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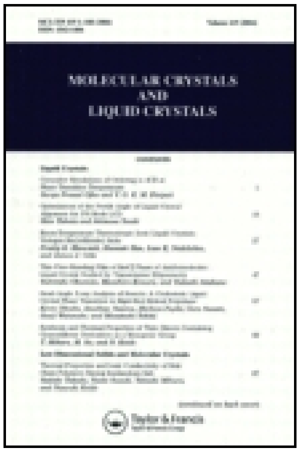

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Exciton States Of Amphiphilic Dye Condensed Matter: From Solution By Way Of LB Film To Crystal

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Exciton States Of Amphiphilic Dye Condensed Matter: From Solution By Way Of LB Film To Crystal

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Photoexcited states of amphiphilic organic dye – anthropyrimidine (AP) in various phases of condensed matter (solution, Langmuir-Blodgett (LB) film, crystal) have been studied by steady-state and time-resolved spectroscopy. Nano- and micro-scale molecular arrangement of each phase of dye condensed matter is discussed.

Keywords: Organic dye, Langmuir-Blodgett film, J-aggregate, nanocrystal

SOLUTIONS

The absorption (curve 1) and fluorescence (curve 2) spectra of diluted solution of AP dye are shown in Fig.1. Curve 1 displays the monomeric absorption of AP whereas weak changes, compared to the monomeric band, can be seen considering the absorption spectrum of concentrated solution (the data are not presented). There are some narrowing and small long-wave shift (about 1 nm) of most intensive band at 506 nm and its vibrational iterations when the concentration of AP dye rises up.

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The fluorescence spectrum of diluted AP solution is especially monomeric whereas time-resolved spectroscopy of concentrated solution reveals the new intensive fluorescence transitions (see curve 3) with enhanced radiative rates (fluorescence lifetime of monomer τ_1 = 11 ns and that of concentrated solution τ_2 = 9,5 ns). These features as we believe indicate the association of AP molecules in concentrated solution in specific manner. It is meant that the constituent aggregate molecules are orientated complanarily as "head to tail", resembling J - aggregate's molecular arrangement. Thus, conception of J - aggregates takes place already in a concentrated solution.

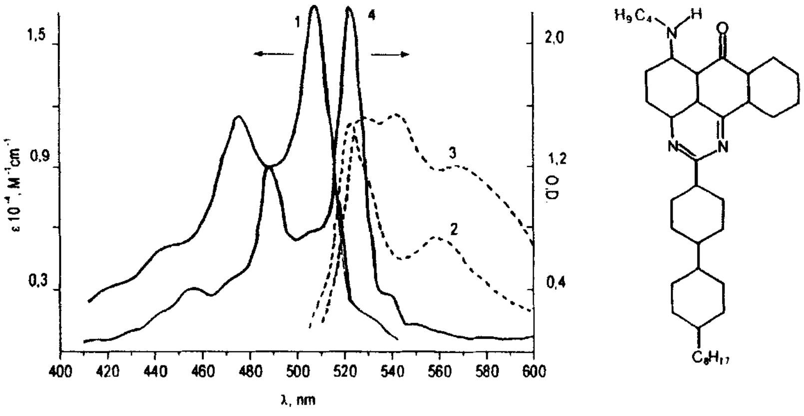

FIGURE 1, Spectral dependence of molecular extinction coefficient of diluted AP solution (curve 1). Steady-state fluorescence spectrum of diluted AP solution (curve 2) and time-resolved fluorescence spectrum were measured at t_d = 20 ns of concentrated AP solution (curve 3) in arbitrary units. Optical density spectrum of AP dye LB film (curve 4) was taken at T = 4,2 K. The solutions of AP dye in dioxane were prepared as diluted solution (concentration C_1 down to 10^{-5} mol/L) and concentrated one ($C_2 = 10^{-4}$ mol/L). 100 layers of AP molecules

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in LB film are organized with X-type. The structure of AP molecule is indicated on the right side of the picture.

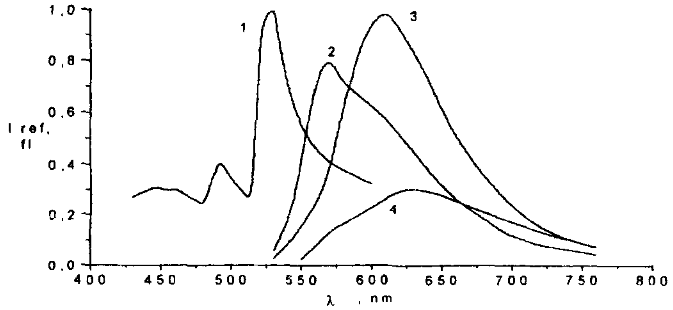

FIGURE 2, Reflection spectrum (curve 1) and time-resolved fluorescence spectra measured at various delay times: 0,5 ns (curve 2), 20 ns (curve 3) and 1 ms (curve 4) of AP dye LB film at T = 77 K.

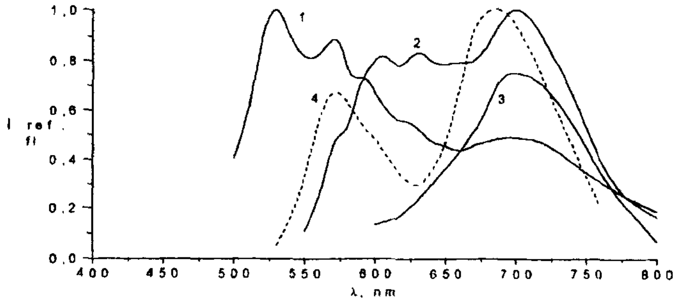

FIGURE 3, Polarized reflection (curves 1, 2 and 3) and steady-state fluorescence (curve 4) spectra of AP dye single crystal at room temperature.

LANGMUIR-BLODGETT FILMS

The absorption spectrum of AP dye LB film is shown in Fig.1, curve 4. Both weak monomolecular bands and intensive ones manifest themselves in

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absorption (also reflection and fluorescence excitation) spectra of LB film. In our case, electronic spectra display a very intensive, narrow and considerable redshifted (about 600 cm^{-1}) band (J - band) caused by optical transitions in J - aggregates. An additional small narrowing and small red shift are inherent in J - band when temperature decreases from room temperature to helium one. Also the typical temperature dependence of fluorescence lifetime of AP dye J - aggregates is observed, i.e. the radiative lifetime considerably decreases, with respect to the monomeric one, when temperature decreases or pump-level increases. Most of these properties can be explained within a band-like approximation.

Figure 2 shows the reflection (curve 1) and the time-resolved fluorescence spectra at various delay times t_d = 0,5 ns (curve 2), 20 ns (curve 3) and 1 ms (curve 4) of AP dye LB film. The fluorescence spectra display few spectral transitions manifesting themselves at certain value of t_d. These transitions are characterized by enhanced fluorescence as well as enhanced radiative decay rates. Both reflection transition at 532 nm, and fluorescence ones at 570, 610 and about 630 nm are due to electronic transitions on J - aggregates. However, J - aggregates, observed on reflection, exist in the ground state, whereas J - aggregates, displayed clearly on fluorescence, are formed only on excitation. Likely, there are interconformal transitions (a realignment of molecules) in stacks of J - aggregates during relaxation. That is why there is no resonance fluorescence in our case. Another reason might be an increasing molecular interaction in "sparse J - aggregate" in an excited state (excimer-like behaviour).

The estimation of a number of coherent-coupling molecules (N) in AP dye J – aggregate is becoming an urgent. That was done [1] from the exchange narrowing and the superradiance considerations which deal with exciton

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delocalization over the N aggregated molecules. The minimal number of coherent-coupling molecules of AP dye J - aggregates was established to be about 6-7. We do speak about the minimum because there are so many reasons that make us do the crude calculation (static and dynamic dephasing of exciton in J-aggregate; energy exchange with J - aggregates of other length or of other molecular arrangement or with triplet states; possibility of quantum mechanical mixing of neutral Frenkel-like exciton of J - aggregate with intra - or inter-molecular charge transfer states).

CRYSTALS

The reflection (curves 1, 2 and 3) and steady-state fluorescence (curve 4) spectra of AP single crystal are shown in Fig. 3. The crystal structure is not uniform. On this reason, the polarized reflection spectra (curves 1, 2 and 3) of different crystal areas, which are parallel to a long crystal axis, are differed. From this figure it is evident that the same spectral transitions at 570, 610 and 630 nm take place in crystal phase of AP. But now these transitions are available already in the ground state. Thus, the intermolecular conformations of excimer-like J - aggregates became proper for a denser condensed matter.

The additional difference is that a new “especially crystal” transition at about 700 nm manifests itself on reflection and fluorescence spectra of AP crystal. Both “common” transitions of LB film and of a crystal, and the “crystal” one may be attributed to various intermolecular conformations differing from each other by overlapping and orientation of molecular macrocycles [2] (fig. 4). The characteristic feature of most redshifted electronic transition at 700 nm is that long hydrophobic tails of neighboring AP molecules in one molecular stake are

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oriented in opposite directions. That is why such intermolecular conformation is not proper for X-type LB film.

Thin polycrystalline films of AP dye were also investigated. The same set of spectral transitions is relevant for such films, but there is a difference of macroscopic scale for the molecular arrangement in single crystals and polycrystalline films. As for single crystals, molecular stacks are parallel to each other and to long crystal axis, but in the case of films, stacks of AP molecules are disposed along radii, forming spherical crystals. The average diameter of spherical crystals can be varied from 0,01 to 1 mm by the thickness of the film. The thickness of a polycrystalline film also influences the manifestation of intermolecular conformations in spherical crystals. The increase in film thickness depresses the transitions at 610 and 630 nm, remaining strong transitions at 570 and 700 nm which respond to most stable intermolecular conformations "a" and "d".

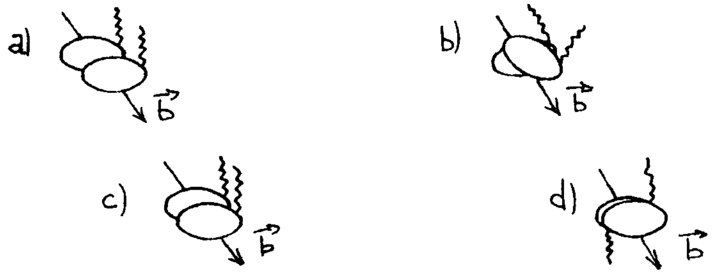

FIGURE 4, The arrangement of AP molecules along b-axis in single crystals (a-d) and along stacking axis of J - aggregates in LB films (a-c).

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