E (for the reason clarified later on, the standard notation $\chi^{(3)}$ for a' is not used). In a system with non-interacting dyes, $\alpha \propto c$ as the contributions of individual dye molecules are additive; for our system, we find $a'(c)$ to be highly nonlinear.

First, we measured a' for 5CB + D4 in the regime of continuous laser generation. We used a single-mode (TEM$_{00}$) CW He-Ne laser ($\lambda = 633\,\mathrm{nm}$, power 75 mW). The focused laser beam with Gaussian profile was incident normally upon the NLC cell of thickness $h = 10\,\mu\mathrm{m}$ with the homeotropic orientation of the director $\mathbf{n}_0(\mathbf{E} \perp \mathbf{n}_0)$. We measured the intensity of light passing through the sample for a fixed diaphragm as a function of the incident light intensity I (I was well below the Jánossy reorientation threshold I_c for all c's [12,13]). The dependence $a'(c)$ is strongly nonlinear, $\alpha'_{633} \sim c^{2.38}$, Figure 1.

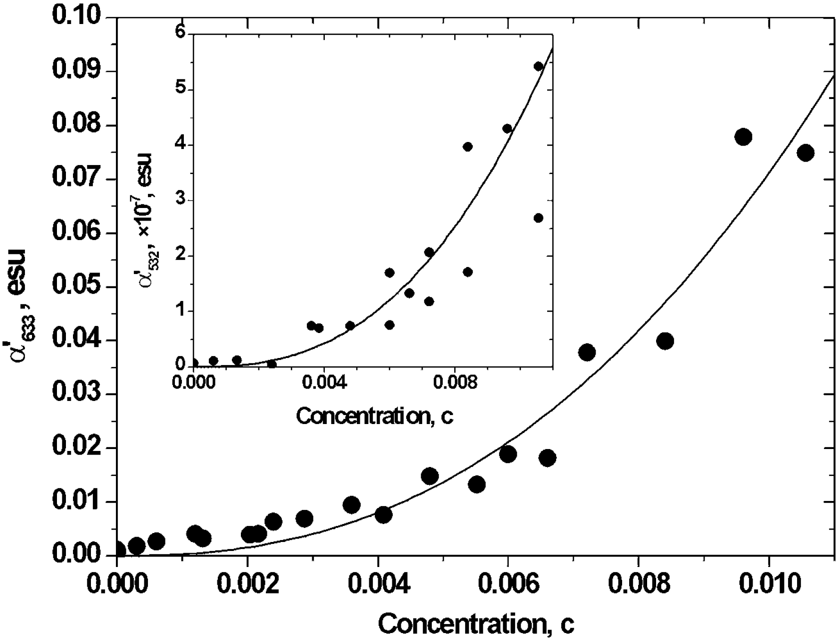

FIGURE 1 Coefficient a'_{633} vs. c; solid line: $a'_{532} \propto c^{2.58}$. Insert: coefficient a'_{532} vs. c; solid line: $a'_{532} \propto c^{2.58}$. Homeotropic 10 μm cell.

In order to exclude the contribution from NLC to the optical response, the same cells were irradiated with picosecond pulses at $\lambda = 532\,\text{nm}$: the absorption of 5CB at 532 nm is low and the response to picosecond pulses is weak [14]. A strongly nonlinear dependence $a'_{532} \sim c^{2.58}$ was observed in this case as well, Figure 1. The nonlinear $a'(c)$ indicates a domination of supramolecular units in the optical response. In contrast, the light absorption coefficient changes linearly with c for W/cm^2 light intensities relevant to the Jánossy effect.

The normalized total transmittance of a given cell $T =$ (total transmittance/linear transmittance) as a function of I is shown in Figure 2. The absorption coefficient of the cell is $A = 1 - T$. For the pure NLC, $T(I)$ very slowly grows. This is because a larger I produces a larger depletion in the angular distribution of the absorbing LC molecules. For exactly the same reason the absorption of individual dye molecules has to be a decreasing function of I [15]. In contrast, we have observed a considerable absorption growth with I even for $I < I_c$. The growth of $A(I)$ *after* the transition can be naturally attributed to the DR towards the field direction. But why does a compatible absorption growth occurs *before* the director starts to turn? This gives

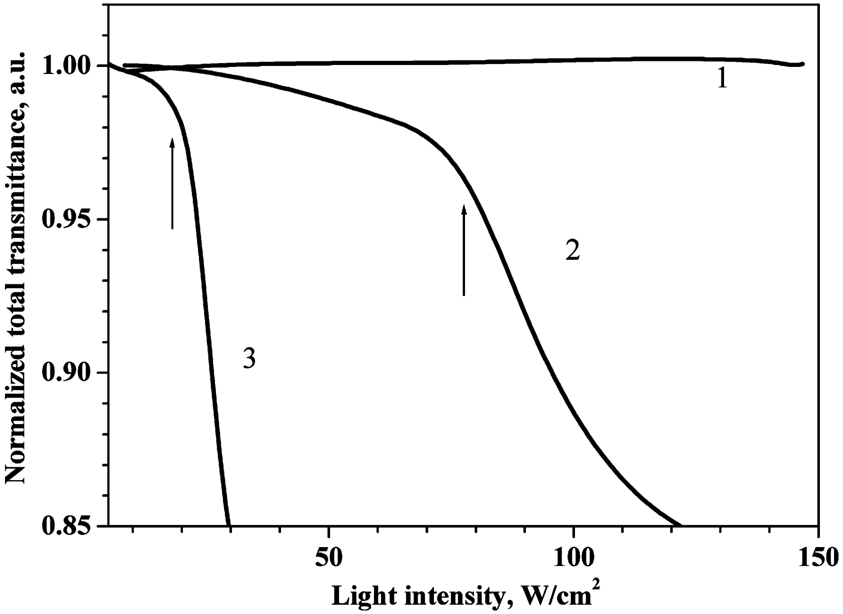

FIGURE 2 Total transmittance (normalized on the linear transmittance) of a 10 μm homeotropic cell vs. I for different c: 1 – pure 5CB, 2 – 0.68 wt.%, 3 – 1.4 wt.%. Arrows show the thresholds of DR.

an impression that the transition dipoles can slightly rotate with respect to the director even before the onset of DR which is difficult to adopt within the assumption of individual dye molecules.

The models considering individual (noninteracting) dye molecules imply that the dye-induced torque on n_0 is linear both in I and c (which is strictly so for $c \to 0$) [1]. The trend linear in c was observed in [15]. For 5CB + D4 we found, in addition to the linear behavior for sufficiently high c, both a non-linear and concentration independent behavior at lower dye concentrations. The threshold of light-induced DR $I_c(c)$ was determined in the homeotropic cells by measuring the on-axis light transmittance vs. I [13]. Figure 3 shows that $cI_c \sim const$ and $I_c \sim 1/c$ only for sufficiently large $c > 0.006$ whereas for smaller c, $0.001 < c < 0.006$, the dependence $I_c(c)$ is much stronger: $I_c \propto c^{-\beta}$ with $\beta \sim 1.5-2$. As in [2,3], for $c = 0.006$ ($\approx$1 wt.%), the threshold I_c is about 0.01 of its value for the pure 5CB. For the lowest concentrations, $c \leq 0.001$, the critical intensity is almost insensitive to the presence of dye and remains close to its value in the pure 5CB.

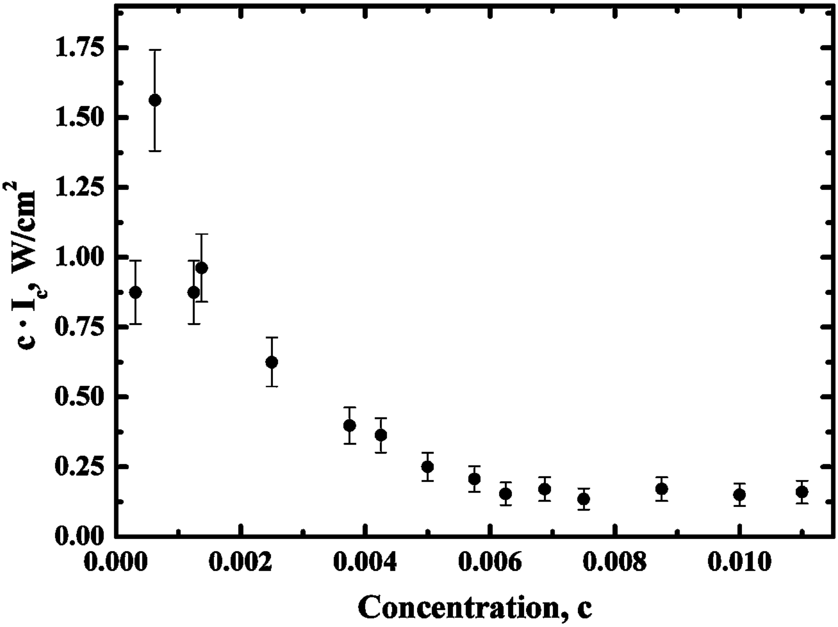

FIGURE 3 Product $I_c(c) \cdot c$ vs. c; homeotropic 10 μm cell.

We now explore how the light induced DR depends on the angle θ_e between $\mathbf{E}$ and $\mathbf{n}_0$, using a planar cell ($\mathbf{n}_0$ is fixed in the plane of the substrate by obliquely deposited SiO_2 layers), which allows us to change θ_e from 0 to 90° by changing the linear polarization of the laser beam ($\lambda = 633\,\mu\text{m}$) normal to the cell. It is known that in azo dye-doped NLC, depending on the angle θ_e, the DR caused by a Gaussian beam can result either in its self-focusing or self-defocusing [16]. The focusing implies that the director reorients towards $\mathbf{E}$, and vice versa. We observed both regimes in our *non azo dye-doped* NLC, namely, a focusing for $52° < \theta_e < 90°$, and defocusing for $0 < \theta_e < 52°$. For $\theta_e = 90°$ ($\mathbf{E} \perp \mathbf{n}_0$), the threshold $I_{c\perp}$ of DR was very close to that for the homeotropic cells. For $\theta_e = 0$ (apparently this geometry has not been studied previously), we found a remarkably strong DR effect with a very low threshold $I_{c||} \sim 0.17\,\text{I}_c$. The difference between $\theta_c = 90°$ and $\theta_c = 0$ is not only quantitative but also qualitative as evident from the dependencies of light transmittance on I, Figure 4. For $\theta_e = 0$, one observes smooth reversible changes without a hysteresis, which is characteristic of the second order transition, Figure 4. In contrast, when $\theta_e = 90°$, DR features a strong hysteresis as in the first order transition.

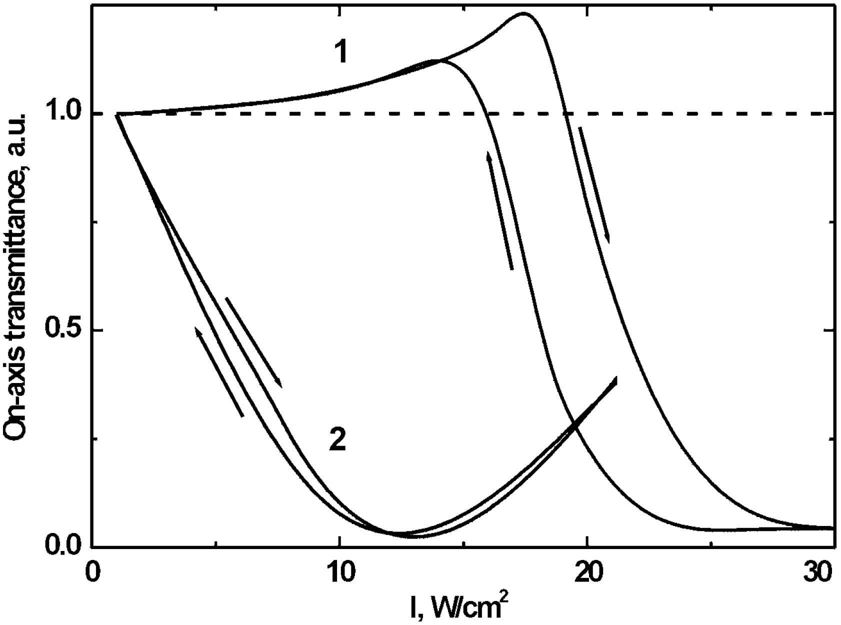

FIGURE 4 Reversibility of the normalized on-axis transmittance of a planar 10 μm cell vs. I, $c = 0.0084$: (1) $\theta_e = 90°$ ($\mathbf{E} \perp \mathbf{n}_0$); (2) $\theta_e = 0°$ ($\mathbf{E} \| \mathbf{n}_0$). Arrows show the variation of I.

MODEL

Below we propose a model of the light-induced DR assuming that the main effect is due to dye aggregation. Let the unit vectors **a** and **d** denote the aggregate axis and the long axis of D4 molecule, Figure 5. We do not assume that **a** and **n** are necessarily parallel and introduce the angle θ_a between them. This is in fact most feasible as the structure of D4 with two phenyl groups sticking out of the molecular plane suggests that a full face-to-face contact of adjacent molecules is difficult.

The electric field of light is $\mathbf{E} = E\mathbf{e}$, and **a** is specified by two angles: θ, the angle made by the initial director $\mathbf{n}_0$ and the perturbed director **n**, and ϕ, made by the planes ($\mathbf{e}$,$\mathbf{n}_0$,$\mathbf{n}$) and ($\mathbf{n}$,$\mathbf{d}$,$\mathbf{a}$). For simplicity, let the aggregation number N_a be the same for all aggregates, and the total number of aggregates be $n_a = cn_0/N_a$. For estimates we assume $N_a \sim 10$; similar numbers are characteristic for chromonic aggregates in aqueous solutions [17,18]. The aggregate is strongly anchored to the director so that the angle θ_a between **a** and **n** is constant: the column

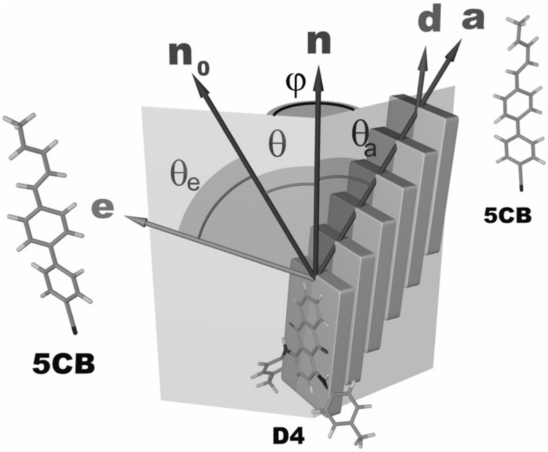

FIGURE 5 Geometry of the columnar aggregate.

can rotate about the director **n**, but not about its own axis **a** as such a rotation would change the orientation of NLC molecules at the aggregate surface.

We first explain why the polarizability a' of D4 aggregates is higly nonlinear whereas the absorption is linear in c. On light absorption, the ground state (g) of dye molecule transforms into the excited (e) state. The absorption and polarizability of dye monomers are proportional to c, regardless of whether they are in the g- or e-state. However, the energy band structure of a conjugated one-dimensional chain of N_a molecules (such as, e.g., J-aggregates) can be similar to that of a semiconductor [8,19]. The g electrons are localized at the individual molecules, the polarizability of the g state is proportional to the aggregate length per one molecule Δl, and the total aggregates' polarizabilitry scales as $n_a N_a \Delta l \propto c\Delta l$. However, the e-electrons are delocalized and can move along the aggregate axis, so that the polarizability of an aggregate with N_e excited molecules is $\propto N_e(N_a\Delta l) \propto N_a^2\Delta l$. Then the total polarizability $\propto n_a N_a^2 \Delta l \propto c N_a \Delta l$ which indeed can be nonlinear since N_a should strongly depend on c [17]. Similar dependence on the aggregation number N_a was observed for resonance light scattering [20] in isotropic solutions [21]. We emphasize that if the excitations were localized at the individual molecules, the polarizability would be linear in c, and thus both the *dye aggregation and delocalization of the excited electrons are necessary* for the nonlinearity. Therefore, both a'_{532} and a'_{633} in Figure 1 have to be attributed to the *excited* molecules in *aggregates*. Then $a'\mathrm{E}^2$ is in fact the *linear* polarizability $\alpha_{L,e}$ of the e-molecules in the aggregates (rather than the hyperpolarizability $\chi^{(3)}$ of the g-molecules): $a'\mathrm{E}^2 = \alpha_{L,e}$. This $\alpha_{L,e} \propto E^2$ since the number of e-molecules $n_a N_e \propto E^2$ (the g-absorption coefficient is included in a'). Thus, the aggregates absorb light in the g-state whereas the induced polarization comes from the e-state. This explains in a unique way why the light absorption is necessary and why it is linear whereas the polarizability is highly nonlinear in c.

The transition dipole moment of the D4 g-molecule is along its long axis **d.** Due to the delocalization, the component along **a** dominates in the field-induced polarization $\mathbf{P}_a$ of an aggregate. The light-aggregate interaction energy can be cast into the form $-(\mathbf{P}_a \cdot \mathbf{E}) = -\Gamma_0 g(\phi, \mathbf{n}, \mathbf{e})$ where $g(\phi, \theta, \theta_e) = (\mathbf{d}(\phi, \theta) \cdot \mathbf{e})^2 (\mathbf{a}(\phi, \theta) \cdot \mathbf{e})^2$ and $\Gamma_0 \propto N_a^2 \Delta l E^4$. This interaction gives rise to the torque on the aggregate. Here we only need its component Γ_α along the vector $\mathbf{n} \times \mathbf{a}$ which obtains as minus the θ_a-derivative of the energy, i.e.,

$$\Gamma_a(\phi, \theta, \theta_e, E) = \frac{\Gamma_0(E)\partial g}{\partial \theta_a} \tag{1}$$

Let us estimate $\Gamma_0 \sim P_a E$. Delocalization of the excited electrons implies an estimate $P_a \sim$ (elementary charge) $\times\, l_m$ where $l_m \sim 10^{-7}$cm is the typical intermolecular size. For $c = 0.01$, Jánossy's critical field $E \sim 0.1$ of the Frederiks threshold $\sqrt{4\pi K/h^2 \Delta\varepsilon}$ where $K \sim 10^{-6}$ dyn is the elastic constant and $\Delta\varepsilon \approx 0.6$ is the dielectric anisotropy for $\lambda = 633\,\mathrm{nm}$. For $h = 10\,\mu\mathrm{m}$ this gives $P_a \sim 5 * 10^{-17}\,\mathrm{esu{\cdot}cm} = 50\,\mathrm{D}$, $E \sim 1$ dyne/esu, and $\Gamma_0 \sim 5 * 10^{-17}$ erg.

In itself, the estimated value P_a is not very large. For example, the permanent dipole moment of a 5CB molecule is $4.3D$ (in the nematic phase, the total polarization due to reorientation of permanent molecular dipoles vanishes in the fast oscillating light field). At the same time, the dipole moment $\overline{P}_{5CB}$ of a $5CB$ molecule induced by the above mean field can be estimated from the dielectric torque $\overline{P}_{5CB} E n_0 \sim 0.01\,\mathrm{K}/h^2$ to give $\overline{P}_{5CB} \sim 10^{-23}\,\mathrm{esu} \cdot \mathrm{cm} = 10^{-5} D << P_a$. If the polarization of a 5CB molecule was induced only by the mean field and thus was close to $\overline{P}_{5CB}$, then the aggregates would considerably contribute to the dielectric permittivity ε. Indeed, per a single aggregate with $N_a \sim 10$ and the dipole moment P_a there are 10^3 molecules of 5CB with the total mean-field-induced dipole moment of just $\sim 10^{-2} D << P_a$. However, experimentally found changes of ε due to D4 are very small. This shows that the dipole moment P_a of an aggregate is nearly compensated by the depolarizing coat of the LC molecules at the aggregate. The 5CB molecules at the very proximity of the aggregate experience the local field up to (elementary charge/l_m^2) $\sim 5\cdot 10^4 E$, their induced dipoles can be up to $5 \cdot 10^4 \overline{P}_{5CB} \sim 0.5D$, and 10^3 molecules of the coat can have the total dipole moment $\sim (-P_a)$ (especially if we take into account that the above estimate P_a is essentially an overestimate, it is considerably larger than that required for the DR transition, see below). The dielectric torque Γ_a (1) acting on the aggregate and the balancing torque $\sim (-\Gamma_a)$ distributed over the LC coat are of opposite signs. Therefore the director field in the coat is distorted. It is not difficult to see that this distortion is mainly a twist about the axis $\mathbf{n} \times \mathbf{a}$ normal to the aggregate's lateral area. The twisted domains attached to the aggregates repel each other. This makes the aggregates effectively thicker by some D_E which depends on their orientation relative to the vectors $\mathbf{E}$ and $\mathbf{n}$. A finite thickness of rods is the reason for the entropy drop. Thus, the entropy of the aggregate subsystem depends on $\mathbf{E}$ relative to $\mathbf{n}$, and if $\mathbf{E}$ is fixed then the tendency to the entropy maximization can result in DR. This thermodynamic mechanism can be very efficient as the mean distance between aggregates' centers $\bar{r} = n_a^{-1/3}$ is close to the inverse biaxial correlation length $\xi \sim 10\, l_m$ [22–25]: as the director derivatives larger than $1/\xi$ are equivalent to highly energetic defects with the biaxial order and reduced scalar order parameter, the elastic repulsion of aggregates is expected to be appreciable.

The twisted domain at a single aggregate can be characterized by the twist amplitude $\delta\theta$. It can be estimated from the equality $\Gamma_a \sim \mathrm{K}(\delta\theta/\bar{r}^2)\,V$ where $V \sim \mathrm{N}_a \Delta S \bar{r}$ is the domain volume and ΔS is the aggregate's lateral area per a constituent molecules. The elastic deformation that two neighboring columns induce in between them under the electric field action depends on their axes $\mathbf{a}(\phi_1, \theta)$ and $\mathbf{a}(\phi_2, \theta)$. It is proportional to the angular difference $\Delta\theta = \delta\theta(\phi_1) - \delta\theta(\phi_2)\cos\Delta\phi$ where $\Delta\phi = \phi_1 - \phi_2$: when the two columns are parallel, $\phi_1 = \phi_2$, the twist vanishes, whereas when they are "antiparallel," $\Delta\phi = \pi$, the difference is maximum and equal to $2\Delta\theta(\phi_1)$. If r_X is *the minimum distance* between the two crossing aggregates, the *maximum twist* is $\delta\theta' = \Delta\theta/r_X$ Then from the inequality $|\delta\theta'| \geq 1/\xi$ one finds that the minimum distance r_X cannot be smaller than

$$D(\phi_1, \phi_2, \mathbf{n}, \mathbf{E}) = D_E \left| \frac{\partial g(\phi_1)}{\partial \theta_a} - \cos\Delta\phi \frac{\partial g(\phi_2)}{\partial \theta_a} \right| \tag{2}$$

where $D_E = \Gamma_0(\mathrm{E})\xi/(\mathrm{K}\mathrm{N}_a \Delta S n_a^{1/3}) \propto \mathrm{E}^4 \propto \mathrm{I}^2$ and $g = g(\phi, \mathbf{n}, \mathbf{e})$. We see that the columnar aggregates repel each other via the field-induced director deformations. The minimum collision distance (2) plays the role of effective correction to the columns' hard core diameter which depends on their orientation relative to the vectors $\mathbf{E}$ and $\mathbf{n}$, grows as E^4, is largest when the columns are “crossed antiparallel,” decreases as $\Delta\phi$ decreases from π, and vanishes for parallel columns.

The free energy density (FED) of our model can be obtained from the Onsager model of long rods [26] where the rod length and diameter are replaced by $N_a\Delta l$ and D and the homogeneous ϕ-distribution is assumed. This FED is the sum

$$f = \frac{K}{2}\left(\frac{d\theta}{dz}\right)^2 + n_0 k_B T \chi X(\mathbf{e},\mathbf{n}) \tag{3}$$

of the elastic term and the entropy drop $\propto \chi X$. Here $\chi(E) = cn_a (N_a\Delta l)^2 D_{\mathrm{E}} = n_0 c^2 \Delta l^2 D_{\mathrm{E}} \propto \mathrm{E}^4$ characterizes the excluded volume and

$$X = \int_0^{2\pi} \frac{d\phi_1 d\phi_2}{4\pi^2} \beta \left| \frac{\partial g(\phi_1)}{\partial \theta_a} - \cos\Delta\phi \frac{\partial g(\phi_2)}{\partial \theta_a} \right| \tag{4}$$

where $b = 2\sin\theta_\alpha \sin(\Delta\phi/2)[1 - \sin^2\theta_\alpha \sin^2(\Delta\phi/2)]^{1/2}$ is sine of the angle made by the two crossing columns.

In the director's reference frame where $\mathbf{n} = (0,0,1)$, $\mathbf{e} = (0, \sin(\theta_e + \theta), \cos(\theta_e + \theta))$ and $\mathbf{a} = (\sin\theta_a \sin\phi, \sin\theta_a \cos\phi, \cos\theta_a)$ we fix $\theta_a, \Delta, \theta_e$ and calculate the FE $\int_0^h f dz$ vs. θ for different Γ_0 and χ. The entropy depletion X does offer a relevant mechanism of DR. X depends on the angle $\theta + \theta_e$ between $\mathbf{E}$ and $\mathbf{n}$ and has a minimum for some $\theta = \theta_{\min}$, Figure 6. For $\theta_e = 90°$, $X(\theta)$ offers a possibility that for sufficiently large θ_a the transition from $\theta = 0$ to θ_m can be of the first order (curve 2) while for larger θ_a it can be of the second order (curve 3). At the same time, the point $\theta = 0$ in the geometry with $\theta_e = 0$ is highly unstable. This picture is exactly what one needs to describe the experiment. We calculated the effect of elasticity ($\theta = 0$ at the cell substrates) for $\theta_a = 52°$, $\Delta = 27°$, and the above values of N_a, c_d, K, and h. The normal field, $\theta_e = 90°$ causes a first order transition from $\theta = 0$ to $\theta_{\min} \approx 43°$ at $\chi_{c\perp} \approx 1.5 \cdot 10^{-6}$ and the inverse transition at $\chi^{**}_{c\perp} \approx 0.49\chi_{c\perp}$. At the same time, the field along the director, $\theta_e = 0$, causes the second order transition at $\chi_{c||} \approx 0.03\chi_{c\perp}$ ($I_{c||}/I_{c\perp} \sim 0.17$). In our model the focusing-defocusing crossover is not related to sign change of the dielectric constant as its origine is thermodynamic rather than dielectric. For our parameters it occurs at $\theta_{e,inv} \approx 50°$. The described theoretical behavior is close to that observed in the experiment. For $c = 0.01$ and the above $\chi_{c\perp}$, the definition of χ gives a small value $D_E \sim 10^{-9}$ cm which demonstrates a high efficiency of the mechanism. The correspondent torque Γ_0 obtained from the definition of D_E is just 2% of the above estimate.

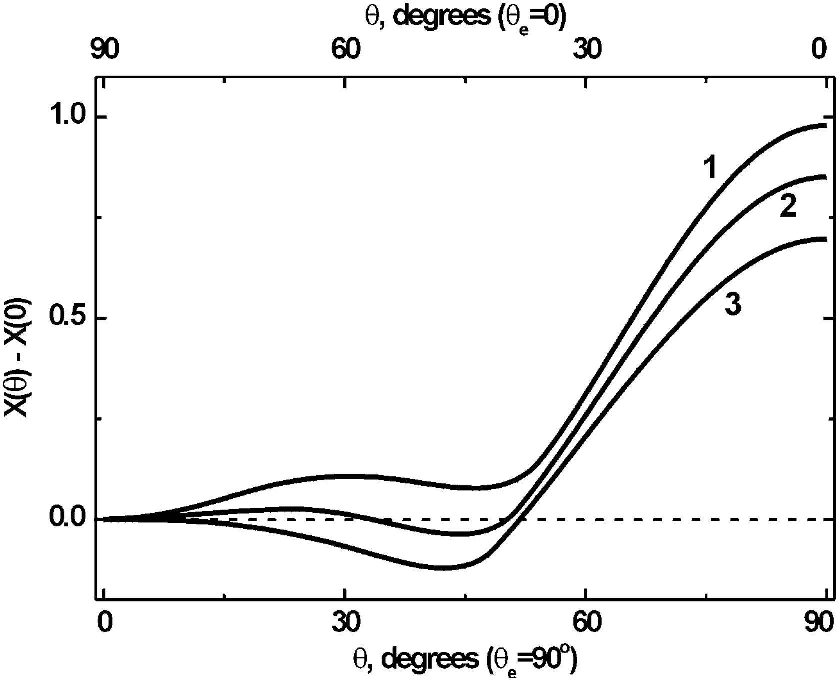

FIGURE 6 Entropy reduction $X(\theta) - X(0)$ for $\theta_e = 90°(\mathbf{E} \perp \mathbf{n}_0$, lower abscissa) and $\theta_e = 0°$ ($\mathbf{E} \| \mathbf{n}_0$, upper abscissa), $\Delta = 30°$: (1) $\theta_\alpha = 45°$, no transition from $\theta = 0$, (2) $\theta_a = 51°$, first order transition to $\theta_{\min} \approx 43°$, (3) $\theta_a = 55°$, second order transition.

To conclude, we showed that the dye aggregation may be an essential ingredient of the physics behind strong enhancement of the DR in a dye-doped thermotropic LC. Further study of the aggregation phenomena in NLCs is in progress.

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