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# Photoluminescence of pentacene solutions in *n*-pentyl-*n'*-cyanobiphenyl

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**Abstract.** We investigated photoluminescence (PL) spectra of pentacene (Pc) in the liquid- and solid-crystalline *n*-pentyl-*n'*-cyanobiphenyl (5CB) matrices. It was shown that the liquid-crystalline matrix behaves as a polar solvent relatively to Pc. Pc and 5CB molecules can form loosely bound donor-acceptor complexes. These complexes may be characterized with their PL spectrum and lifetime that are different from those of molecular Pc. Being heated up to 343 K these complexes are broken down, and Pc molecular radiation is observed in the PL spectra of solutions.

**Keywords:** photoluminescence, pentacene, *n*-pentyl-*n'*-cyanobiphenyl, donor-acceptor complex.

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## 1. Introduction

In recent years much attention has been concentrated on the liquid crystal-organic dye-based composites [1]. The objective of investigations was to find an optimal combination of components for further practical use of such composites in the systems for information display and processing. There are many works dealing with study of both orienting action of a liquid crystal (LC) on impurity dye molecules and induced anisotropy [2, 3].

The number of papers where intermolecular interaction between LC and organic dye has been studied is substantially less. At the same time the LC action on impurity dye molecules is very similar to that of an organic solvent. In organic solvents various processes of intermolecular interaction may occur, such as solvation, aggregation of impurity molecules, formation of donor-acceptor complexes by dye and solvent molecules.

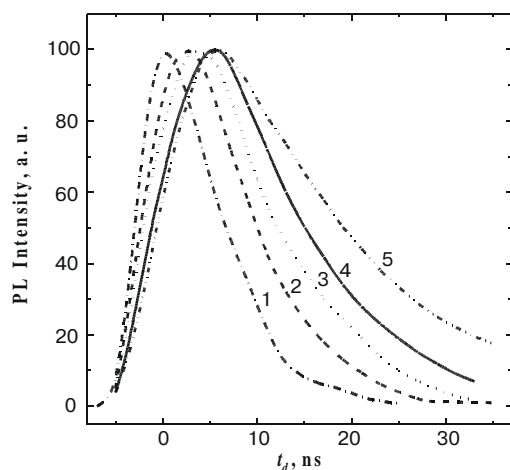
Here, on the grounds of our investigations of photoluminescence (PL) in pentacene-LC solutions, we show that impurity pentacene (Pc) molecules and those of *n*-pentyl-*n'*-cyanobiphenyl (5CB) LC form predominantly loosely bound donor-acceptor and exciplex complexes.

## 2. Experimental technique

We studied time-resolved PL spectra of Pc solutions in the 5CB liquid- and solid-crystalline matrices. A nitrogen laser ( $\lambda_e = 337.1$  nm) was used to excite PL. The

parameters of excitation were as follows: excitation pulse duration  $t_1 = 10$  ns; radiation pulse power  $N = 5$  kW; pulse-recurrence frequency  $f = 100$  Hz. To process the experimental PL quenching curves, we used the curve analog technique and parameter analysis [4-6]. This enabled us to record PL kinetics and spectra of different time delays,  $t_d$ , relative to the laser pulse peak (Fig. 1). When measuring PL spectra at the laser pulse leading edge ( $t_d = -3$  ns), this technique enables to record spectra with resolution of about 0.8 ns, which is determined by the rate of laser pulse rise. The time resolution of our experimental set when determining the PL lifetime  $t$  was about 0.1 ns.

In the curve analog technique a convolution of the response function  $G(t)$  and an arbitrary quenching function  $F(t)$  is calculated at different parameter values. Then one has to select such a calculated curve that fits best the experimental PL quenching curve. In our case, the experimental quenching curve was approximated with the convolution of the excitation pulse and exponential curve,  $\exp(-t/\tau)$ . During PL kinetics registration for reference substances with  $\tau < 0.1$  ns the laser and PL pulses matched. At  $\tau > 0.1$  ns the PL pulse considerably shifted from the laser pulse. This fact makes it possible to measure PL quenching lifetimes from 0.1 ns and up. Due to laser pulse asymmetry and high rate of rise (Fig. 1), one may set the excitation duration from 0.6 to 4 ns when recording PL spectra at the pulse leading edge (negative  $t_d$  values). The SPM-2 monochromator served as spectral instrument; when taking spectra, the slot spectral width was from 0.2 to 0.4 nm.



**Fig. 1.** PL kinetics of 5CB liquid crystal (2) and freshly prepared Pc solutions in 5CB (3, 4) and toluene (5) (1 – form of a laser pulse with  $\lambda_{\text{ex}} = 337.1$  nm).

To prepare Pc solutions in 5CB LC, we used 5CB produced by Merk (Germany) and highly purified crystalline Pc. The temperatures of crystal-LC and LC-isotropic liquid phase transitions in 5CB are 19 and 34 °C, respectively. The Pc single crystals have been obtained using sublimation in helium atmosphere. Study of excitonic absorption and reflection spectra in Pc crystals indicated at their high purity [7]. Low Pc solubility in molecular crystals has been noted in [8]. The highest Pc concentration in pyrene and anthracene crystals was  $C = 10^{-5}$ – $10^{-6}$  mole/mole.

We used two techniques to prepare molecular Pc solutions in LC matrices. According to the first one, single-crystalline Pc has been pre-dissolved in toluene or ethanol. Then the obtained Pc solution in toluene or ethanol was mixed with LC and heated up to 343–353 K. At such temperatures, toluene and ethanol were evaporated, and molecular Pc remained in 5CB (that was in an isotropic phase). In such a way we did manage to obtain Pc concentration in LC of  $10^{-5}$ – $10^{-6}$  mole/mole. According to another technique, highly dispersed powder of crystalline Pc was mixed with 5CB LC and held for a long time. The solution obtained in this way contained both molecular (concentration  $C = 10^{-5}$ – $10^{-6}$  mole/mole) and highly dispersed Pc components.

Our investigations of PL spectra of Pc solutions in toluene or ethanol have shown that form of the spectra changed with time. Along with the bands of Pc molecular PL [8, 9], new bands appeared in the PL spectra of Pc solutions in toluene. These new bands could be related to appearance in solutions of formation of exciplexes or loosely bound charge-transfer complexes (CTC) formed by Pc and solvent molecules. The crystalline Pc component did not fluoresce [10]. Heating the solutions up to 343–353 K restored Pc molecular PL. This served evidence that the formed complexes have broken down. Such a behavior of solvents served to determine the temperature at which the solvent should be evaporated. After

preparation of solutions the Pc molecular component, Pc-5CB molecular complexes and undissolved Pc small crystals have remained in LC.

Following are the results of our studies of PL spectra of Pc solutions in toluene, ethanol or 5CB after solvent evaporation.

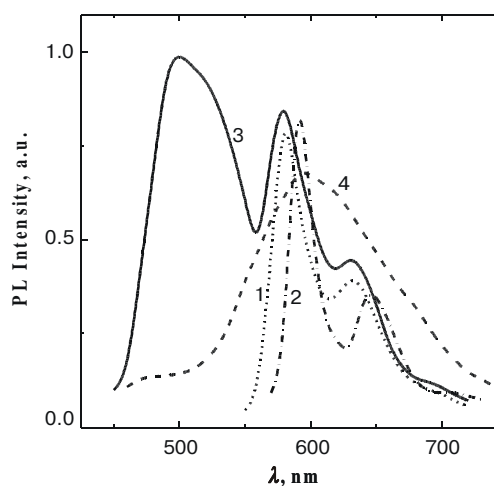
### 3. Experimental results and discussion

#### 3.1. Photoluminescence of pentacene solutions in toluene and ethanol

Shown in Fig. 2 are the PL spectra of as-prepared Pc molecular solution in toluene taken at 300 K (curve 1) and 77 K (curve 2). The PL spectra were measured at the laser pulse peak ( $t_d = 0$ ). A purely electronic band (580 nm) and its vibrational replica (631 nm) are present in the PL spectrum taken at 300 K, as was also stated in [10]. The intramolecular vibration frequency is  $1400\text{ cm}^{-1}$ . The PL lifetime measured in the 580 nm band is 7.5 ns. When temperature drops to 77 K, the PL spectrum (curve 2) somewhat shifts toward longer wavelengths. The purely electronic band is now at 591 nm, while its vibrational replica lies at 645 nm, and the PL lifetime rises upto 14 ns, when temperature decreases down to 77 K.

As was noted above, at 300 K the Pc molecular fluorescence in toluene solution goes down with time. New bands (490 and 510 nm) due to molecular complexes formation by Pc and solvent appear in the PL spectra (Fig. 2, curve 3). The lifetime of new excitation states is decreased and equal to 6 ns. If, however, the solution is heated up to 343 K, then the PL spectrum recovers its original form (curve 1) that is related to fluorescence from the free Pc molecules.

Shown in Fig. 2 (curve 4) is the PL spectrum of the as-prepared Pc solution in ethanol measured at 300 K. This spectrum differs from that of Pc solution in toluene. There



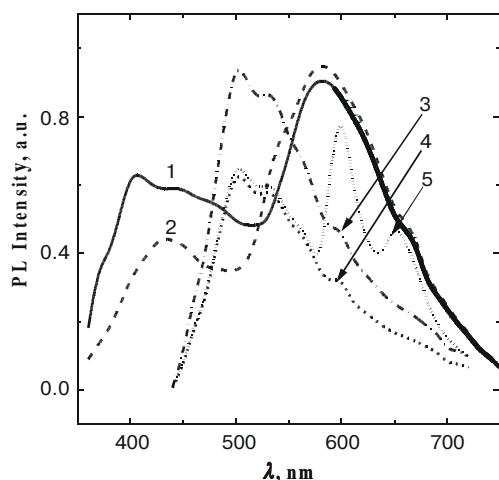
**Fig. 2.** PL spectra of Pc solutions in toluene (1-3) and alcohol (4) taken at  $T = 300$  K (1, 3, 4) and 77 K (2) (concentration  $C = 10^{-4}$  mole/mole;  $\lambda_{\text{ex}} = 337.1$  nm).

is no vibrational structure in the PL spectrum of Pc solution in ethanol. It is a broad structureless band with the peak lying in the vicinity of 600 nm. The PL lifetime in the region of this band is 4 to 4.4 ns. This value is somewhat below than that for Pc molecular fluorescence in toluene solution. The form of this PL spectrum remained the same on long-term keeping of the solution in ambient atmosphere. When the solution is heated up to 343 K, then the PL spectrum shape becomes similar to that of the Pc molecular fluorescence in the freshly prepared Pc solution in toluene (curve 1).

The presented results of our studies of PL spectra for Pc solutions in toluene and ethanol evidence that loosely bound complexes are formed in solutions by Pc and solvent molecules. The excitation states of these complexes differ from those of Pc molecules both in energy and lifetime.

### 3.2. Photoluminescence of pentacene solutions in liquid- and solid-crystalline 5CB matrices

At 300 K the form of PL spectra (Fig. 3, curves 1, 2) of Pc solutions in 5CB LC (obtained by evaporation of solvents that have been used for previous Pc dissolution) did not depend on the solvent type (alcohol or toluene). The form of PL spectra of Pc solutions in LC is similar, in many aspects, to those of Pc solution in ethanol. At Pc in LC concentration about  $10^{-4}$  mole/mole one can set off the regions related to radiation from 5CB (the wavelength  $\lambda < 420$  nm) and complexes formed by 5CB and Pc molecules ( $\lambda > 420$  nm). Two bands (370 and 405 nm) can be set off in the PL spectrum of the LC radiation region (Fig. 3, curve 1) at small ( $t_d = -3$  ns) time delay values. They could be related to the 5CB intrinsic radiation (monomeric and excimeric) [11, 12]. When the time delay is increased up to 15 ns, then the intensities of both monomeric and excimeric radiations go down (Fig. 3,



**Fig. 3.** PL spectra of Pc solution in 5CB after solvent (toluene, alcohol) evaporation taken at  $T = 300$  K (1, 2) and 77 K (3-5) ( $\lambda_{\text{ex}} = 337.1$  nm).

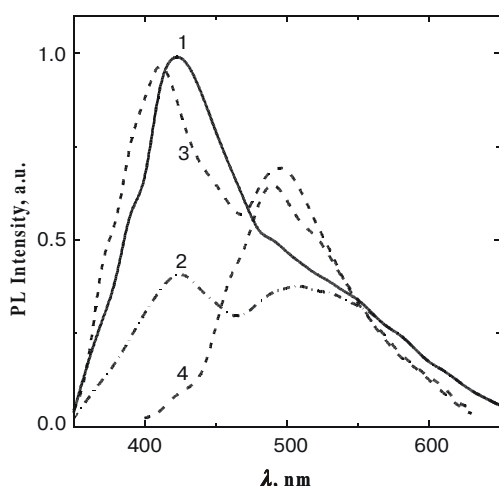
curve 2); the radiation from Pc-5CB molecular complexes is predominant in the PL spectrum (550 and 580 nm bands). The PL lifetimes for these bands are close (4.2 ns). When the Pc in LC solution is heated up to 343 K, then one can observe breaking down of the Pc-5CB molecular complexes; the Pc molecular fluorescence (580 and 631 nm bands) appears in the PL spectra.

When the Pc in 5CB solution is cooled down to 77 K, then radiation from the Pc-5CB molecular complexes (465, 505, 530 and 560 nm bands) prevails in the PL spectrum (Fig. 3, curve 3). If, however, the solid solution is heated up to 343 K and then quickly cool down to 77 K, then part of free Pc molecules have no time to form the Pc-5CB molecular complexes. The lifetimes for excitation states of free Pc molecules and molecular complexes are different. Due to this fact radiation from the Pc-5CB molecular complexes is predominant in the PL spectra of the above solution at 77 K and small time delay values ( $t_d = -3$  ns, Fig. 3, curve 4). When  $t_d$  is increased up to 15 ns, then intense radiation of free Pc molecules is observed (500 and 600 nm bands, Fig. 3, curve 5). The PL lifetime for these two bands is 6.5 and 11 ns, respectively. One can obtain the radiation spectrum for free Pc molecules by subtracting the curve 4 from the curve 5.

For the Pc in LC solutions prepared in the second way, intrinsic radiation of the LC is observed (Fig. 4, curve 1) in the PL spectra taken at 100 K, along with the radiation from the Pc-5CB complexes in the 470–600 nm region. Intrinsic radiation (350–420 nm) of 5CB LC dominates at small ( $t_d = -3$  ns) time delay values. One can set off monomeric (350–390 nm) and excimeric (390–420 nm) radiation of LC in the PL spectrum [9, 10]. Radiation in the 420–470 nm region may be related to that from 5CB molecules that form loosely bound complexes at the Pc crystal surface. When  $t_d$  is increased up to 25 ns, radiation from the Pc-5CB molecular complexes is observed in the PL spectrum at 300 K (curve 2). No radiation from LC and molecular complexes is observed at 77 K in the PL spectra (Fig. 4, curve 3) at small ( $t_d = -3$  ns) time delay values. At  $t_d = 15$  ns only the radiation from molecular complexes is not observed in the PL spectra (Fig. 4, curve 4), 470, 510 and 530 nm bands.

In 5CB molecule a cyanic group (that is strong acceptor of electrons) is present. This fact enables one to assume that even in the ground state 5CB and Pc molecules form  $D^{d+}-A^{d-}$  complexes. Pc molecules serve as electron donors, while cyanic groups are electron acceptors. A partial charge transfer between them is observed even in the ground state. The same interaction occurs between the 5CB molecules and Pc microcrystals inserted in LC. Due to this interaction the Pc microcrystals are gradually dissolving in LC. In this case LC behaves like polar solvent.

In an excitation state the loosely bound donor-acceptor complexes may behave as excimers. In this case the spacing between Pc and 5CB molecules goes down to the equilibrium van der Waals one, and the PL spectra shift toward longer wavelengths. This approaching each other by molecules may be hindered at low temperatures. In-

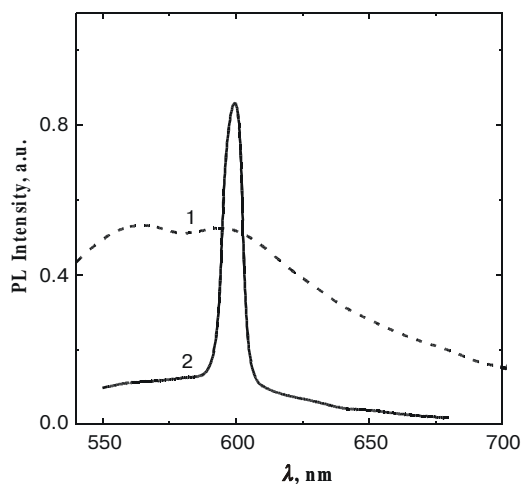


**Fig. 4.** PL spectra of Pc solution (obtained by direct dissolution of Pc finely dispersed crystals) in 5CB taken at  $T = 300$  K (1, 2) and 77 K (3, 4) (delay time  $t_d$  is – 3 ns (1, 3) and 15 ns (2, 4);  $\lambda_{\text{ex}} = 337.1$  nm).

deed, at 300 K the 530, 560 and 590 nm bands are observed in the PL spectra of Pc solutions in LC. After the solutions have been cooled down to 77 K only the 470, 510 and 530 nm bands are observed in the PL spectra. The intensity of the 560 and 590 nm bands is substantially reduced. This fact may indicate at their exciplex nature.

### 3.3. Photoluminescence of pentacene solutions in liquid-crystalline 5CB at different excitation levels

Shown in Fig. 5 are the PL spectra of Pc solution in 5CB LC taken when the solution was excited with the second



**Fig. 5.** PL spectra of Pc solution in liquid-crystalline 5CB taken at low (1) and high (2) excitation level ( $T = 300$  K,  $\lambda_{\text{ex}} = 532$  nm).

harmonic of the Nd:YAG laser ( $\lambda_e = 532$  nm,  $N = 0.1 - 0.5$  MW). The 560 and 590 nm bands are observed in the PL spectrum (curve 1) at low excitation levels (unfocused laser beam). In the long-wavelength spectral region a broad structureless 590 nm band is observed (as in the fluorescence from Pc solution in ethanol). When the excitation level is increased (due to laser beam focusing), then a superradiation occurs (curve 2). One can set off an intense narrow band at 604 nm (with the shoulder near 600 nm) in the spectrum. The 604 nm band may be due to Raman scattering at the 5CB vibrational frequency of  $2260 \text{ cm}^{-1}$ , while the 600 nm band may result from the Pc molecules superradiation. It should be noted that one could observe the 604 nm band also in pure LC (but at higher excitation levels).

## Conclusions

Our investigations of the photoluminescence spectra performed for pentacene solutions in the liquid- and solid-crystalline *n*-pentyl-*n'*-cyanobiphenyl matrices have shown that the liquid-crystalline matrix behaves like polar solvent with respect to Pc. The Pc and 5CB molecules can form loosely bound donor-acceptor complexes. These complexes may be characterized with their spectrum and PL lifetime that differ from those of molecular Pc. Being heated up to 343 K these complexes are broken down, and Pc molecular radiation is observed in the PL spectra of solutions. This radiation can be also observed when, after heating, these solutions have transferred into liquid or solid-crystalline state.

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