

## Effects of liquid crystalline ordering on the luminescence spectra of model compounds with packing-sensitive molecular structure

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Luminescence spectra in liquid crystalline (LC) solvents were measured for stilbene, *p*-terphenyl, *o*-POPOP, 2-(1-naphthyl)-5-phenyloxazole and other compounds commonly used as luminophores or scintillators. The choice of substances was prompted by the ability of their molecules to assume different predominant conformations in different phase states (e.g., standard organic solution vs. melt-grown single crystal). For each compound studied, the luminescence spectra were compared within the sequence "standard organic solution — solution in LC matrix — single crystal". Several distinct cases could be singled out, with the luminescence peak  $\lambda_{max}$  shifted to longer wavelengths, to shorter wavelengths, remaining essentially unchanged, or being split into two separate peaks corresponding to two conformations with close distribution probabilities. For each compound, the observed luminescence behavior could be easily associated with the corresponding changes in the effective molecular shape supposedly induced by the LC and crystal ordering. The obtained data could serve as a basis for future search of efficient liquid crystalline scintillators.

Для стиблена, *p*-терфенила, *o*-POPOP, 2-(1-нафтил)-5-фенилоксазола и других веществ, используемых в качестве люминофоров и сцинтилляторов, измерены спектры люминесценции в жидкокристаллических (ЖК) средах. Выбор объектов обусловлен возможностью их молекул принимать различные конформации в зависимости от фазового состояния. Для каждого люминофора спектры испускания сравнивали в ряду "стандартный органический растворитель — ЖК матрица — монокристалл". В ЖК средах отмечено несколько характерных случаев, когда пик люминесценции  $\lambda_{max}$  сдвигается в длинноволновую область, в коротковолновую, остаётся неизменным или разделяется на два отдельных пика, которым соответствуют две конформации люминофора. Для каждого соединения такое поведение может быть связано с соответствующими изменениями эффективной формы молекулы, индуцируемыми ЖК или кристаллическим упорядочением. Полученные результаты могут служить основой для дальнейшего поиска эффективных ЖК сцинтилляторов.

It is a well-known fact that luminescence spectra of many commonly used luminophores, measured under the same excitation conditions, can be substantially different depending on whether the luminescence is studied in the state of a standard dilute organic solution or, say, for a single crystal sample. One of the obvious examples is

*trans*-stilbene, with its luminescence peak  $\lambda_{max}$  shifted by ~40 nm to longer wavelengths for a single crystal sample as compared with its solution in heptane or cyclohexane [1, 2]. This effect can be routinely associated with stilbene molecules packed in the crystal lattice in a conformation differ-

ent from that occurring in a quasi-free state of the diluted liquid solution.

It has been long known [3] that the average angle between phenyl rings of *p*-substituted cyanobiphenyls can vary from its calculated value for the ideal gas state ( $\sim 42^\circ$ ) to the firmly established value of  $0^\circ$  in the solid crystalline state [4] passing through values of  $\sim 30^\circ$  (isotropic liquid state),  $\sim 20^\circ$  (nematic state) and  $\sim 10^\circ$  (smectic-A state). This suggested that actual effective conformations of stilbene and other luminophore molecules could also be varied in the liquid crystalline state (i.e., when these luminophore substances were introduced into LC solvents).

The importance of this study was supported even more by the expected applications of stilbene, *p*-terphenyl and other similar organic scintillators in the form of pressure-compacted polycrystalline pellets [5–7], where pressure effects could substantially affect the quasi-equilibrium conformational state of the respective molecules [8].

The idea of introducing organic luminophores into a LC matrix is not new in itself. To avoid a long list of references, we would just mention the use of LC+luminophore systems for developing of electrooptical devices with controlled color changes [9], as well as other works [10–12] where such systems were used under the aspect of tunable lasing. Generally speaking, in these works luminescent dopants were used as invariable chemical units, with little attention paid to possible effects of the LC matrix on the luminescence spectrum.

One of the few works describing the effects of the LC solvent upon the luminescent spectra [13] refers to 3-oxy benzanthrone dyes, which displayed a strong shift of the luminescence maximum  $\lambda_{max}$  to the short-wave region (by more than 30 nm) upon dissolution in the nematic matrix ZLI 1840 (no data on its chemical composition were given).

A presumably comprehensive publication on liquid crystal-based scintillators could be found in [14, 15]. In these works, however, the authors used luminophores with knowingly high emission efficiency in cyanobiphenyl-based LC matrices. This could result in technically good luminescence characteristics, but the physico-chemical problem remained untouched. It has been known [16–18] that cyanobiphenyl liquid crystals show their own luminescence, the intensity of which is of the same order of magnitude as compared with that of stilbene or similar compounds introduced into

the LC matrix in quantities of several per cent. Moreover, further complications arise from the fact that cyanobiphenyls can show excimer bands with their intensity depending upon the confined geometry [19]. This makes cyanobiphenyls (and, consequently, most of the standard LC matrices) clearly unacceptable as solvents for studies of LC ordering upon luminescence.

Thus, the idea of our study was (a) to use a LC matrix that would not be a source of its own luminescence capable to interfere with the luminescence coming from the introduced dopants, and (b) to use organic luminophores of relatively simple chemical structure and known characteristics, allowing a simple and unambiguous interpretation of conformational changes in their molecular structure that could be induced by the nematic matrix.

The LC host used was a nematic mixture ZhK-805 (50:50 % mixture of 4-butyl- and 4-hexyl-*trans*-cyclohexanecarboxylic acids).

The luminescent dopants included: *trans*-stilbene, *p*-terphenyl (*p*-Tph), pyrene, *o*-POPOP, 2,5-diphenyloxazole (PPO), 2-(1-naphthyl)-5-phenyloxazole (NPO). The dopants were dissolved in the LC matrix in the isotropic phase with subsequent cooling to the nematic state.

The absorption and steady-state luminescence spectra were measured in a standard cell (thickness  $\sim 10$  microns) with planar alignment of LC at room temperature using a Hitachi 330 spectrophotometer and a Fluoromax-4 spectrofluorimeter. The concentrations used ensured optical density similar to diluted ( $\sim 10^{-4}$ – $10^{-5}$  M) solutions in hexane.

The measured photoluminescence spectrum of nematic ZhK-805 is shown in Fig. 1. For comparison the luminescence spectrum of commonly used nematic LC matrix 5CB measured under the same conditions is shown on the same picture. The intrinsic fluorescence intensity of 5CB is several orders of magnitude higher than that of ZhK-805. Moreover, the broad shape of 5CB spectrum, in fact, reflects a superposition of the monomer emission at 320–380 nm and emission of 5CB aggregates in the long-wavelength region (380–500 nm), including excimers (405 nm), *J*- and *H*-dimers (at 395 and 380 nm, respectively) [16, 19]. Thus, we chose ZhK-805 as a LC solvent for luminescent dopants because of its negligibly low intrinsic fluorescence intensity.

For all compounds we studied absorption spectra in the LC matrix and a standard organic solvent, and photoluminescence

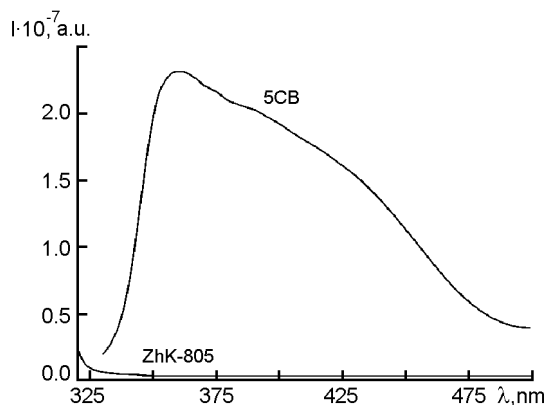


Fig. 1. Photoluminescence spectra of LC matrix 5CB and Zhk-805 measured under the same conditions in our experiments,  $\lambda^* = 320$  nm.

spectra in LC, isotropic solvent, and in crystalline form.

It has been known that some *trans*-stilbene derivatives in the isotropic solutions form supramolecular aggregates, which are manifested in the luminescence spectra [20]. So, in the first stage of our studies we attempted to validate our idea that LC order could facilitate aggregation of stilbene molecules. However, no such evidence was found — it seems that excimer-type aggregation is really limited to some of stilbene derivatives [20], but is not observed for stilbene itself. In ZhK-805 matrix, as compared with hexane solution, for stilbene we observed an insignificant red shift (about 4 nm) of absorption spectrum (Fig. 2), without change in its shape. However, in the same conditions photoluminescence spectrum in LC demonstrated strong bathochromic shift (22 nm) with respect to hexane solution. The position of stilbene spectrum in the LC was a sort of intermediate between the isotropic solvent and a single crystalline sample. It is worth mentioning that for *p*-TPh the same qualitative picture was observed, but the red shift of the photoluminescence spectrum in LC matrix with respect to the isotropic solution was much smaller (4 nm), which presumably reflects the fact that conformational movements of benzyl rings in *p*-TPh is more restricted than in stilbene. This hypothesis is supported by the fact that stilbene polycrystalline samples appeared to be more sensitive to combined pressure-temperature effects than those of *p*-TPh [8].

*o*-POPOP is known for its large Stokes shift due to flattening of its molecules in the excited state [21]. In the LC matrix, we observed no significant changes in the

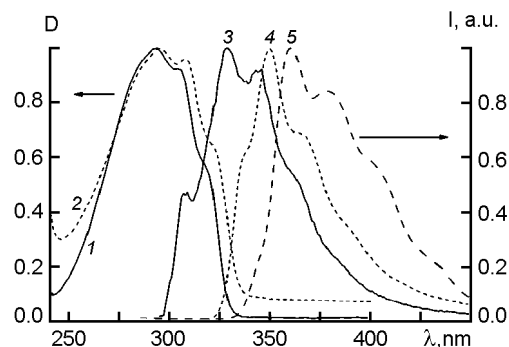


Fig. 2. Absorption (1, 2) and luminescence (3–5) spectra of stilbene,  $\lambda^* = 260$  nm: 1, 3 —  $10^{-5}$  M solution in hexane; 2, 4 — 2 % solution in ZhK-805; 5 — single crystal sample.

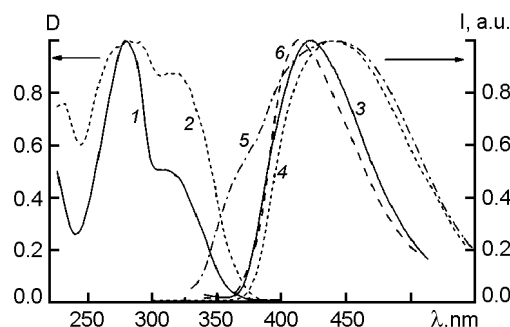


Fig. 3. Absorption (1, 2) and luminescence (3–6) spectra of *o*-POPOP,  $\lambda^* = 260$  nm: 1, 3 —  $10^{-5}$  M solution in hexane; 2, 4 — 3.6 % solution in ZhK-805; 5 — 3.6% solution in 5CB, 6 — single crystal sample.

shape and position of *o*-POPOP absorption spectra (Fig. 3). But in the emission spectra we observed broadening of the peak and increasing of the Stokes shift (by ~20 nm) in the LC solvent as compared with the isotropic matrix. This effect was approximately of the same order of magnitude in LC matrices of different chemical nature and polarity — ZhK-805 and 5CB (Fig. 3, curves 4, 5). A short-wave shoulder at 350–360 nm in curve 5, Fig. 3, corresponds to emission of the pure 5CB matrix). This suggests that in these cases the key role is played not by the chemical nature of the solvent, but just by the presence of LC ordering. As distinct from the cases of stilbene and *p*-TPh, the *o*-POPOP single crystal emission spectrum was blue-shifted with respect to LC and even isotropic solutions of *o*-POPOP. This can be explained by the restraint of *o*-POPOP molecule conformation changes in the crystalline form and their more flexible state in solutions. The LC environment facilitates additional flattening of the luminophore molecules in the excited

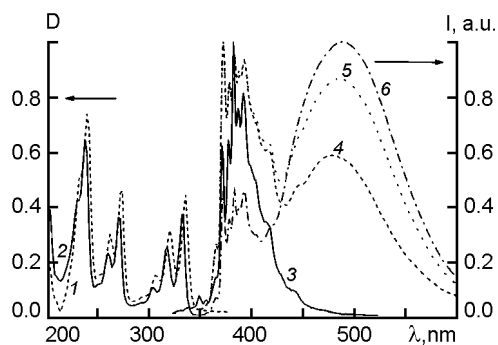


Fig. 4. Absorption (1, 2) and luminescence (3–6) spectra of pyrene,  $\lambda^* = 317$  nm: 1, 3 —  $10^{-5}$  M solution in hexane; 4 — 0.2 % solution in ZhK-805; 5 — 1 % solution in ZhK-805; 2, 6 — 2 % solution in ZhK-805.

state, causing an increase of the Stokes shift.

Unlike the previous cases, absorption and emission spectra of pyrene demonstrated absolutely the same behavior in LC and isotropic solvents. No spectral shift depending on the solvent ordering could be noted (Fig. 4). In the LC matrix we observed the excimer formation fully corresponding to the well-known pyrene properties in the isotropic solutions [22,23]. A broad excimer band appeared at  $\sim 475$  nm and slightly shifted to the long wavelength with increased pyrene concentration. It can be assumed that, because of its rigid structure and very small anisotropy, pyrene has no reasons for changing its conformation or obtaining a preferred orientation in a LC matrix, which results in the observed similarity of the measured spectra in isotropic and anisotropic solvents.

For PPO and NPO (well-known organic luminophores of similar chemical structure [24]) we obtained qualitatively similar results, which (as it could be expected) were more pronounced in the case of NPO. Changing the solvent from isotropic (hexane) to anisotropic (ZhK-805) led to a slight blue shift ( $\sim 4$  nm) in the absorption spectra of NPO (Fig. 5). The changes in emission spectra were more pronounced. Instead of a single luminescence peak noted in the isotropic solution at  $\sim 389$  nm, two marked peaks appeared in the LC solvent at  $\sim 378$  nm and  $\sim 447$  nm (Fig. 5). The position of the long-wavelength peak (447 nm) is rather close to the photoluminescence peak of NPO crystalline powder (449 nm) [24]. Additional microscopic observations showed no dopant crystallization from LC solution.

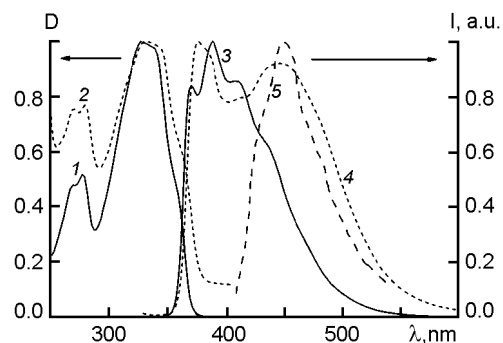


Fig. 5. Absorption (1, 2) and luminescence (3–5) spectra of NPO,  $\lambda^* = 320$  nm: 1, 3 —  $10^{-4}$  M solution in hexane; 2, 4 — 2.7 % solution in ZhK-805. 5 — crystalline powder; data from [24].

We can ascribe this effect to the existence of two favored conformations of NPO (and PPO) in LC environment. One conformation corresponds to the planar-shaped conformation of NPO molecule with naphthyl group in plane with the phenyloxazole moiety, as in the case of crystalline state of NPO. This conformation corresponds to the long-wavelength photoluminescence peak at  $\sim 447$  nm, and NPO molecules are coplanar to molecules of LC matrix. The other conformation is close to that predominant in the isotropic solution with the naphthyl group perpendicular to the phenyloxazole moiety and to the plane of LC molecules. Because of the shortening of  $\pi$ -conjugated chain, in this case the luminescence peak is blue-shifted ( $\sim 378$  nm).

Thus, it can be concluded that luminescence spectra of many compounds in the LC solvents show substantial differences as compared with their spectra in the isotropic organic solution and crystalline state. The effect of the LC ordering on the photoluminescence peak position ( $\lambda_{max}$ ) of the substances studied is due to favoring of their certain conformations by LC environment.

For stilbene and *p*-TPh in LC matrix,  $\lambda_{max}$  takes intermediate position between isotropic solvent and crystal.

For *o*-POPOP, the Stokes shift in the LC matrix was further increased because of LC ordering facilitating flattening of the luminophore molecule.

There were no remarkable changes of  $\lambda_{max}$  position for pyrene because of its rigid structure and little anisotropy that remain the same in the different phase states.

For NPO and PPO,  $\lambda_{max}$  splits into two separate peaks corresponding to two confor-

mations induced by the LC matrix with close distribution probabilities.

The obtained effect of LC environment on emission properties of organic luminophores, together with detailed study of mesomorphic and physico-chemical properties of such doped LC systems [25], could serve as a basis for future search of efficient liquid crystalline scintillators.

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## Вплив рідкокристалічного впорядкування на спектри люмінесценції модельних речовин з молекулярною структурою, чутливою до ефектів пакування

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Для стільбену, *n*-терфенілу, *o*-POPOP, 2-(1-нафтіл)-5-фенілоксазолу та інших речовин, що використовуються як люмінофори та сцинтилятори, отримано спектри люмінесценції у рідкокристалічних (РК) середовищах. Вибір об'єктів зумовлено можливістю їх молекул приймати різні конформації в залежності від фазового стану. Для кожного люмінофора спектри випромінювання порівняно у низці "стандартний органічний розчинник — РК матриця — монокристал". Знайдено декілька різних випадків у РК середовищах, коли відбувається зсув піка люмінесценції  $\lambda_{max}$  у довгохвильову чи короткохвильову область, положення  $\lambda_{max}$  залишається незмінним, або пік розділяється на два окремих, які відповідають двом конформаціям люмінофора. Для кожної сполуки така поведінка може бути пов'язана з відповідними змінами ефективної форми молекули, які індуюються РК або кристалічним впорядкуванням. Отримані результати можуть служити основою для подальшого пошуку ефективних РК сцинтиляторів.