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The orientational behaviour of some aminoanthraquinone dyes in E8 and ZLI-1132 nematic solvents and effect of addition of carbon nanotubes

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Guest–host liquid crystal displays have been widely utilised because of their many advantages such as colour, wide viewing angle and high brightness. For practical guest–host applications, it is important to choose dyes with a high ability of orientation in the liquid crystal matrix. In this work, two different nematic liquid crystals (E8 and ZLI-1132) were separately doped with three different dyes (1,2-, 1,4- and 2,6-diaminoanthraquinone). Their solubilities, textures, phase transition temperatures and order parameters were determined. At the second stage, single-walled carbon nanotubes (CNTs) were added (0.05% m/m) to these solutions and the same parameters (except solubilities) were studied again. The highest solubility and order parameter values were attained with 1,4-diaminoanthraquinone dye in ZLI-1132 nematic host. When CNTs in a small amount were added to the dye mixtures as co-dopant, the further increases in order parameters (S) were observed in mixtures with low S values. These dyes and CNTs did not significantly destabilise the mesomorphic phase of nematic hosts. An appreciable change in textures was not observed with addition of dopant(s).

Keywords: guest–host systems; nematic liquid crystal; aminoanthraquinone dye; carbon nanotube; order parameter; phase transition

1. Introduction

Nematic liquid crystal displays (LCDs) are widely employed as an indispensable component in modern display devices due to many of their alluring features such as flatness, low power consumption and full colour capability [1]. Dye doped LCDs are also commonly known as guest—host (G-H) LCDs. In these systems, a small amount of a dye is dissolved in a nematic liquid crystal; the dye molecules become aligned in the liquid crystal matrix and hence can be oriented from one direction to another along with the liquid crystal molecules on the application of an electric field. The phenomenon of aligning the guest molecules by the liquid crystal molecules is called guest–host interaction [2].

The performance of guest–host type liquid crystal displays is governed by the solubility, stability and molecular orientation of dyes in the liquid crystal medium [3]. Therefore dyes in different chemical structures, especially anthraquinone and azo ones, have been studied as dopant. Anthraquinone dyes are known to be much more stable than azo compounds [4]. The dyes used in G-H LCDs normally absorb in the visible spectrum. With proper surface treatment, in one state the dye/LC mixture does not absorb light strongly while in other state it does. This is the basis of almost all dye doped LCDs. The absorption is usually increased with the help of a polariser or by the addition of a suitable amount of a chiral dopant in a nematic host [2].

Recently, new approaches such as the doping of nanoparticles such as fullerene and carbon nanotubes (CNTs) into LCs were proposed to overcome the limitation of the physical properties of LCs [5–9]. Among several particles, CNTs are very interesting because they have anisotropic shape as LCs and they interact with liquid crystal molecules strongly. They show high conductivity along the tube length but have very low conductivity across the diameter. It is known that the long axis of CNTs is aligned parallel to the LC director on the absence of voltage [5, 10].

In this work, two different nematic liquid crystals were separately doped with three different dyes based on aminoanthraquinone. Secondly, a small amount of single-walled carbon nanotubes (SWCNTs) was added to these solutions. Their solubilities, textures, phase transition temperatures and order parameters were determined and discussed by comparing them to each other.

2. Materials and methods

Dyes and carbon nanotubes used in the experiments were supplied by Aldrich Chemical Company (Germany), and nematic liquid crystals and organic solvent from Merck (Germany). They were used

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without further purification. The composition of liquid crystals (E8 and ZLI-1132), which have high positive dielectric anisotropy, are shown in Figure 1 [11, 12]. The structures of dyes (1,2-, 1,4- and 2,6-diaminoanthraquinone) were shown in Figure 2.

First, the dyes were dissolved separately in each of the nematic liquid crystals and their saturated solutions were prepared using an excess of the dye. The concentration of dye was limited at 5% (mass/mass) by dissolving 5 mg of dye in 95 mg of liquid crystal.

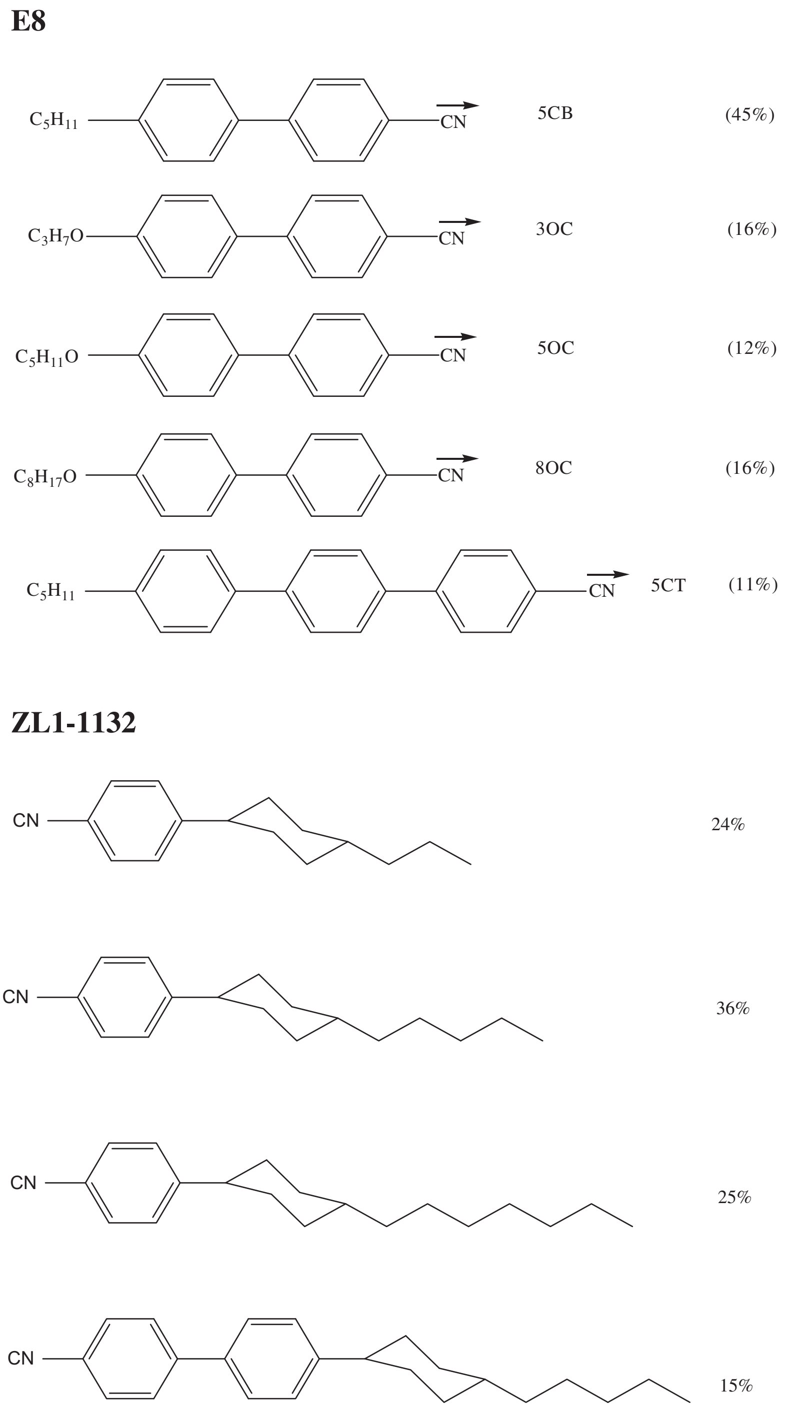
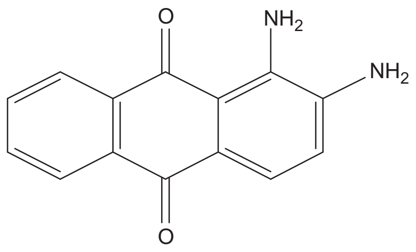
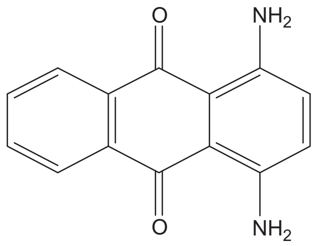


Figure 1. Composition of nematic liquid crystals.

1,2-Diaminoanthraquinone (dye 1)



1,4-Diaminoanthraquinone (dye 2)



2,6-Diaminoanthraquinone (dye 3)

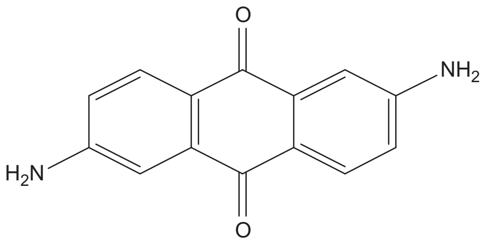


Figure 2. Structure of dyes.

A shaking water bath (Selecta Unitronic, USA) was used to assist solubility. For this purpose, mixtures were kept in the bath for a period of 18 hours at 20°C. After shaking, undissolved dye was separated by centrifugation at 14,000 rpm for 15 min. This sediment was dissolved in 100 ml acetone and the concentration of the diluted solution was determined spectrophotometrically at the maximum absorption wavelength, $\lambda_{\text{max.}}$ The solubilities of the dyes in the liquid crystals were then calculated [13]. The absorption spectra were scanned on a Perkin Elmer Lambda 900 UV-Vis-NIR double beam spectrophotometer. The sample holder was a quartz cell with the path length of 10 mm.

For further studies, saturated solutions of dyes in liquid crystals were prepared to determine the order parameters. By shaking the dye/LC mixtures, dyes were dissolved thoroughly in nematic hosts. At the second stage, small amounts of single-walled carbon nanotubes (0.05% m/m) were mixed with dye/LC mixture under the reinforcement of sonication effect for 1 h to promote dispersion [9].

For spectroscopic evaluation of the order parameter (S), liquid crystal cells were supplied by ForeSea Technologies (USA). Surface-stabilised sandwich cells of 5 μm thickness were filled with the mixtures by capillary action. The mixtures formed thin oriented layers between the two glass plates of the cell with an area of 1 cm × 1 cm. By using the samples with planar homogeneous orientation in the LC cell, absorption spectra were scanned on a Perkin Elmer Lambda 900 UV-Vis-NIR double beam spectrophotometer equipped with sheet polarisers. All measurements were performed at room temperature. The orientational order parameters of the dyes dissolved in LC were calculated from the polarised components of the absorption spectra [14].

The nematic–isotropic phase transition temperatures and associated enthalpy changes of pure hosts and mixtures were determined by differential scanning calorimeter (DSC) (Perkin Elmer DSC Diamond). DSC experiments were carried out in the temperature range from 40 to 100°C. Heating and cooling rates were 10°C/min [15].

For the optical microscopy experiment, a Leica DFC 280 microscope equipped with a heating stage (Linkam Scientific Instruments, Model TS1500) was utilised. Digital pictures were acquired using the snappy interface and software. The samples were heated at elevated temperature (100°C) in a glass-coated quartz cell until the nematic LC structure became optically isotropic, and then cooled to ambient temperature. During this operation, the textures of the samples were photographed at various temperatures [7]. The sample hot stage and cooling unit were connected to a programmable temperature controller (Linkam, Model THMS600).

3. Results and discussion

When determining the colour hue in G-H LCDs, the maximum absorption wavelength of the absorption spectrum is very important [16]. Depending on the mutual interactions between dye molecules and solvents (E8, ZLI-1132 and acetone), the maximum absorption wavelength of dyes had different values. These are shown in Table 1.

The solubilities of the dyes in the nematic liquid crystals were determined spectrophotometrically. All absorption measurements were recorded at the maximum absorption wavelength, $\lambda_{\max}$, and the solubilities of the dyes in the liquid crystals were then calculated. The highest solubility value (1.47%) was

Table 1. Maximum absorption wavelengths, solubilities and order parameters of aminoanthraquinone dyes in liquid crystal mixtures.

	λ_{max} (nm)			Solubility (% m/m)		S (without CNT)		S (with CNT)	
Dye	Acetone	E8	ZLI-1132	E8	ZLI-1132	E8	ZLI-1132	E8	ZLI-1132
1	508	507	494	0.58	0.83	0.61	0.66	0.54	0.62
2	547	560	553	0.93	1.47	0.63	0.71	0.62	0.68
3	458	465	460	0.29	0.37	0.11	0.14	0.15	0.25

attained with dye 2 and dye 3 dissolved in low ratio (Table 1). All dyes have the same molecular structure except for a difference in the position of the amino groups. However, due to this difference, the solubilities were substantially different [17]. In particular, *ortho*-position (dye 1) and *para*-position (dye 2) (diamino)-substituted dyes had higher solubilities than the other position-substituted dye (dye 3). The highest solubility values were attained with ZLI-1132 nematic host. This observation could be attributed to the fact that ZLI-1132 has more mobility (less steric effect) compared with E8, and therefore solubilities increased because the interactions between the dye molecules and liquid crystal molecules are increased and strengthened [3].

Substances (dye or nanotube) added to a nematic LC affect its orientation order. The method based on polarised absorption spectra was used to measure the order parameters (S) in LC systems that include dyes. At this stage, the order parameters were calculated from the absorption of polarised light using Equation (1):

$$S = \frac{A(\mathrm{II}) - A(\perp)}{A(\mathrm{II}) + 2A(\perp)}, \tag{1}$$

where A(II) and A($\perp$) are the absorbances (at λ_{max}) of light polarised parallel and perpendicular to the orientation axis of liquid crystal respectively [18]. The S values obtained with E8 were lower than those with ZLI-1132 (Table 1). This result may be attributed to the steric effect [3]. The highest value was attained with dye 2 in ZLI-1132.

Our experimental results also indicate that the order parameter is a function of the natures of the guest and host, the molecular structure of the dyes, and intermolecular interactions between the molecules of the dye and the LC host. In particular, hydrogen bonding interactions could lead to an increase in the order parameter of the dyes in the liquid crystal medium [2]. Hydrogen bonding can occur between amino (–NH_2) groups in these dyes and cyano (–CN) groups in liquid crystals. While amino groups act as hydrogen-bond donors, cyano groups are hydrogen-bond acceptors. This bonding enables the continuity of conjugate structure in the cell. Conjugate systems are widely used to improve charge injection/transport properties [19]. So high values may be attributed to the number of hydrogen bonds formed between the liquid crystal and these dyes, and its stability. The order parameter is found to be very low for dye 3 in all mixtures. These results indicate that either the nematic ordering is low or the orientation of the transition dipole moment is not parallel to long axis of the molecule.

When a small amount of CNTs was added to the dye mixtures as co-dopant, the greatest increases in S values were observed with dye 3 (Table 1). These increases may also be explained by the efficient contact between the dye and liquid crystal achieved with nanotubes in mixtures with low S values [20]. But it caused a negative effect in other LC/dye mixtures which had strong interactions between the dye and liquid crystal molecules.

DSC studies were performed to determine the nematic to isotropic phase transition temperature and the value for the enthalpy change of this transition. An example thermogram is shown in Figure 3. The phase transition temperatures of dye/LC and nanotube/dye/LC systems and melting enthalpies obtained with DSC are given in Table 2. Enthalpy changes in nematic–isotropic phase transitions were small. These values may be attributed to structural features of the liquid crystals and the order of the molecules in nematic phase [15].

The different values of the nematic–isotropic phase transition temperature (T_{NI}) obtained for different cases reveal that T_{NI} was dependent on the size and shape of the dye molecule, as well as on the mutual interactions between the molecules [18]. ΔT_{NI} denotes the shift of T_{NI} with respect to the value for the pure LC. Experimental results indicate that all the additives (dye and nanotube) added to the nematic liquid crystal influence the range of the mesophase, causing either a decrease or an increase in the nematic–isotropic transition temperature of the pure host. These additives did not significantly destabilise the nematic phase

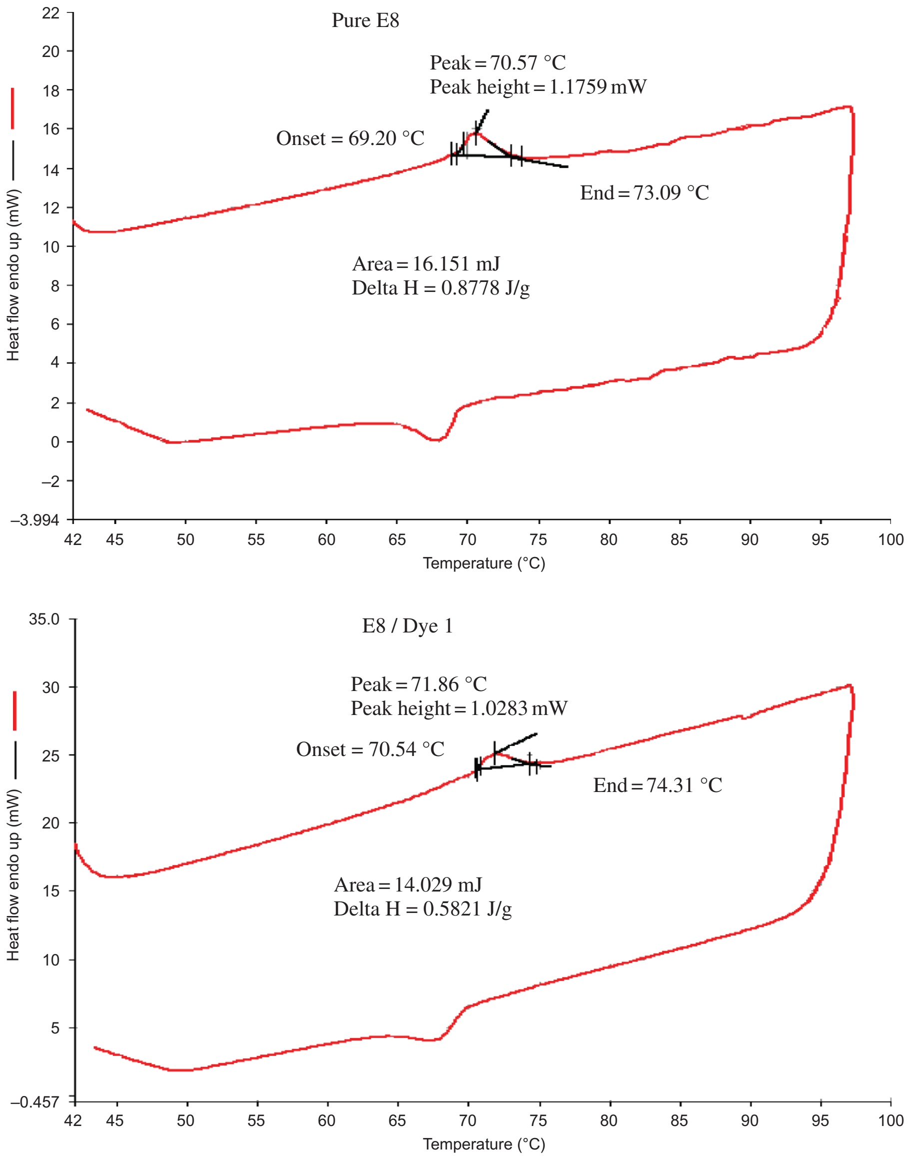


Figure 3. DSC thermograms of pure liquid crystal E8 and liquid crystal E8 doped with dye 1.

Table 2. Phase transition temperatures (°C) and melting enthalpies (J/g) determined by DSC.

Dye	SWCNT	LC	T_{NI} (°C)	ΔT_{NI} (°C)	ΔH (J/g)
–	–	E8	70.57	–	0.8778
1			71.86	+1.29	0.5821
2			70.22	–0.35	0.5902
3			71.42	+0.85	0.7345
–		ZLI-1132	72.67	–	1.6773
1			73.10	+0.43	14.428
2			73.01	+0.34	14.141
3			73.19	+0.52	14.052
1	0.05% (m/m)	E8	71.37	+0.80	0.9169
2			70.77	+0.20	0.6464
3			71.21	+0.64	0.8792
1		ZLI-1132	74.42	+1.75	21.001
2			71.98	–0.69	14.384
3			72.82	+0.15	18.605

Note: T_{NI} is the nematic–isotropic phase transition temperature.

of the liquid crystalline host (ΔT_{NI} is not less than -1.4°C) [21].

Finally, the textures of the dye/LC and nanotube/dye/LC systems were photographed at various temperatures using a polarising microscope. An example texture is shown in Figure 4. The textures of the liquid crystals did not change much with the addition of dopant(s) [22].

4. Conclusions

The orientational ability of some aminoanthraquinone dyes dissolved in two commercial liquid crystalline mixtures was investigated. The changes in order parameters of these mixtures were determined by adding a small amount of carbon nanotubes to them. The changes in nematic to isotropic phase transition temperatures, textures and solubilities were

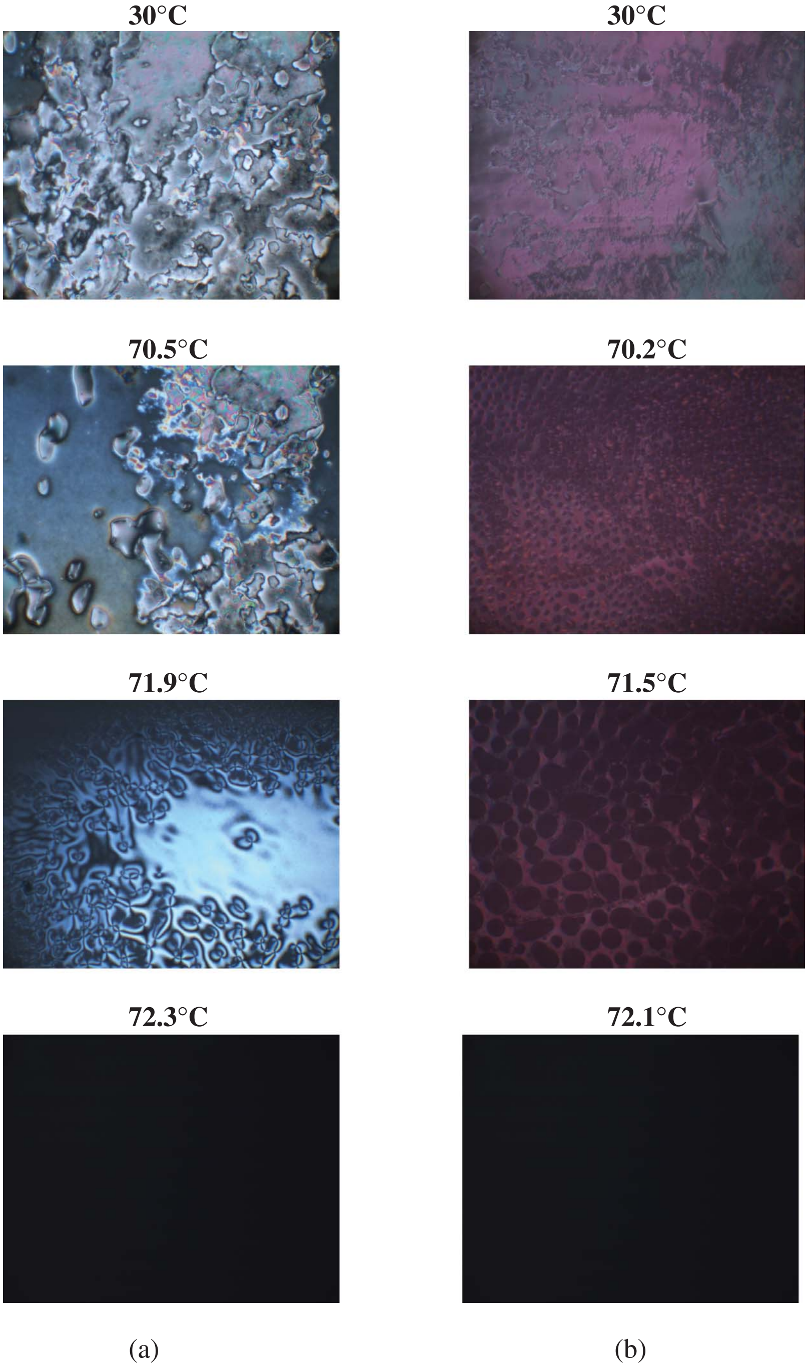


Figure 4. Textures of liquid crystal E8 at various temperatures: (a) pure; and (b) doped with dye 2.

also determined for dye-doped nematic liquid crystals. The solubilities at room temperature changed remarkably depending on the position of amino groups and the interactions between the dye and liquid crystal molecules. Solubilities and order parameters in E8 were lower than those in ZLI-1132. The high values of order parameter may be attributed to the number of hydrogen bonds formed between the liquid crystal and these dyes, and their stability. The addition of carbon nanotubes to dye/LC solutions resulted in an increase in order parameters only when using dye 3. The orientation of the dyes in the liquid crystal matrices was satisfactory except with dye 3 (values of S greater than 0.4 are acceptable, but not optimal, for liquid crystal application). In addition, an important change in the phase transition temperatures of liquid crystal doped with dye and nanotube was not observed and they were close to those of pure LC. ΔT_{NI} values stayed within the limitations given in the literature. A negative change in textures could not be recorded.

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