



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 31 Aug 2006

To cite this article: V. I. Alekseeva, L. E. Marinina, L. P. Savvina, N. Kh. Ibrayev & A. M. Zikirina (2005): Spectral and Luminescent Properties of Nile Red Dye in Langmuir-Blodgett Films, *Molecular Crystals and Liquid Crystals*, 427:1, 159/[471]-166/[478]

To link to this article: <http://dx.doi.org/10.1080/15421400590892163>

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## Spectral and Luminescent Properties of Nile Red Dye in Langmuir-Blodgett Films

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*We report the investigation findings of monolayers behaviour of nile red new synthesized amphiphilic analog at the air/water interface and its spectral-luminescent properties in solvents of various polarity and in Langmuir-Blodgett films consisting of dyes and stearic acid mixture. It is shown, that electronic absorption spectra of films depends on the presence of two monomer types of various spatial conformations. The position of the films fluorescence band is identical to a case of polar medium.*

**Keywords:** dye; fluorescence; Langmuir-Blodgett film; nile red; singlet state

## INTRODUCTION

Nile red is related to the class of oxazine dyes and is widely applied as a laser dye and an active material for light-emitting diodes [1,2]. The usage of nile red as a fluorescent probe for definition of micropolarity of medium has been shown in works [3–5]. Sensitivity of luminophore to polarity of medium is stipulated by substantial growth of dipole moment of the molecule at its transferring in the excited singlet state. Such feature of the molecule is connected with its structure, the electron-donating diethylamino group attached to an electron withdrawing

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rigid aromatic fragment by means of a single bond makes the rotate of one group about the other possible. In polar medium electron transfer from diethylamino group to an acceptor of a benzene ring is accompanied by a twist of one moiety about the other. The geometrical deformation of the molecule results in a modification of the dipole moment that is reflected in spectral and luminescent properties of the dye. In work [6] from the mixed Langmuir-Blodgett films molecules non-amphiphilic nile red and stearic acid double fluorescence which authors connect with the existence in the monomer monolayer of planar and perpendicular conformation was observed.

In works [7–9] it has been shown, that spectral and luminescent properties of xanthene dyes in Langmuir-Blodgett films depend on nanoarchitecture of the monolayer. By a modification of the surface pressure in the monolayer it is possible to influence dimensional orientation carboxphenil ring concerning the plane of the molecule that results in alteration of bands of absorption and fluorescence. In the given work study outcomes of spectral and fluorescent properties of the new amphiphilic nile red dye in solutions of different polarity and Langmuir-Blodgett films are reduced.

## EXPERIMENTAL METHODS

The molecular structure of the dye is shown on Figure 1. The dye was synthesized in Russian Scientific Centre (NIOPIC).

Monomolecular films were generated at the air-water interface in Langmuir bath. There was used bidistilled and deionized water. The surface tension of water was 72.8 dyn/cm at pH = 5.6 and at T = 20°C. In order to draw on the subphase surface solutions of the dye and stearic acid in chloroform are used. Stearic acid was refined by crystalline modification from ethanol solution. Before drawing quartz substrates for a period of several hours were withstood in chrome mixture. After flush with a great deal of distilled water and drying, the surface of the substrate was polished.

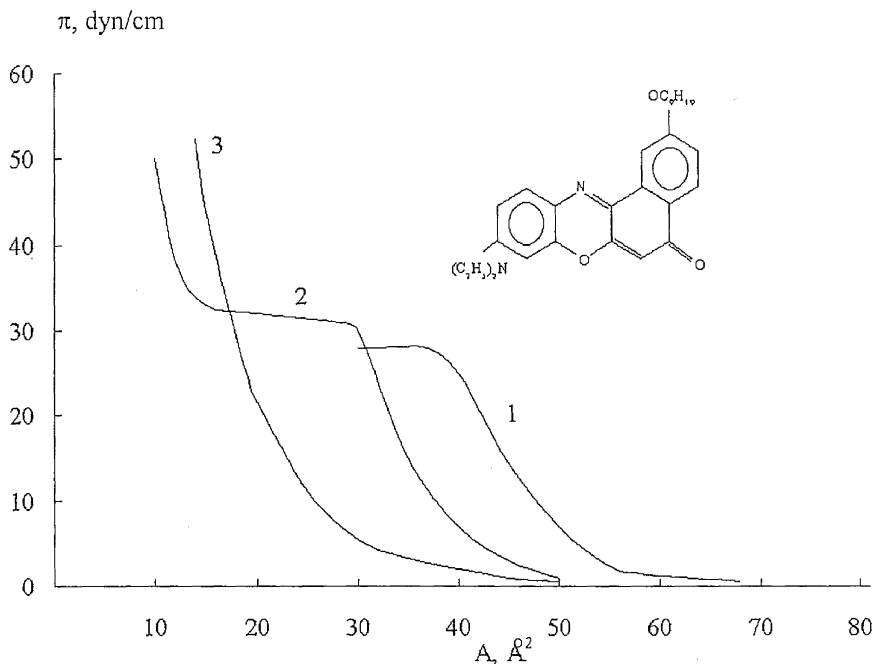
There have been received films of clear luminophore and bipropellant monolayers of dye molecules and Stearic acid at a modification of luminophore concentration from 2 mol% up to 100 mol%. The transmission of monolayers on quartz substrates was carried out by the vertical method according to Z- and Y-types at travelling speed of the plate 0.02 mm/sec and pressure of transmission  $\pi = 27$  dyn/cm. The transfer coefficient of the mixed films has made  $0.96 \pm 0.2$ . In case of clear dye it was much lower.

Absorption and fluorescence spectra were recorded by standard spectroscopic devices.

## RESULTS AND DISCUSSION

Figure 1 shows  $\pi$ -A-isotherm for the dye monolayer (the curve 1). It represents a case of the liquid-extended film with a horizontal field at values  $\pi = 28$  dyn/cm and  $A < 38 \text{ \AA}^2$ . From the obtained curve the area occupied by one dye molecule equal to  $A = 50 \pm 5 \text{ \AA}^2$  has been defined. It is possible to assume, that in the liquid-condensed state (lower than  $\pi = 28$  dyn/cm) the close packing of molecules perpendicularly to the water surface is observed. Such structure of the monolayer is traced from proximity of the limiting area  $A = 50 \pm 5 \text{ \AA}^2$  and efficient cut of the molecule along the lengthy axis of its aromatic fragment ( $55.83 \text{ \AA}^2$ ). The last value was rated from geometrical sizes of Nile Red molecule in vacuum by method MMP2/10/.

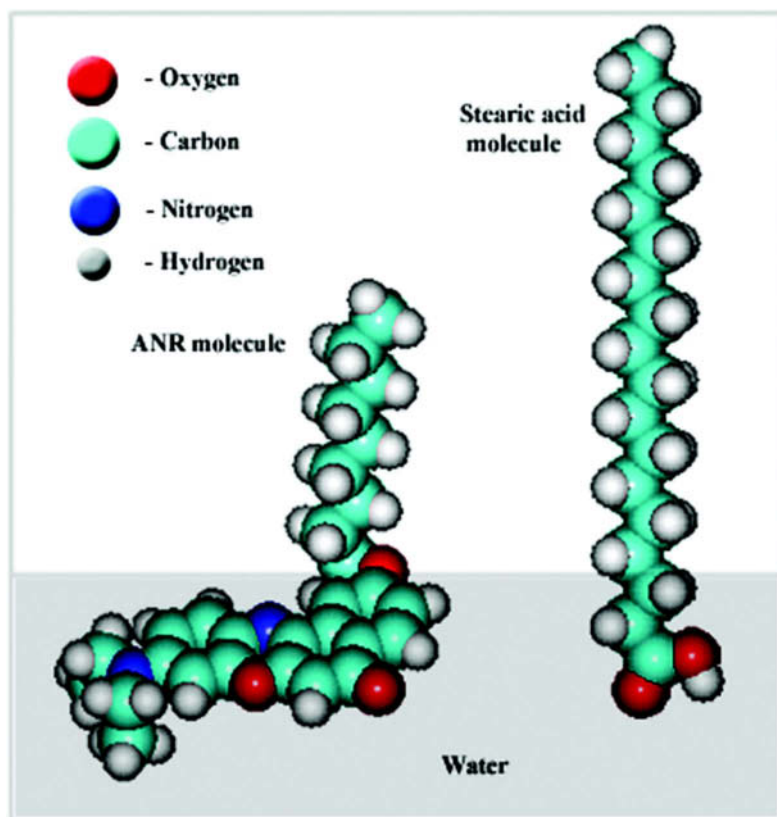
The appearance of the plateau on the curve 1 can be caused by conformational changes in the monolayer. Probably dye molecules rearrange so that to stand on the perpendicular to the water surface, or some molecules appear outside the layer. At the values of surface



**FIGURE 1**  $\pi$ -A-isotherm of monolayers of ANR (1), ANR + SA (2) and SA (3) molecules on the water surface. In the inset the structural formula of ANR dye is shown.

pressure  $\pi$  conforming to the horizontal field of isotherm 1, on the sub-phase surface the deformation of the monolayer is visually observed, and an inhomogeneous film is formed. More homogeneous is not formed at sonicating of the monolayer even for a period of several hours. Therefore, the observable inflection apparently indicates a collapse of the condensed phase. Figure 2 schematically shows dye and stearic acid molecules orientation on the water/air interface.

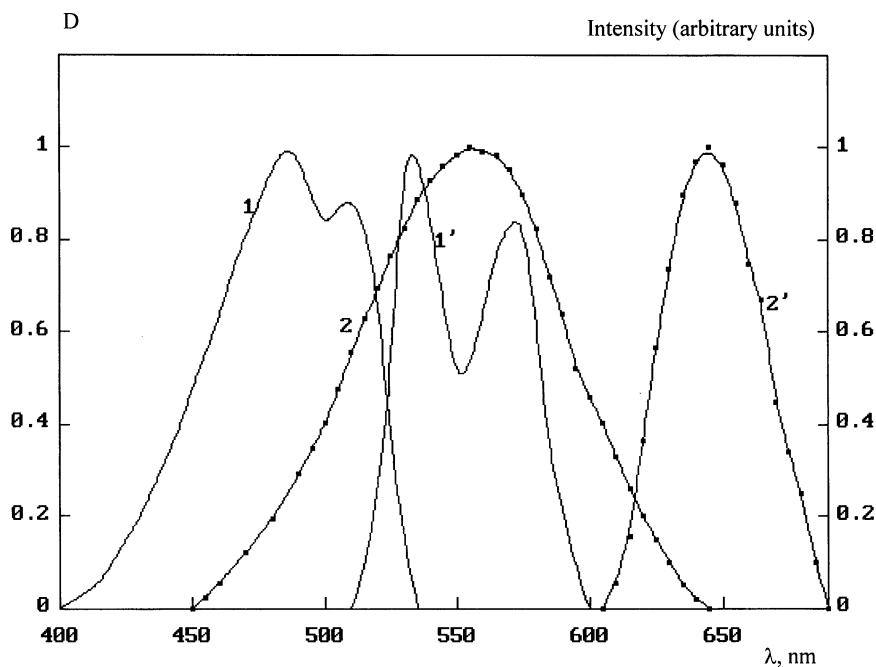
Figure 1 also shows the isotherm for the mixed monolayer of dye molecules and Stearic acid (the curve 2,  $C_{\text{dye}} = 50 \text{ mol}\%$ ). At low pressure the mixture behaves so, as if the film surface is determined by molecular sizes of luminophore. The pressure of the collapse in this case is  $\pi = 31 \text{ dyn/cm}$ . It can be connected with the small effect of cohesion with Stearic acid molecules. Above 35 dyn/cm the average area comes



**FIGURE 2** Schematic representation of ANR and stearic acid molecules orientation on the water/air interface.

to  $10 \text{ \AA}^2$  per one molecule. It indicates appearance of closely packed Stearic acid monolayer. Dye molecules are displaced out off the film. Further the pressure sharply increases at  $\pi = 48 \text{ dyn/cm}$  until Stearic acid layer will also start collapsing. The form of isotherms does not depend on the correlation of the mixture components concentration. The increasing of Stearic acid molar ratio results only in the modification of length of the horizontal area. Such situation is typical for the mixture of two mutually unsolvable elements/11/.

Figure 3 shows absorption and fluorescence spectra of Nile red in heptane (curves 1, 1') and ethanol (curves 2, 2'). It is evident from the picture, that the absorption spectrum maxima shifts from 485 nm in heptane up to 555 nm in ethanol. The fluorescence spectrum in heptane has a maximum at  $\lambda = 530 \text{ nm}$ . In ethanol the fluorescence maximum is  $\lambda = 640 \text{ nm}$ . The observed solvatochromic shifts in the absorption and fluorescence band maxima are according to the conclusions of works connections of works [6,12] in which authors connect analogous spectral regularities and growth of medium polarity with

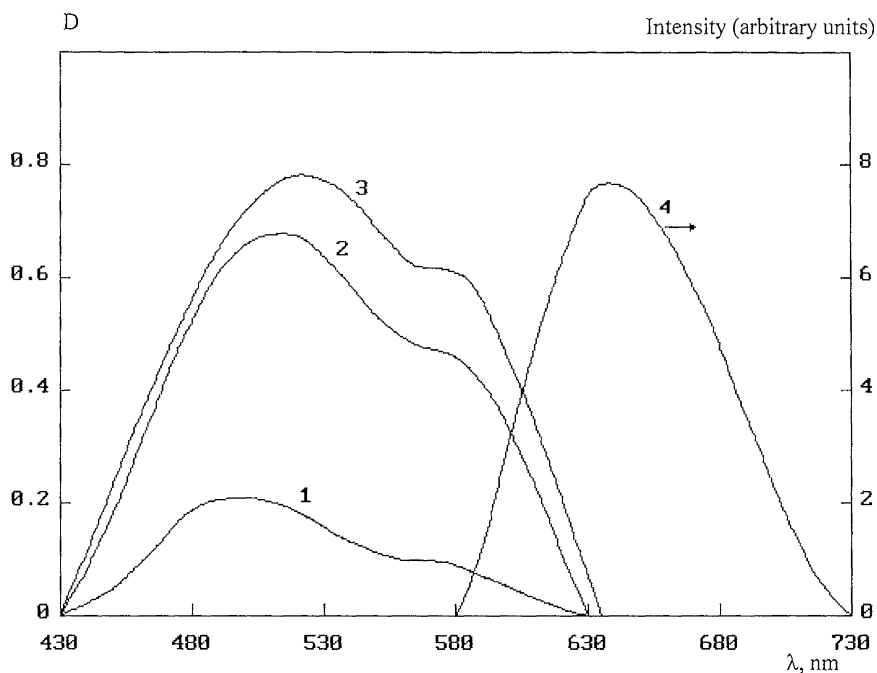


**FIGURE 3** Absorption (1, 2) and fluorescence (1', 2') spectra of ANR in heptane (1, 1') and ethanol (2, 2').

increase of dipole moment Nile red molecules in an excited singlet state because of the intramolecular electron transferring.

Figure 4 shows absorption spectra (curves 1–3) of the mixed Langmuir-Blodgett films Nile Red and Stearic acid at their various ratios. In the 430–630 nm region the broad absorption band with two distinct maxima is observed. The usage of the first derivative absorption spectrum method has shown, that short-wave peak for the lowest dye concentration (the curve 1) is  $\lambda = 495$  nm and shifts to  $\lambda = 520$  nm at the ratio of dye and Stearic acid 3:1. The long-wavelength peak  $\lambda_{\text{max}} = 560$  nm for 1:20 also has small red shifts at increase of dye concentration. The ratio of a long-wavelength maximum intensity to short-wave intensity grows with the increase of dye concentration in the monolayer.

Fluorescence spectrum (Fig. 4, the curve 4) is a structureless broad band with a maximum at 640 nm. The increase of dye concentration in the indicated interval of the monolayer has led only to the rise of integral fluorescence intensity without a modification of the spectral



**FIGURE 4** Absorption (1–3) and fluorescence (4) spectra of the mixed ANR and SA LB films at their various ratios in a monolayer: 1 – 1:20; 2 – 1:1; 3 – 3:1; 4 – 1:1.

distribution. It is remarkable, that the position of a band of fluorescence corresponds to a case of highly polar medium around of a fluorescence centre.

Presence in absorption spectra of two maxima, probably, should be referred to the presence of two types of Nile red monomeric molecules with various orientation of diethylamino group. The comparison of film absorption spectra with liquid solution absorption spectra shows, that short-wave maximum is formed by planar molecules, and maximum at 580 nm – shape molecules with perpendicular orientation of diethylamino group. Formation of monomeric structures with conformation, typical for highly polar medium, can take place in the monolayer at water/air interface when the main part of a molecule, except a hydrophobic fragment, is immersed into the water. Such molecular structure can be also stored at transferring of a monolayer to the firm substrate [7]. Common long-wavelength shift of Langmuir-Blodgett film spectra concerning liquid solution spectra and their broadening testify to a dispersion of  $S_1$ -levels because of the local heterogeneity of films structure [13]. Therefore to receive separate spectra is impossible. Existence of only one fluorescence band at  $\lambda_{\max} = 640$  nm testifies, that in the mixed films of Nile red and Stearic acid fluorescence centres are, mostly, molecules with perpendicular orientation of diethylamino group. The absence of molecule fluorescence having maximum of absorption at 500 nm can be connected with migration of excited energy on inhomogeneously extended  $S_1$ -levels and its localization on the singlet-excited level of nonplanar molecules.

Thus, as a result of the carried examinations it is revealed, that molecules of Nile red synthesized amphiphilic analog derivate with stearic acid stable monolayers at water/air interface. In the liquid-condensed state of the monolayer the plane of chromophore part of dye molecules is oriented perpendicularly to water surface. The given orientation of luminophore molecules in the monolayer is also stored at its transferring on the firm substrate.

Absorption spectra of firm Langmuir-Blodgett films can be considered as a superposition of two types spectra of monomeric molecules with planar and perpendicular orientation of diethylamino group concerning the plane chromophore part. The position of the fluorescence film band is typical for a case of polar medium around the fluorescence center.

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