

Dye-Induced Enhancement of Optical Nonlinearity in Liquids and Liquid Crystals

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Optical nonlinearity of liquid crystals (LC) in the isotropic phase can be enhanced by 1 order of magnitude by dissolving 0.1% of anthraquinone dye in the LC. The enhancement decreases by $\sim 30\%$ when the LC transforms into the nematic phase. The same guest-host effect also exists in non-LC liquids. It can be explained by a model based on the change of guest-host interaction induced by optical excitations of the dye. [S0031-9007(96)01985-0]

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Guest-host interaction is a subject of high interest in many disciplines. Recently, it has received a great deal of attention in the field of liquid crystals (LC) because of its potential applications to displays and other optoelectronic devices. In one case, it was found that the unusually strong optical nonlinearity of nematics LCs can be further enhanced dramatically by a small amount of dye dissolved in LC [1–5]. The strong optical nonlinearity of pure nematic LC is known to be a result of optical-field-induced collective reorientation of LC molecules [6–8]. A cw laser intensity of 100 W/cm^2 can readily induce a refractive index change of ~ 0.1 by this mechanism [7]. It has led to many interesting nonlinear optical effects in LC with possible applications [9]. Now with mixing of only 1% of certain anthraquinone dyes into the LC host, this giant nonlinearity can be further increased by 2 orders of magnitude if the optical field resonantly excites the dye molecules [1,2]. According to Ref. [2], this happens because the linearly polarized optical field excites the dye molecules and creates anisotropic orientational distributions of the dye molecules both in the excited state and in the ground state. The change of guest-host interaction between dye and LC molecules upon excitation then results in the enhanced molecular reorientation of LC. However, a microscopic understanding of the guest-host interaction responsible for this effect is still missing.

One may also ask if the same effect exists in LC in the isotropic phase, or more generally, in liquids without a mesomorphic LC phase. In this Letter, we show that this is the case, using 1-amino-anthroquinone (AAQ) dye and alkylcyanobiphenyls $\text{CN}(\text{C}_6\text{H}_4)_2\text{C}_n\text{H}_{2n+1}(\text{nCB})$ with $n = 2, 3, 5, 8$ as guest and host materials, respectively. Note that 5CB and 8CB have mesophases while 2CB and 3CB have not. In all cases, we found significant enhancement of the optical nonlinearity. The enhancement increases with the alkyl chain length or n . In the cases of 5CB and 8CB, the enhancement decreases by $\sim 30\%$ when the LC transforms into the nematic phase. These results may provide useful clues for a better understanding of this fascinating guest-host interaction problem.

The optical-field-induced reorientation of LC molecules results from interaction between field and field-induced dipoles on the molecules that can be described by the interaction free energy density:

$$F_{\text{INT}} = -\frac{1}{4} \chi_{ij} E_i E_j = F_{\text{INT}}^0 - \frac{1}{6} \Delta\chi Q_{ij} E_i E_j. \quad (1)$$

Here, $\chi_{ij} = \bar{\chi} + \frac{2}{3} \Delta\chi Q_{ij}$ is the optical susceptibility tensor, $\bar{\chi}$ is the average susceptibility, $Q_{ij} = Q(\frac{3}{2} n_i n_j - \frac{1}{2} \delta_{ij})$ is the order parameter tensor with Q being the scalar order parameter and \mathbf{n} the director describing the average direction of molecular orientation, $\Delta\chi$ is the susceptibility anisotropy of a perfectly aligned LC medium with $Q = 1$, \mathbf{E} denotes the optical field, and F_{INT}^0 is independent of Q_{ij} . The orientational ordering of LC, defined by Q_{ij} , is usually obtained by minimizing the total free energy $\int F d^3r$, with

$$F = F_0 + F_{\text{INT}}, \quad (2)$$

where F_0 is the free energy density of the medium in the absence of the field. In the isotropic phase, the molecules originally have no orientational ordering. The nematiclike order Q is induced by the applied optical field \mathbf{E} , with \mathbf{n} parallel to \mathbf{E} . The free energy density reduces to [10]

$$F = \frac{1}{2} a(T - T^*)Q^2 + \frac{1}{3} BQ^3 + \frac{1}{4} CQ^4 - \frac{1}{6} \Delta\chi Q|E|^2, \quad (3)$$

where a, B, C, D , and T^* are characteristic constants of the LC and the spatial variation of Q is neglected. To induce a measurable Q , the optical field must be sufficiently strong and therefore a pulsed laser is often needed. The induced Q is then time dependent and obeys the dynamic equation;

$$\nu \frac{dQ}{dt} + a(T - T^*)Q = \frac{1}{6} \Delta\chi |E(t)|^2, \quad (4)$$

with ν denoting the viscosity. In the above equation, the higher-order terms of Q have been neglected since Q is generally much smaller than 1. In the nematic phase, a cw laser beam is intense enough to reorient the director

\mathbf{n} , but the scalar order parameter Q can hardly be changed ($Q = Q_0$). Equation (2) then takes the form [10]

$$F = \frac{1}{2} K_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} K_2 [\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + \frac{1}{2} K_3 [\mathbf{n} \times (\nabla \times \mathbf{n})]^2 - \frac{1}{4} \Delta \chi Q_0 (\mathbf{n} \cdot \mathbf{E})^2, \quad (5)$$

where K_i are the Frank elastic constants. In the special case where the laser beam is normally incident on a homeotropically aligned LC cell, minimizing the free energy shows that molecular reorientation occurs only when the laser intensity exceeds the so-called Fréedericksz transition threshold $I_{\text{th}} = c\sqrt{1 + 4\pi\bar{\chi}}(K_3/\Delta\chi Q_0 d^2)g(\phi/d)$, when d is the sample thickness, ϕ is the laser beam diameter, and g is a numerical function [9].

In the presence of dye impurities, the optical field can also interact with LC via dye molecules. To the lowest order of Q_{ij} and \mathbf{E} , this additional interaction takes the form

$$F_{\text{INT}}^a = -DQ_{ij}E_iE_j, \quad (6)$$

where D is a constant. Now with F_{INT} in Eq. (2) replaced by $F_{\text{INT}} + F_{\text{INT}}^a$, the interaction strength is increased by a factor of $(1 + \eta)$, with $\eta = 6D/\Delta\chi$. This leads to an enhancement of the optical reorientation by a factor of $(1 + \eta)$ for both isotropic and nematic phases. In particular, we find $Q' = (1 + \eta)Q$ for the isotropic phase and $I'_{\text{th}} = I_{\text{th}}/(1 + \eta)$ for the nematic phase, with the prime denoting the dye-doped case. The result here suggests that isotropic and nematic phases of LC should experience the same enhancement in optical reorientation with dye doping.

In the experimental investigation, we used the optical Kerr effect to measure the light-induced reorientation of molecules in isotropic liquids [11]. A linearly polarized, frequency-doubled, Q -switched Nd:YAG laser at 532 nm was employed as the pump beam to induce molecular reorientation in the liquid medium. Its wavelength is inside the broad absorption band of AAQ peaked at 490 nm. The pulse duration is 20 ns and the repetition rate is 2 Hz. The induced molecular reorientation gave rise to an optical birefringence $\delta n(t) = (4\pi\Delta\chi/\sqrt{1 + 4\pi\bar{\chi}})Q(t)$ that was probed by a cw He-Ne laser beam polarized at 45° from the pump field at the input and analyzed by a crossed polarizer at the output. The transmitted probe beam appeared as a pulse and was measured by a photomultiplier and a gated integrator. With $(2\pi/\lambda)\delta n(t)d \ll 1$ (λ is the wavelength of the probe laser), the time-integrated signal that we measured is $S \propto \int_{-\infty}^{\infty} [(2\pi/\lambda)\delta n(t)d]^2 dt$. In the case of the isotropic LC at a temperature close to the isotropic-nematic (I - N) transition, the pump pulse was much shorter than the orientational relaxation time of the medium. From Eq. (4), we obtain for pure and dye-doped LC, respectively,

$$S \propto \frac{(\Delta\chi)^4}{1 + 4\pi\bar{\chi}} \frac{1}{v} \frac{1}{a(T - T^*)} d^2 \mathbf{F}^2 \quad (7)$$

and

$$S' = (1 + \eta)^2 S, \quad (8)$$

where \mathbf{F} is the average pump flux in the medium. At the temperatures where the orientational relaxation time of the isotropic liquid is comparable with or shorter than the pump pulse width, Eq. (7) is no longer valid, but the quadratic dependence of S on \mathbf{F} and Eq. (8) still hold. For accurate determination of η , we constructed a composite cell with two components sandwiched between the same two glass substrates, one filled with pure liquid and the other with dye-doped liquid. The cell was 0.7 mm thick and was placed in an oven with temperature controlled to better than 0.1 K. Such a geometry guarantees the same temperature and cell thickness for the pure and dye-doped samples.

To measure the enhancement factor in nematic LCs, we used a frequency doubled, cw mode-locked, Nd:YAG laser at 532 nm to induce reorientation of the LC director and measure the Fréedericksz transition threshold ratio of pure and dye-doped LC cells that are homeotropically aligned by n , n -dimethyl- n -octadecyl-3-aminopropyl-trimechoxysilyl chloride (DMOAP)-coated glass substrates. The threshold was determined by the sudden appearance of a ring pattern in the far field due to self-phase modulation of the laser beam in the LC medium [7].

Figure 1 shows the integrated optical Kerr signals from pure and AAQ-doped isotropic 5CB samples versus the pump flux. As expected from Eqs. (7) and (8), both signals depend quadratically on \mathbf{F} . The signals from the dye-doped 5CB is much larger than that from the pure one, which means that the optical reorientation of isotropic LC is indeed enhanced by dye doping.

We have also measured the temperature dependence of the integrated optical Kerr signals of pure and AAQ-doped 5CB in the isotropic phase. The results are shown

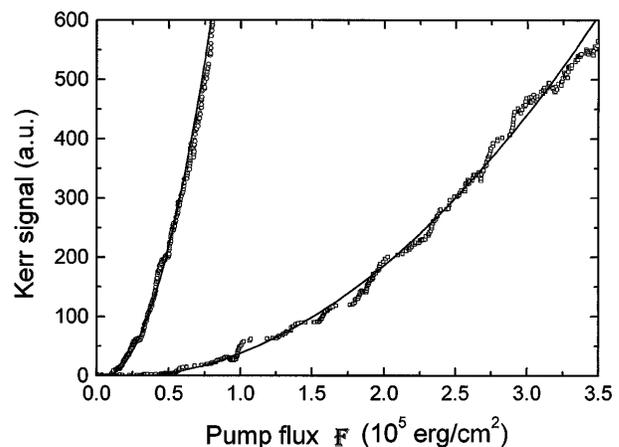


FIG. 1. Integrated optical Kerr signals vs the pump flux. Squares are for pure 5CB and circles for 0.05% AAQ-doped 5CB. Solid curves are quadratic fits. Temperature of the sample is 37°C.

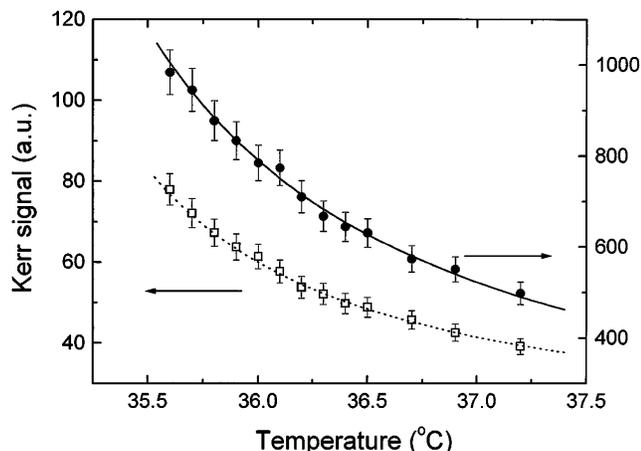


FIG. 2. Integrated optical Kerr signals vs temperature. Open squares are for pure 5CB and solid circles for 0.03% AAQ-doped LC. Curves were obtained from fitting using Eqs. (7) and (8).

in Fig. 2. Here again, the signal from the dye-doped 5CB is much larger than that from the pure one. Both signals are inversely proportional to $T - T^*$ as predicted in Eqs. (7) and (8). The apparent critical temperature T^* was found to be 34.2 °C and 34.5 °C for dye-doped and pure LC samples, respectively. The temperature difference of 0.3 °C came from laser heating of the dye-doped LC. The I - N transition temperatures of pure and dye-doped LC exhibit the same difference under irradiation of the pump laser. The above result indicates that η does not have a critical dependence on $T - T^*$ even in the pretransitional region where the LC molecular correlation sets in critically. This shows that such a correlation in the host material is not important for our guest-host effect.

The measured enhancement in AAQ-doped isotropic 5CB was found to be directly proportional to the dye concentration, as shown in Fig. 3. This is expected for low dye concentrations at which the interactions between dye molecules are insignificant. Also displayed in Fig. 3 are the η values for different dye concentrations in the nematic phase. We found $\eta(\text{nematic})/\eta(\text{isotropic}) = 0.65$. The difference in η between the isotropic and nematic phases could be a result of our neglect of the higher order terms of Q_{ij} in F_{INT}^a , as we shall discuss later.

Finally, we have studied the effect in liquids that have no mesomorphic LC phases. We found that 2CB and 3CB also exhibit significant enhancement in the light-induced molecular reorientation from dye doping although they are not LC materials. This indicates that enhancement in optical reorientation due to guest-host interaction is a generic effect not restricted to LC. Figure 4 shows η of AAQ-doped n CB versus n . The enhancement appears to increase with the alkyl chain length. This is presumably related to the increasing anisotropy of n CB with increasing n .

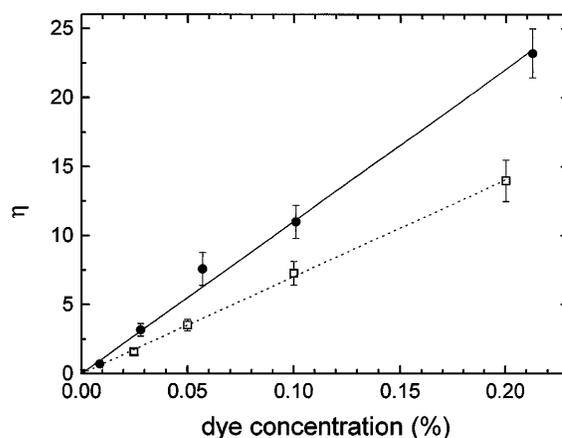


FIG. 3. η vs dye concentration of AAQ-doped 5CB. Solid circles are for the isotropic phase at 37 °C. Open squares are the nematic phase at 32 °C. Lines are linear fits.

To understand this guest-host effect on a microscopic level, we adopt the physical picture suggested by Jánossy [2]. The two important aspects here are the selective excitation of dye molecules and the change of guest-host interaction upon excitation. Dye molecules oriented with their stronger transition dipoles parallel to the pump beam polarization have a higher probability of being excited. Consequently the excited dye molecules should appear to have an anisotropic orientational distribution. The interaction between the anisotropic host and dye molecules then tends to align the host molecules towards the average orientation of the excited dye molecules. The excitation also creates an anisotropic distribution of the opposite sense for dye molecules in the ground state that counters the reorienting action of the excited dye molecules. If the excited dye-host molecular interaction V_e is different from the ground state dye-host molecular interaction V_g , then a net reorienting torque on the host molecules exists. Assuming that V_e and V_g take the phenomenological form $V_i(\mathbf{r}, \mathbf{l}, \mathbf{l}'') = V_i^0(r) + \delta V_i(r)(\mathbf{l} \cdot \mathbf{l}'')^2$ for anisotropic molecular interaction, ($i = g$ or e), with \mathbf{l} and

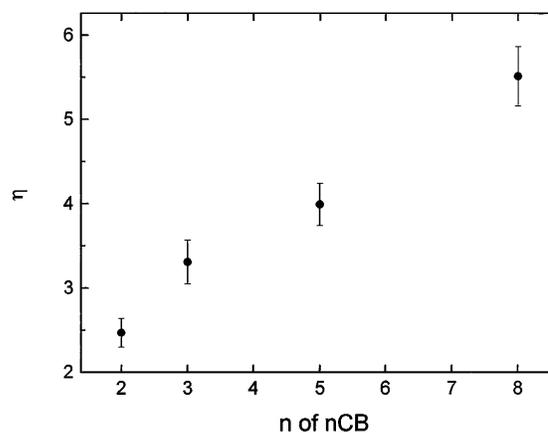


FIG. 4. η of 0.05% AAQ-doped n CB at 80 °C versus the alkyl chain length of n CB.

\mathbf{l}'' being the unit vector along the long axis of the host and dye molecules, respectively, and \mathbf{r} the separation between the two molecules, we obtain the following free energy density for the total guest-host interaction:

$$F_{INT}^a = \frac{4}{9} nn'' \left(\int [\delta V_e(r) - \delta V_g(r)] d^3 r \right) Q_{ij}'' Q_{ij}. \quad (9)$$

Here, n and n'' are the number density of the host and excited dye molecules, respectively, and $Q_{ij}'' = \langle \frac{3}{2} l_i'' l_j'' - \frac{1}{2} \delta_{ij} \rangle_{f''}$ with $\langle \rangle_{f''}$ denoting the average over the orientational distribution f'' of the excited dye molecules.

In the case of an isotropic host medium, f'' is uniaxial with the symmetry axis along the optical field direction \mathbf{e} and $Q_{ij}'' = Q'' (\frac{3}{2} e_i e_j - \frac{1}{2} \delta_{ij})$. The number density of the excited dye molecules is given by $n'' = (\sqrt{1 + 4\pi\bar{\chi}} \lambda \bar{\alpha} \tau / 32\pi^2 \hbar) |E|^2$, with λ being the wavelength of the pump laser, $\bar{\alpha}$ the absorption coefficient in the isotropic phase, and τ the lifetime of the excited states. Equation (9) reduces to Eq. (6) with $D = -(n\sqrt{1 + 4\pi\bar{\chi}} \lambda \bar{\alpha} \tau Q'' / 48\pi^2 \hbar) \int [\delta V_e(r) - \delta V_g(r)] d^3 r$. Assuming that the orientational relaxation time of the dye molecules, τ_r , is much longer than τ [12] so that rotational diffusion of the dye molecules can be neglected in the calculation, the orientational distribution f'' can be approximated simply by the angular dependence of the dye molecule excitation, i.e., $f'' \propto (\mathbf{l}'' \cdot \mathbf{e})^2$, from which we can find $Q'' = 0.4$. From our experimental result, i.e., $\eta \approx 10$ for 0.1% AAQ-doped 5CB ($\alpha = 1.5 \text{ mm}^{-1}$), we then obtained $\int [\delta V_e(r) - \delta V_g(r)] d^3 r \approx -2 \times 10^{-35} \text{ erg} \cdot \text{cm}^3$ ($-2 \times 10^{-48} \text{ J} \cdot \text{m}^3$ in SI units), assuming $\tau = 1 \text{ ns}$ which is estimated from our fluorescence measurement. Considering only nearest-neighbor interaction between dye and LC molecules (with $r \sim 1 \text{ nm}$), we found $\delta V_e - \delta V_g \sim 5 \times 10^{-3} \text{ eV}$ ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ in SI units). Such a change can easily arise from the electronic structural change of anthraquinone dye molecules upon excitation [13]. For dye in $n\text{CB}$, because the anisotropy of $n\text{CB}$ increases with the increase of the alkyl chain length, both δV and F_{INT}^a should increase with n . The optical anisotropy of $n\text{CB}$, however, comes mainly from the biphenyl ring, and therefore F_{INT} hardly changes with n . This makes the enhancement increase with n , as observed.

In nematic LC, the dye molecules tend to align with the LC molecules. Our dichroism measurement on a homogeneously aligned AAQ-doped 5CB sample showed that AAQ molecules had roughly the same orientational distribution as that of 5CB molecules. In such a case, n'' and Q_{ij}'' depend on Q_{ij} and hence F_{INT}^a must contain higher-order terms of Q_{ij} . This should make the dye-induced enhancement in the nematic phase different from that in the isotropic phase. Again neglecting rotational diffusion

of dye molecules so that the orientational distribution of the excited dye molecules can be approximated by $f''(\mathbf{l}'') \propto (\mathbf{l}'' \cdot \mathbf{e})^2 \cdot f(\mathbf{l}'')$, where the initial orientational distribution of the dye molecules is assumed to be the same as that of the LC molecules denoted by f , we can reduce Eq. (9) to the form of Eq. (6), but with D replaced by $\tilde{D} = -\{n\sqrt{1 + 4\pi\bar{\chi}} \lambda \bar{\alpha} \tau \int f(\mathbf{l}'') [(\mathbf{l}'' \cdot \mathbf{n})^2 - (\mathbf{l}'' \cdot \mathbf{n})^4] d^2 \mathbf{l}'' / 16\pi^2 \hbar\} \int [\delta V_e(r) - \delta V_g(r)] d^3 r$. Note that \tilde{D} now depends on the scalar order parameter Q_0 of the LC. Knowing $Q_0 = 0.5$ for 5CB at 32°C [14], we found $\tilde{D} = 0.72D$ and $\eta(\text{nematic}) = 0.72\eta(\text{isotropic})$, which roughly agrees with our experiment result.

To conclude, we have demonstrated for the first time that mixing dye into isotropic LC can enhance the optical Kerr effect dramatically. Only 0.1% of dye dopant can enhance the Kerr coefficient by 1 order of magnitude. This enhancement decreases by $\sim 30\%$ when the LC becomes nematic. The same effect also exists in non-LC host materials. This guest-host effect can be explained by a model based on selective excitation of the dye molecules and change of guest-host interaction upon dye excitation.

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