Characterization of Pure and Mixed Langmuir and Langmuir-Blodgett Films of Some Fluorescent Naphthalimide Dyes

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Langmuir and Langmuir-Blodgett (LB) films formed of some fluorescent dyes, derivatives of 4-aminonaphthalimide, and their binary mixtures with the liquid crystal 4-heptyl-4′-cyanobiphenyl (7CB) have been studied. Surface pressure versus mean molecular area isotherms for Langmuir films have given information about the alignment of molecules in a monomolecular layer at the air/water interface. The absorption and fluorescence spectra of LB films have revealed the occurrence of aggregates among dye molecules. In the ground electronic state some fraction of aggregates of J-type have appeared, while in the excited state the excimers have been created. The latter statement has been confirmed by additional absorption and fluorescence measurements performed for dyes dissolved in 7CB and placed in sandwich cells of 10 μm in thickness.

Key words: Naphthalimide Dye; Liquid Crystal; Langmuir-Blodgett Film; Electronic Absorption Spectra; Fluorescence Spectra.

1. Introduction

Recently, the display devices based on organic materials own very attractive prospects. It is forecasted that in a short time, organic light emitting diodes (OLEDs) [1] will be strongly competing with the today most popular displays, namely liquid crystal displays. Since the highest driving efficiency can be achieved when the organic layer in OLED is self-emitting, the materials with high luminance, high efficiency, saturated emission and substantial lifetime are intensively sought. A very important matter for the organic layer used in OLEDs is also that it is a good charge transporter. It is well known that the transport of charge carriers in organic compounds will be favoured by increasing molecular order. One of the possibilities to achieve highly ordered molecular layers is the utilization of the Langmuir-Blodgett (LB) technique [2 – 4]. This technique is a unique method which allows to fabricate ultrathin ordered layers from certain molecules or particles, the architecture of which can be manipulated with ease. This allows to optimize specific physical parameters of a material and therefore LB films are today an integral part in the field of molecular electronics [2].

The first required step for the successful LB film fabrication is creating a stable compressible monolayer at the air/water interface (Langmuir film) [2 – 5]. It is well known that water-insoluble amphiphilic molecules are able to form Langmuir films, and that they can be transferred onto solid substrates forming LB films [2 – 5]. There are, however, other molecules, which, despite being non-amphiphilic, can form stable Langmuir and LB films. Among them are such dyes as rhodamine B [6], pyrene [7], porphyrins [8, 9], phthalocyanines [9, 10], derivatives of perylene [11 – 14], derivatives of fluorescein [15], and derivatives of naphthoylenebenzimidazole [16 – 21]. Some years ago it was found in our laboratory that also several derivatives of 1,8-naphthalimide can create stable monolayers at interfaces [16 – 20]. Recently, novel groups of 1,8-naphthalimide (derivatives of 4-aminonaphthalimide) were synthesized [22], which are characterized by brilliant yellow colour and emit light with very high quantum yield in the spectral region advantageous for human eye, thus can be utilized as organic dyes or luminophors. First of all these compounds were prepared for colouration of polyester fabrics [22]. In our recent paper [23] we found, however, that derivatives of 4-aminonaphthalimide orient well in a liquid crystal matrix and do not destabilize the mesophase region of the liquid crystalline host. Therefore, they are very attractive for an application in passive and active guest/host

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liquid crystal displays [24]. In this paper we would like to check, if these dyes can be also utilized as an active layer in OLEDs.

We present the results of the study of Langmuir and LB films formed of derivatives of 4-aminonaphthalimide and their mixtures with the liquid crystal, 4-heptyl-4′-cyanobiphenyl (7CB). The analysis of the run of the surface pressure-mean molecular area isotherms for Langmuir films allows to estimate the molecular organization in monolayers at the water surface.

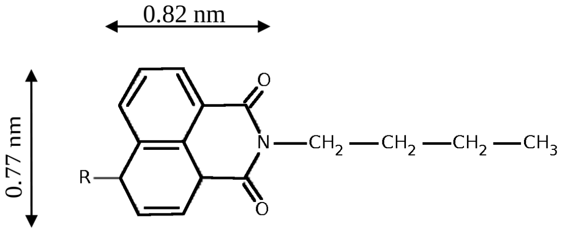
The electronic absorption and fluorescence measurements were used to determine the spectral properties of the dyes and the intermolecular interactions in ultrathin ordered films.

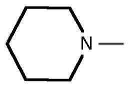
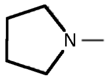
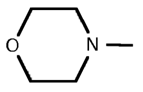
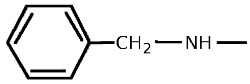
2. Experimental

The set of the dyes investigated consists of six derivatives of 4-aminonaphthalimide. Their synthesis is described in [22]. The chemical structure of the dyes, confirmed by ^{1}H NMR analysis, is given in Table 1. The liquid crystal 4-*n*-heptyl-4′-cyanobiphenyl (7CB) was purchased from the Dąbrowski Laboratory at the Military University of Technology, Warsaw (Poland) and was used without further purification. Solutions of dyes and 7CB were prepared in chloroform. Chloroform was of spectroscopic quality (Uvasol, 99.9%) obtained from Merck.

Langmuir and Langmuir-Blodgett films were formed in a Minitrough 2 (KSV Instruments Ltd., Finland). This trough was equipped with two barriers for monolayer compression. Water deionized by a Millipore Milli-Q system (Millipore Corporation, Austria) with a resistivity of 18.2 MΩ · cm was used as a subphase. The subphase temperature was maintained by a cooling circulator and kept constant at (20 ± 1) °C. Pure dyes **1**–**6** and their mixtures with 7CB in chloroform solution were spread drop by drop from a microlitre syringe (Hamilton, England). The chloroform was allowed to completely evaporate over a period of at least 15 min before compression of the monolayer commenced at a constant sweeping speed of 5 mm/min. The surface pressure π, at the air/water interface was measured by a Wilhelmy plate balance as a function of the mean molecular area A (π-A isotherm). Each isotherm was recorded at least three times to ensure the reproducibility of the results. Standard trough cleaning procedure was adopted between measurements.

Table 1. Molecular structure of dyes investigated.



dye code	R
1	
2	
3	$CH_3(CH_2)_3NH$ —
4	$(CH_3)_2N$ —
5	
6	

Langmuir monolayers were transferred onto solid substrates by the vertical dipping method with a lifting speed of 2 mm/min. Polished quartz plates (35 × 10 × 1 mm^3) were used as solid substrates with a hydrophilic surface. The transfer was made at surface pressures below the collapse point, which corresponds to the stage of the formation of the compressed monolayer. The dipping stroke was 25 mm. The transfer ratio was estimated by calculating the ratio of the decrease in the subphase area to the area on the substrate coated by the layer. Values between 1.00 and 1.20 were obtained. Successful deposition of pure 7CB and dye/7CB mixtures took place only on first raising the substrate.

The UV-Vis absorption spectra of LB films were recorded on a Varian CARY 400 spectrophotometer, and the fluorescence measurements were carried out with a photon-counting spectrofluorimeter built in our laboratory and described in detail in reference [25].

The exciting light was the 436 nm line from a high-pressure mercury lamp. Both in the absorption and fluorescence measurements the incident light beam was normal with respect to the film plane. The spectra were recorded for various molar fraction (X_M) of a dye, from 1.0 to 0.1 at room temperature. In order to analyze the spectra in wide range of a dye concentration, some supplementary absorption and fluorescence measurements of 4-amino-naphthalimide derivatives dissolved in 7CB were performed in sandwich cells made of two glass plates separated by the spacer of 10 μm in thickness. Such cells allowed to record absorption and fluorescence spectra of dye/7CB mixtures at X_M from $3.6 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$. In order to avoid additional (anisotropic) effects, all measurements in the cells were made in the isotropic phase of 7CB (T = 44 °C).

3. Results and Discussion

3.1. Surface Pressure-Mean Molecular Area Isotherms

The measurement of the surface pressure versus the average area available for one molecule at the constant temperature (π-A isotherm) is the most basic and widely used technique for the characterization of Langmuir films [2–5]. For monolayers, π is defined as the surface tension of pure subphase minus the surface tension of the subphase/monolayer system. In our experiment, the isotherms were recorded both during the compression and expansion processes and no significant differences in the two runs were found. We take this to indicate that equilibrium conditions have been attained.

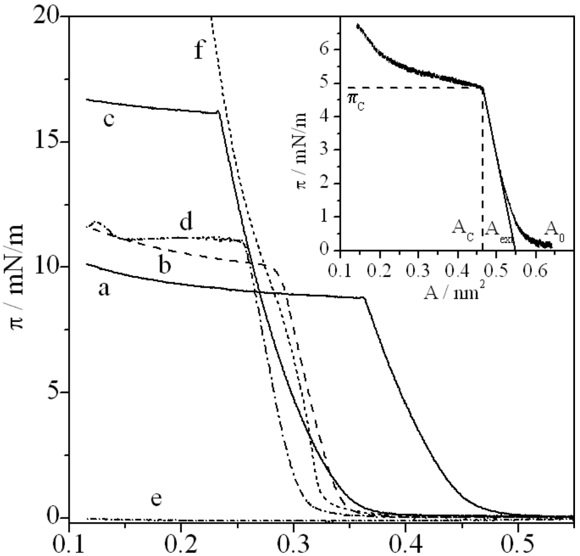


Fig. 1. Surface pressure-mean molecular area isotherms for Langmuir films of dyes **1**–**6**: **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), and **6** (f).

Table 2. Values of the area per molecule, collapse pressure π_c and average angle ϕ_{av} between the normal to the water surface and rigid molecular cores, for derivatives of 4-amino-naphthalimide mixed with 7CB in Langmuir films for various molar fractions X_M.

Substance	X_M	A_0/nm^2	A_{ext}/nm^2	A_C/nm^2	π_C/mN·m^{-1}	ϕ_{av}/deg
1/7CB	1.0	0.52	0.42	0.36	8.7	35
	0.8	0.43	0.31	0.30	9.0	30
	0.6	0.41	0.32	0.25	9.4	26
	0.4	0.41	0.31	0.26	8.7	29
	0.3	0.44	0.34	0.31	7.3	40
	0.2	0.47	0.38	0.32	6.0	40
	0.1	0.46	0.38	0.33	5.3	43
2/7CB	1.0	0.38	0.34	0.28	9.8	26
	0.8	0.38	0.30	0.24	9.8	24
	0.6	0.37	0.29	0.25	10.0	26
	0.4	0.37	0.31	0.25	8.3	28
	0.3	0.44	0.34	0.27	6.8	38
	0.2	0.46	0.39	0.31	5.6	38
	0.1	0.42	0.37	0.31	5.2	40
3/7CB	1.0	0.40	0.31	0.23	16.2	21
	0.8	0.42	0.32	0.23	15.7	23
	0.6	0.43	0.33	0.25	14.2	26
	0.4	0.44	0.35	0.27	9.8	30
	0.3	0.53	0.42	0.33	7.7	40
	0.2	0.50	0.42	0.35	7.1	44
	0.1	0.51	0.44	0.37	5.4	50
4/7CB	1.0	0.36	0.30	0.25	10.9	23
	0.8	0.28	0.22	0.16	10.4	16
	0.6	0.25	0.19	0.14	10.1	14
	0.4	0.32	0.27	0.21	7.8	23
	0.3	0.34	0.31	0.25	5.9	34
	0.2	0.38	0.33	0.28	5.8	34
	0.1	0.43	0.40	0.33	5.2	43
5/7CB	0.5	0.25	0.22	0.16	6.4	17
	0.4	0.32	0.26	0.21	7.2	23
	0.3	0.34	0.31	0.23	6.3	26
	0.2	0.37	0.33	0.26	5.9	31
	0.1	0.40	0.40	0.30	5.1	38
6/7CB	1.0	0.38	0.33	0.29	8.0	27
	0.8	0.40	0.36	0.30	9.1	30
	0.6	0.36	0.32	0.25	11.6	26
	0.4	0.37	0.31	0.24	13.2	27
	0.2	0.39	0.36	0.30	6.8	37
	0.1	0.46	0.43	0.35	5.1	46
7CB	0.0	0.47	0.43	0.37	4.9	52

Figure 1 shows π-A isotherms for derivatives of 4-aminonaphthalimide under investigation. It is seen that, except dye **5**, all other dyes form a compressible

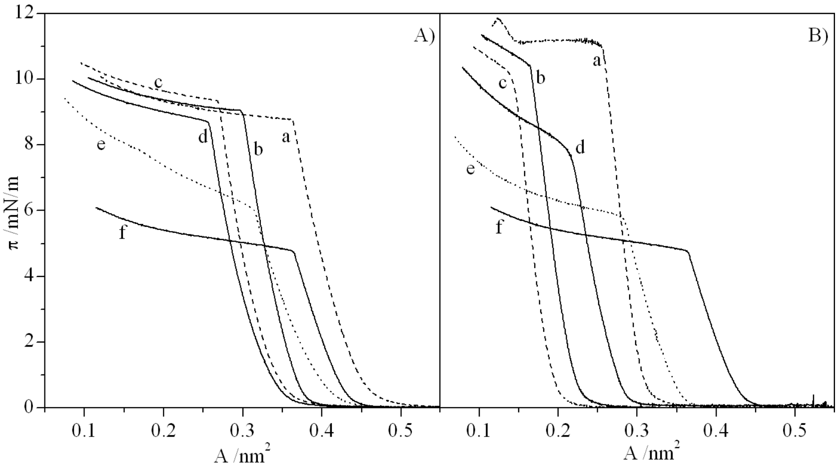


Fig. 2. Surface pressure-mean molecular area isotherms for Langmuir films of **1**/7CB (A) and **4**/7CB (B) mixtures; the molar fraction of dye $X_M = 1.0$ (a), 0.8 (b), 0.6 (c), 0.4 (d), 0.2 (e), and 0.0 (f).

floating monolayer at the air/water interface. The increase in π begins at the area equal to A_0 being the first edge of the phase transition. It indicates the formation of the compressed monolayer, which collapses at the area A_C and the surface pressure π_C. The collapse point is recognized as the point in the isotherm where the ratio $\partial\pi/\partial A$ begins to decrease due to the next phase transition.

The shape of π-A isotherm for derivatives of 4-aminonaphthalimide is strongly dependent on the molecular structure of the substituent R. In the case of the dyes **1** – **4**, behind the collapse point a broad plateau region is observed, however with the different surface pressure value, while in the case of dye **6**, the pressure rises monotonically with a decrease of the available area. The steepness of the isotherms is also different for various dyes, which means that not only the stability, but also the rigidity of the monolayer strongly depends on the substituent R.

The examples of π-A diagrams for Langmuir films formed from dye/7CB mixtures are shown in Figure 2, together with the isotherms of pure compounds. The π-A isotherms for **1**/7CB (Fig. 2A) and **4**/7CB (Fig. 2B) mixtures with different molar fraction (X_M) of a dye are presented there. The π-A run for pure liquid crystals 7CB is in agreement with that given in literature [26].

Table 2 contains the characteristic values of π-A isotherms for the Langmuir films of pure dyes, 7CB and dye/7CB mixtures with different X_M of a dye. The following data are presented: A_0 – the value of the area at which π starts to rise, A_{ext} – the value of the area obtained by extrapolating the tangent of the tilt angle of the π-A plot (the part representing the compensated monolayer creation) to $\pi = 0$ (see insert in Fig. 1), A_C – the value of the collapse area, and π_C – the value of the collapse pressure. It is seen that dye **5** mixed with 7CB is able to create the Langmuir film up to $X_M = 0.5$.

A cross-sectional area of the naphthalene skeleton with two –C=O groups, being the rigid central part of molecules of 4-aminonaphthalimide derivatives, calculated on the basis of the space-filling model, including van der Waals radii of the terminal atoms [27], is 0.63 nm^2. Thus, the results presented in Table 2 for pure dyes show that in compressed monolayers the molecules neither lie flat at the water surface nor assume the edge-on configuration. It is reasonable to assume that the rigid cores of the molecules must be tilted with respect to the water surface. Table 2 contains the values of the tilt angle ϕ_{av} estimated as the average angle between the rigid molecular core of the dyes investigated and the normal to the water surface in compressed monolayer just before the collapse point.

From the analysis of the shapes of the isotherms and the data given in Table 2 for the Langmuir films formed from binary mixtures of derivatives of 4-aminonaphthalimide with the liquid crystals 7CB follows that the packing density of molecules as well as the rigidity and the stability of the monolayer at the air/water interface depend strongly not only on the molecular structure of the dye substituent but also on the film composition. The value of π_C for 7CB is smaller, whereas A_{ext} and A_C values are greater, than the appropriate values for the dyes investigated (except of dye **1**, where the values of A_{ext} and A_C for 7CB and the dye are similar). With the rise of the dye content in the mixture, π_C increases and A_C decreases, although

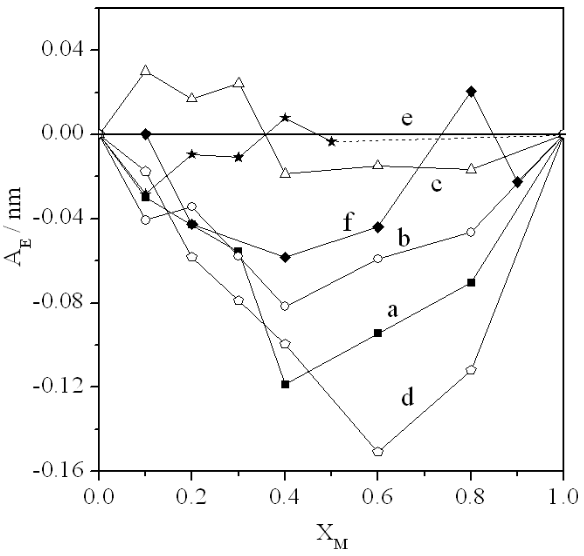


Fig. 3. Plot of excess of mean molecular area A_E for Langmuir films of dye/7CB mixtures versus the molar fraction of a dye X_M at $\pi = 3.5$ mN/m: **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), and **6** (f).

irregularly. The smallest A_C values are observed for mixtures with X_M of a dye between 0.4 and 0.8, depending on the dye. They are accompanied with the highest value of π_C. This indicates that at such a concentration of the dye the most dense molecular packing at the water surface occurs and simultaneously the film has the greatest stability.

The changes of the isotherm run with the Langmuir film composition for the dye/7CB mixtures indicate on interactions between dye and liquid crystal molecules. The kind of these interactions can be followed in Figure 3, in which the excess of the average area per molecule, A_E, as a function of X_M of a dye for the dye/liquid crystal mixtures in the Langmuir films is presented. A_E is defined as follows [5]:

$$A_E = A_{12} - (X_{M1}A_1 + X_{M2}A_2), \tag{1}$$

where A_{12} is the average molecular area in the two-component film, X_{M1} and X_{M2} are the molar fractions of the components, and A_1 and A_2 are the single component areas at the same π. For the data given in Figure 3 the values of A were taken at $\pi = 3.5$ mN/m.

The value of A_E is very helpful to establish whether in Langmuir films formed of binary mixtures the miscibility or the phase separation occurs. If A_E is equal to zero, the average area per molecule follows the additivity rule, $A_{12} = X_{M1}A_1 + X_{M2}A_2$, which means that in the mixture ideal mixing or complete immiscibility occurs. Deviation from zero, either positive or negative, indicates miscibility and non-ideal behaviour. The positive deviation from additivity rule is characteristic for miscible components with repulsive intermolecular interactions [5, 28]. The negative deviation means a contraction of the two-component films due to attractive interactions between dye and liquid crystal molecules [5, 28]. For dyes **1**, **2** and **4** mixed with 7CB the negative deviation in whole concentration range is observed. In the case of **6**/7CB mixture the negative deviation occurs at lower concentration, and at higher X_M the value of A_E is about zero. A_E values for **3**/8CB and **5**/8CB systems indicate that the interactions between dye and liquid crystal molecules are not very strong and their kind changes with the mixture composition. When $A_E \approx 0$, in order to decide whether in the mixture the complete mixing or the phase separation of components occurs, a second criterion is needed. Additional information about the miscibility can be obtained from the surface phase rule [5]. This rule states that if the components are immiscible, the equilibrium spreading pressure (ESP) should be constant, independently of the mixture composition. In some cases, however, the ESP value is difficult to determine and, therefore, for systems where the Langmuir film collapse point is easily detectable, it is sufficient to estimate the collapse pressure π_C instead of ESP. The dependence of π_C on the composition of the Langmuir films formed from the dye/liquid crystal mixtures can be inferred from the data given in Table 2. In all the cases a change of π_C is observed, which for the mixtures of 7CB with dyes **1**, **2**, **4** and **6** confirms the miscibility of both components deduced on the basis of A_E. For **3**/7CB and **5**/7CB mixtures we can assume that we deal here also with good miscibility.

Knowing the angles ϕ for pure compounds and taking into account the mixture composition we try to estimate the average angle which create the rigid cores of molecules with the normal to the water surface in the mixed Langmuir films. The estimated values for mixtures of derivatives of 4-aminonaphthalide with 7CB are gathered in Table 2. From the data given in this table follows that the presence of 7CB molecules affects the alignment of dye molecules at the air/water interface. At the small dye content ($X_M \leq 0.4$) the increase of ϕ_{av} is observed, meaning that, in the mixed Langmuir films, the dye molecules assume more tilted arrangement with respect to the water surface.

Table 3. The maximum position λ_{max} and the half-bandwidth δ of the long wavelength absorption band of **1** – **6** in chloroform ($X_M = 10^{-7}$) and mixed with 7CB, in sandwich cell ($X_M = 5 \cdot 10^{-2}$) and in LB film ($X_M = 0.6$).

dye code	chloroform $X_M = 10^{-7}$		7CB, sandwich cell $X_M = 5 \cdot 10^{-2}$		7CB, LB film $X_M = 0.6$	
	λ_{max}/nm $\Delta\lambda = \pm1$ nm	δ/cm^{-1} $\Delta\delta = \pm10$ cm^{-1}	λ_{max}/nm $\Delta\lambda = \pm1$ nm	δ/cm^{-1} $\Delta\delta = \pm20$ cm^{-1}	λ_{max}/nm $\Delta\lambda = \pm1$ nm	δ/cm^{-1} $\Delta\lambda = \pm50$ cm^{-1}
1	410	4460	413	4560	429	4550
2	442	3470	445	4230	460	4200
3	430	3590	435	4000	453	3950
4	415	4470	415	4860	434^a	–^{b}
5	395	4510	398	3820	404^c	3900^c
6	424	3930	429	3940	442	3850

^{a} $X_M = 0.4$, ^{b} impossible to determine, ^{c} $X_M = 0.5$.

3.2. Electronic Absorption Spectra

The most stable monolayer on the water surface among dyes under investigation forms dye **3** (π_C is the highest – see Table 1). This is probably due to the presence of the long alkyl chain attached to the main molecular core, which plays the role of the hydrophobic part. Only the floating monolayer of pure dye **3** could be successfully transferred on the quartz slide. Other dyes made the LB films not before they were mixed with the liquid crystal 7CB.

Figure 4 shows the long wavelength absorption spectra of pure dye **3** in the LB films (solid curve) and, for comparison, dissolved in chloroform at $X_M = 10^{-7}$ (dashed curve), while in Figure 5 the absorption spectra for pure dye **3** (curve f), pure 7CB (curve a) and dye/liquid crystal mixtures at various molar fractions X_M of a dye (curves b – e) in the LB films are presented. Table 3 lists the positions of the maximum and the half-bandwidths of the long wavelength absorption band for dyes **1** – **6** in chloroform and mixed with 7CB, in the sandwich cell at the highest possible concentration ($X_M = 5 \cdot 10^{-2}$) as well as in the LB film at $X_M = 0.6$. Because of very small values of the absorbance, the uncertainty in the estimation of the half-bandwidth of the LB films is large and the values should be treated only as informative ones.

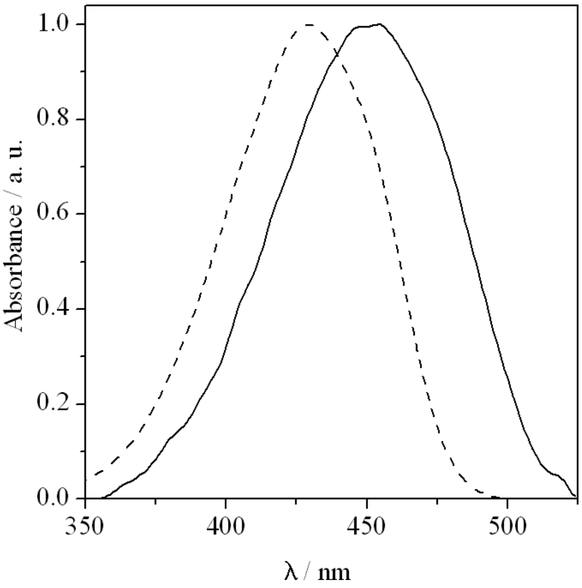


Fig. 4. Normalized long wavelength absorption spectra of pure **3** in LB film (solid curve) and in chloroform at $X_M = 10^{-7}$ (dashed curve).

The absorption spectra of 4-aminonaphthalimides in 7CB measured in the sandwich cell, except of dye **5**, reveal spectral broadening in comparison with those in chloroform, but the position of the maximum of the absorption band shifts no more than 5 nm. However, in LB films a bathochromic shift (up to 24 nm for pure dye **3**) is observed. Note that the molecular structure of the substituent R influences both the wavelength of the maximum and the width of the band. For various dyes the changes of the absorption maximum position of LB films with respect to those in chloroform are also different.

The shift and the broadening of the absorption band of **1** – **6** mixed with 7CB can be caused at least by three factors: (i) the different polarity of 7CB and chloroform, (ii) the surface interactions, occurring both in the sandwich cell and in the LB film, and (iii) the creation of some aggregates fraction between dye molecules. In many papers [6, 7, 14, 15, 18 – 21, 29] similar changes in the absorption spectrum of various dyes embedded in LB films with respect to that in diluted solutions were observed and they were explained mainly by the latter factor. Therefore, we attributed the broadening of the absorption band and the maximum shift of dyes **1** – **6** in 7CB to the occurrence of aggregates. Indeed

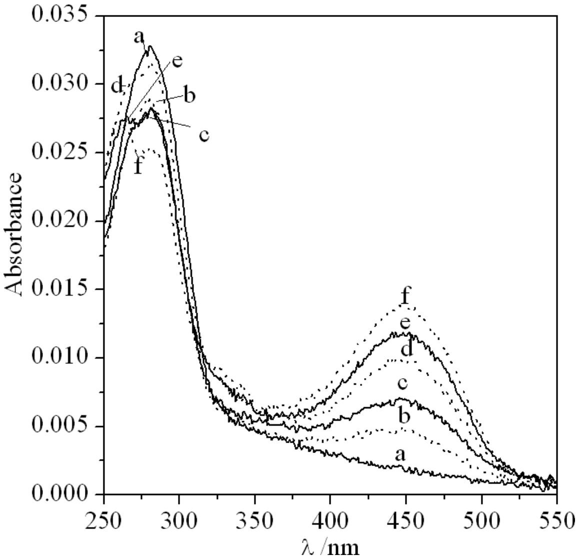


Fig. 5. Absorption spectra of **3**/7CB mixtures in LB films; the molar fraction of dye $X_M = 0.0$ (a), 0.2 (b), 0.4 (c), 0.6 (d), 0.8 (e), and 1.0 (f).

neither an additional peak, nor a shoulder, which would directly indicate on the dimers formation in the ground state, is observed, but the absorbance of the band corresponding to the dye does not vary proportional to its concentration. For example, the content of **3** in 7CB in LB films, which absorption spectra are shown in Figure 5, decreases by a factor of 5, and the absorbance of the long wavelength band related to **3** decreases no more than 4-fold. The changes of the band related to the liquid crystal (≈ 280 nm) are difficult to distinguish because of the overlapping of the absorption bands of the dye and the liquid crystal in this region of the spectrum. The lack of the proportionality between the dye content in the mixture and the absorbance value occurs for all the dyes. This seems to confirm the suggestion that small fraction of aggregates of dyes **1**–**6** in the LB films is present already in the ground electronic state.

Because the molar extinction coefficient of **1**–**6** is quite large over 10,000 [22, 23], in the LB films one can expect the dipole-dipole interaction leading to the exciton coupling. On the basis of the molecular exciton model [30, 31], it is known that the interaction between transition dipoles results in the splitting of the energy level of the excited state into two levels with higher and lower energy relative to the undisturbed excited state (Davydov splitting).

Assuming the parallel configuration of dyes **1**–**6** molecules in the dimer, the co-planar arrangement of the absorption transition moments can be considered. In this case the transition to one of the excited states, corresponding to an antiparallel alignment of dipole moments, is forbidden, while the energy difference between the excited monomer state and the exciton state depends on the angle θ between the dipole transition moment of the molecule and the vector joining the centers of two dipoles [31]. When the alignment of the dipole moments in the aggregates is such that $0° < \theta < 54.7°$, the exciton band is located energetically below the monomer band causing a bathochromic shift of the absorption spectrum, and created aggregates are called J-aggregates [32]. For $54.7° < \theta < 90°$, the exciton band is located energetically above the monomer band causing a hypsochromic shift, and corresponding aggregates are referred to as H-aggregates [32]. When $\theta = 54.7°$, no shift in the absorption spectrum is observed, and the aggregates are then called I-aggregates [33].

The broadening of the absorption band of **1**–**6** in the LB films as compared to that characteristic of monomers with the red shift of the absorption maximum position, implies that, in the case of derivatives of 4-aminonaphthalimide, we are dealing with creation of some fraction of J-aggregates in the ground electronic state.

3.3. Fluorescence Spectra

Figure 6 shows the fluorescence spectra of pure dye **3** in the LB film (solid curve) and, for comparison, dissolved in chloroform at $X_M = 10^{-7}$ (dashed curve), while in Figure 7 the fluorescence spectra for **2**/7CB mixtures at various molar fractions X_M are presented. Table 4 shows the positions of the maximum and the half-bandwidths of the fluorescence band for dyes **1**–**6** in chloroform and mixed with 7CB, in the sandwich cell at the lowest ($X_M = 7.3 \cdot 10^{-3}$) and highest ($X_M = 5 \cdot 10^{-2}$) concentrations used. In Table 5 the positions of the maximum and the half-bandwidths of the fluorescence band for all the dye/7CB mixtures investigated in the LB film as well as the ratios of the fluorescence intensity value of the appropriate mixture to that of dye/7CB mixture at $X_M = 0.1$ are listed. The data are given for mixtures up to the maximal value of X_M at which the deposition was possible, so the values for the LB film of pure dye **3** are presented, too.

The significant red shift of maximum positions for all the dyes and the broadening of the fluorescence

Table 4. The maximum position λ_{max} and the half-bandwidth δ of the fluorescence band of **1** – **6** in chloroform ($X_M = 10^{-7}$) and mixed with 7CB in sandwich cell ($X_M = 1.7 \cdot 10^{-3}$ and $5 \cdot 10^{-2}$).

dye code	chloroform $X_M = 10^{-7}$		7CB, sandwich cell $X_M = 7.3 \cdot 10^{-3}$		7CB, sandwich cell $X_M = 5 \cdot 10^{-2}$	
	λ_{max}/nm $\Delta\lambda = \pm 1$ nm	δ/cm^{-1} $\Delta\delta = \pm 10$ cm^{-1}	λ_{max}/nm $\Delta\lambda = \pm 1$ nm	δ/cm^{-1} $\Delta\delta = \pm 20$ cm^{-1}	λ_{max}/nm $\Delta\lambda = \pm 1$ nm	δ/cm^{-1} $\Delta\delta = \pm 20$ cm^{-1}
1	514	2370	519	2400	521	2500
2	503	2410	517	2440	522	2460
3	501	2490	510	2420	512	2560
4	500	2230	514	2520	517	2560
5	514	2270	514	2340	515	2260
6	496	2330	518	2500	512	2400

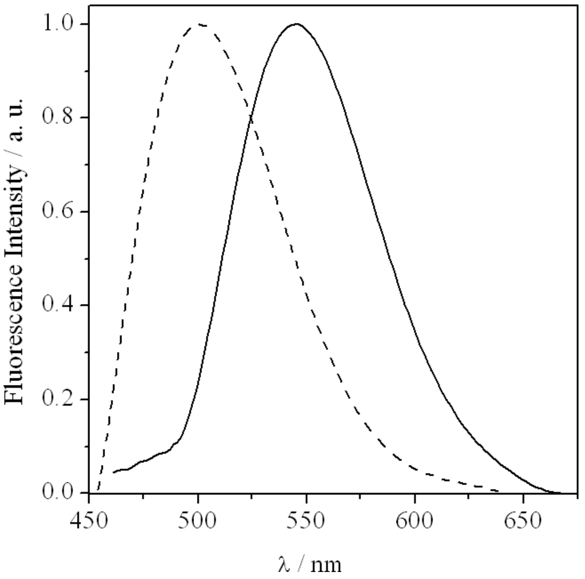


Fig. 6. Normalized fluorescence spectra of pure **3** in LB film (solid curve) and in chloroform at $X_M = 10^{-7}$ (dashed curve).

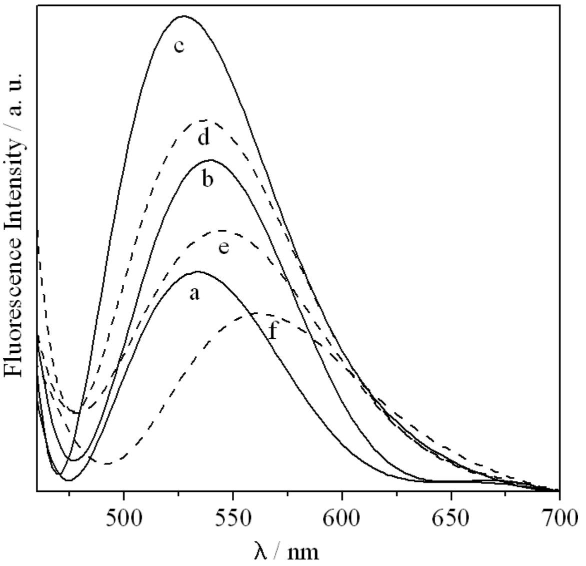


Fig. 7. Fluorescence spectra of **2**/7CB mixtures in LB films; the molar fraction of dye $X_M = 0.1$ (a), 0.2 (b), 0.3 (c), 0.4 (d), 0.6 (e), and 0.8 (f).

band in the LB films with respect to the appropriate values in the solution are seen. From comparison of the results obtained from the fluorescence (Table 5) and absorption measurements (Table 3) follows that a distinct bathochromic shift of the fluorescence peak has no reflection in the absorption spectra. Therefore, we can speculate that we are dealing here with the fluorescence of excimers which originate from an interaction between molecules in the ground and excited state and are often observed in the solid phase of flat aromatic molecules [34]. The excimer creation in the LB films was previously observed for pyrene [7], perylene-like dyes [11 – 14], derivatives of naphthoylenebenzimidazole [18 – 21], and also for some derivatives of 1,8-naphthalimide [18 – 20]. Some confirmations of the occurrence of the excimers of dyes **1** – **6** in the LB films can be founded in fact that in spite of the absorbance growth with the dye content (although not proportional to X_M – see Figure 5 for example), observed for all the dye/7CB mixtures, the fluorescence intensity behaves differently for various dyes. For dyes **1** and **5** the fluorescence intensity increases up to the maximal concentrations used, but considerably slower than the rise of X_M (note that for these dyes the transfer only for relatively small dye concentrations was possible). In the case of dyes **2** and **4** the fluorescence intensity increases only up to some X_M value and next starts to diminish. For dyes **3** and **6** we observed first a decrease of the fluorescence intensity and at the higher concentrations – a small increase. Taking into account the changes of the absorbance and the fluorescence intensity with the rise of X_M, we can conclude that the

Table 5. Maximum position λ_{max} and half-bandwidth δ of fluorescence band of **1**–**6** mixed with 7CB in LB films at various molar fractions X_M.

dye code	X_M	λ_{max}/nm $\Delta\lambda = \pm 1$ nm	δ/cm^{-1} $\Delta\delta = \pm 50$ cm^{-1}	$F_{mix}/F_{0.1}$
1	0.1	536	2650	1.00
	0.3	545	2550	1.47
	0.6	548	2700	1.90
2	0.1	534	2650	1.00
	0.3	527	3050	2.16
	0.8	561	3050	0.82
3	0.1	530	2350	1.00
	0.4	543	2750	0.70
	0.8	549	2750	0.43
	1.0	543	2850	0.62
4	0.1	512	–	1.00
	0.3	519	2500	3.54
	0.4	537	2550	2.60
5	0.2	526	2500	1.00
	0.4	527	2550	1.43
	0.5	529	2500	1.76
6	0.1	520	2300	1.00
	0.4	531	2550	0.41
	0.8	550	2450	0.25
	0.9	539	2600	0.39

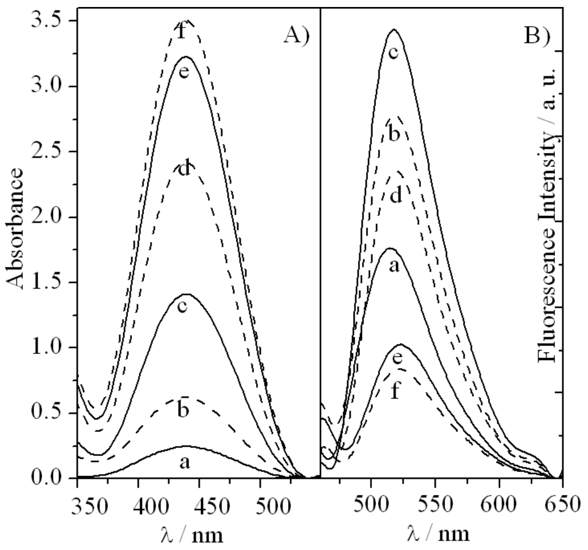


Fig. 8. Absorption (A) and fluorescence (B) spectra of **2** in 7CB at T = 44 °C (isotropic phase) in sandwich cell; the molar fraction of dye: $3.6 \cdot 10^{-3}$ (a), $7.3 \cdot 10^{-3}$ (b), $1.7 \cdot 10^{-2}$ (c), $2.6 \cdot 10^{-2}$ (d), $3.5 \cdot 10^{-2}$ (e), and $5.0 \cdot 10^{-2}$ (f).

interaction between two dye molecules in the dimers created in the electronic ground state is very weak and the overall shape of the absorption spectrum of **1**–**6** in 7CB is monomer-like, even in the LB films. However, the decrease (or very slow increase) of the fluorescence intensity with the rise of a dye concentration would indicate the excimer formation because the reduction of the fluorescence efficiency as a result of the concentration quenching is a well known effect for molecular aggregates [34, 35].

The supplementary measurements of the fluorescence for dyes **1**–**6** mixed with 7CB at various concentrations in sandwich cells were carried out. The results for dye **2** are shown in Figure 8, as examples. It is seen that already at much smaller dye concentrations than used in the LB films, the fluorescence quenching is observed. Dyes **4** and **6** behave similarly as dye **2**: the fluorescence intensity grows up to $X_M = 1.7 \cdot 10^{-3}$ and at higher concentrations it decreases. For dyes **1** and **5** the fluorescence intensity increases with the rise of the dye content up to $X_M = 5 \cdot 10^{-2}$, but only a little at higher concentrations, whereas in the case of dye **3** a fluorescence intensity decrease with X_M is observed. These facts, together with the shift of the fluorescence maximum and some broadening of the fluorescence band with respect to these parameters in the dilute solution (see data in Table 4), can indicate that some fraction of excimers of derivatives of 4-aminonaphthalimide is present in the mixtures with 7CB already at concentrations used for measurements in the sandwich cell. In the LB films when the dye concentration in 7CB is higher than in the sandwich cell, the fluorescence band maximum shifts to the longer wavelengths, and the half-bandwidth increases, indicating that more and more molecules come together and form excimer configurations. However, one should keep in mind that the results obtained from the measurements in the sandwich cell and in the LB film cannot be compared directly, as in both cases the molecules are in different conditions. The measurements in the sandwich cell were made in the isotropic phase of 7CB, thus molecules were randomly distributed; in LB films molecules were organized in a specified way: as a result of the compression of the Langmuir film they were arranged mutually parallel (see Section 3.2). Such an arrangement favours interactions between dipole moments of dye molecules. An increase of the fluorescence intensity observed for dyes **3** and **6** at $X_M \gtrsim 0.8$ in the LB films can be explained in the term of the occurrence of sufficiently good conditions to overlap in the way enabling the genuine excimers creation already at lower dye content in the mixture.

4. Conclusions

Six derivatives of 4-aminonapththalimide (**1**–**6**), together with their binary mixtures with the liquid crystal 7CB have been investigated in Langmuir and Langmuir-Blodgett films. Except of dye **5**, having a morpholine ring in the substituent R, all other dyes have been able to create themselves stable and compressible monolayers at the air/water interface. However, the transfer of the floating monolayer on the quartz slide was possible only for pure dye **3**. Dyes **1**, **2**, **4**, **5** and **6** could make the LB films after they were mixed with 7CB at a definite molar fraction X_M. The maximal value of X_M was different for various dyes indicating the influence of the nature of the substituent R on the formation of stable monolayers at interfaces.

The analysis of π-A isotherms of the Langmuir films has revealed that properties of the monolayer on the water surface (packing density, stability, and rigidity) depend not only on the structure of dye molecules but also on the mixture composition. Both components of the dye/7CB mixtures were good miscible over the whole range of X_M.

For the LB films the absorption and fluorescence spectra were recorded. Additionally, the mixtures of dyes with 7CB in the sandwich cells of 10 μm in thickness have been studied as a function of a dye concentration. The shape of the absorption spectra of **1**–**6** mixed with the liquid crystal suggests a tendency to formation of aggregates between the dye molecules in the LB films, already in the ground electronic state. The detailed analysis of the fluorescence spectra allow to conclude that in the excited state, derivatives of 4-aminonaphthalimide can create molecular configurations giving the excimer emission. The energy and the intensity of this emission strongly depend on the dye concentration as well as on the dye molecular structure. The smallest tendency to aggregation and, as a result, the smallest fluorescence quenching with the rise of the dye content reveal dyes **1** and **5**. This indicates that the presence of the piperidine or morpholine ring in the substituent R hinders the interactions between dye molecules. However, when the pyrrolidine ring is present in the substituent (dye **2**), the tendency to creation of aggregates in the excited state is the highest.

In final conclusion it should be emphasized that the LB films formed of some derivatives of 4-aminonaphthalimide could be consider as promising products to use as active layers in OLEDs, but the dyes have to be first embedded in a stabilizing matrix, e. g. in one of thermotropic liquid crystals. However, in order to improve the fluorescence efficiency LB films of more than one layer should be made. Thus, another liquid crystal than 7CB or one of fatty acids need to be used as the matrix. This will be subject of our further investigations.

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