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CONFORMATIONAL EFFECTS AND PHOTOLUMINESCENCE SPECTRA OF NANOCOMPOSITES 5CB LIQUID CRYSTALS–CARBON NANOTUBES[1]

Specific temperature dependences (10–300 K) of the emission band maximum, its intensity and half-width in the luminescence spectra of 5CB liquid crystals and 5CB + carbon nanotube nanocomposites are observed. The analysis of the luminescence spectra and thermal properties of the studied systems has shown that the observed features are due to polymorphic transformation of 5CB and conformational changes of its molecules.

Keywords: liquid crystals, luminescence, carbon nanotube, conformational changes.

1. Introduction

The nanocomposites on the basis of liquid crystals (LC) have attracted attention because of unique physical properties and possibilities of their practical application. The introduction of minute amounts of nanoparticles of different nature, shape, and size into the LC matrix allows one to change the properties of the resulting nanocomposites. Of particular importance are composites of carbon nanotubes (CNT), which are dispersed in liquid crystals. Composites LC–CNT are currently a subject of numerous studies [1–4]. In particular, the authors of [1, 2] reported original results regarding the formation and the structure of aggregates of CNT dispersed in 5CB liquid crystal. Their results clearly demonstrated an increase in the number of aggregates and their size with time. In addition, the nematic-isotropic transition in 5CB liquid crystal with carbon nanotubes was studied by the differential scanning calorimetry (DSC) method [1,2]. Subsequently, the influence of the CNT concentration on the isotropic-nematic and nematic-smectic phase transitions in 8CB liquid crystal has been studied by the DSC [3]. The self-organization of CNT clusters in 5CB liquid crystal, starting with a certain CNT concentration, leads to the percolation transition reflected in the electrical conductivity behavior and in the appearance of optical singularities [1, 4]. The state of art in the physics of LC–CNT nanocomposites is well presented in [1–4], and the current researches of these composites were preceded by the numerous works devoted to the luminescence properties of pure LC [5–10].

Interesting results were obtained in [6]. By the analysis of the time-resolved fluorescence spectra of nematic and isotropic phases of 5CB LC, it was shown that the luminescence bands in the regions 340–360 nm and 380–400 nm are related to the monomer and excimer emissions, respectively. The analysis of the literature shows that the majority of papers de-

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voted to the luminescence of cyanobiphenyls, including 5CB liquid crystal, dealt with its solutions and mesophase structures. A relatively small number of papers were devoted to the spectral properties of a solid crystalline phase, in particular, to the low-temperature luminescence of 5CB LC [11–14].

This paper presents the results of our experimental study of the luminescent and thermal properties of 5CB LC and composites 5CB LC with CNT, as well as a comparative analysis of their properties. The essential advantage of our work, in contrast to other studies, is the use of low temperatures from 10 K to 300 K, and the use of different methods (luminescence and DSC). This has allowed us to establish the relationship between the experimentally observed changes in the luminescence spectra and the physical processes at the microscopic level, as well as to propose a mechanism of influence of nanotubes on the structure of LC.

2. Experimental

The luminescence spectra were measured with a MPF-4 Hitachi (inverse linear dispersion 3 Å/mm) spectrofluorimeter in the spectral interval 300–600 nm with the use of the 315-nm line for the excitation. The measurements were carried out in the temperature range 10–300 K on heating, by using a helium cryostat equipped with a system of automatic temperature regulation with an accuracy of (±0.1 K). The calorimetry experiments were done with a differential scanning calorimeter (Perkin-Elmer DSC-7). The measurements were carried out on cooling and heating at a rate of 5 K/min. 5CB nematic LC was purchased from Merck (Germany). The phase transition temperatures for the crystal-nematic and nematic-isotropic liquid states are 296.8 and 308.4 K, respectively. The carbon nanotubes were about 20–30 nm in diameter, and their length was approximately 5–10 microns. 5CB composites were prepared by the addition of relevant quantities of CNT to 5CB in the isotropic liquid state ($T = 310$ K). The samples were sonicated for 5 min, by using an ultrasonic disperser. Ultrasonication is a generally accepted technique to obtain highly homogeneous dispersed nanotube samples. The samples were placed in quartz tubes with the inner diameter of 3 mm and the height of 25 mm. Before measurements, the samples were rapidly cooled by the direct immersion to liquid helium.

3. Results and Discussion

It is commonly believed that the luminescence of 5CB LC is caused by the emission of monomers and dimers. The formation of different conformations of 5CB molecules in monomer and dimer structures determines the complexity of the spectral shape of the luminescence band. This is most clearly manifested itself at low temperatures. At room temperature, the emission of dimers contributes mainly to the luminescence. At temperatures below the crystallization temperature of 5CB LC (crystallization point 296.8 K), the composite transforms into solid crystalline state. Its luminescence is mainly due to the emission of monomers.

The temperature-dependent fluorescence spectra of 5CB LC in the temperature range from 10 to 297 K are shown in Fig. 1. It is seen that these spectra differ significantly in the shape and the position of bands. The positions of the bands at the maximum ($\lambda_{\max}$) and their half-widths ($\Delta\lambda$) and relative intensities (I) at temperatures from 10 K to 297 K are shown in Fig. 2. First, we compare the luminescence spectra of 5CB LC measured at 10 and 297 K (Fig. 1). It is seen that the spectrum at 297 K is shifted relative to the spectrum at 10 K to the red side by 27 cm^{-1}. At the same time, the intensity and the shape of the luminescence band change significantly. When the temperature increases, the solid crystalline state of 5CB transforms into the nematic LC phase, resulting in the increased number of dimers. Due to the strong dipole interaction between molecules in dimers, the molecules become more planar (flat). Moreover, it is known [7] that the electron

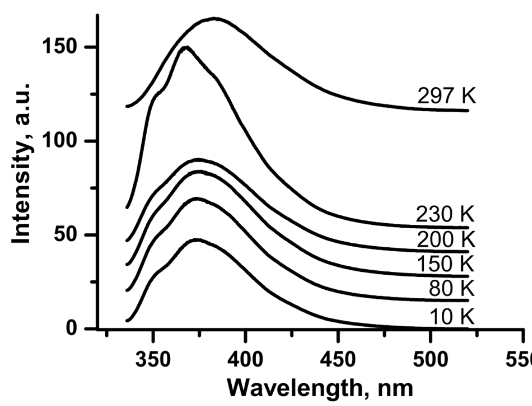

Fig. 1. Luminescence spectra of 5CB LC at various temperatures

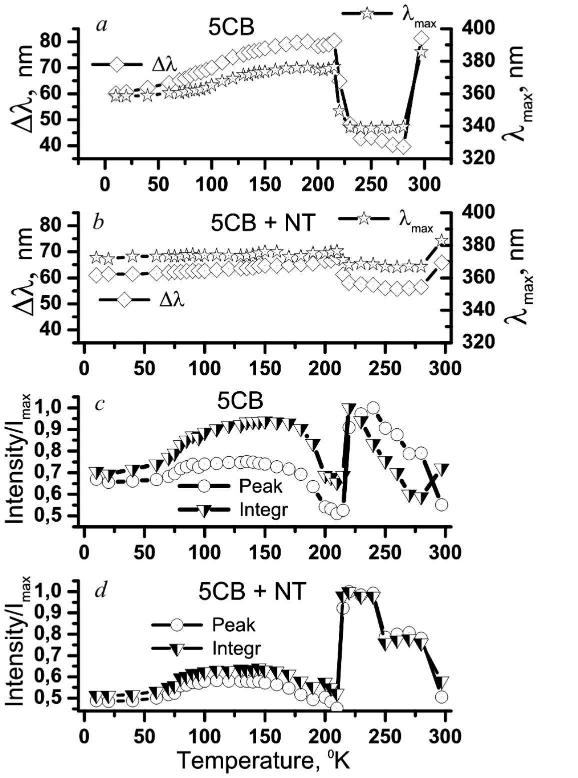

Fig. 2. Temperature dependence of the position of the band at the maximum ($\lambda_{\max}$), its half-width ($\Delta\lambda$) (*a, b*), and peak and integral intensities (*c, d*) in the luminescence spectra of pure 5CB and 5CB-CNT composite

energy level of a 5CB molecule is reduced during the transition from the twisted conformation in the solid crystalline state to the planar (flat) one in the nematic LC phase. Therefore, during the transformation of 5CB from the solid crystalline state into the liquid nematic state, the formation of dimers with planar (flat) conformation of the molecules occurs. This explains the observed red shift of the spectrum at 297 K compared to the spectrum at 10 K.

Values of position of the band at the maximum ($\lambda_{\max}$) and its half-width ($\Delta\lambda$) in luminescence spectra of 5CB LC and 5CB LC + CNT composite at various temperatures

T, K	5CB		5CB + CNT	
	($\lambda_{\max}$), nm	($\Delta\lambda$), nm	($\lambda_{\max}$), nm	($\Delta\lambda$), nm
10	358.5	60.2	372.4	61.0
297	385.7	81.2	382.8	65.9

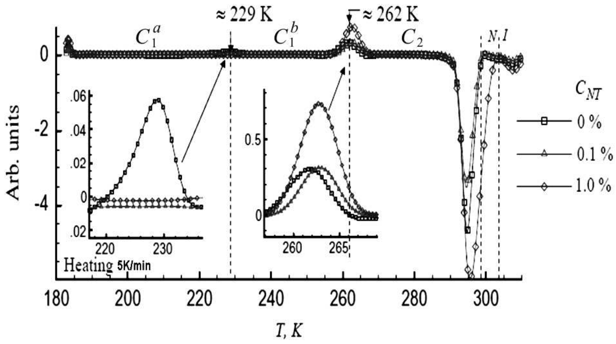

Fig. 3. DSC thermograms of 5CB–CNT composites at various concentrations of CNT measured on heating

It should be noted that among the first were authors of [15, 16] who paid attention to the dependence of the molecule conformations on the temperature at the nematic-isotropic phase transition in 5CB LC and 6CB LC.

With respect to different values of the red shift of the fluorescence bands in pure 5CB and its nanocomposite, it can be assumed that, in the latter case, some of the molecules are linked to the surface of nanotubes. Due to this linking, a steric restriction of the conformational mobility of 5CB molecules occurs. This explains a smaller red shift of the band in the luminescence spectrum of 5CB–CNT composite relative to that in pure 5CB.

The most interesting are the results of the temperature dependence of the luminescence band parameters such as $\lambda_{\max}$, $\Delta\lambda$, and I in the fluorescence spectra of 5CB and 5CB-CNT (Fig. 2). It is essential that an increase in the temperature in the interval 220—230 K leads to a sharp (abrupt) decrease of the parameter values. However, with increasing the temperature up to 297 K (a vicinity of the crystal-to-nematic phase transition), the parameter values begin to increase sharply again (Fig. 2).

Attention should be paid to the fact that the values of ($\lambda_{\max}$) and ($\Delta\lambda$) in the luminescence spectra of 5CB LC are substantially greater than in 5CB-CNT composite (Fig. 2, Table). In pure 5CB, they are ($\lambda_{\max} = 27.2$) and ($\Delta\lambda = 21.0$ nm), respectively, while, in 5CB-CNT, they are ($\lambda_{\max} = 10.4$) and ($\Delta\lambda = 4.9$ nm). Thus, the presence of CNT complicates the corresponding conformational changes of 5CB molecules.

With the aim of interpretation of the observed temperature changes in the fluorescence spectra, the thermal properties of the systems were examined within the DSC method. As mentioned above [1,2], the DSC method was widely used previously for the study of the phase transitions in a nematic-isotropic composite 5CB LC–CNT. Furthermore, the results of DSC measurements of pure 5CB LC in the interval 200–320 K are presented in [17].

It is of interest to compare the behavior of the DSC thermograms recorded on heating with the luminescent spectra. Figure 3 shows the typical DSC thermograms of pure 5CB LC and its composite at various CNT concentrations. There are two exothermic peaks at 229 and 262 K on the thermograms.

The first one ($C_1^a \to C_1^b$) corresponds to the low-temperature phase transition of the crystal-crystal type inside the metastable phase C_1. The possibility of such intracrystalline transition was indicated in [18]. The first peak at 229 K on the DSC thermogram correlates with the anomalous behavior of the luminescence parameters at ∼230 K (Fig. 2). The second peak at 262 K on the DSC thermogram corresponds to the transition of the metastable phase C_1^b into the stable crystalline phase C_2. It should be noted that the peak at $T = 262$ K, ($C_1^b \to C_2$), in the DSC thermogram has no analog in the luminescence spectrum. The stable crystalline phase melts at 297 K, by passing into the nematic LC phase ($C_2 \to N$). It can be seen that there is a correspondence between the endothermic peak at 297 K in the DSC thermogram and changes in the luminescence parameters at $T = 297$ K. The presence of CNT in LC has a different effect on the intracrystalline phase transition in different temperature intervals: they suppress this process at $T \approx 229$ K, but intensify it at 262 K. Possible reasons for this fact are discussed in [19].

4. Conclusions

The investigations of pure 5CB LC and the 5CB LC + CNT composite in a wide temperature range have revealed some correlations between the spectral luminescent and thermal properties of these two systems. It is shown that, as the temperature increases from 10 to 297 K, their fluorescence spectra are shifted to the red side by 27 and 11 nm, respectively. This fact is associated with the formation of dimers during the transition of 5CB from the solid-crystal phase to the liquid crystal nematic state. As a result, planar conformations of molecules are realized in the LC nematic state, which leads to the experimentally observed red shift of the band in the fluorescence spectra. The comparison of the anomalous temperature behavior in the fluorescence spectra (position of band maxima and their half-widths and relative intensities) and the results of DSC show that the temperatures 229 and 262 K correspond to intracrystalline transitions of the crystal-crystal type, and the temperature 297 K corresponds to the transition from the solid crystal phase to the nematic LC one. Thus, basing on the experimental data, we can conclude that the observed temperature transformations of the luminescent and thermal properties of 5CB LC and the 5CB LC + CNT composite in the temperature range 10–297 K are due to conformational changes in 5CB molecules during the phase transformations.

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КОНФОРМАЦІЙНІ ЕФЕКТИ І СПЕКТРИ ФОТОЛЮМІНЕСЦЕНЦІЇ НАНОКОМПОЗИТІВ РІДКИЙ КРИСТАЛ 5CB–ВУГЛЕЦЕВІ НАНОТРУБКИ

Р е з ю м е

У спектрах люмінесценції рідких кристалів 5CB і гетерокомпозитів 5CB–карбонові нанотрубки виявлені характерні температурні (10–300 K) залежності зміщень максимумів смуг, їх півширин та відносних інтенсивностей. На основі комплексного аналізу даних з люмінесценції та вимірів диференціальної скануючої калориметрії показано, що особливості, які спостерігаються, пов'язані з поліморфними перетвореннями та конформаційними змінами молекул 5CB.