Photoluminescence of Nematic Liquid Crystal Doped with Anthraquinone Dye

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Abstract

Photoluminescence and absorption spectra of nematic liquid crystal 5CB doped with an anthraquinone dye (AQ) have been studied. An effective energy transfer from the fast relaxing S_1 level of 5CB with intensive PL band at 410 nm to slowly relaxing AQ level with PL band at 724 nm is discovered. On the basis of these results we reconstruct the energy level diagram that explains the stages of energy transfer process in the host-guest system.

Key words: liquid crystal, organic dye, photoluminescence, energy transfer

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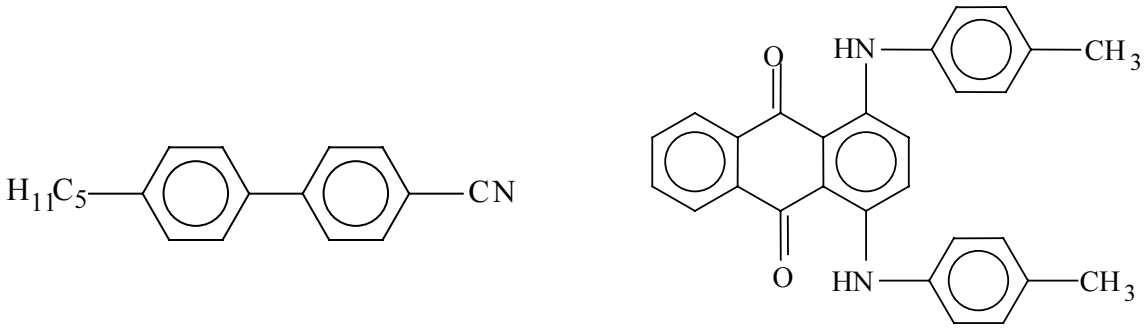
Introduction

Liquid crystals (LC) are well known [1] as promising materials for optical devices because of their giant nonlinear optical (NLO) response. In particular, orientation of molecules in LC samples may be changed by illumination with polarized light. It has been revealed [2] that a system consisting of nematic LC doped with a small amount (~1%) of organic dye exposed to intense light exhibits reorientation response, which is about two orders of magnitude higher than that of a pure LC matrix. This phenomenon is often referred to as Janossy effect. The nature of this phenomenon has been discussed in several works. The main hypotheses put forward for this aim describe it in terms of effective molecular interactions between the host and guest molecules [3] or the aggregates of the latter [4]. In frame of the model by Janossy [3], the excitation is transferred from the dye host molecules, changing "mechanical" properties of the system such as diffusion constant, etc. According to *Nazarenko* and co-workers [4], formation of supramolecular aggregates of dopant molecules in the LC matrix is responsible for the effect and the excitation of these aggregates induces an extra torque in the guest-host system. Irrespective of the model adopted, however, it is the guest-host interaction that plays a principal part in these processes.

The aim of this paper is to present results of spectroscopic studies for the host-guest system consisting of an anthraquinone dye dissolved in nematic liquid crystal 5CB. Our results provide information about energy transfer in the system and kinetics of its deactivation.

Experimental details

The system investigated in this work was 1,4 – di (p - aminotoluene) - 9 , 10 - anthraquinone (hereafter referred to as anthraquinone-containing dye and abbreviated as AQ) dissolved in 4-cyano-4'-pentylocyanobiphenyl (5CB) liquid-crystalline matrix (see Fig. 1 for



a) b)

Fig. 1. Chemical formulae of 5CB liquid crystal (a) andanthraquinone-containing dye AQ (b).

chemical formulae of the molecules). NLO properties of this system have been intensively investigated and are reported in [4-6]. The LC material was doped with various dye concentrations (up to 1.6 wt. %). The experiments were performed in the cells, in which alignment of 5CB molecules was induced by coating glass substrates with orientant layers. These orientant layers provided either normal or tangent anchoring direction of 5CB molecules and therefore induced either homeotropic or planar orientation, respectively. The thickness of LC layer was set to be 10 μm. All the spectra were recorded at the room temperature.

The transmittance spectra were recorded with a Perkin Elmer Lambda 35 UV-VIS-IR spectrophotometer in the spectral range of 250–1100 nm. The samples (pure or doped 5CB) were placed in the cells used later in independent NLO experiments and were measured against the air as a reference. The absorption spectra were calculated after taking the absorption of the cell material and the reflection from the cell surfaces into account. The photoluminescence (PL) was excited with continuous-wave lasers: a He-Cd laser (Omnichrome Series 56, λ=325 nm, P= 20 mW), He-Ne laser (LGN–208, λ=633 nm, P= 1.5 mW), diode laser (Coherent Radius 405-25 EP, λ=405 nm, P= 25 mW) or a pulsed nitrogen laser (Spectra Physics 337203-00, λ=337 nm, τ_p=5 ns (FWHM), E_p=300 μJ). In some experiments, a 150 W Xe–lamp was used. Then the exciting radiation was passed through a Hitachi F-4500 monochromator (for the continuous excitation spectra) or TRIAX with a grating 300 grooves per mm (for the pulsed excitation spectra). The PL emission and excitation spectra were recorded with a Hitachi F-4500 spectrofluorimeter, using a photomultiplier registration (the continuous excitation) and Ocean Optics HR4000CG-UV-NIR CCD spectrometer (the pulsed excitation). The spectra were corrected for the emission spectrum of Xe-lamp. Time-resolved emission spectra were recorded using Acton Research Spectra Pro-275 with CCD Princeton Inst. LN/CCD 512TK/S-UV and Acton Research Spectra Pro-2300 with CCD Princeton Inst. PI-MAX2 System. The spectra were corrected for spectral sensitivity of CCD matrix calibrated with a wolfram lamp with the colour temperature of 3500 K.

Results and Discussion

The absorption spectra of the guest-host system under study are shown in Fig. 2a. Pure 5CB is transparent in the visible range. The spectrum of 5CB has a single band in the near UV with the maximum at 325 nm that coincides with the PL excitation spectrum (cf. Fig. 3). This is in agreement with the data taken from [7,8]. The absorption spectrum of AQ dissolved in 5CB (see Fig. 1a) in the visible region contains the band at 420 nm and the doublet with the maxima at 620 and 660 nm. The same absorption spectrum of AQ has been reported in [9,10]. The solutions of AQ in the common solvents exhibit

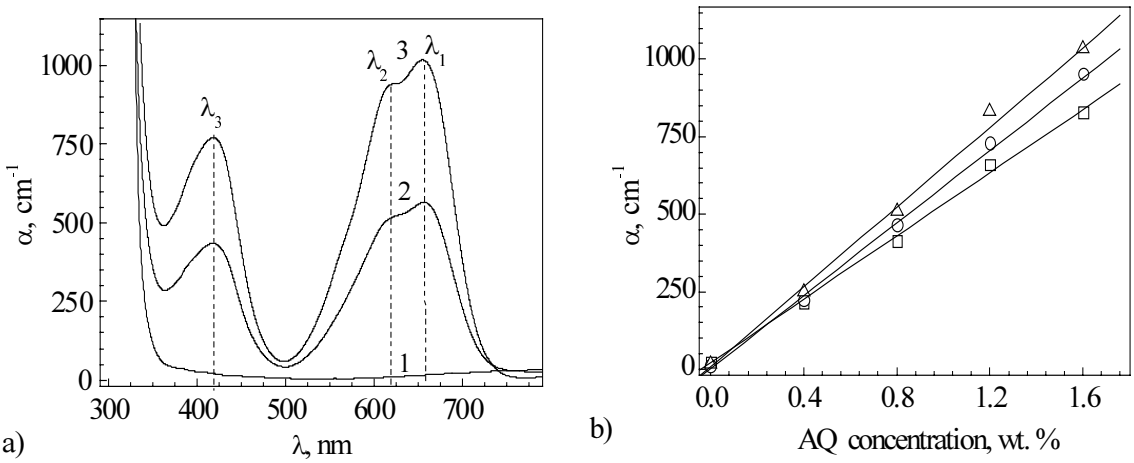


Fig. 2. (a) Absorption spectra for AQ-5CB system at various dopant weight concentrations: 1 – 0.0% (pure 5CB), 2 – 1.0% and 3 – 1.6%. The dashed lines indicate the positions of band maxima. (b) Peak absorbances versus dye concentration for the AQ bands: Δ – 656 nm (λ_1), ○ – 622 nm (λ_2) and □ – 417 nm (λ_3). The lines indicate linear fits.

shifts of all the bands by approximately 10–20 nm, depending on the solvent polarity. In the 5CB solutions, absorbances of the bands due to AQ obey the Lambert-Beer law up to 1.6 wt % as shown in Fig. 2b (the solubility of AQ in 5CB is about 1.8% at the room temperature). The molar absorbances calculated from these dependences amount to about 2.72×10^4; 2.43×10^4 and 2.14×10^4 dm^3 mol^{-1} cm^{-1} respectively for λ_1=656 nm, λ_2=622 nm and λ_3=417 nm.

As we have mentioned in the preceding section, the PL spectra were excited essentially at the two wavelengths: 320 nm (close to the maximum of the absorption spectrum of 5CB and in accordance with the maximum of the excitation spectrum) and 337 nm. Fig. 3 shows the emission and excitation spectra of the pure 5CB.

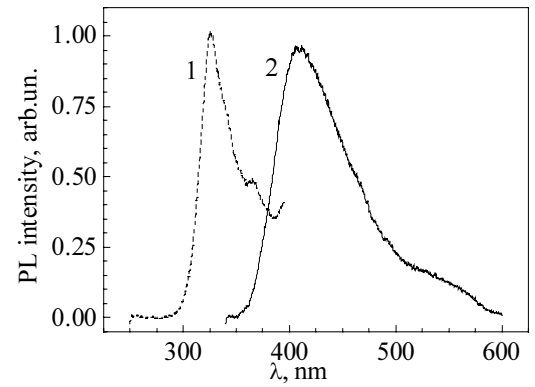


Fig. 3. (1) PL spectrum of pure 5CB (excitation at 320 nm) and (2) excitation PL spectrum of 5CB (monitoring at 410 nm).

The emission spectra in the spectral range under investigation contain a prominent asymmetric band peaking about at 410 nm. The same band has been observed elsewhere [8,11] and ascribed to excimer $S_0 \leftarrow S_1$ emission of the 5CB. For some samples, the long-wavelength tail develops into a weak band with the maximum at ~ 525 nm. As the relative intensity of the long-wavelength feature is found to depend on the origin of the material and on the sample prehistory, we attribute it to an unspecified impurity and neglect it in our further considerations. The excitation spectrum shows intensive peak at 320 nm. This wavelength corresponds to the position of the absorption band of 5CB which, according to theoretical calculations, is associated with the lowest transition [12].

The PL spectra of AQ-5CB solutions excited at 337 nm are shown in Fig. 4a. The luminescence intensity of the 410 nm band sharply decreases with increasing dopant concentration, this also being true of the long-wavelength tail. At the same time, very weak

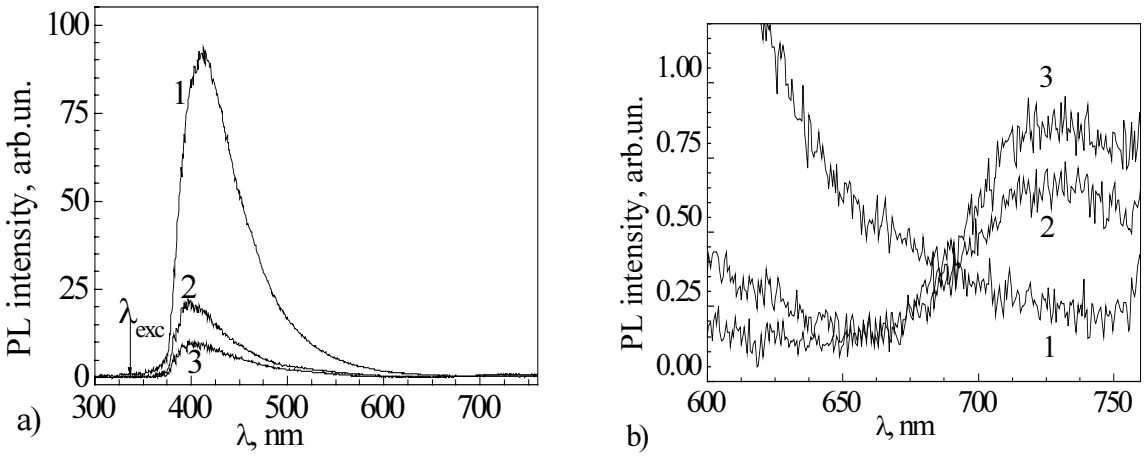


Fig. 4. (a) PL spectra of 5CB cells with various dopant concentrations, (b) magnified IR range: 1 – 0%, 2 – 1% and 3 – 1.4%. The excitation is performed with a pulsed nitrogen laser (τ_p=5 ns, λ=337 nm). The arrow indicates the excitation wavelength.

band with the maximum located at 724 nm appears in the near IR region. Its intensity increases with increasing dopant concentration (see Fig. 4b).

The PL spectra recorded under the excitation at 320 nm exhibit an even sharper dependence on the dopant concentration. The intensity ratio taken for the 410 nm band in the pure 5CB and that of the AQ-5CB solution containing as little as 0.2 wt% of AQ is approximately equal to 7. Such a drastic reduction of the intensity of 5CB band cannot be explained by increased absorption of the exciting light, because the difference in the absorption coefficients at 320 nm for the two systems (the pure 5CB and 5CB doped with 0.2% AQ) is about 6% (4700 and 5000 cm^{-1}, respectively). Similarly, the effect cannot be explained by enhanced absorption of the emitted light in the guest-host system: the absorption of 5CB at 320 nm is stronger than that of AQ in the solution at 410 nm (4700 and 100 cm^{-1}, respectively). Thus, we have to suppose availability of energy transfer of some kind between the matrix and the dopant.

Fig. 5 shows the excitation (curves 1 and 2) and the emission (curves 3 and 4) spectra recorded in the regions of long-wavelength tail of the main 5CB peaks (i.e., between 600 and 900 nm for the emission and between 280 and 500 nm for the excitation). The PL spectra of the pure 5CB and 5CB doped with 1.4% AQ are presented as the curves 3 and 4, respectively. In the spectral range covered by the figure, the spectrum of 5CB contains a tail of the main peak. In the dye-doped sample, however, a band appears in the near IR region, which is centred nearly at 724 nm (i.e., at the same wavelength as that appearing in the spectra shown in Fig. 4b). The PL excitation spectra were monitored at the wavelength 724 nm. Apart from a tail of the UV peak of 5CB, the spectrum of the pure 5CB (curve 1) does not contain any feature. The spectrum of the dye-doped sample (see curve 2) exhibits additionally a band with the maximum at 415 nm (i.e. at the position of an absorption peak of AQ – see the data [9] and Fig. 2).

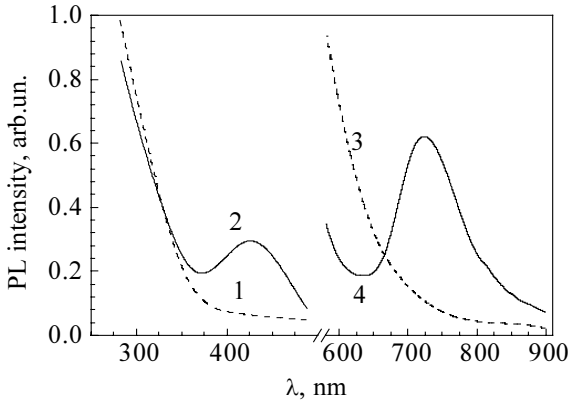


Fig. 5. PL excitation spectra monitoring at 724 nm (curves 1 and 2) and PL spectra (curves 3 and 4) of 5CB (1, 3) and 5CB doped with 1.4% AQ (2, 4) excited at 420 nm.

Moreover, the shape of the band remains unchanged upon excitation of 5CB sample doped with 1.4 wt% of AQ at 405 and 633 nm. The excitation wavelengths correspond to different absorption bands of the dye (see Fig. 2), though the PL spectra are identical. This finding may be explained by assuming a common relaxation channel to the emitting level.

An important spectral feature of the system is good correspondence between the emission spectrum of the host matrix and the absorption spectrum of the guest molecule. The spectra shown in Fig. 6 exhibit an almost complete overlap that defines effective pathway of the energy transfer from the matrix to the dopant.

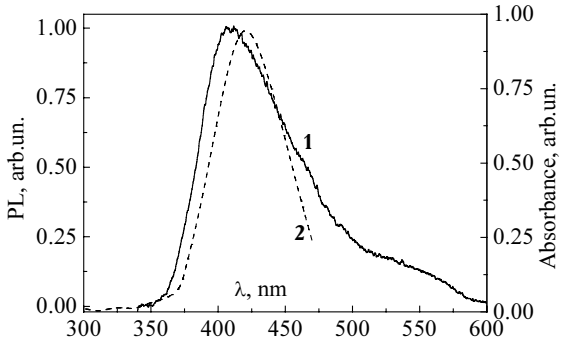


Fig. 6. Comparison of PL emission spectrum of 5CB (1) and absorption spectrum of AQ (2). The curves are normalized to their maxima.

Investigation of temporal parameters of the excitation relaxation processes has been carried out using the time-resolved PL spectroscopy. Both the pure 5CB and the dye-doped systems have been studied. The samples have been excited with a pulsed nitrogen laser (λ = 337 nm, duration of the pulse 5 ns) for various delays and widths of the sampling gate, the shortest delay time for the gated registration system being 10 ns. Fig. 7 displays the results obtained for the pure 5CB (see figure a), and the 5CB doped with 1.4 wt% AQ (figure b). In both cases the curves labelled as (1) refer to the integral spectra and the curves (2) to the time resolved spectra obtained with the delay 10 ns and acquisition window width 10 ms. The acquisition times between the curves differ effectively only by the initial 10 ns but the intensity of the main PL band of 5CB decreases by the factor of 20. Assuming that the decay is single-exponential, one can estimate the upper limit for the effective time constant of the process(es) responsible for the fast decay in 5CB to be about 3 ns. The result is consistent with those reported in [7,8,11], where the relaxation time has been estimated as 100 ps.

The spectra of 5CB doped with 1.4% AQ measured in the same regime are presented in Fig. 7b. A major difference between the integral spectra of the pure 5CB and the dye-doped system is a pronounced difference in their intensities, being about one order of magnitude, whereas the intensity of the slow component decreases only by the factor of 2.

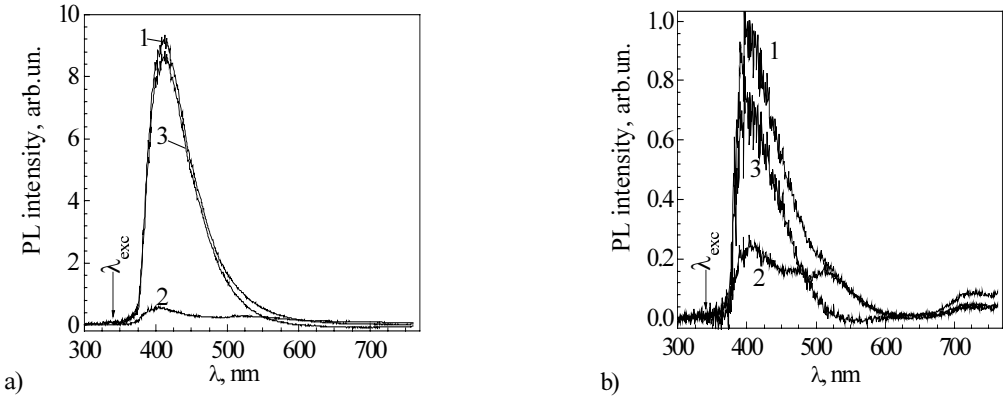


Fig. 7. Time-resolved PL spectra excited with a nitrogen laser (λ=337 nm) for 5CB (a) and 5CB doped with 1.4% AQ (b). Acquisition time: (1) integral spectrum, (2) from 10 ns till 10 ms and (3) differential curves between (1) and (2).

Simultaneously, a build-up of the band at 724 nm characteristic of AQ can be seen. These data seem to indicate that the main part of the energy transfer takes place during the first 10 ns.

Another important point is the decay kinetics for the excited state of AQ. A comparison of curves 1, 2 and 3 in Fig. 7b allows us to estimate qualitatively the time constant controlling this process as being shorter than 10 ms. A better estimate could be get from the time resolved spectra measured with different delay times and widths of the acquisition window, being changed logarithmically from 10 ns up to 10 ms. We have always set the delays and the widths of the acquisition window to be equal to one another, in order to keep the registration system at the same dynamic range. The intensities at 724 nm extracted from these spectra are presented in Fig. 8. Assuming non-overlapping bands and a single-exponential decay of PL, the luminescence intensity I is expressed by the integral

$$I = \int_a^b A(\lambda)\exp(-t/\tau)dt = \\ = A(\lambda)\tau(\exp(-a/\tau) - \exp(-b/\tau)) = \\ = B(\lambda)(\exp(-a/\tau) - \exp(-b/\tau)) \qquad (1)$$

where B is the amplitude, a the delay time and (b-a) the window width. Since $b=2a$ in our case, we get the following equation for I:

$$I = B(\lambda)(\exp(-a/\tau) - \exp(-2a/\tau)) \qquad (2)$$

Fitting the experimental data shown in Fig. 8 with Eq. (2) enables one to obtain the value $\tau = 3$ ms for the time constant. Such long times are usually due to phosphorescence and so we should attribute the decay of the 724 nm band to the emission from the triplet state of AQ.

The results of our experiments supplemented with the literature data [7,8,11] allow us to put forward a consistent diagram of energy levels and transitions in the 5CB–AQ system (see Fig. 9).

Upon exposition to irradiation of a suitable wavelength, 5CB molecules can be excited to their S_1 state located approximately at 3.9 eV. In the pure 5CB, the excitation is followed by a fast (of the order of tens of picoseconds) formation of an excimer [7] that emits at 410 nm (3.02 eV). The lifetime of the excimer is of the order of 10^{-10}–10^{-9} s. Additionally, our experiments reveal the existence of a slow emitting state of almost the same energy, whose nature remains to be explained.

In the 5CB–AQ host-guest system, a parallel (and more efficient) channel of deactivation is opened: the energy of the excimer (and, possibly, also of the slow state) is transferred to the S_m state of the dye. Due to the $S_m \rightarrow S_1 \rightarrow T_1$ intersystem crossing, the triplet state of AQ is populated, its energy amounting to 1.74 eV and its lifetime, in the order of magnitude, being from a fraction of millisecond to a few milliseconds. The excitation of the AQ molecules to their singlet levels relaxes along the same channel that quenches the PL in 5CB, with the phosphorescence at 724 nm.

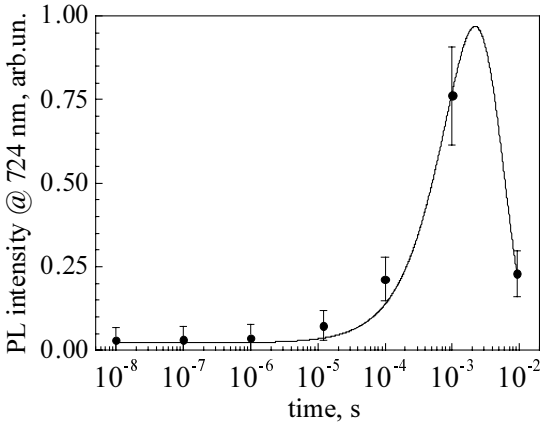


Fig. 8. Temporal response of PL signal at 724 nm excited with nitrogen laser pulses in 5CB doped with 1.4 wt% AQ. The dots represent experimental data and the line is the best fit curve that uses Eq. (2) with the time constant $\tau = 3$ ms.

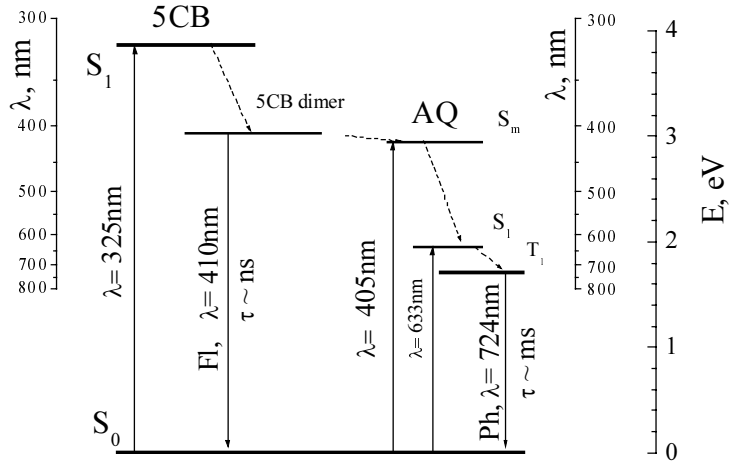


Fig. 9. Simplified diagram of energy levels for 5CB doped with AQ. The notation Fl corresponds to fluorescence and Ph to phosphorescence. The vibrational levels are not indicated.

Conclusions

Our experiments provide information about the path for the energy transfer between the host and guest molecules in the 5CB–AQ system, resulting in creation of a long-lived excited state of the dye molecule. The PL spectrum of the pure 5CB exhibits an intensive band with the maximum at about 410 nm. This band is efficiently quenched by AQ molecules in the dye-doped mixed systems. A decrease in the intensity of the 410 nm band is accompanied by a build-up of a new band peaking at 724 nm, whose intensity increases with increasing AQ concentration. The presence of the dye manifests itself in the appearance of additional band in the PL excitation spectrum, peaking about at 417 nm. This wavelength corresponds to a peak appearing in the absorption spectrum of AQ and is close to the maximum of the main PL band of 5CB. The overlap between the emission band of 5CB and the absorption band of AQ creates favourable conditions for efficient excitation transfer from the LC matrix to the dopant, reflected in the efficient quenching of the emission from 5CB.

The lifetimes for the excited molecules of matrix and dopant have been estimated from the measurements of time-resolved spectra. The upper limit of the lifetime for S_1 state in the 5CB dimer is of the order of 10^{-9} s, in agreement with the literature data [7,8,11]. Additionally, our experiments have revealed the existence of a state of approximately the same energy, emitting in the millisecond range, whose origin still remains to be explained.

In the mixed systems, the energy of S_1 state of the 5CB dimer is efficiently transferred to the (non-emitting) S_m state of the dye. The transfer is facilitated by almost complete overlap of the emission spectrum of the matrix and the absorption spectrum of the dye in the vicinity of 417 nm. Finally, T_1 state of AQ is populated via intersystem crossing. The lifetime of the excited T_1 state is of the order of 10^{-3} s.

The long-term relaxation creates conditions for delocalization of charge and increase in molecular polarizability. The strong interactions and slow relaxation of the excited state can explain the origin of the anomalous influence of AQ dopant in the Janossy effect.

Acknowledgements

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