

## Structure and Physicochemical Properties of Cation Polymethine Dyes in Langmuir–Blodgett Films

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**Abstract**—The physicochemical properties of monomolecular layers of amphiphilic cation polymethine dyes (i.e., thia- and oxacarbocyanines) on the surface of a water subphase are studied along with the conditions of Langmuir–Blodgett (LB) film preparation. The area occupied by one dye molecule in the liquid-stretched and liquid-condensed states of a monolayer is determined. Based on a comparison of experimental and theoretically calculated areas, the nature of dye packing in monolayers is studied by means of molecular mechanics using data from conformation analysis. The spectral and luminescent properties of cationic polymethine dyes in various media are investigated. Excimer fluorescence is observed in LB films. The excimers in LB films are found to arise not from monomers but from dye dimers. A possible mechanism of their formation is considered.

**Keywords:** Langmuir–Blodgett films, polymethine dyes, optical properties.

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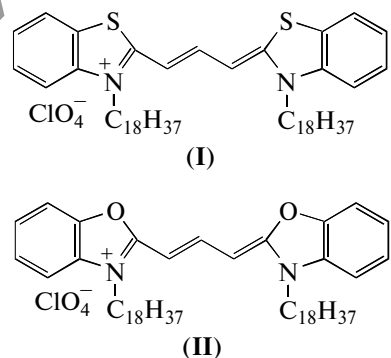
### INTRODUCTION

New functional materials with specific optical properties for nanophotonics and optoelectronics are now the subject of intensive research [1, 2]. The Langmuir–Blodgett (LB) technique for producing multi-molecular systems based on optically active centers is extremely promising [3]. Polymethine dyes with elevated (fatty) aliphatic radicals are very promising centers of this type [4], since this class of organic dyes has the broadest range of photophysical and photochemical properties [5]. The orderly packing of polymethine molecules in LB films stimulates the formation of self-organized J- and H-aggregate nanostructures, which are unique converters of light energy [6, 7].

In this work, we study the effect of substituting benzoxazole and benzothiazole in the molecules of amphiphilic polymethine dyes on the spectral and luminescent properties of luminophores in solutions and LB films.

### EXPERIMENTAL

The classical cation polymethine (cyanine) dyes thiacyanocyanine (I) and oxacyanocyanine (II) [8] were used in our experiments:



Our solvents were ethyl alcohol and chloroform, and our polymer was polyvinylbutiral (PVB). The solvents were purified by way of double distillation. The dye concentration in solutions was varied in the range of  $10^{-6}$  and  $10^{-4}$  mol/L. In our polymer matrix, its concentration was  $\sim 5 \times 10^{-4}$  mol/L. Monomolecular films were formed at the water/air interface in a Langmuir bath. Twice-distilled deionized water was used. The water's surface tension at pH 5–6 and a temperature of 20°C was 72.8 mN/m. The two component monolayers of dye molecules and stearic acid (SA) were prepared at dye concentrations of 9, 17, and 50 mol %. Isotherms of monolayer compression were measured at a temperature of 20°C. The monolayers were transferred onto nonluminescent quartz substrates using the Z-type vertical method at transfer pressure  $\pi_{\text{trans}} = 28$  mN/m and a 0.02 mm/s speed of

## Spectral luminescent characteristics of dyes I and II

Solvent	$\lambda_{\max}^{\text{ab}}, \text{nm}$	$\Delta\tilde{\nu}_{1/2}, \text{cm}^{-1}$	$\varepsilon \times 10^{-5}, \text{L mol}^{-1} \text{cm}^{-1}$	$f$	$\mu, \text{D}$	$\lambda_{\max}^{\text{fl}}, \text{nm}$	$\Delta\tilde{\nu}_{1/2}, \text{cm}^{-1}$	$\phi$
Dye I								
Ethanol	559	974	1.7	0.69	9.06	585	1524	0.07
Chloroform	568	927	2	0.82	9.92	595	1523	0.15
PVB	566	974	—	—	—	587	1700	—
Dye II								
Ethanol	485	1325	1.3	0.82	9.18	510	2029	0.27
Chloroform	490	1860	1.1	0.74	8.79	515	1680	0.17
PVB	490	1953	—	—	—	515	1700	—

plate movement through the monolayer. The films were 20 monolayers thick.

Absorption and fluorescence spectra were measured on a Solar CM 2203 spectrofluorimeter. Quantum fluorescence yield  $\phi_{\text{fl}}$  was determined relative to a standard, i.e., an ethanol solution of rhodamine 6G ( $\phi_{\text{fl}} = 0.95$ ) [9]. Delayed fluorescence was measured via flash photolysis. Dyes I and II were photoexcited using ZhS-18 and SS-5 light filters, respectively; the flash time was  $10^{-5}$  s. Prior to measurements, the solutions were degassed to a residual pressure of  $10^{-4}$  mm Hg; polymeric films were placed in an optical cryostat whose residual pressure was  $10^{-4}$  mm Hg.

## RESULTS AND DISCUSSION

In the first series of experiments, we studied the spectral and luminescent characteristics of dyes I and II in ethanol, chloroform, and PVB. The table shows the positions of their maxima ( $\lambda_{\max}$ ) and half-widths ( $\Delta\tilde{\nu}_{1/2}$ ) of the absorption (ab) and fluorescence (fl) bands, the molar extinction coefficients ( $\varepsilon$ ) in the

maxima of the absorption bands, and the quantum fluorescence yields ( $\phi_{\text{fl}}$ ).

The oscillator strengths ( $f$ ) and dipole moments ( $\mu$ ) of the first electron transition  $S_0 \rightarrow S_1$  (see table) were calculated from the absorption spectra of dyes I and II in ethanol and chloroform.

As can be seen from Fig. 1, the absorption and fluorescence spectra of dyes in liquid solvents and PVB have the virtually identical universal form characteristic of organic dyes [8, 9]. The maxima of the spectral bands differ slightly because of differences between the polarity parameters of the solvents [8].

The solutions of dyes I and II in the working range of concentrations obey the Lambert–Beer law, indicating that the investigated dyes were present in our solutions in the monomeric nonassociated state.

Cationic polymethines are known [8] to aggregate in polymeric matrixes, considerably distorting their absorption and fluorescence spectra relative to solutions. In our case, however, introducing dyes I and II into the polymeric matrix had no measurable effect on the absorption spectra or the aggregation of dyes, since

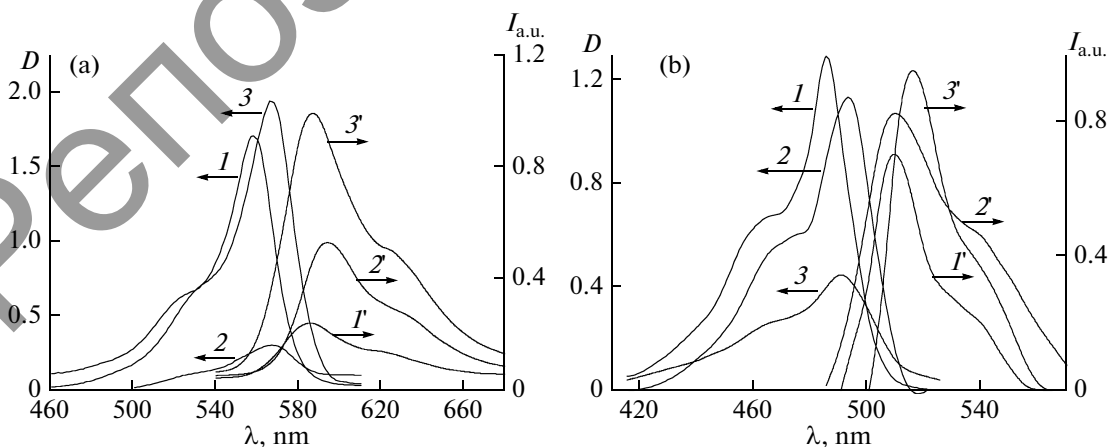
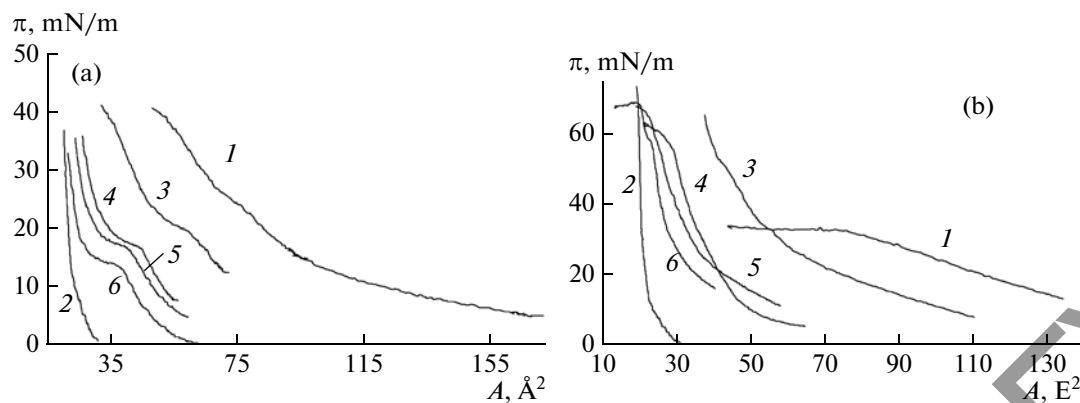


Fig. 1. Absorption (1–3) and fluorescence (1'–3') spectra of dyes (a) I and (b) II in ethanol (1, 1'), chloroform (2, 2'), and PVB (3, 3').



**Fig. 2.**  $\pi$ - $A$  isotherms of mixed monolayers of dyes (a) **I**, (b) **II** and SA at different dye concentrations ( $c_{cr}$ , mol %): 1-100; 2-0; 3-50; 4-25; 5-17; 6-9.

the nucleophilic salvation of cations **I** and **II** by polar groups of PVB hinder their association.

Polymethine dyes of types **I** and **II** have no bulky substitutes in their polymethine chains, and heavy atoms exhibit weak fluorescence and low quantum yields of intercrossing conversion (ICC) in the triplet state but have high quantum yields of trans-cis photoisomerization in the singlet excited state [8]. The low values of the ICC quantum yields of dyes **I** and **II** are confirmed by the lacking of dyes' delayed fluorescence (DF) in solutions and their low intensities in polymeric matrix, ensuring the considerable rigidity of chromophores. The DF spectrum of dyes in the polymer coincided with the spectrum of fast fluorescence. DF intensity fell along with temperature, testifying to its thermal activation nature [9]. The times of DF decay were found to be 6.5 and 10 ms for dyes **I** and **II**, respectively, at room temperature and a residual pressure of  $10^{-4}$  mmHg.

In our second series of experiments, the phase states of monomolecular layers of the dyes were studied on the surface of an aqueous subphase.

The isotherms from the compression of dye **I** films are shown in Fig. 2a; the  $\pi$ - $A$  isotherm of the pure dye monolayer (curve 1) is characteristic of the liquid state. The liquid-stretched film state is maintained up to a pressure of 15 mN/m, when a transition to the liquid-condensed phase occurs. The limit areas occupied by one molecule change from  $190 \text{ \AA}^2$  for the liquid-stretched state to  $110 \text{ \AA}^2$  for the liquid-condensed state. Conformational analysis of the dye **I** molecule's spatial structure, performed by molecular mechanics in an MM+ force field [10], established that the chromophore part of the molecule had a virtually flat structure. It occupies an area of  $138 \text{ \AA}^2$ . Comparing the experimental and theoretical values of the areas, we may assume that the area equal to  $190 \text{ \AA}^2$  corresponds to when the chromophore part of the molecule is arranged parallel to the surface of aqueous subphase. Raising the pressure reorients the chromophore slightly, with the chromophore plane partially deviat-

ing from the plane of the aqueous subphase's surface. This is confirmed by the bend on the isotherm at a pressure of 25 mN/m. At 40 mN/m, the dye monolayer collapses.

The isotherms of stretching mixed dye **I** monolayers (Fig. 2a) indicate the formation of more compact films. For all ratios at constant  $\pi$ , the area of mixed monolayers was within the limits of the additive value error:

$$A_{ml} = x_1 A_1 + x_2 A_d,$$

where  $A_{ml}$ ,  $A_1$ , and  $A_d$  are areas attributable to individual molecules in a mixed monolayer, an SA monolayer, and a dye monolayer, respectively, at a given pressure  $\pi$ ;  $x_1$  and  $x_2$  are the molar parts of the SA and dye, respectively, in a mixed monolayer. This indicates that the two-component monolayers of dye **I** and SA mix well [11]. It follows from the results of conformation analysis that one molecule of stearic acid can be enclosed in the cavity formed between the alkyl radicals of dye **I** molecules. The close packing principle results in the formation of more condensed dye monolayers.

The stretching isotherms of the pure dye **II** monolayer and its mixing with SA at various ratios of their components are presented in Fig. 2b. The  $\pi$ - $A$  isotherm of the pure monolayer is typical of the liquid-extended state with an implicit expression of collapse. The pressure rises slowly as the area attributable to one molecule grows. The limit area occupied by molecule is  $170 \text{ \AA}^2$  at transfer pressure  $\pi_{trans} = 28 \text{ mN/m}$ . The geometrical sizes of chromophoric parts of dyes **I** and **II** differ negligibly. We may therefore assume that the experimentally obtained value for the area of dye **II** corresponds to the parallel orientation of its chromophore relative to the water's surface.

Mixtures of SA and dye **II** molecules form more condensed layers with denser molecular packing. Like polymethin **I**, its two-component monolayers mix well.

Monolayers of dyes **I** and **II** were transferred onto solid supports via Z-type vertical lift. Noncentrosymmetric multimolecular films were formed. The transfer coefficient ( $K$  being the ratio of the shrinking monolayer area to the area of substrate) grew as the SA concentration rose ( $K = 0.50$  for the LB film with  $c_{cr} = 100$  mol %;  $K = 0.92$  for the LB film with  $c_{cr} = 9$  mol %).

In closely packed multimolecular dye films, effective aggregation processes occur that are revealed by changes in the form and position of the maxima of absorption and luminescence bands. Since the chromophores of neighboring monolayers in Z-type films are separated by long hydrocarbon radicals, the dye aggregates form within the limits of one monolayer. Figure 3 shows the absorption spectra of dye **I** LB films.

The spectral curves have two maxima. The ratio of intensity between them depends on the  $c_{cr}$  in a film. As it rises, the short-wave maxima grow while the long-wave maxima diminish. The absorption spectrum of the LB film with  $c_{cr} = 9$  mol % is close to that of dye **I** in chloroform. The dye molecules in this film exist mainly in monomeric form; the long-wave band with  $\lambda_{max} = 580$  nm corresponds to these. The short-wave band with  $\lambda_{max} = 518$  nm observed in the films with high dye contents belong to molecular aggregates. In the coordinates of optical density ( $D$ ) divided by the number of molecules attributable to an area unit ( $\sigma$ ), all of the spectral curves cross at the isosbestic point (Fig. 3), indicating that there were only two absorption centers in each film: monomers and dye aggregates.

According to the exciton model of molecular aggregates [12], the excited  $S_1$  level in dimers splits to yield two sublayers with greater and lower energies, respectively. The probability of transitions from the ground state to one of the excited states depends on the mutual disposition of the dipole moments of the electron transition  $S_0 \rightarrow S_1$  among the monomers in a dimer. With a parallel disposition of the moments, the allowed transition is short-wave; with a head-to-tail disposition, the transition is long-wave. The short-wave band in the spectrum of LB films is consequently due the absorption of sandwich-type dimers. As was already noted, however, it follows from an analysis of the compression isotherms of dye **I** monolayers that the chromophores are oriented parallel to the subphase surface at transfer pressure  $\pi_{trans} = 28$  mN/m on the surface of the aqueous subphase. Such conformation favors the formation of planar dimers, the presence of which should result in a long-wave band with respect to the absorption of monomers. This discrepancy can be explained if we assume that the chromophore part of a dye molecule nevertheless emerge from the aqueous subphase's surface while growing on a rib. At this disposition of molecules, they effectively form dimers with a sandwich structure within the limits of one monolayer. According to conformational analysis, the limit area of an **I** molecule is  $60 \text{ \AA}^2$ , less than the experimental values for perpendicular chro-

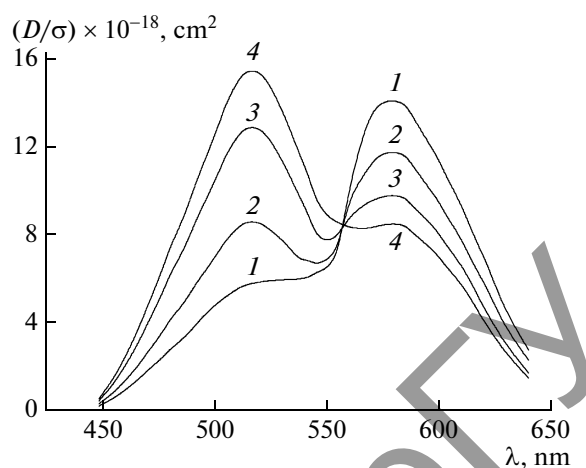


Fig. 3. Absorption spectra of LB films at different concentrations of dye **I** ( $c_{cr}$ , mol %): 1—9, 2—17, 3—50; 4—100.

mophore orientation and a vertical disposition of hydrocarbon radicals relative to the subphase's surface. The hydrocarbon tails in the monolayers of amphiphilic molecules are frequently known to be inclined relative to the water's surface, and the limit area occupied by dye molecules is thus increased [11]. In a pure dye monolayer the dimers, are oriented chaotically relative to each other and yield a monolayer in the liquid-stretched state that corresponds to its low ordering. The SA molecules in mixed monolayers occupy the available cavities between dye dimers. As was noted above, SA molecules can also be incorporated between the hydrocarbon radicals of a dye molecule. This results in a denser packing of monolayers and thus to the mixed monolayer transitioning to a more condensed state.

A variety of dye dimer conformations were analyzed to clarify the possible packing of dye molecules in a monolayer. Calculations were performed for the dimers of dye **II**, in which the molecular planes were parallel and shifted such that the hydrocarbon tails of the first molecule lay between the chains of the second molecule (Figs. 4c, 4d). The conformation presented in Figs. 4a, 4b had an energy of 21.2 kcal/mol, less than the energy of a single molecule (35 kcal/mol) and demonstrating the considerable energy advantage of this conformation. The distance between chromophores was  $4 \text{ \AA}$ . The energy of conformation presented in Figs. 4c, 4d was 31.5 kcal/mol. There was also an energy advantage relative to a single molecule, but it was 10 kcal/mol less than for the first dimer. Other conformations of dimers were considered as well, but they were less favorable energetically than the one shown in Fig. 4.

Polymethine dyes in the condensed state can form more complex aggregates than dimers (e.g., J-aggregates) [1, 6, 7]. One of the main structures of J-aggregates is brick-like layers whose building blocks are c- and d-type dimers (Fig. 4). However, the results from

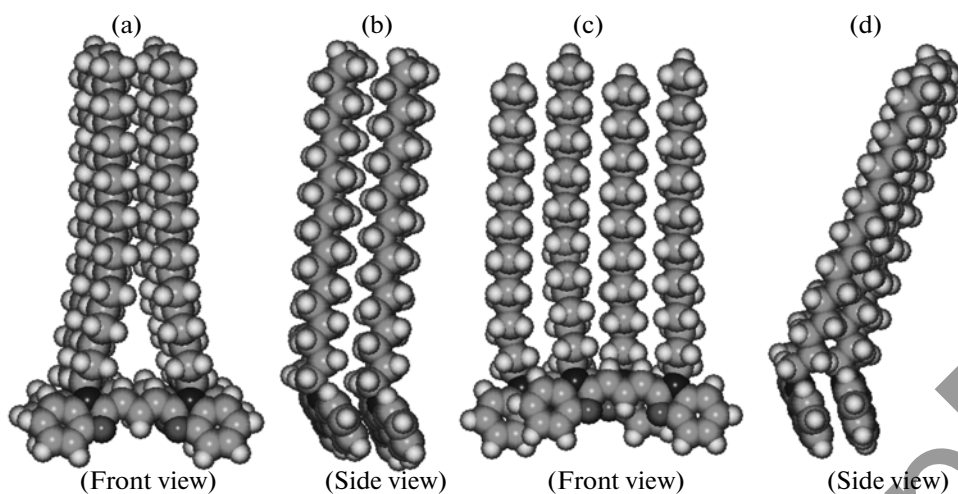


Fig. 4. Hypothetical conformations of dye II dimers simulated by means of molecular mechanics.

conformational analysis of dye II dimers and the spectral data of LB films show that sandwich-type dimers form in both monolayer and LB films. For this conformation of dimers, the angle of the slope between hydrocarbon radicals and the subphase's surface is  $71^\circ$ , at which the calculated molecular area corresponds to experimental values.

Effects similar to those of dye I LB films are observed in the absorption spectra of dye II LB films. As the dye concentration grows, short-wave dimer bands appear in the spectra. According to our conformational analysis of molecules (Figs. 5a, 5b), the most stable dimers are those of the sandwich type. The angle of the slope of dye I molecules' hydrocarbon chains to the surface of the aqueous subphase is  $50^\circ$ .

Two bands appear in the fluorescence spectra of dye I LB films upon excitation at the maximum of the dimeric absorption band (Fig. 5). The position of the more intense short-wave band with a maximum at 595 nm corresponding to monomeric emission coin-

cides with the fluorescence band of dye I in solutions. The position of the maximum of the broad long-wave band changes from 645 to 670 nm as the concentration of dye in mixed LB films grows, and it lies at a wavelength of 650 nm for the pure dye LB film. In mixed LB films, increased dye concentration raises the ratio between the intensities of long-wave and short-wave bands (Fig. 5). At  $c_{cr} = 9$  mol %, the first band takes the form of a shoulder; at  $c_{cr} = 50$  mol %, the intensities of both bands are commensurable. The quantum yield of film fluorescence declines upon an increase in  $c_{cr}$ .

These results can be explained as follows. As was noted above, sandwich-type dimers are found alongside monomers in dye I LB films, in which long-wave electron transitions are forbidden in the dipole approximation [12]. As result, dimers of this type generally cannot luminesce. Hence, the long-wave band in the fluorescent spectrum of dye I LB films cannot be attributed to dimers. The absence of additional bands in the absorption spectrum of these films and the presence of broad structureless fluorescence bands with large Stokes shifts testify to the excimer nature of long-wave emissions.

More favorable conditions for the formation of dye excimers can be created in LB films than in liquid solutions. Classic excimers are formed from unexcited M and excited  $M^*$  monomeric molecules. To accomplish this, they must not only manage to encounter one another in the  $M^*$  molecule's lifetime but turn to face each other with opposite charges to form labile  $M \cdots M^*$  donor-acceptor complexes owing to the electrostatic attraction of these charges. The times of polymethine dye diffusion in solutions are usually longer than the lifetimes of their excited state [13]. It is therefore quite rare for excimers to form from the monomeric M and  $M^*$  molecules of polymethins in solution.

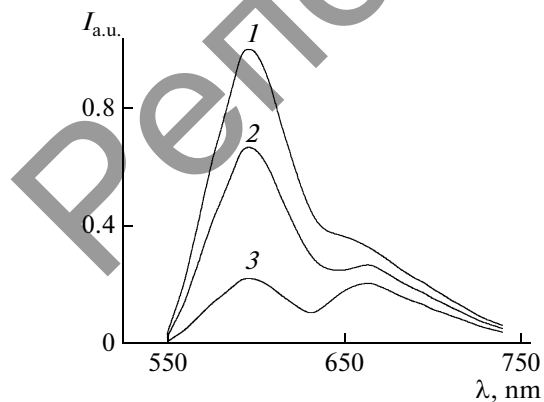
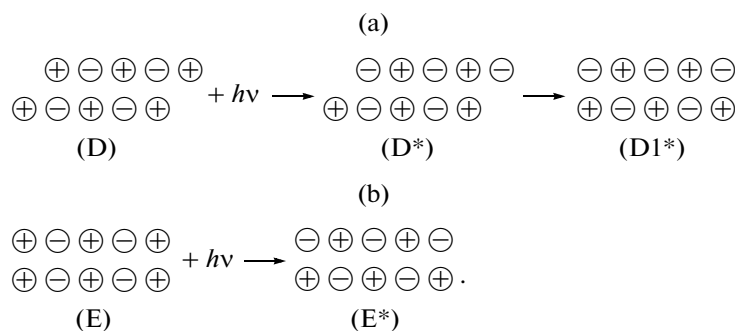


Fig. 5. Fluorescence spectra of LB films at different concentrations of dye I ( $c_{cr}$ , mol %): 1—9; 2—17; 3—50.



**Fig. 6.** Scheme of the formation of excited dimers in (a) solutions and (b) excimers in LB films based on cationic polymethine dyes.

It should be less likely for such things to occur in LB films, since there is no possibility of the molecules reorienting themselves after excitation. At high dye concentrations, the dyes are capable of aggregating both in solutions and in films. Planar polymethine with no voluminous substituents in type **I** and **II** carbocyanine molecules form associates with sandwich structures [8]. Along with dispersion interactions between the light polarized bonds of  $\pi$ -systems, they can be stabilized by the electrostatic attraction of the opposite charges of polymethine chain atoms in which partial positive and negative charges alternate. For the electrostatic stabilization of monomeric molecules in a dimer, they must be shifted such that their opposite charges overlap each other. Structure D in (Fig. 6a) the scheme of excited dimer formation in solutions and (Fig. 6b) excimer in LB films based on cationic polymethine dye corresponds to such a disposition.

It can easily form in solution. Upon the absorption of a light quantum, the sign of the charge in the polymethine dye chain is reversed [8]. Since this is a one-quantum process, a single dimer molecule is recharged, resulting in an excited dimer structure. The repulsion between the identical charges of its monomeric molecules prevents the formation of excimers. For these to form, they must be shifted relative to one other along their long molecular axes (structure D1\*), which takes time. Their emergence from dimers is therefore problematic in solution.

It follows from conformational simulations and from the experimental isotherms presented above that the formation of E type sandwiches is preferable in LB films of dyes. The disposition of such monomers in a dimer with identical charges opposite one another is apparently due to the laws of dense packing and is originally determined by the directional orientation of the hydrophilic and hydrophobic parts of the dye molecule in the polar and nonpolar phases of the initial solution, respectively. It is then fixed by compression under pressure. Upon the absorption of light quanta by E-type dimers in LB films of dyes, monomeric molecules are strongly attracted to one another due to the emergence of opposite charges forming

excimers. It is revealing that their formation from dimers in LB films does not require the reversal or shift of charged centers relative to one another, since it occurs when excimers form in solutions. Their formation in the first instance is thus more advantageous than in the second.

The number of dimers grows as the dye concentration increases, as is confirmed by the changes in the absorption spectra of LB films (Fig. 3). As result, the number of excimers also grows, raising the intensity of the long-wave band. Depending on the concentration of dye in a film, the shifts of this band are due to the influence of the short-wave band, which when added to the long-wave band moves the latter into the range of low frequencies in the overall spectrum. It is interesting that the intensity of the long-wave band is low for an LB film of an individual dye. The denser molecular packing in more condensed mixed dye and SA layers more allows them to adopt conformations that are energetically more advantageous for the formation of excimers in a dimer. The drop in the fluorescence quantum yield of LB films with rising dye concentration due to the migration of electron excitation energy from monomers to nonluminescent dimers, which serve as energy traps. The existence of energy transfer is confirmed by the excimer band observed along with the monomeric band in the film's fluorescence spectrum upon excitation of the monomer absorption band.

Two bands are also observed in the luminescence spectrum of dye **II** LB films: a monomeric (515 nm) and a broad excimer band (600 nm). The short-wave band is lower in intensity at all dye concentrations, and the long-wave band is higher in intensity. This indicates that excimers are formed in dye **II** LB films more effectively than in dye **I** LB films, since oxygen atoms create fewer steric hindrances to sandwich formation in oxacarbo-cyanine **II** than sulfur atoms in thiooxacarbo-cyanine **I**. The intensity of the long-wave maximum increases with rising dye concentration.

## CONCLUSIONS

The spectral and luminescent properties of new amphiphilic cationic polymethine dyes in solutions, polymeric matrices, and Langmuir–Blodgett films were studied. The spectral and luminescent properties of thiocarbocyanine were found to be virtually identical.

Our study of the phase behavior of single and mixed monolayers on the surface of a water–air interface established that adding fatty acid results in denser packing of the dye molecules in a monolayer and raises the coefficient of film transfer onto solid substrates.

The spectral and luminescent properties of dyes both in solutions and in LB films were shown to differ substantially. The short-wave band of dimer absorption was observed along with the monomeric absorption band in solid LB films. A conformational analysis of dye dimers was conducted for different conformations to study the possible packing of dye molecules in a monolayer. The formation of sandwich-type dimers was found to be preferable for both thiocarbocyanine and oxacarbocyanine.

Low-intensity excimer fluorescence was observed along with intense emission band of monomers in the fluorescence spectra of thiocarbocyanine LB films. For oxacarbocyanine, the intensity of excimer fluorescence was considerably higher than the intensity of monomer emission. This can be explained by differences between the processes of dye molecule aggregation. They form sandwich-type associates both in solutions and in LB films, but their structures differ. In solutions, the monomeric molecules in dimers are shifted relative to each other along their long axes. In LB films, they are strictly parallel. Such dispositions and the dense molecular packing in these films results in dye excimers being formed from dimers. The for-

mation of excimers is intense in LB films based on oxacarbocyanine molecules, since oxygen atoms create fewer steric hindrances to sandwich formation in carbocyanine than do the sulfur atoms in thiocarbocyanine.

## REFERENCES

1. E. A. McArthur, J. M. Godbe, D. B. Tice, and E. A. Weiss, *J. Phys. Chem. C* **116**, 6136 (2012).
2. I. V. Kurdyukova and A. A. Ishchenko, *Russ. Chem. Rev.* **81**, 258 (2012).
3. L. M. Blinov, *Sov. Phys. Usp.* **31**, 623 (1988).
4. H. Kuhn, D. Mubiuss, and H. Bucher, *Physical Methods of Chemistry I* (Wiley, New-York, 1972), p. 577.
5. A. A. Ishchenko, *Russ. Chem. Rev.* **60**, 865 (1991).
6. F. Würthner, T. E. Kaiser, and C. R. Saha-Möller, *Angew. Chem., Int. Ed. Engl.* **50**, 3376 (2011).
7. B. I. Shapiro, *Nanotechnol. Russia* **3**, 139 (2008).
8. A. A. Ishchenko, *Structure and Spectral Luminescent Properties of Polymethine Dyes* (Naukova Dumka, Kiev, 1994) [in Russian].
9. L. V. Leyshin and A. M. Saletskii, *Luminescence and Its Measurements* (Mosk. Gos. Univ., Moscow, 1989) [in Russian].
10. T. Clark, *A Handbook of Computational Chemistry* (Wiley, New York, 1985).
11. A. Adamson, *The Physical Chemistry of Surfaces* (Wiley, New York, 1976).
12. A. S. Davydov, *Theory of Molecular Excitons* (Nauka, Moscow, 1968; Plenum Press, Oxford, 1971).
13. R. Grigonis, N. A. Derevyanko, A. A. Ishchenko, and V. Sirutkaitis, *Quantum Electron.* **31**, 1027 (2001).

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