# Fullerene-dispersed nematic liquid crystal structures: dynamic characteristics and self-organization processes

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## Contents

**Abstract. A possible way to speed up the operation of liquid crystal structures based on nematic mixtures with a charge transfer complex between a fullerene and an organic molecule donor fragment is studied using pyridine and polyaniline monomers and polymers as systems with the donor – acceptor interaction. Self-organization is established to occur in such structures. A more than an order of magnitude reduction in switching time is shown to be achievable. A possible physical mechanism of accelerating the liquid crystal dipole reorientation stimulated with intermolecular complex formation is discussed.**

## 1. Introduction. Statement of the problem

Since the First International Congress on Liquid Crystals (LCs) held at Kent State University, OH, USA, in 1965, the implications of these systems associated with various aspects of laser and liquid crystal display technologies, thermo-optics, and medicine have been the subject of considerable debate among researchers. Indeed, LCs, being a unique mesomorphic phase of matter, combine properties of both solids (long-range orientational order, manifestations of Bragg diffraction) and liquids (fluidity, viscosity) [1 – 3]. Important features of LCs are weak dispersion forces between molecules and strong orienting fields. An intrinsic characteristic of the liquid crystal state is unidirectional (nematic structure) or bidirectional (smectic structure) ordering, albeit not in three dimensions as in a real crystal. In other words, this state is more structured than the liquid one but less so than the solid phase. The order parameter of an LC is the degree of its regularity characterized by the deviation of the

direction of the long axis of a molecule from that of the LC director,

$$S = \frac{3\langle\cos^2\theta\rangle - 1}{2} , \qquad (1)$$

where $\theta$ is the angle formed by the long axis of a molecule and the director and $S$ is such that $0.3 - 0.4 < S < 1$ [3].

The orienting power of LCs is used in the development of composite materials. LCs align suspended particles, acting as matrices easily controllable by elastic forces and by thermal, magnetic, light, and electric fields. By way of example, an electric field applied to a liquid crystal or an electric current passing through a medium produces effects that do not occur in other electro-optical media. These effects include, for example, the Freedericksz effect, that is, a change of director orientation in an electric or magnetic field. The altered transmission state of an LC medium undergoing the Free-dericksz effect makes it possible, in principle, to study the time course of the system's reaction to an external impact and its subsequent relaxation to the initial state. Such studies and the search for the new methods to reduce the switching time of LC media are of primary importance for the solution of a variety of problems pertaining to opto-electronics, laser techniques, medicine, and certainly liquid crystal display technology.

It is worthwhile to note that the use of liquid crystals as electro-optic switches, laser gates, light modulators, cavity mirrors, display monitors, and some other real-time systems requires not only a high speed of operation but also good contrast and modulation characteristics [4]. But these goals cannot be pursued by simply choosing a unique basic device setup or by somehow arranging its elements or components. As a rule, the improvement of one characteristic, e.g., either the operating speed range or the sensitivity, compromises the resolving power. On the other hand, the available methods for the enhancement of the resolving power slow down the spread of charge carriers when the potential pattern is formed in recording optical information in a medium and thus affect the performance. Holographic studies of liquid crystals provide a plausible explanation of this controversy. Indeed, the resolving power determined from the relation between the diffraction efficiency and the spatial frequency depends on

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the depth of the phase relief and its correspondence to the intensity distribution in the interference grating created in the layer. When a thin grating with sinusoidal variation of transmission is recorded in a photosensitive structure, the intensity of the diffraction maximum of the $i$th order, $I_i$, is described, in accordance with the criterion proposed in Ref. [5], by the expression

$$I_i = \frac{J_i^2(\Delta\Phi_{\max} - \Delta\Phi_{\min})}{2}, \qquad (2)$$

where $(\Delta\Phi_{\max} - \Delta\Phi_{\min})$ is the phase modulation depth and $J_i$ is the order-$i$ Bessel function of the first kind.

The depth of the phase modulation is related to the thickness of the liquid crystal layer by the direct proportionality dependence [4]

$$\Delta\Phi = \frac{2\pi d\Delta n}{\lambda}, \qquad (3)$$

where $d$ is the thickness of the electro-optical layer, $\Delta n$ is the birefringence of the liquid crystal, and $\lambda$ is the radiation wavelength acting on the electro-optical medium.

Thus, it follows from (2) and (3) that the thickening of the liquid crystal layer must lead to deeper phase modulation and therefore to a stronger electro-optical response that determines diffraction efficiency. However, it is the thinning of electro-optical crystals that is normally used to improve time-related structural parameters. In other words, it is technically difficult to enhance the operating speed while retaining high resolution power, hence, the need to search for new ways to optimize dynamic and modulation characteristics of liquid crystal devices based on the results of investigations into photophysical processes that proceed in electro-optical media under the effect of either an electric field or laser radiation.

We recall that there are a number of classical approaches to the improvement of the switching time in nematic liquid crystal (NLC) cells that are frequently used for practical purposes [4]. They include increased supply voltage and the aforementioned thinning of the crystalline structure, as well as a change in viscosity, e.g., by heating the medium or adding an extra amount of organic solvent, and the application of certain technical adjuncts, such as pulsed feeding and illumination, the choice of the delay time between the exciting laser pulse and the external voltage pulse, etc. [6, 7]. Naturally, it is possible to proceed from simple to complex, that is, to radically change the structure by using a fast-acting smectic instead of an NLC. This, however, encounters two serious obstacles, one being the high cost of smectic LC and the other being the difficulty of aligning smectic layers. The lamellar structure of the smectic liquid crystalline phase is easily disturbed when the geometric relief of the orienting surface is formed by friction. These difficulties are practically nonexistent in work with simple nematic systems, e.g., cyanobiphenyls.

In addition to the well-known classical methods of optimizing nematic characteristics, new physical principles are now used for the purpose, such as the introduction of photosensitive components, e.g., dyes, into a liquid crystal [8, 9]. The addition of dyes increases the absorption efficiency of a composite system and affects the related photoconductivity. As a result, these structures exhibit a marked photorefractive effect accounting for the efficacious modulation of laser radiation that passes through a liquid crystal sensitized

by a special dye. Such crystals are composite materials, the so-called polymer-dispersed liquid crystals (PDLCs). The control process for these materials is as follows [10]. A liquid crystal, e.g., a nematic, is chosen such that its refraction index for an ordinary beam, $n_0$, is close to that of a polymer matrix, $n_{\mathrm{p}}$. In the initial state, there is a refraction index gradient created by an arbitrary director orientation at the LC– polymer interface; it accounts for the strong light scattering by such a composite. When an electric field or a light signal propagating normally to the cell surface ($n_0 \cong n_{\mathrm{p}}$) is applied, the refractive index gradient is very small and the LC director is oriented along the field or the light wave electric vector. In this case, there is no scattering and the system becomes more transparent. One of the factors contributing to the equality of refractive indices is heating of the liquid crystal [11], up to its transition to the isotropic state, by an intense light or a strong electric current. After either effect is eliminated, the composite returns to the initial, scattering state. It is worth noting that the size of LC droplets in the polymeric matrix may vary in a rather broad range from 0.1 to 20 μm and the LC concentration in the polymer amounts to 35–40% or more. Thus, it should be borne in mind that the term 'polymer-dispersed liquid crystal' does not adequately reflect the existence of the two PDLC types that are most extensively studied today; these are polymer matrices containing LC droplets (as a rule, measuring not more than 100 nm) and systems in which the matrix LC layer includes dyes, polymeric components, stabilizers, and various photosensitive compounds. Studies involve both fast-acting smectics and classical nematic compositions.

At present, PDLCs are increasingly employed in a variety of spheres, and the area of their application constantly widens due to the development of new liquid crystal and polymer compositions and to the improvement of their processing technologies. These developments are promoted by the use of nano-objects, including LC nanodroplets [12]. It has been shown that the introduction of LC droplets with a linear size of $\sim 100$ nm substantially alters the order parameter of composite materials and may increase the efficiency of electro-optic modulation of light by the end product. Moreover, the unique optical and nonlinear optical properties of liquid crystals including PDLCs and PDLC-based devices find wide applications in laser physics as promising systems that effectively limit laser radiation, due to the presence of fullerenes in their composition, and facilitate reversible recording of optical information [13–19]. For fullerene-enriched liquid crystal systems containing no introduced polymeric matrix, the limiting threshold is taken to be roughly $\leqslant 0.09$ J cm$^{-2}$. When resonant nonlinearities of nematochiral liquid crystals are used, the same parameter is $10^{-6}$ J cm$^{-2}$. Laser switches based on polymer-dispersed systems set the laser radiation power to within $\leqslant 0.3$–0.4 J cm$^{-2}$. Thus, liquid crystal systems with fullerenes including polymer-dispersed ones with such a low limiting threshold can be used in multistage systems for the protection of human eyes from laser radiation (safe energy density is assumed to be $\sim 10^{-7}$ J cm$^{-2}$). Both the limiting threshold and the spectral range of real PDLC-based protective devices and their dynamic properties can be controlled by using various photosensitive compounds.

The suitable photosensitive components include complexes in which the charge is transferred between an organic donor (monomer, polymer, or nanoparticle) [20–23] and a fullerene as a strong electron acceptor with the electron
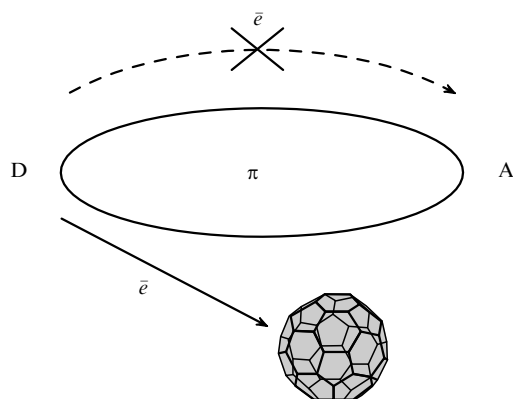
**Figure 1.** Schematic representation of the donor – acceptor interaction between a fullerene molecule and the donor component of a fullerene-containing composite.



**Figure 2.** Sandwich liquid-crystal structures.

affinity energy in the range 2.3 – 2.65 eV; this value is frequently in excess of a similar parameter for intramolecular acceptor fragments of organic molecules. For comparison, the acceptor fragment of pyridine family molecules, e.g., 2-cyclooctylamino-5-nitropyridine (COANP), is an $NO_2$ group linked to the donor fragment via a benzene ring. A single $NO_2$ molecule or radical is characterized by an electron affinity energy of 2.3 eV, but the same $NO_2$ group bound to the benzene ring has an electron affinity energy of only 0.54 eV [24]. This value is 4 times smaller than the same parameter for a fullerene. In another donor – acceptor system with a polyimide molecule with a triphenylamine fragment as the donor and diimide as the acceptor, the latter has the electron affinity energy 1.12 – 1.46 eV [25], i.e., twice as small as that of the fullerene. Figure 1 depicts a feasible scheme of the donor – acceptor interaction in a fullerene-containing composite. The new complex having a larger dipole moment [26] enhances polarizability of the system and thus ensures its more efficacious control when applying an external electric field or a light pulse.

The present paper outlines a promising way to improve the performance of nematic liquid crystal structures during the experimental process of system self-organization. We examine the switch-on and switch-off times of nematic fullerene-containing dispersed LCs (FDLCs) based on charge-transfer complexes of 2-cyclooctylamino-5-nitropyridine (COANP) – fullerene and polyaniline (PANI) – fullerene. Also, the reader is referred to the publications reporting the use of the magnesium phthalocyanine – fullerene system.

## 2. Experimental conditions

FDLC cells are classical multilayered structures (Fig. 2) formed by two glass (quartz) substrate layers, conducting and orienting coats, and an electro-optic liquid-crystalline layer into which a photosensitive additive is introduced. The last of these is either a monomer electron-donor molecule of COANP or a PANI polymer with $C_{60}$ and/or $C_{70}$ fullerenes as acceptors. Fullerene powders containing 99% and 97% of $C_{60}$ and $C_{70}$, respectively, were provided by Alfa Aesar (A Johnson Matthey Company, USA). Thin films of indium and tin oxides were used to form the conducting coats. The proper alignment of the electro-optical layer was achieved by the use of orienting polymer coats of photoinsensitive polyimides that ensured a small tilt of LC molecules relative to the
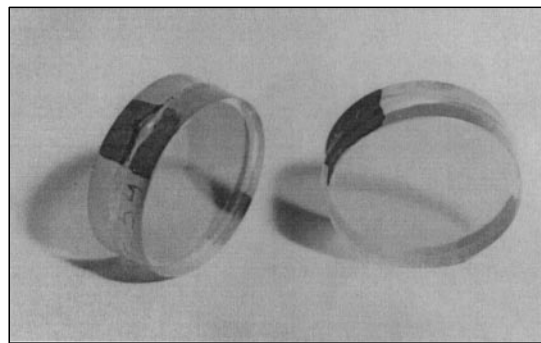
substrate surface [27]. The orienting films were synthesized by the treatment of 3% polyimide solutions in tetrachloroethane under centrifugation.

The experiments were conducted on S-type cells with an initially planar orientation. The electro-optical layer consisted of standard nematic LC systems with positive optical ($\Delta n$) and dielectric ($\Delta\varepsilon$) anisotropy: NLC1282 ($\Delta n = 0.164$, $\Delta\varepsilon = 9.9$), NLC1289 ($\Delta n = 0.168$, $\Delta\varepsilon = 10$), and E7 ($\Delta n = 0.224$, $\Delta\varepsilon > 0$). The layer thickness varied from 10 to 12 μm. As mentioned earlier, molecules of the donor – acceptor complex were introduced into the bulk of the LC systems under study. The ratio of the photosensitive to electro-optic components was 1 : 2 and 1 : 4 for COANP and PANI, respectively. We note that the COANP structures were preliminarily sensitized with $C_{60}$ and/or $C_{70}$ fullerenes (see Refs [20, 28] for COANP sensitization by fullerenes) and the PANI system with a $C_{60}$ fullerene [22]. The fullerene concentration was 0.5 – 5% by weight of the pure COANP and varied from 0.5 to 8 weight percent of the pure PANI. Efficacious sensitization of COANP by a dye was first demonstrated in [29]; in this study, the pure COANP had the absorption edge at 420 – 430 nm. The earliest absorption spectra of fullerene-doped COANP solutions were presented in Refs [28, 30] and of a thin-film composite in Refs [20, 31]. Sensitization by dyes resulted in long wavelength bands in the absorption spectra near 600 nm; an additional 800 nm band was recorded in the spectra of fullerene-doped nanocomposites. Figure 3 presents the absorption spectrum of a thin-film
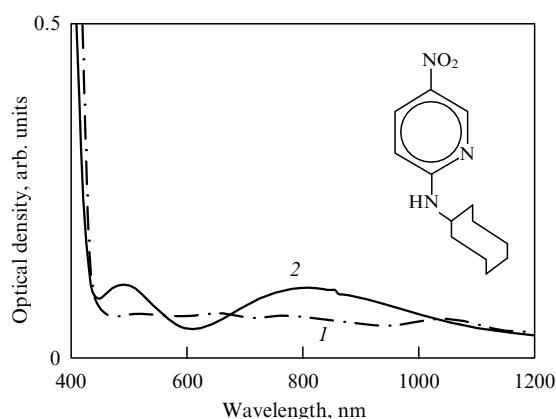


**Figure 3.** Absorption spectra of thin films: *1* — pure COANP sample, *2* — COANP – $C_{70}$ structure. The inset shows the structure of the COANP molecule.

of a $COANP-C_{70}$ composite and the inset shows the structural formula of the COANP molecule.

External voltage was applied to the cells in the form of rectangular pulses with the amplitude from 10 to 60 V, duration from 10 to 100 ms, and repetition frequency from 0.5 to 2000 Hz. The measured parameter was the passage of $He-Ne$ laser radiation through a cell at $\lambda = 633$ nm. The light spot focused on the sample was $3-3.5$ mm in diameter.

The experiment was designed to determine the incremental times of the electro-optical response in the first transmission oscillation and the transition to the adjacent extremum on the S-curve corresponding to a change in the phase delay by $\pi$. The switch-on time was determined from the increment of the electro-optical response from 0.1 to 0.9 and the switch-off time from the decrease of the electro-optical response from its maximum level to 0.1. The concentration dependence of the switch-on time was obtained for the $LC-PANI-C_{60}$ structure.

## 3. Discussion

Figure 4 illustrates the dependence of the switch-on time of all studied dispersed liquid crystalline structures containing fullerene complexes on the control action parameters in two situations: in the absence of self-organization (the cells were made immediately after the preparation of LC mixtures) and following the self-organization process in the same structures (the cells were made and left at room temperature for a few days after sensitization of LC compositions). The data obtained indicate an abrupt change in time parameters in the latter case. Specifically, the system studied undergoes ordering and transits to a thermodynamically more favorable state resulting in a molecular rearrangement, biaxiality, and potential change of the order parameter. Figures 5a, b present microphotographs of such structural process in a $COANP/C_{70}$-based crystalline system. It is readily apparent that the structure passes to a state essentially different from the initial one. Characteristic uniaxiality of the pure LC structure changes to biaxiality following the introduction of a charge-transfer complex. Photography in polarized light reveals well-apparent regions with altered birefringence and
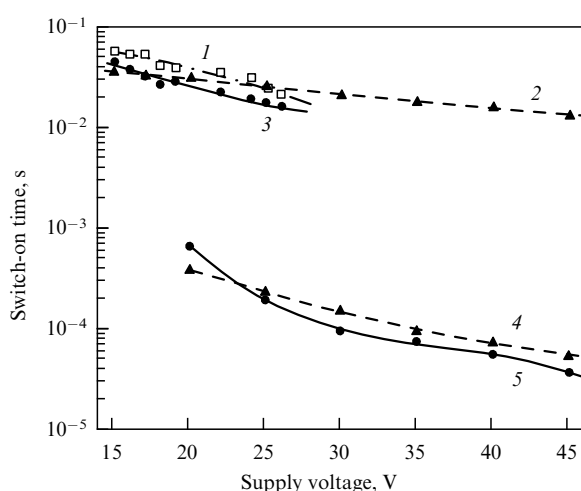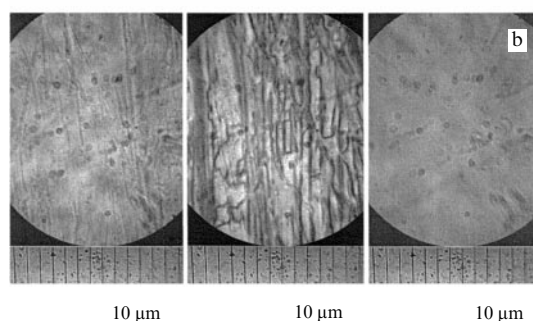
**Figure 5.** (a) Micrograph of an $LC-COANP-C_{70}$ structure. (b) Micrographs of LC structures: pure NLC (left), $LC-COANP-C_{70}$ (middle), $LC-COANP$ (right). Scale division at the bottom is 10 μm.

the clearly visible domain structure of sensitized LC. In addition, a shift in the upper substrate results in a slight distortion of the molecular arrangement, which returns after a time to the previously reached self-ordered state. The analysis of the micrographs shows that the introduction of nano-objects in the form of fullerene-containing complexes may induce a substantial change in the rotational dynamics of the LC director in the sensitized mesophase. The main idea consists in the creation of an additional field gradient by a more efficient charge transfer between the organic donor (monomer, polymer, or nanoparticle) and the acceptor (fullerene) with the subsequent twist of the LC-dipoles along the coupled donor – fullerene system.

We qualitatively analyze the above process. By way of example, we consider a small local volume of our medium, substantially smaller than the incident wavelength. Indeed, for a system of dimensions smaller than the optical wavelength (633 nm in our experiment; for comparison, fullerene molecules are $0.65-0.7$ nm in size according to some publications [32, 33]), the most important optical characteristic is the induced dipole, whose dependence on the applied local field can be expressed through dipole polarizabilities $\alpha^{(n)}$ [34]. These are in turn related by the proportional dependence to the nonlinear sensitivities $\chi^{(n)}$ and are inversely proportional to the considered unit cell volume $v$:
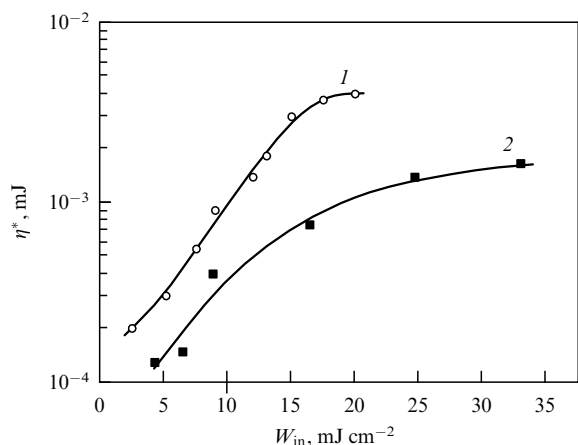
$$\chi^{(n)} = \frac{\alpha^{(n)}}{v} . \tag{4}$$

**Figure 4.** Dependence of the switching time on the supply pulse amplitude for NLC systems containing pure COANP (*1*), $PANI-C_{60}$ (*2*, *4*), and $COANP-C_{70}$ (*3*, *5*). Initial characteristics (*1 – 3*) and after completion of self-organization (*4, 5*).

**Figure 6.** Plots of the first-order response of the diffraction ($\eta^*$) versus the input density of the laser radiation energy ($W_{in}$) for a COANP/$C_{70}$-based PDLC (5 weight %) at a laser pulse of 20 ns ($1$) and 400 ps ($2$).



**Figure 7.** Plots of switch-on ($1$) and switch-off ($2$) times versus the $C_{60}$ concentration in an LC–PANI–fullerene structure. Supply pulse parameters: amplitude $A = 30$ V, duration $\tau_p = 30$ ms, repetition frequency $1/T = 2$ Hz.

It has been shown in Ref. [21] that the third-order non-linear sensitivity $\chi^{(3)}$ of a sensitized COANP/fullerene-based LC system is much more pronounced than can be computed from the analysis of a photo-induced change in the refractive index (and hence, $\chi^{(3)}$) of a nonsensitized structure. Indeed, the response in the first order of diffraction in recording a thin amplitude-phase hologram in an LC–COANP–fullerene structure varies from $2 \times 10^{-4}$ to $3.7 \times 10^{-3}$ mJ as the incident energy density changes from 2.5 to 17.5 mJ cm$^{-2}$. Figure 6 shows the dependences of the response in the first order of diffraction for an LC–COANP–$C_{70}$-based structure. The photo-induced value of the refractive index for a COANP-based LC structure with fullerenes can be estimated using the known relation for the calculation of the experimentally measured diffraction intensities (see Ref. [35]) in combination with the aforementioned film thickness and light spot diameter. In this way, the refractive index in the nanosecond range of the laser pulse lengths has been found to vary from $7.3 \times 10^{-4}$ to $1.4 \times 10^{-3}$. These values of the refractive index are larger than the thermal constituent $\Delta n$ characteristic of LC structures ($\sim 10^{-5}$) and two orders of magnitude in excess of the response of a nonsensitized COANP system.

Thus, it can be suggested based on the available experimental data and the known relation between nonlinear sensitivity and polarizability of the system given by expression (4) that both the dipole polarizabilities of the local microvolume and the macroscopic polarization of the system are on the whole higher for an LC mesophase with the introduced fullerene-containing complex than for a pure LC mixture. The literature on the smectic state, including polymer-dispersed LC systems [36], gives evidence that polarization of a system is inversely proportional to time parameters; in other words, enhanced polarization of the system accelerates photophysical processes and thus increases the small switching times of the smectic mesophase. The authors of Ref. [36] experimented with a three-micron PDLC system containing smectic LCs and estimated the incremental response time as $\sim 150$ μs with the exciting pulse amplitude 20 V; the switch-on time was $\sim 40$ μs at the pulse amplitude 40 V. The values of time-related parameters obtained in the present work are close to those reported in Ref. [36]. It should be noted, however, that we used structures
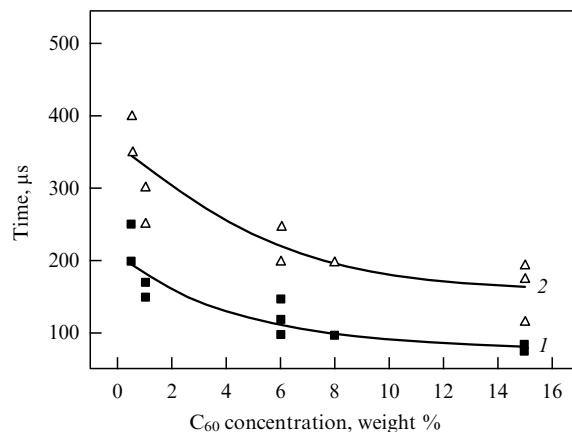
three times as thick as those in Ref. [36] and also studied nematics, not smectics. It appears that the recording of switch-over times in a range of hundreds of microseconds for a sensitized fullerene-doped NLC complex actually reflects a nematic–smectic quasitransition, and this does not disagree with the recorded time parameters (see Fig. 4).

Thus, the introduction of a charge-transfer donor–fullerene complex with an additional dipole moment into the NLC mesophase (see the results of the quantum-chemical calculation [26] and the above qualitative consideration of the relevant process indicating a consistent enhancement of polarization in the nonsensitized structure) may accelerate molecular rearrangement in the system. We note that the appearance of the additional dipole moment may be promoted by the effective generation of charges in certain structures, such as PANI-based ones, under the effect of light; also, it stimulates charge separation between the donor and the fullerene, leading to an overall increase in system polarization. Therefore, the orientation of LCs occurs when the bulk mesophase is modified by introducing an additional amount of the distributed organic donor–fullerene system characterized by enhanced polarization and aligning the LC director along the dipole vector; it substantially improves the performance of the system. This observation is strongly confirmed by studies of the dependence of the switch-on and switch-off times of the electro-optical response on the introduced fullerene additive. Such a dependence for an LC–PANI–fullerene system is depicted in Fig. 7. It can be seen that a rise in the fullerene concentration by at least 0.5 – 5% weight percent of the matrix PANI leads to a decrease in the switch time, probably owing to an increased number of charge-transfer complexes involved in the rearrangement of LC dipoles. This dependence was verified by observations of the direct and reverse changes in the supply pulse amplitude.

We now return to the main idea. The novelty of the present study and interpretation of its results consists in the fact that we have managed to separate, at the stage of technological synthesis of specimens, two LC states differing in molecular arrangement: nematic and, probably, smectic or (to be precise) quasismectic ones; the latter was induced by the introduction of a fullerene-containing charge-transfer complex rather than by the direct field or light effect fairly well known from the literature [37, 38].

Returning once again to the time dependences obtained in experiments, we emphasize that time-related characteristics of LCs are significantly modified by the introduction of photosensitive charge-transfer complexes, which cause a more prominent change in the reorientation rate of LC dipoles in a self-organizing structure. It is worth noting that cells prepared from self-organizing structures had switch-over times two orders of magnitude better than reported in earlier studies. We managed to realize a transition from the millisecond to the microsecond range (dozens of microseconds at the driving voltage with an amplitude of 50 V), which is characteristic of the smectic liquid crystalline state. Moreover, our experiments demonstrated that all the structures under study had practically identical time parameters when the applied voltage was about 30 V. This observation requires further experimental and theoretical verification. Even now, however, our data suggest the leveling effect of organic donors, in good agreement with the theoretical results in Ref. [39], where the authors showed a threshold increase in the system's order parameter at a given amplitude of the driving voltage. This increase was associated with the correlation of the order parameter inside an LC droplet and the order parameter of its immediate surroundings in the LC mesophase.

The results of investigations considered in this paper suggest that the physical mechanism of the accelerated twist of LC dipoles facilitating the switch of a sensitized NLC may be related to the molecular complex formation process in a coupled nanostructured organic system during the creation of an additional field gradient and the enhancement of polarization. This process appears to stimulate a change in the order parameter of the system in the case of a potential nematic – smectic quasitransition upon the introduction of a fullerene-containing complex. Measurement of the order parameter by X-ray structural analysis constitutes a promising line of further research.

It should be noted that the process of complex formation in the structures studied thus far was confirmed by spectral measurements (absorption spectra, photoconductivity [20–22]), mass spectrometry (see, e.g., Ref. [40]), quantum-chemical simulation [26], nonlinear optical measurements of photoinduced effects in various media [18–21, 40, 41], etc. We compared our findings with the relevant data obtained by other groups of researchers. The results are summarized in the table that illustrates the evolution of notions about dynamic and electro-optic characteristics of LC media after the introduction of dyes and charge-transfer complexes into their structure. Attention is focused on polymer-dispersed nematic compositions, although some data on the optimization of switching times concern separated photolayer – LC structures.

To conclude, studies of new liquid-crystalline materials containing various photosensitive additives and methods for the optimization of electro-optical characteristics of these systems promote their application in opto-electronics, laser and display technologies, medicine, and, in the future, solar energetics. They also contribute to a deeper understanding of basic processes in these media during their interaction with light and especially laser radiation. Naturally, this problem and a feasible approach to its solution as outlined in this paper are of special interest for the development and improvement of liquid-crystal display monitors. The author hopes that the present study will stimulate further investigations in this area, attract attention of more researchers, and

possibly receive the most adequate theoretical substantiation. The last is strongly needed bearing in mind that the present study took no account of the likelihood of the direct interaction between fullerenes and the LC matrix via a CN-group of cyanobiphenyls.

## 4. Conclusion

This study was focused on time parameters and effects of self-organization in FDLC systems containing organic donor – fullerene complexes. It has demonstrated a reduction of switching times by two orders of magnitude. The analysis of the calculated photoinduced variation in the refractive index (allowing for the assessment of nonlinear sensitivity), results of quantum-chemical simulation, and microscopic data confirm additional polarization of the system. The process of complex formation is shown to induce a transition from the nematic state to a more regular quasismectic one. The analysis emphasizes the following major results of the study:

(1) The introduction of fullerenes and/or fullerene-containing charge-transfer complexes markedly affects order parameter dynamics in NLC structures.

(2) Organic donor – fullerene complexes function as activators of the self-organization processes in an LC system, ensuring a more ordered arrangement of LC molecules.

(3) Organic donor – fullerene complexes stimulate potential transition from the nematic mesophase to the smectic one.

(4) After thermodynamic equilibrium is established, the time-related characteristics of all systems under study (monomer-, polymer-, or nanocrystal-based) are practically independent of the nature of the organic donor (see Refs [23, 48] for a system composed of magnesium phthalocyanine nanocrystals, fullerenes, and LCs).

(5) The results of the study have implications for the optimization of characteristics of LC displays and the dynamic parameters of liquid-crystal space – time light modulators operating in real time.

**Table.** Operating speed range of liquid-crystal composites.

| LC composition | Layer thickness, μm | Radiation wavelength, nm | Parameters of driving voltage pulses: amplitude ($A$, V), duration ($\tau$, ms), repetition frequency ($1/T$, Hz) | Switch-on/off time, ms | Potential mechanism of improved operating speed of an LC composite | Note | References |
|---|---|---|---|---|---|---|---|
| NMC + orange dye | 30 | 514.5 | — | 20 | Switching effect produced by enhanced thermal nonlinearity | Interruption of continuous laser beam | [42] |
| 100 nm LC droplets in the polymeric matrix | 12 – 36 | | | | Effect of electric field on the order parameter was assessed. Account was taken of the order parameter inside the droplet and its coincidence or discrepancy with PDLCs. Conclusion: decrease in the order parameter at low driving voltages and its increase at high ones (over 35 V) | Possible change in the electro-optical response is predicted | [39] (theoretical study) |
| NLC + monomer + stabilizer | 13 – 36 | 632.8 | $1/T = 100$ Hz | 0.5/0.7 | Change in the order parameter | Induced phase shift and, incidentally, time parameters were evaluated | [12] |
| NLC + PMMA + azo dye | 36 | Ar$^+$ — recording, He – Ne — reading | $A = 100$ V $1/T = 100$ Hz; max up to $1/T = 2000$ Hz | 5/5 | *Cis-trans* photoinduced isomerization | Diffractional variations in intensity $\eta$ versus spatial frequency $\Lambda$; $\Lambda = 200 - 100$ mm$^{-1}$, $I = 5 - 350$ W cm$^{-2}$, $V = 0 - 100$ V | [43] |
| NLC + PMMA + dye | 36 | 514.5 | | Seconds | The idea of polymerization was rejected because the response was independent of polarization of the recording beams. The study was focused on the photorefractive effect inside the droplets | The presence of the dye had the following consequences: (1) increased absorption resulted in the heating of the medium, (2) the dye functioned as the charge generator for the photorefractive effect; the internal field strength was estimated at 0.03 V μm$^{-1}$ (within a few minutes after irradiation) | [9] |
| Nematic + DRed-1 dye (dispersed red-1) | 32 | 532 and 670 | | 74 | Photoisomerization; variation in the system's order parameter taking dichroism of the dye into account | Interruption of continuous laser beam for 0.2 s. The response time and the value of $\eta$; $\Delta n = 9.6 \times 10^{-4}$ | [44] |
| NLC + rhodamine 6G; LC-containing polymers; separated by the photolayer – LC system | 15 | 532 | Constant voltage of 10 V | 10 ms – 1 s, the largest total value 100 ms | Enhanced photogeneration of charge carriers in the bulk of the LC mesophase; a change in $\Delta n$ | Also evaluated were $n_2$ and $\chi^3$. One conclusion concerns the necessity to decrease the dye concentration in order to diminish thermal nonlinearity | [8] |

**Table** (continued).

| LC composition | Layer thickness, μm | Radiation wavelength, nm | Parameters of driving voltage pulses: amplitude ($A$, V), duration ($\tau$, ms), repetition frequency ($1/T$, Hz) | Switch-on/off time, ms | Potential mechanism of improved operating speed of an LC composite | Note | References |
|---|---|---|---|---|---|---|---|
| Photolayer – LC system, sensitization by a $C_{60}:C_{70}$ mixture (85 : 15%) | 5 – 10 | 532 | $A = 30 - 60$ V $\tau = 30 - 300$ ms $1/T = 0.2 - 7$ Hz | 5 – 10 | Accelerated transition processes at the photolayer – LC interface under the effect of fullerenes | Predicted conservation of high resolution upon a slight decline in the switching time | [45] |
| COANP + $C_{60}$ + NLC | 10 – 12 | 633 | $A = 30 - 50$ V $\tau = 30 - 60$ ms $1/T = 50$ Hz | 6 – 2.5/15 – 10 | Reorientation of LC dipoles when the accelerated twist of $C_{60}$ and $C_{70}$ molecules in the external field is taken into consideration | The mixture was supplemented by a high molecular weight polyimide-based plasticizer | [46] |
| COANP + $C_{70}$ + NLC + plasticizer | 10 – 12 | 633 | $A = 30 - 50$ V $\tau = 30 - 60$ ms $1/T = 50$ Hz | 4 – 2/12 – 8 | Effect of the accelerated $C_{60}$ and $C_{70}$ molecules on the reorientation of LC dipoles in the external field | Twist rate of $C_{60}$ and $C_{70}$ molecules depending on fullerene nature. The plasticizer/LC ratio was also varied to assess the effect on molecular mass dynamics | [47] |
| COANP + $C_{70}$ + NLC | 10 – 12 | 532 | | | A model of the LC dipole twist model is proposed | Calculated photoinduced change in the refractive index ($\sim 10^{-3}$) and also $n_2$ and $\chi^{(3)}$ | [21] |
| COANP + $C_{70}$; $N$-(4-nitro-phenyl)-$L$-proline | 10 – 12 | 532; 805 | | | A conclusion: donor – acceptor interaction must be taken into consideration as a mechanism of photoinduced effects in PDLCs | Studies were carried out in nano-, pico-, and femtosecond ranges | [19] |
| NLC + magnesium phthalocyanine + $C_{70}$ | 10 – 12 | 633 | $A = 30 - 50$ V $\tau = 1 - 100$ ms $1/T = 0.2 - 100$ Hz | 1/3 | Formation of fullerene – phthalocyanine complex | The cells were prepared immediately after mixing components of the composite | [23, 48] |
| NLC + polyaniline + $C_{60}$ | 10 – 12 | 633 | $A = 30 - 50$ V $\tau = 1 - 100$ ms $1/T = 0.2 - 100$ Hz | 30 – 17/90 – 70 | Formation of fullerene – polyaniline complex | Polyaniline molecular mass $\sim 15000$. The results were compared with earlier ones | [49] |
| COANP + $C_{70}$ + NLC | 10 | | $1/T$ up to 2000 Hz | 0.05/0.2 | Formation of fullerene – organic donor complex | Measurements were made after the completion of self-organization | [50] |
| NLC + polyaniline + $C_{60}$ | 10 | | $1/T$ up to 2000 Hz | 0.07/0.22 | | | |
| NLC + magnesium phthalocyanine + $C_{70}$ | 10 | | $1/T$ up to 2000 Hz | 0.045/0.10 | | | |

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