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# Molecular Crystals and Liquid Crystals

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## Possible Transition of Fullerene-containing Nematic Liquid Crystal to Smectic Phase

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Self-organization in liquid crystal compounds based on the charge-transfer complexes between an organic donor and a fullerene has been first investigated. The switch-on time of 50  $\mu$ s has been obtained. The results are discussed from the viewpoint of the transition from the nematic phase to the smectic one, which is caused by a complex formation.

**Keywords:** charge-transfer complexes; fullerene; liquid crystal; self-organization; switching

Electrically- and light-addressed liquid crystal (LC) systems are being intensively investigated and improved in last decade. The reason is that they are of low (up to 100 V) operating voltage, good threshold characteristics, and high uniformity, as well as of high sensitivity, resolution, and speed. Moreover, these devices are easily controllable.

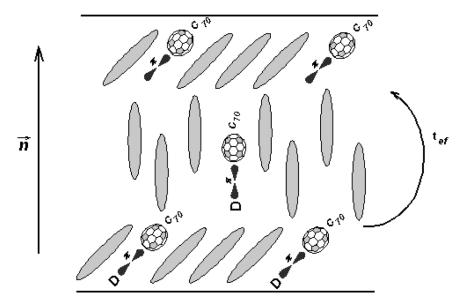
The authors would like to thank Dr. I. Yu. Denisyuk (Vavilov State Optical Institute, St. Petersburg, Russia) and Dr. N. M. Schmidt (Ioffe Physical Technical Institute, St. Petersburg, Russia) for their help in the microscopic measurements. This work was supported by RFBR grant No. 04-03-32249-a.

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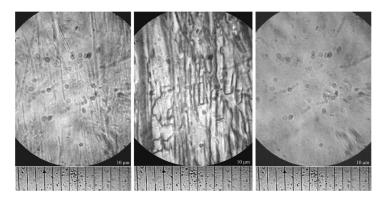
The speed is a very important characteristic of LC devices. To enhance the speed various cases are applied. Apart from changing geometric dimensions of the structure and characteristics of the supply voltage, the modification of the physical-chemical properties of nematic liquid crystal (NLC) is used. In particular, photosensitive substances (e.g., dyes [1,2]) are introduced into NLC. They increase the absorption of the compound and its photoconductivity. In this case, the photorefractive effect is observed, resulting in an efficient modulation of a laser beam transmitted through LC sensitized with the dye.

Charge-transfer complexes between an organic donor (monomer, polymer, nanoparticles) [3–6] and fullerenes can be as the photosensitive component. The new complex has a high dipole moment [7] and hence it increases the polarizability of the compound. This effect improves the control of the NLC structure. The re-orientation of the NLC dipoles is schematically presented in Figure 1.

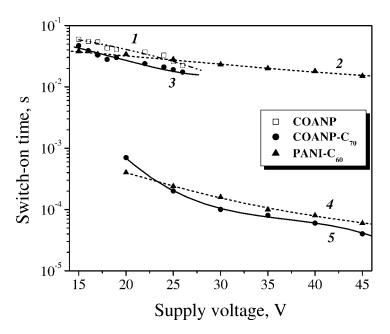
In the present paper the  $10\,\mu m$  NLC cells with the fullerene complexes based on 2-cyclooctylamine–5-nitropyridine (COANP) [3,4] and polyaniline [6] were investigated. As a result, the unique effect was established. It was found that the exposure in a few days resulted in the self-arrangement of the NLC system with the fullerene complex.



**FIGURE 1** The re-orientation mechanism of the NLC-compound with the charge-transfer complex between an organic donor and fullerene under an external action. Fullerene  $C_{70}$  is used as the acceptor.



**FIGURE 2** The optical microscopic images of the structures based on: pure NLC (*left*); the mixture of LC, COANP and  $C_{70}$  (*center*); and the mixture of LC and COANP (*right*). Below is shown the scale (1 point is equal to  $10 \,\mu m$ ).

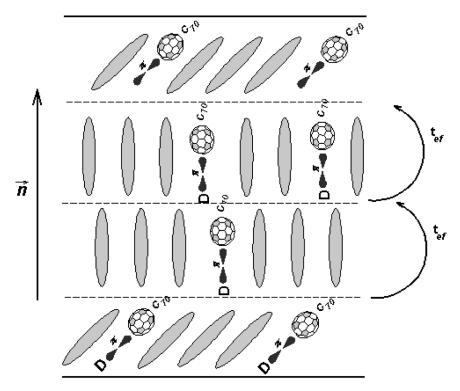


**FIGURE 3** The dependence of the time-on on the amplitude of the supply voltage pulse for the LC-systems with the complexes based on: (1) — pure COANP; (2,4) — PANI– $C_{60}$ ; and (3,5) — COANP– $C_{70}$ . The initial characteristics (1–3) and the ones after the self-arrangement (4–5).

The microscopic study allowed the transition to be revealed from the nematic phase to the smectic one. The optical microscopic images are shown in Figure 2.

The drastic change in the time-on of the cells became the main result of the self-arrangement. The dependence of the time-on on the amplitude of the supply voltage pulse is presented in Figure 3. As the result of the self-arrangement, the ultra-short time-on was obtained. For the initial compounds, the time-on fell in the range 40–160 ms, which was typical of the nematic liquid crystals. After the self-arrangement, the time-on was up to three orders of magnitude shorter. Thus, the time-on was obtained to be typical of the smectic liquid crystals.

In this case, the re-orientation of the LC dipoles can be schematically presented in Figure 4. It should be noticed that the close values of the time-on were observed at the supply voltage pulse amplitude of



**FIGURE 4** The re-orientation mechanism in the smectic phase of the fullerene-containing LC compounds investigated.

TABLE 1 Speed of Modified Liquid Crystals

| Modified LC compound   | Layer thickness,<br>µm | Laser<br>wavelength,<br>nm       | Supply<br>voltage                        | $t_{ m on}/t_{ m off},{ m ms}$ | Ref.                |
|--|------------------------|----------------------------------|--|--------------------------------|---------------------|
| NLC + orange dye $NLC (LC drops of diameter)$ $100 nm in polymor metric)$  | 30 $12-36$             | 514.5                            | I  | 20 theory                      | [11]                |
| NLC + dipentaerythrol hydroxy penta<br>acrylate (DPHPA) + stabilizer   | 13–36                  | 632.8                            | Positive pulse $1/T=100\mathrm{Hz}$      | 0.5/0.7                        | [12]                |
| NLC + PMMA + azodye  | 36                     | $Ar^+ - record$<br>633 - readout | $A=100\mathrm{V} \ 1/T=100\mathrm{Hz}$ : | 5/5                            | [13]                |
| NLC + PMMA + dye   | 36                     | 514.5<br>539 and 670             | (  | seconds                        | [2]                 |
| NLC + ryoe (Linear) NLC + rhodamine 6G; LC-polymers;   | 15                     | 532                              | cw 10V                                   | 10  ms- 1  s/100  ms           | ΞΞ                  |
| Separated systems of photolayer-LC Sensitization with a full-tene mixture $C_{co} + C_{co}$  |                        | 532                              |  | 5–10                           | [15]                |
| $\rm COANP + C_{60} + NLC$   | 10–12                  | 633                              | 30-50  V; 30-60  ms<br>1/T = 50  Hz      | 6-2.5/15-10                    | [16]                |
| ${ m COANP} + { m C}_{70} + { m NLC} + { m plasticizer}$ ${ m COANP} + { m C}_{70} + { m NLC}$ ${ m COANP} + { m C}_{70};$ ${ m COANP} + { m C}_{70};$ ${ m Mod aniton bound} { m Mod aniton bound} { m Complianol} { m Complex conditions}$ | 10-12 $10-12$ $10-12$  | 633<br>532<br>532; 805           | }<br> <br>                               | 4-2/12-8 Possible model        | [16]<br>[3]<br>[17] |
| $NLC + phthalocyanine + C_{70}$  | 10–12                  | 633                              | 30-50  V; $1-100  ms0.2-100  Hz$         | 1/3                            | [2]                 |
| $ m NLC+polyaniline+C_{60}$ $ m NLC+COANP+C_{70}$ (after self-oreanization)  | $10-12 \\ 10$          | 633<br>633                       | "_<br>to 2000 Hz                         | $30-17/90-70 \ 0.2/0.05$       | [18]<br>present     |
| NLC + polyaniline + C <sub>60</sub> (after self-organization)  | 10                     | 633                              | to $2000\mathrm{Hz}$                     | 0.22/0.07                      | present             |

about 25 V. This fact was indicative of negligible contribution of the organic donor and directly agreed with the data of Ref. [8]. In that paper it was theoretically demonstrated that, in this range of the supply voltage pulse amplitude, the order parameter of the system increased that was associated with correspondence of the order parameter within the LC drop with the close surrounding of the mesophase.

It follows from our results that the mechanism of the accelerated rotation of the LC dipoles is likely to be caused by the order parameter change during the transition from the nematic to the smectic induced the fullerene-containing complex introduction. The complex formation was supported by the data of absorption and luminescence spectra, mass-spectroscopy, non-linear measurements of light-induced effects, and a quantum-chemical simulation [3,5,7,9,10].

Analyzing our experimental results and literature data, the place of material studied and their dynamic characteristics can be indicated. The results are shown in Table 1.

In conclusion, it should be emphasized that the organic donor – fullerene complex significantly influences the temporal characteristics of the LC compounds investigated. The complex stimulates the self-arrangement of the LC system (the nematic–smectic transition). After the establishment of thermodynamic equilibrium with the new order parameter, the dynamic characteristics of the systems are independent of the organic donor.

Moreover, in our case, the molecular weight of the organic donor affects the rotation time of the LC dipoles. However, this effect calls for future investigations. Nevertheless, the investigations of the new liquid crystal materials with different photosensitive components allow them to be applied in optoelectronics and laser technology.

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