POLYMERS
AND LIQUID CRYSTALS

Photoelectric Properties of a Self-Ordered Molecular Disperse Structure Based on a Polar-Dye Solution in a Liquid-Crystal Matrix

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Received March 6, 2007

Abstract—An analysis of photoluminescence spectra and nonlinear optical properties revealed the effect of polar-dye aggregates in a liquid-crystal matrix on the formation of an ordered molecular disperse structure. As the dye is aggregated in the liquid-crystal matrix, there is a certain concentration of the dye below which only second-harmonic generation occurs upon laser excitation at 1064 nm, while above this concentration, this generation occurs in combination with intense two-photon-induced photoluminescence. An applied electric field or intense ultraviolet illumination is found to change both the molecule orientation and the conditions of molecule aggregation.

1. INTRODUCTION

Liquid crystals (LCs) have properties of a crystal and a liquid and can easily change their orientation under weak external influences, which can be used to control their properties. When molecules of certain dyes are introduced into a liquid-crystal matrix, they are arranged [1–4] and their nonlinear optical properties strengthen [2–4]. The orientation ordering of dye molecules in an LC matrix is usually related to the anisotropy of their physical properties and their strongly elongated shape. Although an LC matrix has weak nonlinear optical properties, the orientation ordering of a dye and the frequently observed collective response of dye molecules in the LC matrix to weak external influences open up fresh opportunities for the application of such systems in nonlinear optics. In many cases, the significant increase in the nonlinear optical properties of dye solutions in an LC matrix is thought to be caused by the collective properties of aggregated dye molecules and the formation of molecular disperse structures. The synthesis of new materials requires a knowledge of the effect of both the molecular and supramolecular structures of these materials on their nonlinear optical properties.

In [1], we detected the *J* aggregation of astrofloxine molecules and the formation of molecular disperse structures in a cyanobiphenyl LC matrix. Such structures have high cubic nonlinearity and, at a low level of infrared (IR) laser excitation, exhibit intense up-conversion photoluminescence (PL) in the visible region induced by two-photon absorption.

In this work, we consider the effect of the aggregation of polar-dye molecules in a 4-*n*-pentyl-4'-cyanobiphenyl (5CB) LC matrix on their PL and nonlinear optical properties. Having an elongated shape, the dye molecules and nanoaggregates made of them are oriented along LC molecules and form ordered ensembles. In contrast to astrofloxine, crystals of the dye under study are noncentrosymmetric, and the introduction of this dye into the LC matrix makes second-harmonic generation (SHG) and two-photon-induced PL (TPL) possible. The up-conversion emission intensity depends substantially on the dye concentration. Since SHG can occur only in noncentrosymmetric molecular structures, the appearance and intensity of SHG can be used to trace the formation of noncentrosymmetric dye nanoaggregates and ordered ensembles made of this dye.

2. EXPERIMENTAL

We studied time-resolved and steady-state spectra of solutions of a dye (1-(4-dimethylaminophenyl)-3-(4-bromephenyl)-4-cyano-4-(2,4-diamino-3,5-dicyanopyridynyl)-1,3-butadiene (*D*Br)) in liquid-crystal and solid matrices of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) and acetonitrile upon one- and two-photon laser excitation. The structural formula of the dye molecule is shown in the inset to Fig. 1.

To prepare 5CB–*D*Br solutions, the *D*Br dye was mixed with an LC at the required weight proportions and then heated to 70–80°C. At these temperatures, the major part of the *D*Br dye is in a molecular form in a
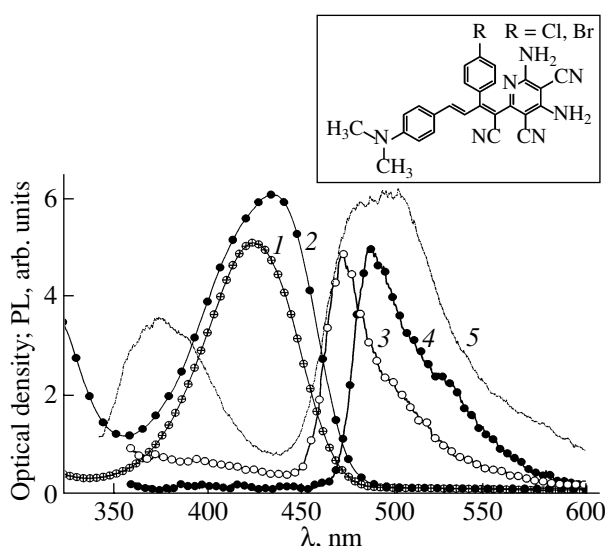
Fig. 1. Absorption and PL spectra of molecular solutions of the *D*Br dye in acetonitrile or 5CB LC: (*1, 3*) absorption (at 301 K) and PL (77 K) of a *D*Br solution in acetonitrile, respectively; (*2, 4*) absorption and PL of the as-prepared 5CB–*D*Br solution (at 301 K), respectively; and (*5*) PL of a 5CB–*D*Br solution (77 K). The inset shows the structural formula of the dye molecule.

Fig. 2. Schematic diagram of the spectral system: *M* stands for monochromator; PEM, for photoelectric multiplier; DL, for delay line; OS, for pulsed sampling oscilloscope; PC, for computer; *S*, for sample; L_1, L_2, L_3, and L_4 are lenses; F_1 and F_2 are filters; Lamp is a DRSh-250-2 mercury lamp; and PD is photodiode.

solution. The temperatures of the crystal–LC and LC–isotropic liquid phase transitions in 5CB are 18 and 35°C. When a 5CB–*D*Br solution passes from the isotropic to the LC phase, which occurs as the temperature decreases, the dye solubility decreases substantially. In an LC solution, dye molecules are aggregated to form colloids. When the *D*Br concentration in the solution is well above the solubility threshold, a molecular disperse structure forms.

As will be shown below, the formation of colloids causes bands characteristic of *D*Br single crystals to appear in the PL spectra. Therefore, we assume that the cores of the colloids represent noncentrosymmetric crystalline nanoaggregates of *D*Br molecules, which then interact with both 5CB and *D*Br molecules. As the *D*Br concentration increases further, the colloids grow and precipitate to form a gel. As follows from the PL spectra, the precipitated gel is similar to *D*Br crystals; however, unlike these crystals, it has high plasticity and a lower melting temperature. Using an LC as a solvent, we were able to specify a certain orientation of *D*Br molecules and nanoaggregates with respect to the director field in the LC cell and vary this orientation using an external electric field. To this end, solutions were placed between two quartz plates with an orienting agent or with deposited transparent electrodes made from a conducting layer (a mixture of indium and tin oxides). We examined both homeotropic and planar LC orientations.

To excite PL, we used the following radiations: the radiation of a nitrogen laser (λ_e = 337.1 nm, exciting
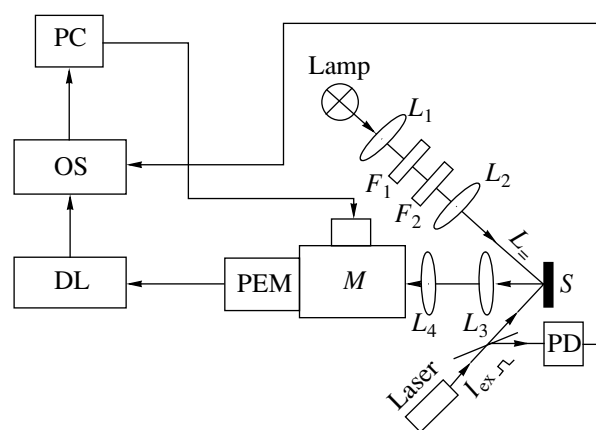
pulse time t_1 = 9 ns, peak power N = 5 kW, pulse repetition frequency f = 100 Hz), the fundamental harmonic of an Nd : YAG laser (λ_e = 1064 nm, t_1 = 10 ns, N = 0.05–1.0 mW, f = 100 Hz), and the second harmonic of an Nd : YAG laser (λ_e = 532 nm, N = 0.1–0.5 mW, f = 50 Hz). Time-resolved PL spectra were recorded with a stroboscopic system [4, 5], which made it possible to record PL kinetics and spectra with various delay times t_d with respect to a laser pulse. The time resolution of the system was about 0.1 ns for determining the PL lifetime and 0.7 ns for measuring PL spectra. To record PL spectra, we used an MDR-12 monochromator. The spectral slit width for measuring PL spectra was 0.2–0.4 mm. The schematic diagram of the spectral system is shown in Fig. 2.

3. ABSORPTION AND ONE-PHOTON-INDUCED PHOTOLUMINESCENCE

In the ground state, *D*Br molecules are polar due to partial electron transfer from the donor dimethylamino groups to the acceptor cyano groups. The absorption maximum of molecular *D*Br solutions ($C = 5 \times 10^{-5}$ mol/l, T = 301 K) in acetonitrile (related to intramolecular charge transfer) is located at 425 nm (Fig. 1, curve *1*). In an excited state, the charge separation increases; as a result, the dipole moment of the molecule increases substantially and the PL band maximum has a significant Stokes shift. For weakly concentrated ($C = 5 \times 10^{-5}$ mol/l) *D*Br solutions in acetonitrile at room temperature and 77 K, the maximum of the *D*Br molecular emission is located at 473 nm (Fig. 1, curve *3*).

At low *D*Br concentrations in an LC matrix and acetonitrile, the absorption spectra of these solutions are similar. However, the PL spectra of these solutions
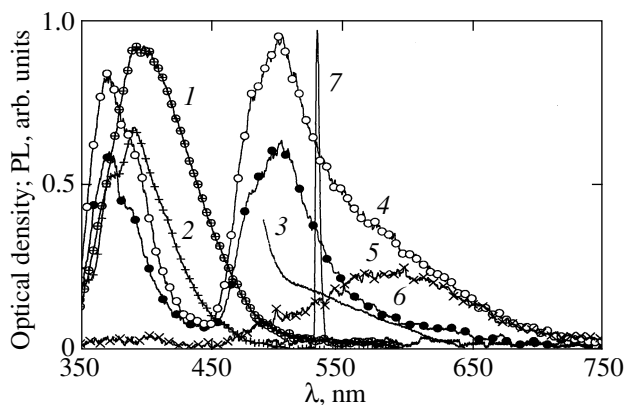
Fig. 3. PL spectra of the 5CB–DBr molecular disperse system: (*1*, *2*) steady-state PL of the initial 5CB LC at 301 and 4.2 K, respectively; (*3*) absorption band edge of 5CB–DBr colloids; (*4*) steady-state PL of a 5CB–DBr solution; (*5*) time-resolved PL of 5CB–DBr solutions measured at delay times of 15 and 0.7 ns, respectively; and (*7*) PL excited by a focused laser beam at λ = 1064 nm.

exhibit substantial differences related to the fact that, at room temperature, most DBr molecules in the LC matrix are in predimer states and, in an excited state, form exciplexes with 5CB molecules.

Curve *2* in Fig. 1 shows the absorption spectrum of an as-prepared 5CB–DBr solution with a dye concentration close to 1 wt %. Since the absorption of the 5CB LC lies in the spectral range λ < 300 nm, the band at 435 nm can be associated with the molecular absorption of DBr. At 301 K and λ > 450 nm, the Pl spectra of this solution (Fig. 1, curve *5*) contain a band representing a superposition of bands with maxima at 480 and 505 nm, which correspond to the emission of DBr molecules and 5CB–DBr exciplexes. At 77 K, only the molecular emission of DBr is observed (Fig. 1, curve *4*) because of structural difficulties induced by exciplex formation.

Exciplexes (complexes forming upon the interaction of excited molecules with electron donors or acceptors) play a key role in many photophysical and photobiological processes. They are intermediate products of intramolecular electron transfer in an excited state. Exciplexes between 5CB and DBr molecules form so that, in the ground state, their static dipole moments compensate each other and they form a centrosymmetric system. This behavior is supported by the fact that SHG is not observed in an as-prepared DBr solution in 5CB or a DBr solution of the same concentration in acetonitrile under intense IR laser excitation.

When an as-prepared DBr solution in 5CB is stored for a time, a polar molecular disperse system is formed. In this system, some DBr molecules form 5CB–DBr predimer structures and the other molecules form colloids, which represent polar nanoaggregates uniformly distributed and oriented in the LC matrix. The spectral characteristics of this solution are given in Fig. 3.

SHG is observed when this molecular disperse solution is excited by a focused (*d* = 1 mm) laser beam at a wavelength of 1064 nm and when the signal is measured in backscattering geometry (Fig. 3, curve *7*). This observation indicates qualitative changes in the solution, namely, the formation of polar nanoaggregates and their orientation ordering in the LC matrix. After the molecular disperse solution is excited by a focused IR laser beam, the SHG intensity changes slowly, which can indicate additional orientation of the polar particles in the laser radiation field. Thus, the appearance of SHG can be used to detect the formation of an ordered ensemble of noncentrosymmetric nanoaggregates in a 5CB–DBr solution at a certain DBr dye concentration. Our studies demonstrate that, if Cl substitutes for Br in the DBr molecule, the SHG signal disappears. According to the calculation data from [6], the SHG signals of similar molecular compounds with Cl and Br are close. Therefore, the macroscopic nonlinearity is mainly determined by the specific features of the crystal structure and the type of DBr molecule packing in the unit cell.

Studying the PL spectra makes it possible to reveal the molecular structure of a molecular disperse solution and interaction processes in it. For comparison, Fig. 3 shows the steady-state PL spectrum of the initial 5CB LC (curves *1*, *2*) and the steady-state (curve *4*) and time-resolved (curves *5*, *6*) PL spectra of the molecular disperse solution excited by laser radiation with λ = 337 nm. Upon ultraviolet (UV) excitation, emission appears from both the LC matrix (λ < 450 nm) and the dissolved dye (λ > 450 nm). The PL spectra of 5CB were measured at 301 K (Fig. 3, curve *1*) and 4.2 K (curve *2*). The Pl spectra of the 5CB–DBr solution were measured at 301 K.

The PL of 5CB in the molecular and LC states was studied in [5, 7–9]. In the range 340–360 nm, the PL of 5CB contains a band (shoulder) polarized along the long axis of the molecule and related to the monomeric emission from the ^1L_a state [8]. The corresponding band in the absorption and PL excitation spectra is located at 280 nm. On the long-wavelength side of the monomeric PL band, bands at 375, 395, and 405 nm can be distinguished by time-resolved spectroscopy [5]; they correspond to different associates of 5CB molecules. The PL with a long lifetime (τ = 22 ns) at 400–405 nm (Fig. 3, curve *1*) is characteristic of classical excimers. The corresponding predimer pairs usually form from noncoplanar 5CB molecules via sandwich packing. Due to steric limitations in the ground state, 5CB molecules in these pairs are spaced a large distance (0.4–0.6 nm) apart. In an excited state, the distance between 5CB molecules decreases to 0.35 nm [5], which leads to an increase in their interaction and excimer formation. When interacting with DBr molecules, one of the 5CB molecules in a predimer pair is replaced by a DBr molecule. In an excited state, such a mixed 5CB–DBr predimer pair generates exciplex emission. The main difference

between exciplex emission and excimer emission is that the former appears between two different molecules and is related to significant intermolecular electron transfer in an excited state, whereas excimer emission is mainly caused by intermolecular resonance energy transfer. At low temperatures ($T < 77$ K), the band at 405 nm is not observed because of steric obstacles and only molecular emission and physical-dimer emission (bands at 375 and 395 nm, respectively) are detected.

The PL bands at 375 and 395 nm are clearly visible in the low-temperature PL spectra of 5CB (Fig. 3, curve *2*, $T = 4.2$ K). This fact indicates that this emission does not have activation character and is not related to excimers. These bands are assumed to correspond to physical dimers whose bond is much stronger than that in the dimer pairs generating excimers upon photoexcitation. In the PL excitation spectra of the 5CB LC [5], the bands corresponding to the PL bands at 375 and 395 nm are located at 265 and 310 nm; they are shifted toward shorter and longer wavelengths, respectively, with respect to the monomeric absorption band at 280 nm. This finding suggests that dimers of both the *H* and *J* types of aggregation (sandwich and linear packing, respectively) are formed in a macroscopic volume of 5CB. Under this assumption, we can attribute the Pl band at 395 nm to *J*-type dimers. The 375-nm band can correspond to *H* dimers provided that emission is generated from a partly relaxed state. *H*-type dimers can form only sufficiently coplanar conformers. In an excited state, they can approach each other to a distance at which their collective properties manifest themselves. Thus, the presence of several PL bands in the long-wavelength region of the spectrum can easily be explained by the coexistence of various *H*- and *J*-type molecular associates (predimer and dimer pairs) formed by molecules with different stereometry and degrees of bonding.

The presence of various 5CB-molecule aggregates in the initial LC matrix should cause, in addition to 5CB–*D*Br predimer pairs, the formation of more complex *H*- and *J*-type aggregates in a 5CB–*D*Br molecular disperse solution. The PL spectrum of a 5CB–*D*Br molecular disperse solution (Fig. 3, curve *4*) contains bands at 375, 505, and 580 nm. The molecular and excimer PL of 5CB in the spectral region $\lambda < 405$ nm is quenched due to the formation of exciplexes with *D*Br molecules, and the PL lifetime decreases to 0.3 ns. The PL in this spectral region is mainly determined by the emission of physical *H*-type 5CB dimers. The PL in the region $\lambda > 450$ nm can be related to the emission of the molecular and aggregated forms of *D*Br. The steady-state Pl spectrum (Fig. 3, curve *4*) contains an intense band of the exciplex emission of 5CB–*D*Br with a maximum at 505 nm. Its long-wavelength wing ($\lambda > 520$ nm) corresponds to the emission of more complex aggregated forms of the dye, which can be distin-

guished by time-resolved spectroscopy. The PL spectra measured at a delay $t_d = 0.7$ ns after the excitation of a sample by a laser pulse (Fig. 3, curve *6*) mainly contain exciplex (5CB–*D*Br) emission, specifically, a band at 505 nm. The monomeric emission of the *D*Br dye is substantially quenched due to exciplex formation and manifests itself in the form of a weak short-wavelength shoulder. The PL lifetime in the 505-nm band is 0.3 ns, which is close to the PL lifetime of LC molecules in predimer pairs.

It should be noted that, when passing to a colloid, the intensity of the 395-nm band (caused by the formation of *J*-type 5CB associates) in the PL spectra of the LC matrix decreases substantially. This fact indicates that, apart from the formation of exciplexes between 5CB and *D*Br molecules, more complicated mixed linear aggregates are also formed in the colloids. The degree of linearity of the aggregates can be estimated by studying the PL anisotropy. The 5CB–*D*Br exciplexes are aggregated according to the *H* type, and the more complicated linear aggregates (whose emission spectrum lies on the long-wavelength side of the 505-nm band of exciplex emission) are formed according to the *J* type. The longer the aggregate, the larger the shift in its band toward longer wavelengths. The broad structureless band at 580 nm (Fig. 3, curve *5*) in the time-resolved spectra recorded at a delay time $t_d = 15$ ns can be related to the emission of uniformly distributed colloids, which are more complex aggregates than exciplexes. The PL lifetime in the 580-nm band is 7.5 ns.

4. DICHROISM
IN THE PHOTOLUMINESCENCE SPECTRA

Studying the PL anisotropy makes it possible to find the orientation of transition dipole moments with respect to the configuration of molecules and nanoaggregates in the molecular disperse system. By definition [10], PL anisotropy R_n is

$$R_n = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}), \qquad (1)$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the PL polarized along and perpendicular to the plane of exciting-light polarization (to the direction of the electric-field vector **E** of the light wave), respectively.

The PL anisotropy was measured for two cases: the anisotropy R_1 corresponds to the case where the vector **E** of the light wave is parallel to the axis of LC molecules in the measuring cell and R_2 corresponds to the case where vector **E** is normal to the axis of LC molecules. In the absence of energy transfer, light is absorbed by the molecules whose transition dipole moment vectors lie in the plane of the electric-field vector of exciting light. Therefore, only properly oriented molecules are excited and, hence, fluorescent. PL polarization theory is considered in [10, 11]. In partic-
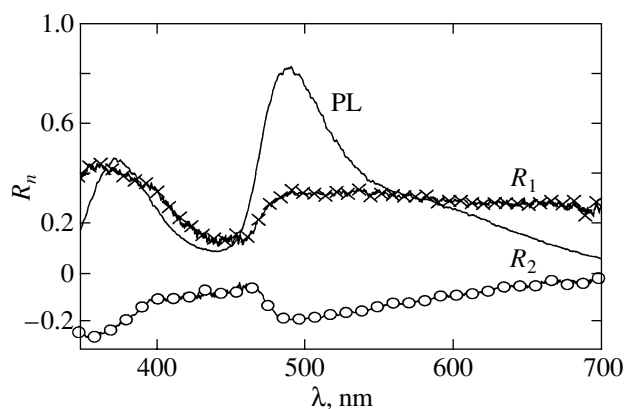
Fig. 4. Anisotropy (R_1, R_2) and PL spectra of a colloidal 5CB–DBr solution.

Fig. 5. Schematic image of (a) 5CB–DBr exciplexes and (b) polar DBr nanoaggregates in an LC matrix.

ular, it has been shown that, in the case of unmovable chaotically oriented molecules, R_n depend on the angle θ between the dipole-moment vectors of absorption and emission transitions [5]:

$$R_n = (3\cos^2\theta - 1)/5. \qquad (2)$$

Many molecules have an angle θ of either 0° or 90°; in this case, the anisotropy is 0.4 or –0.2, respectively. For completely anisotropic molecular layers, the anisotropy parameter R_1 should be equal to unity for light excitation with **E** parallel to the orientation axis.

Figure 4 shows the R_n spectra of a colloidal 5CB–DBr solution. A 20-μm-thick sample had the planar orientation and was excited by vertically polarized laser radiation with λ_e = 337 nm at a temperature of 296 K. The R_1 curve corresponds to the situation where the orientation axis of the sample is parallel to the direction of laser excitation, and the R_2 curve corresponds to the case where the sample is orthogonal to the direction of laser-radiation polarization. Having an elongated shape, 5CB molecules in an LC layer are oriented mainly along the director axis. As for DBr molecules, their long axes are expected to be also parallel to 5CB molecules.

The wavelength dependences of R_n (Fig. 4) demonstrate the presence of two directions of transition dipole moments caused by the aggregation of 5CB and DBr molecules. The main transition dipole moment is normal to the long axes of 5CB and DBr molecules and gives positive anisotropy. The light absorption is a maximum in the case where the light electric-field vector E is parallel to the long axes of 5CB and DBr.

Indeed, the value of R_1 in the emission range of the 5CB matrix (the emission range of physical dimers, 375 nm) is close to 0.6, which indicates a high degree of orientation of 5CB molecules along the LC director axis. In the emission range of exciplexes, R_1 = 0.4 and R_2 = –0.2. The negative value of R_2 in the emission range of exciplexes indicates that, in addition to selec-
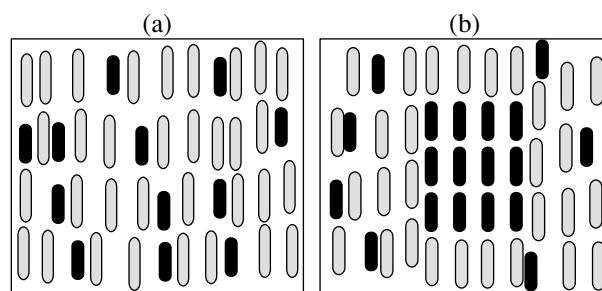
tive excitation and emission of the ^1L_a states with a transition moment oriented along the long axis of the 5CB molecule, there is an emission component with a transition moment orthogonal to the long axis of the 5CB molecule. This component is caused by the H-type aggregation of DBr molecules and the orthogonal transition moment induced by electron transfer between the donor and acceptor parts. The PL anisotropy in the range λ > 505 nm is characteristic of predominantly one-dimensional molecular aggregates whose transition dipole moments are oriented along the director in the LC matrix. When an aggregate is excited normal to its orientation, this anisotropy is close to zero. In the low-temperature PL spectra, these aggregates generate bands at 518 and 550 nm, which are a manifestation of exciton properties, namely, molecular properties (518-nm band) and charge-transfer properties (550-nm band). The manifestation of quasi-one-dimensional exciton properties is typical of certain crystals with intramolecular charge transfer [12], including DBr crystals, in which the long axes of molecules are parallel to the transition dipole moment for Frenkel excitons and are perpendicular to the transition dipole moment for charge-transfer (CT) excitons.

At a low concentration, the DBr molecules are close in size to the 5CB molecules and, when substituting for them in predimer pairs, are oriented in the same direction. In the excited state, they form 5CB–DBr exciplexes (Fig. 5a). As the DBr molecule concentration increases, small linear aggregates are formed in the LC matrix (Fig. 5b). In the PL spectra, these aggregates are manifested in the form of bands that are shifted toward the long-wavelength side from the exciplex band and predominantly polarized along the director axis. The study of the polarization reflection spectra of DBr single crystals demonstrates that the planes of DBr molecules in them are normal to the crystal growth direction. The DBr single crystals have a shape strongly elongated in the growth direction. Obviously, this situation can also occur in DBr crystalline nanoaggregates in the LC matrix. The growth of an aggregate along the growth direction can result in its reorientation, with its long axis becoming parallel to the director axis and with the axes of DBr molecules being perpendicular to it. On the other hand, the growth of aggregates leads to
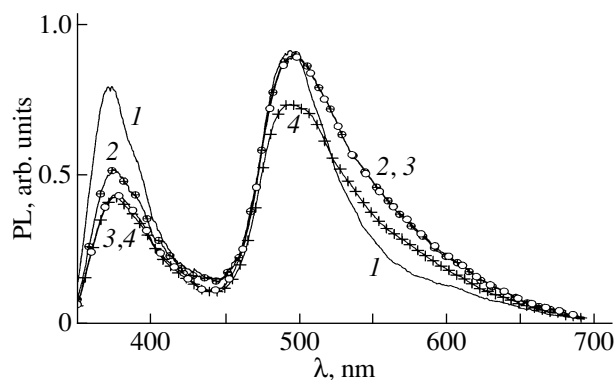
Fig. 6. PL spectra of the 5CB–*D*Br molecular disperse system measured with nanosecond-scale time resolution (*1*, *2*) without illumination and (*3*, *4*) with additional illumination by a mercury lamp.
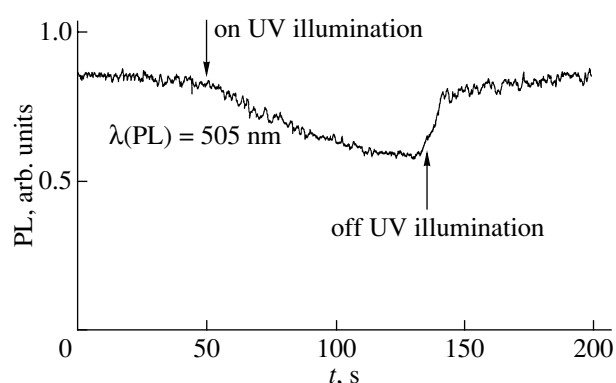

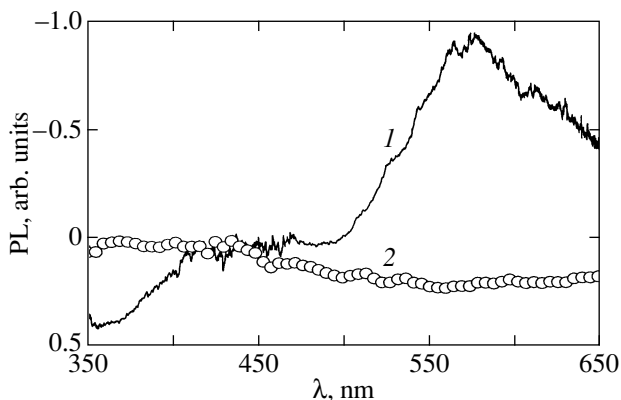**Fig. 7.** PL kinetics at a wavelength $\lambda = 505$ nm when UV illumination is turned on and off.

Fig. 8. Relative changes in the PL spectra (*1*) after illumination is turned off and (*2*) during illumination.

their precipitation and gel formation. Indeed, the study of the PL spectra of *D*Br aggregates in gel demonstrates that they generate a band at 600 nm characteristic of the corresponding single crystals.

5. EXTERNAL INFLUENCES ON MOLECULAR AGGREGATION AND PHOTOLUMINESCENCE ANISOTROPY

The aggregation of molecules in a 5CB–*D*Br molecular disperse solution can be affected by intense illumination or an external electric field. The time-resolved PL spectra (with a time resolution of several nanoseconds) generated by pulsed laser excitation (at a wavelength of 337 nm) are changed when the solution is additionally illuminated by an intense steady luminous flux from a high-pressure DRSh-250-2 mercury lamp through certain filters (Fig. 2). When PL is measured with nanosecond-scale time resolution, the steady-state PL spectrum does not contribute to the recorded PL spectrum. If the laser beam is intercepted and the steady illumination is retained in this measurement geometry, steady-state PL is not detected by the measuring apparatus. The influence on the PL ns-spectra is maximal for illumination with $\lambda < 500$ nm. The effect of steady illumination on the PL ns-spectra can be related to photochemical and structural changes in the 5CB–*D*Br molecular disperse system. We think that the effect of UV illumination is not photochemical, since the initial PL spectra are restored in several minutes after illumination is turned off.

Figure 6 shows the PL spectra of the molecular disperse system measured with ns-scale time resolution. A 100-µm-thick layer of the molecular disperse solution was located between two quartz plates and was not oriented. Curve *1* represents the initial PL ns-spectrum, and curve *4* illustrates the PL ns-spectrum under additional illumination by the mercury line $\lambda = 365$ nm. In the PL spectrum, the bands at 375 and 505 nm (i.e., in the ranges of dimer LC emission and exciplex 3 5CB–*D*Br emission) are seen to be quenched. Moreover, the emission of aggregates in the spectral region $\lambda > 505$ nm is also observed. After steady illumination is turned off, the 505-nm band intensity in the PL ns-spectrum (Fig. 6, curve *2*) is restored, the PL of aggregates in the region $\lambda > 505$ nm becomes stronger, and the band at 375 nm remains quenched. Figure 7 shows PL kinetics at a wavelength $\lambda = 505$ nm when UV illumination is turned on and off. The time it takes for the spectrum to be restored after illumination is about 2 min. It takes longer time for the initial spectrum to be restored (Fig. 6, curve *1*). Subsequent cycles of measuring the PL spectra without and with illumination oscillate between curves *2*, *4*, and *3* in Fig. 6.

Figure 8 shows relative changes in the spectra of pulsed PL under steady illumination. Curve *1* ($\Delta PL/PL = (PL(2) - PL(1))/PL(1)$; PL data are taken from Fig. 6) reflects relative changes in the PL spectra after illumination is turned off. Curve *2* ($\Delta PL/PL = (PL(4) - PL(2))/PL(2)$; PL data are taken from Fig. 6) reflects changes in the PL spectra measured during illumination. As follows from the spectra in Figs. 6 and 8 and from the dynamics of PL quenching during steady illumination (Fig. 7), there are two mechanisms of the
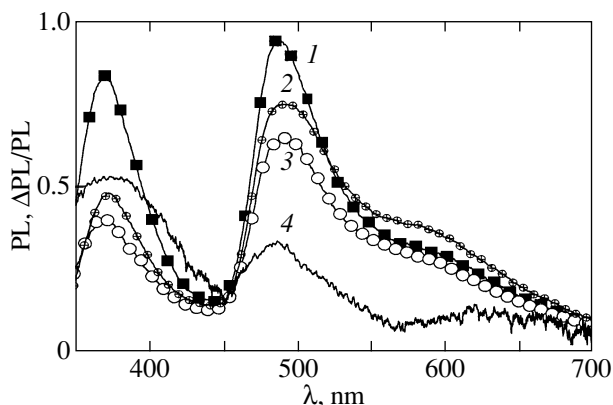
Fig. 9. Steady-state PL spectra in a partly disordered region of the LC cell (*1, 2*) without an electric field and (*3*) at a voltage of 1 V (*f* = 10 kHz). (*4*) Voltage-induced relative changes in the PL spectrum.

effect of illumination on the PL spectra. The increase in the PL intensity after illumination is turned off in the emission range of aggregates (λ > 500 nm) can be related to their growth due to the attachment of closely spaced excited molecules from dimer pairs to them. The decrease in the concentration of predimer pairs induced by their interaction with aggregates can quench the PL in the emission ranges of exciplexes and pred-imer 5CB pairs. The quenching of PL over a wide spectral region during illumination can also be associated with the reorientation (selective photo-orientation) of molecular aggregates for which the transition dipole moment and the illumination-induced dipole moment (which is related to intermolecular charge transfer) differ in direction. These aggregates interact with a light wave through an induced dipole moment and tend to be reoriented, which results in PL quenching. After illumination is turned off, the molecular disperse structure relaxes to a stable state with temperature.

6. EFFECT OF AN ELECTRIC FIELD ON THE PHOTOLUMINESCENCE OF A 5CB–*D*BR MOLECULAR COLLOIDAL SOLUTION

Since dye molecules and aggregates made of them have an elongated shape, their orientation in a homeotropic cell should also be homeotropic. In an electric field, dye molecules in a homeotropic cell rapidly change orientation and many of them acquire planar orientation. This is accompanied by changes in the PL of both an LC and the dissolved dye. In the excited state, exciplexes represent polar molecular structures because of intermolecular charge transfer and their orientation in an LC matrix can also be affected by an external electric field.

Figure 9 shows the steady-state PL spectra in a partly disordered region of the cell without an applied voltage (curves *1, 2*) and at a voltage of 1 V varying at

a frequency *f* = 10 kHz (curve *3*). Curve *1* is the initial Pl spectrum of the as-prepared molecular colloidal solution, and curve *3* shows the spectrum for the case of applied voltage *U*. Curve *4* reflects the relative change ΔPL/PL(0) = (PL(0) – PL(1 V))/PL(0) in the PL spectrum after the voltage is applied.

Our experiments show that, in the region of the cell with a small fraction of planar orientation, the effect of an electric field lower than 100 V on the PL intensity is virtually absent (not shown in Fig. 9). PL is mainly quenched in a disordered region in a sample. An applied electric field mainly affects the PL in the LC emission region (350–400 nm) and the exciplex band (490–505 nm) and weakly affects the emission of elongated *D*Br dye aggregates (band at 590 nm).

The electric-field-induced changes in the Pl spectra of LC with a dissolved dye are explained by the fact that some LC and *D*Br molecules in a homeotropic cell have planar orientation and that this orientation changes into homeotropic orientation in an electric field. Pl quenching is related to the fact that the principal dipole moment of the optical transition in the dye molecule is directed along its long axis; therefore, the reorientation of such molecules decreases absorption and, hence, the PL intensity. In time (after several cycles of applied voltage), the PL quenching in the spectral regions given above decreases and the PL spectrum acquires the shape shown in Fig. 9 (curve *2*).

The spectrum is seen to undergo changes identical to those occurring during intense steady UV illumination (Fig. 6). In both cases, excited molecular dipoles are slowly reoriented under the action of either an applied voltage or light, which leads to the quenching of the dimer (5CB) and exciplex (5CB–*D*Br) PL and to an increase in the PL of extended aggregates. It is obvious that the interaction that causes aggregate growth appears at a certain critical angle between excited 5CB and 5CB–*D*Br molecules and linear aggregates having similar orientations. Thus, we can reorient polar molecules and affect their aggregation in the 5CB–*D*Br molecular colloidal system via an applied electric field or intense UV illumination (λ < 400 nm).

7. UP-CONVERSION PHOTOLUMINESCENCE

When a solution containing more than 10 wt % *D*Br in an LC matrix is prepared at room temperature, the colloids increase in size and precipitate to form a gel. Figure 10 shows the PL spectra of an excited gel. The steady-state PL spectra of the molecular disperse solution and gel recorded at room temperature for λ < 450 nm are similar (Fig. 10, curve *1*). They become different in the spectral region λ > 450 nm. As the dye concentration increases, the relative PL intensity in this region increases. Curves *2* and *3* illustrate the spectrum of one-photon-excited PL for delay times of 0.7 and 20 ns, respectively. In the time-resolved PL spectra, the maximum of the long-wavelength PL band shifts from

570 to 600 nm (Fig. 10, curve *3*) and the PL lifetime increases from 7 to 15 ns depending on the *D*Br concentration in the LC matrix and the delay time.

When the gel is excited by a focused ($d = 1$ mm) laser beam at a wavelength of 1064 nm, intense SHG and PL are observed (Fig. 10, curve *4*). The measurements of the dependences of the PL and SHG intensities on the exciting IR laser irradiation intensity demonstrate that they are proportional. This finding indicates that the detected PL is two-photon-excited PL (TPL). As is seen from Fig. 10, the one-photon-excited PL and TPL spectra of the 5CB–*D*Br gel are similar.

The aggregation of *D*Br molecules in a colloidal solution results in an intermolecular interaction between them in the crystalline phase. As a result, intermolecular charge transfer between the donor and acceptor fragments of two neighboring molecules (i.e., the formation of an intermolecular CT exciton) is possible in the ground state along with intramolecular charge transfer in predimer structures. Such properties were observed in crystalline weak-charge-transfer complexes [13], in which CT excitons whose wave functions are delocalized within two or a larger number of molecules appear in the excited state along with Frenkel excitons. In the absorption spectra of colloids, the intermolecular CT-absorption band manifests itself as a shoulder on the long-wavelength ($\lambda > 500$ nm) edge of the intramolecular absorption band (Fig. 3, curve *3*). The presence of intermolecular charge transfer in the 5CB–*D*Br molecular disperse system is supported by the fact that recombination PL with a lifetime of about 1.5 s occurs at low temperatures in the red region. It is detected upon UV laser excitation ($\lambda = 337$ nm), when free charge carriers can be generated. CT-exciton PL takes place in the red region upon laser excitation ($\lambda = 532$ nm), when CT excitons can be excited and free charge carriers cannot be generated. The PL lifetime in the 600-nm band related to the emission of CT excitons is 12 ns at room temperature and 22 ns at 4.2 K.

The intermolecular charge transfer energy W_{CT} can be written as

$$W_{CT} = I_D - A - E_C - P + (C \pm K) \mp U, \qquad (3)$$

where I_D is the donor ionization potential; A is the electron affinity of the acceptor; E_C is the energy of the Coulomb attraction between the donor (D^+) and acceptor (A^-); P is the energy of the medium polarization by dipole $\mu_{D^+A^-}$; $(C + K)$ and $(C - K)$ are the energy of the Coulomb repulsion between unpaired electrons for their singlet and triplet orientations, respectively; K is the exchange repulsion energy; and U is the contribution of a covalent-bond structure to the polar state [14].

One-photon and two-photon transitions in molecular crystals obey different selection rules and give complemented spectroscopic information with respect to
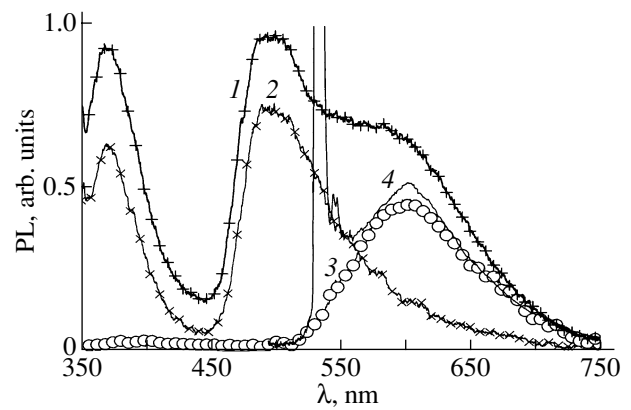

Fig. 10. (*1–3*) One- and (*4*) two-photon-excited PL spectra for a gel of the 5CB–*D*Br molecular disperse system at 301 K: (*1*) steady-state PL; (*2, 3*) time–resolved PL for delay times of 0.7 and 20 ns, respectively; and (*4*) SHG and PL excited by a laser beam at $\lambda = 1064$ nm.

each other. In the dipole approximation, the probability W of absorption of two photons with a frequency ω and the corresponding electric-field polarization **e** has the form [3, 14]

$$W(\omega, \mathbf{e}) \propto N\omega^2 F^2 \sum_f |M_{fg}|^2 \delta(2\omega - \omega_{fg}), \qquad (4)$$

where g and f stand for the ground and final states of a two-photon transition, respectively; M_{fg} is the composite matrix element of the transition between the g and f states; $\hbar\omega_{fg} = E_f - E_g$ is the energy difference between the g and f states; F is the exciting-light intensity; and N is the density of molecules or unit cells in the medium.

In a medium with a center of symmetry, the ground state is nondegenerate and electronic states can be divided into even (g) and odd (u) states. In the dipole approximation, one-photon g–g or u–u transitions are forbidden; however, two-photon transitions between these states are allowed. Thus, using two-photon absorption spectroscopy, one can probe new electronic states that cannot be detected during one-photon absorption.

Crystals consisting of polar molecules can be both centrosymmetric and polar. For crystals with a center of symmetry, SHG is forbidden. If a system loses its inversion symmetry and has a static dipole moment, its ground state is degenerate and has no symmetry [8]. In this case, transitions between the ground and excited states for one- and two-photon light absorption are not rigorously forbidden. M_{fg} for a molecular system with a center of symmetry can be expressed as [3, 14]

$$M_{fg} = \sum_i \frac{2 p_{fi} p_{ig}}{\omega - \omega_{ig}} - 2\frac{\Delta\mu_{fg} p_{fg}}{\omega}, \qquad (5)$$

where $\Delta\mu_{fg} = \mu_{ff} - \mu_{gg}$ is the difference static dipole moment (projection onto direction **e**) between the final and ground states, p_{ij} is the matrix element of the transition dipole moment (projection onto direction **e**) between different (i, j) states, and $\hbar\omega_{ij} = E_i - E_j$ is the energy difference between states i and j. The main contribution to the two-photon transition probability is supposed to be made by the intermediate i states that are close to the g and f levels.

The coefficients of the one- and two-photon absorption of a two-level system without an inversion center can be written as

$$\alpha(\omega) \propto p_{fg}^2 \delta(\omega - \omega_{fg}),\qquad(6)$$

$$\alpha(2\omega) \propto p_{fg}^2 \Delta\mu_{fg}^2 \frac{F(\omega)}{\hbar\omega}\delta(2\omega - \omega_{fg}).\qquad(7)$$

The TPL intensity is

$$I_{PL} = \eta\alpha(2\omega)I^2,\qquad(8)$$

where η is the PL quantum yield.

The SHG intensity is specified by the polarizability squared; for charge-transfer crystals, this polarizability is [4]

$$\beta_{CT} = \frac{3e^2\hbar^2 W_{CT}f\Delta\mu_{fg}}{2m[W_{CT}^2 - (2\hbar\omega)^2]}.\qquad(9)$$

Here, β_{CT} depends on the characteristic radiation quantum energy $\hbar\omega$, the electron charge e and mass m, the energy gap W_{CT}, the oscillator strength f of the transition to the CT state, and the change in the dipole moment $\Delta\mu_{fg}$ upon this transition. To achieve the maximum value of β_{CT}, it is desirable to have molecules (crystals) in which an electronic transition has an energy close to $2\hbar\omega$ and does no fall inside the absorption band. Moreover, the oscillator strength should be high and the dipole moment should change significantly during this transition. These conditions coincide with the conditions required for effective absorption upon two-photon excitation of PL [3, 14]. However, TPL is observed from states $E_{TPL} \le 2\hbar\omega$. In our case, $\hbar\omega$ is related to the light-quantum energy for IR excitation. Therefore, until the sizes of polar nanoaggregates for which $W_{CT} > 2\hbar\omega$ are smaller than a critical size, only SHG takes place upon the IR excitation of 5CB–DBr solutions. As the nanoaggregates grow, the ionization energy of the molecular structure decreases (because of possible molecular conjugation in the aggregates) and the polarization energy increases (because of collective intermolecular charge transfer in the crystalline aggregates). As follows from Eq. (3), W_{CT} should decrease. When $W_{CT} < 2\hbar\omega$, TPL appears along with SHG.

8. CONCLUSIONS

Our studies have demonstrated that, being in molecular and aggregates forms, the polar DBr dye dissolved in an LC matrix forms an ordered polar molecular colloidal phase in which DBr molecules and aggregates are oriented along the LC director (5CB). This system has nonlinear optical properties and exhibit SHG and TPL when excited by IR laser radiation, depending on the dye concentration.

At low dye concentrations, apart from the emission of the LC matrix, we have also detected the molecular and exciplex PL of 5CB–DBr. An increase in the dye concentration leads to the formation of nanoaggregates, which can precipitate to form a gel at a certain DBr concentration.

When an ordered molecular colloidal solution is subjected to one-photon excitation, its PL spectra contain the bands of DBr exciplexes and nanoaggregates. The two-photon excitation ($\lambda_e = 1064$ nm) of this solution is accompanied by second-harmonic generation (SHG). The gel subjected to two-photon excitation exhibits SHG and intense two-photon-induced PL, and its one-photon excitation near 600 nm is accompanied by intense PL characteristic of crystalline CT transitions.

When the 5CB–DBr molecular colloidal system is subjected to an electric field or intense UV illumination ($\lambda < 400$ nm), polar molecules in it can be reoriented and the processes of their aggregation can be controlled.

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Translated by K. Shakhlevich

SPELL: 1. exciplexes, 2. noncentrosymmetric, 3. exciplex, 4. centrosymmetric, 5. excimers, 6. unpaired