Spectral properties of naphthalimide dyes mixed with 4-heptyl-4'-cyanobiphenyl (7CB) in Langmuir-Blodgett films

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Langmuir-Blodgett (LB) films formed of some fluorescent dyes, namely derivatives of 4-aminonaphthalimide, and their binary mixtures with the liquid crystal 4-heptyl-4'-cyanobiphenyl (7CB) have been studied. The electronic absorption and fluorescence spectra were recorded. On the basis of these spectra, the spectral properties of the dyes and the intermolecular interactions in ultrathin ordered films were determined. The conclusions about the tendency to the creation of aggregates by dye molecules in LB films have been drawn. The measurements of absorption by using linearly polarised light have allowed us to determine the arrangement of the dye and liquid crystal molecules on the air-solid substrate interface.

Keywords: Langmuir-Blodgett film, naphthalimide dye, liquid crystal, absorption spectra, fluorescence spectra.

1. Introduction

In the 21st century, modern electronic devices require larger and larger miniaturization. Therefore it is necessary to use in them materials in scale of the order of micro- to nanometers. The smaller systems become the faster and they can operate more economically. Unfortunately, it is more and more difficult and expensive to produce them. Indeed a certain progress on the way to miniaturization of three-dimensional (3D) systems is still expected, but the future belongs to electronic devices using single molecules or their small aggregates as functionalized materials. Various nanotechnologies can be here helpful, it is searching for quick, reliable and economically efficient methods which will produce systems on the nanoscale. The Langmuir-Blodgett (LB) method is considered as one of the most versatile techniques for fabricating two-dimensional (2D) ordered layers from some molecules and colloid particles [1–3], the architecture of which can be easily manipulated. This gives the possibility of optimization of physical (especially electro--optical) parameters of the material used and therefore the LB layers are today integral part of the knowledge connected with molecular electronics. Already several years ago Stapff *et al.* [4] proposed to use LB technique to obtain the ordered layer for organic light emitting diodes (OLEDs). Recently OLEDs [5] have attracted a great deal of research interest due to their promising application in full-colour flat-panel displays [6], which can be strongly competitive to the most popular today liquid crystal displays (LCDs).

On the other hand, fabrication of ultra-thin layers by means of LB technique is very useful to study molecular aggregates, especially of organic compound molecules. These layers give molecules the opportunity to be in highly oriented environments, similarly as it takes place in solid matrix, where the phenomenon of the molecular aggregation is often observed. The molecular aggregates are characterized by different physico-chemical properties in comparison with those of monomeric systems [7]. In particular, they display intriguing optical properties and therefore attract attention as novel functionalized materials for application in molecular electronics and photonics.

In this paper we present the results of the spectroscopic study of Langmuir-Blodgett films formed of some 1,8-naphthalimide dyes (derivatives of 4-aminonaphthalimide) and of their mixtures with the liquid crystal 4-heptyl-4'-cyanobiphenyl (7CB), used as supporting matrix. The derivatives of 4-aminonaphthalimide are known as organic dyes with very high quantum fluorescence yield and good orientation in 7CB [8]. The aim of our study was to determine spectral properties of the dyes and the intermolecular interactions in ultrathin ordered films deposited on the solid substrate. Additionally, we would like to check the possibility of utilization of the LB films of the dyes as active layers in OLEDs.

2. Experimental

2.1. Materials

The set of the dyes investigated consists of twelve derivatives of 4-aminonaphthalimide. Their synthesis is described

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in Ref. 9. The chemical structure of the dyes, confirmed by ^{1}H NMR analysis, is given in Fig. 1. The study of monolayers of dyes **1-6** fabricated by means of LB technique was already reported [10]. Here, the supplementary results are given and some results from Ref. 10 are quoted in order to compare them with the data for newly investigated dyes **7-12**. The liquid crystal 4-*n*-heptyl-4'-cyanobiphenyl, 7CB (Fig. 1) 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 spectroscopic quality (Uvasol, 99.9%) obtained from Merck.

2.2. Methods

Monolayers at the air-water (Langmuir films) and air-solid substrate (LB films) interfaces were prepared using Mini-trough 2 (KSV Instruments Ltd., Finland). Milli-Q water was used as a subphase and polished quartz plates with hydrophilic surface were used as solid substrates. Pure compounds **1-12** and their mixtures with 7CB in the whole range of the molar fraction of the dye X_M were spread onto subphase from chloroform solutions. The temperature of the subphase was main-
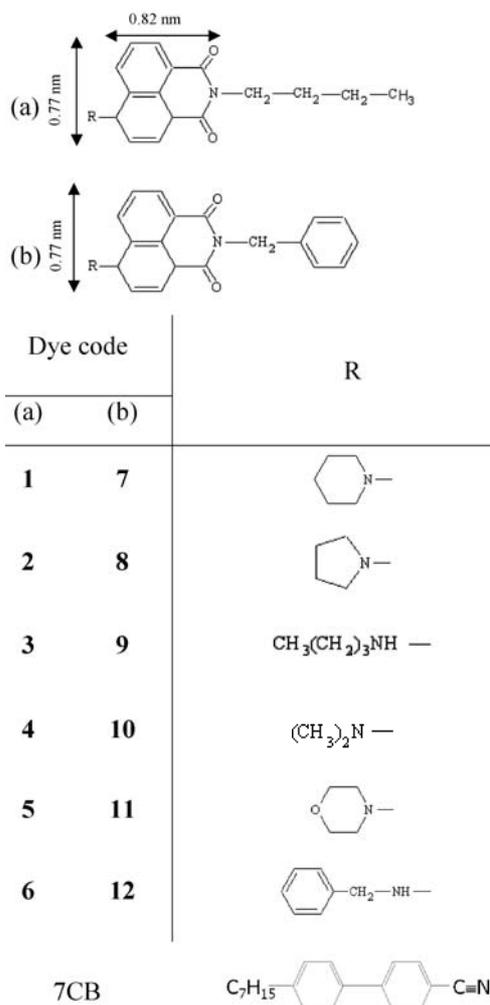
tained by cooling circulator and kept constant at 20 ±1°C. The transfer of the monolayer from the water surface onto the quartz substrates was made below the collapse point, which corresponds to the stage of the formation of the compressed monolayer. The transfer rate was 5 mm/min. The successful deposition of the film onto the quartz was possible only on raising the substrate. Repeated attempts to transfer a floating monolayer onto quartz plates failed. Therefore, only one dipping and one raising were made. The transfer ratio [11] obtained was between 1.00 and 1.20. Further experimental details are reported in Ref. 10.

The absorption spectra of LB films were recorded in the UV-Vis region by means of a spectrophotometer CARY 400, while the fluorescence measurements were carried out by using a photon-counting spectrofluorimeter built at our laboratory and described in detail in Ref. 12. The exciting light was 436 nm line from high-pressure mercury lamp.

In the absorption measurements, by using polarised light, Glan-Thomson polarisers and an angular sample holder were used. The measurements were performed in the geometry presented in Fig. 2. α is the angle between the normal to the quartz slides and the direction of the incident light. The spectra were run at the incidence angle α of 0° and 30°. On the basis of the polarised absorption spectra, the linear dichroism (LD) was determined. Following N'souk-poé-Kossi *et al.* [13] we defined LD by

$$LD = \frac{A_P - A_S}{A_P + A_S}, \qquad (1)$$

where A_P and A_S are the absorbance values at the band maximum for the light polarised parallel and perpendicularly to the plane of incidence, respectively.

LD can be connected with the angle of incidence α in the following way [13]

$$LD_a = \frac{2 - \tan^2 \beta}{\tan^2 \beta [(1 + \cos^2 \alpha) / \sin^2 \alpha] + 2}, \qquad (2)$$

where β is the angle between the transition dipole moment vector and the normal to the plane of the LB film.

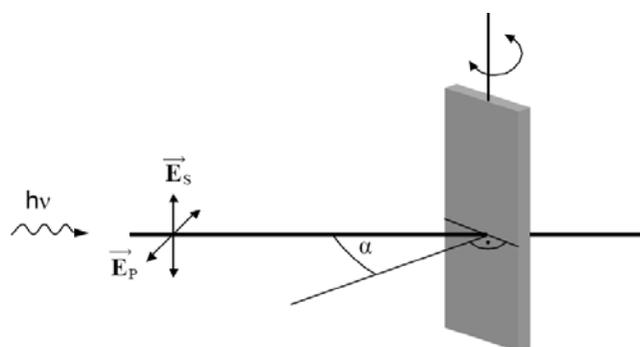
Fig. 1. Molecular structure of compounds investigated.

Fig. 2. Geometry for the polarised absorption measurements. $\vec{E}_P$ and $\vec{E}_S$ are the electric vectors of the incident light polarised, respectively, parallel and perpendicularly to the plane of incidence. α is the incidence angle.
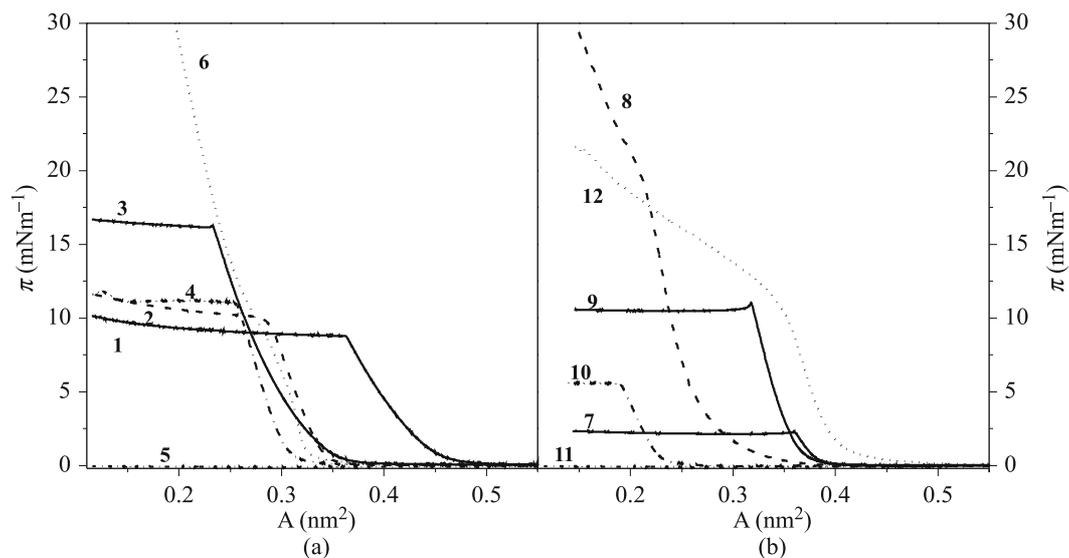
Fig. 3. Surface pressure-mean molecular area isotherms for Langmuir films of dyes **1**-**6** (a) (after Ref. 10) and dyes **7**-**12** (b).

Equation (2) is valid if the molecules in the monolayer are distributed in the cone, uniformly on the slide surface, with their transition moment tilted at the angle β with respect to the normal. In this case, LD for $\alpha = 0°$ should be equal to zero.

In order to analyse the spectra in wide range of a dye concentration, some supplementary absorption and fluorescence measurements of 4-aminonaphthalimide derivatives dissolved in 7CB ($X_M = 7.3\times10^{-3}$–5×10^{-2}) were performed in sandwich cells made of two glass plates separated by the spacer of 10 µm in thickness. 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

Figures 3(a) and 3(b) show the dependence of the surface pressure π on the average area available for one molecule A (π-A isotherm) for derivatives of 4-aminonaphthalimide under investigation. It can be seen that, except of dyes **5** and **11**, all other dyes form a compressible floating monolayer at the air-water interface. After spreading chloroform solution of **5** and **11** at the water surface at the through, we observed large patches of the dye, and the surface pressure did not rise upon the reduction of the area. However, when these dyes were mixed with 7CB at appropriate concentrations, compression was possible and we obtained π-A isotherms, which for Langmuir films of **11**/7CB mixtures are shown in Fig. 4. In all the cases, the increase in π begins at the area being the first edge of the phase transition and 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 Langmuir films were deposited onto quartz slides below the collapse point keeping the surface pressure constant. The transfer of monolayers of dye **7** and of its mixture

with 7CB was made at $\pi = 2$ mN/m, whereas monolayers of all other dyes and/or of their mixtures with the liquid crystal were transferred at $\pi = 3.5$ mN/m. From the dyes of group (a) (Fig. 1) only pure dye **3** could be successfully transferred from the water surface on the quartz slide, whereas from the dyes of group (b) the transfer was possible for pure dyes **7**, **8**, **9**, and **12**. This indicates that not only the molecular structure of the substituent R, but also that of the second substituent plays role in the formation of the stable LB films. All other dyes made the LB films only when they were mixed with the liquid crystal 7CB.

Figures 5, 6, and 7 show the exemplary results of the absorption and fluorescence measurements. In Figs. 5 and 6,
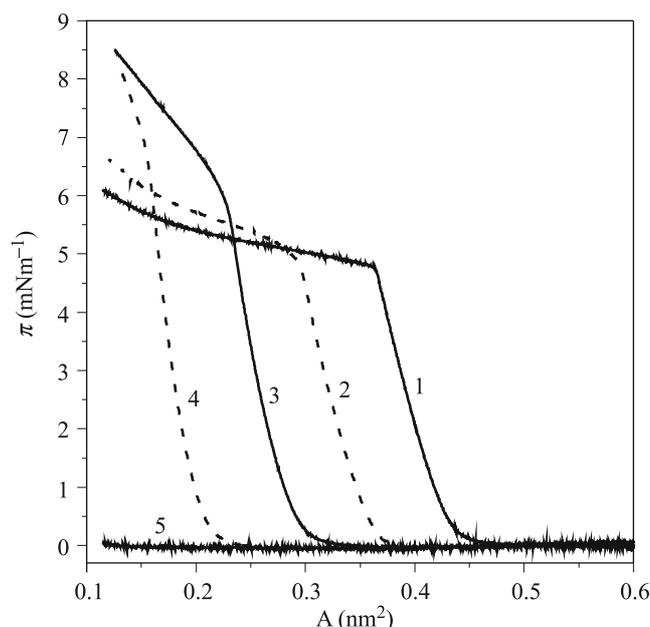

Fig. 4. Surface pressure-mean molecular area isotherms for Langmuir films of 7CB (1) and **11**/7CB mixtures for $X_M = 0.2$ (2), 0.4 (3), 0.6 (4), and 0.8 (5).
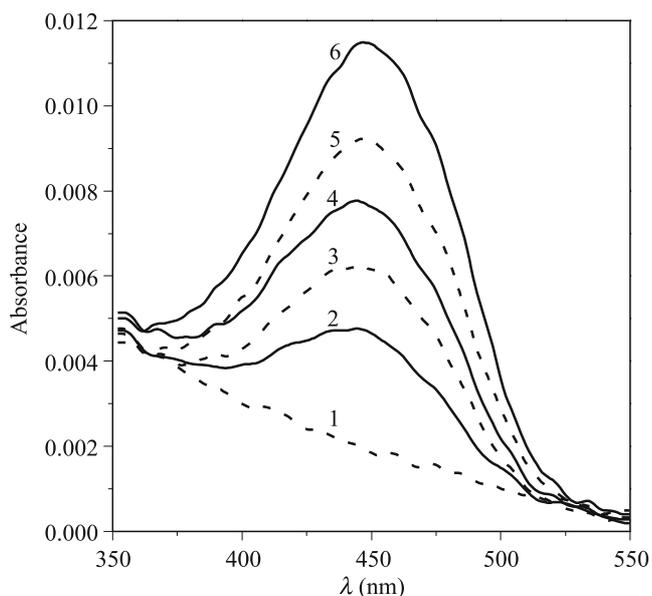
Fig. 5. Absorption spectra of **9**/7CB mixtures in LB films: the molar fraction of dye $X_M = 0.0$ (1), 0.2 (2), 0.4 (3), 0.6 (4), 0.8 (5), and 1.0 (6).
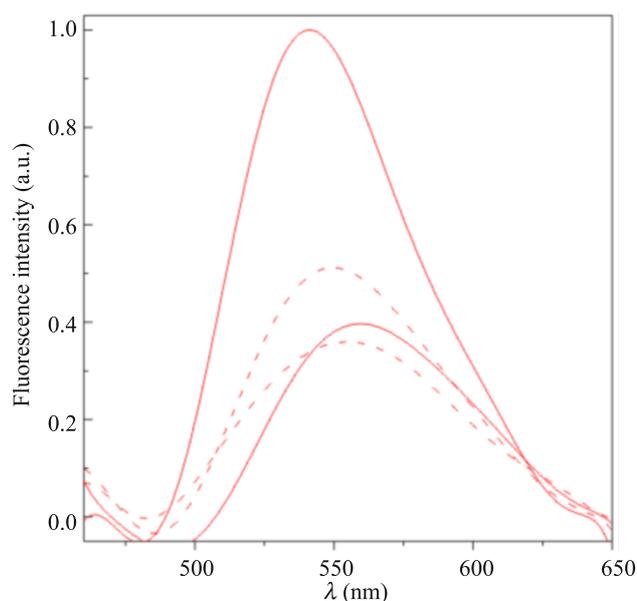

Fig. 6. Fluorescence spectra of **9**/7CB mixtures in LB films: the molar fraction of dye $X_M = 0.2$ (1), 0.4 (2), 0.6 (3) and 1.0 (4).

respectively, the absorption and fluorescence spectra of LB films of pure dye **9** and **9**/7CB mixtures at various X_M of a dye are presented. Figure 7 shows, however, the absorption and fluorescence spectra of dye **10** dissolved in 7CB at different concentrations and measured in the sandwich cells.

Table 1 lists the positions of the maximum λ_{max} and the half-bandwidths δ of the long-wavelength absorption band for dyes **1**-**12** in chloroform and mixed with 7CB, in the LB films, mostly at $X_M = 0.6$, and in the sandwich cells at the highest possible concentration ($X_M = 5\times10^{-2}$). It should be here noted that because of very small absorbance, the uncertainty in the estimation of the δ values for the LB films is

large. Moreover, the half-bandwidth depends on the temperature, thus the direct comparison of this value in the LB film (the measurement at the room temperature) and in the sandwich cell (the measurement at 44°C) is not possible. So, the values given in Table 1 should be treated only as informative ones.

Table 2 shows the positions of the maximum and the half-bandwidths of the fluorescence band for dyes **1**-**12** in chloroform and mixed with 7CB, in the sandwich cell at the lowest ($X_M = 7.3\times10^{-3}$) and highest ($X_M = 5\times10^{-2}$) concentrations used. In Table 3, the positions of the maximum and the half-bandwidths of the fluorescence band for LB films

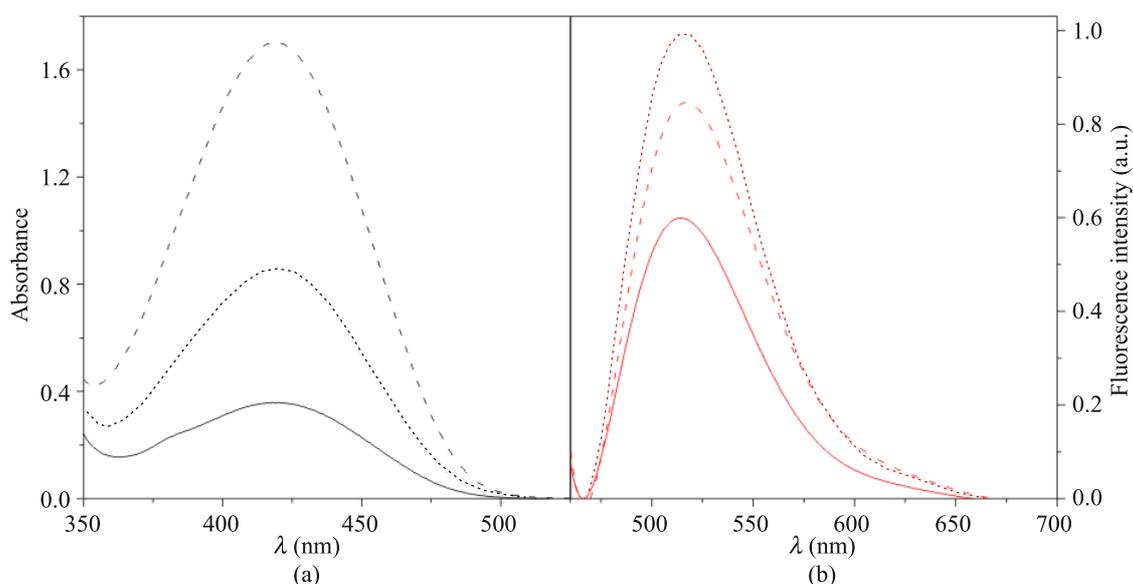

Fig. 7. Absorption (a) and fluorescence (b) spectra of **10** in 7CB at $T = 44$°C (isotropic phase) in sandwich cell, the molar fraction of dye: 7.3×10^{-3} (1), 1.7×10^{-2} (2), and 5.0×10^{-2} (3).

Table 1. The maximum position λ_{max} and the half-bandwidth δ of the long wavelength absorption band of dyes **1-12** in chloroform ($X_M = 10^{-7}$) and mixed with 7CB, in sandwich cell ($X_M = 5\times10^{-2}$) and in LB film ($X_M = 0.6$). Data for dyes **1-6** are taken from Ref. 10.

Dye code	Chloroform $X_M = 10^{-7}$		7CB, sandwich cell $X_M = 5\times10^{-2}$		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} $\Delta\delta = \pm50$ cm^{-1}
1	410	4460	413	4560	429	4550
2	442	3470	445	4240	460	4200
3	430	3590	435	4000	453	3950
4	415	4470	415	4860	434[a]	_[b]
5	395	4510	398	4080	404[c]	3900[c]
6	424	3930	429	3940	442	3850
7	413	3740	411	4320	418	4100
8	443	3500	445	3640	455	4400
9	428	3670	435	3720	446	3700
10	418	4380	419	4440	442	_[b]
11	393	4400	395	4400	396	4250
12	425	3730	429	3740	443	3700

[a]$X_M = 0.4$, [b]impossible to determine, [c]$X_M = 0.5$

of pure dyes and the dyes mixed with 7CB at chosen (representative) X_M are listed. The ratios of the fluorescence intensity value of the appropriate mixture to that of the dye/7CB mixture at the lowest X_M are presented too.

Figure 8(a) shows the polarised absorption spectra recorded at $\alpha = 0°$ for **12**/7CB mixture, as an example, in the LB films. It is seen that the linear dichroism for the light in-

cident perpendicularly to the quartz surface ($LD_{\alpha=0}$) is zero. This means that the vertical movement of the quartz slide during deposition did not disturb the homogeneity of the molecular alignment. For other compounds investigated we obtained also $LD_{\alpha=0} = 0$. Thus, the angle β could be calculated from Eq. (2) on the basis of the spectra measured at the angle $\alpha \neq 0°$. The spectra of polarised absorption compo-

Table 2. The maximum position λ_{max} and the half-bandwidth δ of the fluorescence band of **1-12** in chloroform ($X_M = 10^{-7}$) and mixed with 7CB in sandwich cell ($X_M = 7.3\times10^{-3}$ and 5×10^{-2}). Data for dyes **1-6** are taken from Ref. 10.

Dye code	Chloroform $X_M = 10^{-7}$		7CB, sandwich cell			
			$X_M = 7.3\times10^{-3}$		$X_M = 5\times10^{-2}$	
	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} $\Delta\delta = \pm20$ 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
7	512	2040	518	2440	523	2500
8	507	2300	511	2400	527	2500
9	494	2520	507	2600	512	2500
10	499	2260	513	2440	516	2500
11	503	2100	513	2460	513	2500
12	496	2350	506	2660	506	2600

Table 3. Maximum position λ_{max} and half-bandwidth δ of fluorescence band of **1-12** mixed with 7CB in LB films at various X_M.

Dye code	X_M	λ_{max}/nm $\Delta\lambda = \pm 1$ nm	δ/cm^{-1} $\Delta\delta = \pm 50$ cm^{-1}	$F(X_M)/F(X_M^{min})$
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
	0.6	544	2900	1.19
	0.8	561	3050	0.82
3	0.1	530	2350	1.00
	0.6	545	2700	0.51
	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
	0.6	549	2500	0.20
	0.9	539	2600	0.39
7	0.2	545	2500	1.00
	0.6	548	3050	1.16
	1.0	548	2850	1.64
8	0.2	549	2500	1.00
	0.6	524	2350	5.21
	0.7	539	2350	2.07
	1.0	548	2450	1.00
9	0.2	541	2450	1.00
	0.4	549	2650	0.51
	0.6	555	2850	0.36
	1.0	559	2600	0.40
10	0.2	537	2250	1.00
	0.4	537	2300	1.30
	0.6	543	2350	1.15
11	0.2	527	2350	1.00
	0.4	526	2450	1.20
	0.6	526	2500	1.35
12	0.2	536	2700	1.00
	0.6	541	2600	0.68
	0.8	524	2650	0.50
	1.0	521	2600	0.40

nents recorded at $\alpha = 30°$ for **12/**7CB mixture are presented in Fig. 8(b) whereas the values of β for all the dyes investigated in the LB films at various X_M of the dye are listed in Table 4. These are mean values of the results obtained at the incidence angles $\alpha = 30°$ for at least three independently prepared samples.

4. Discussion

From the results presented in Fig. 3, it is seen distinctly that the nature of the isotherms of Langmuir films of dyes **1-12** strongly depends on the structure of both substituents to the rigid core of the dye molecule. In some cases, behind the col-
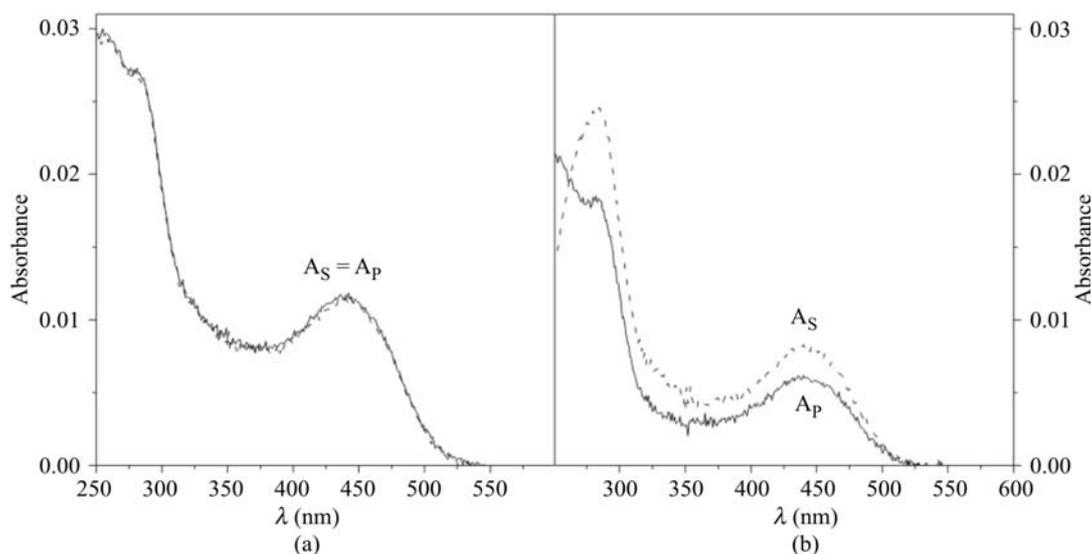
Fig. 8. Polarised absorption spectra of **12**/7CB mixtures ($X_M = 0.6$) in LB films at $\alpha = 0°$ (a) and 30° (b).

lapse point a broad plateau region is observed, however, with the different surface pressure value, while in the others, the pressure rises monotonically with a decrease in the available area. However, the shapes of all π-A isotherms obtained for dyes **1-12** were similar to those which can be found in literature for other compounds [1–3,11,14–18]. No significant differences in the isotherms runs during compression and expansion processes were observed meaning that the monolayers formed were stable. The creation of the compressible Langmuir film was not possible only when the morpholine ring was

Table 4. Values of an angle between absorption transition moment and normal to quartz slide in LB films of dye/7CB mixtures.

Mixture	X_M	β/deg	Mixture	X_M	β/deg
7CB	1.0	68			
				0.2	77
	0.2	67		0.4	65
1/7CB	0.4	73	**7**/7CB	0.6	66
	0.6	71		0.8	69
				1.0	68
	0.2	73		0.2	79
2/7CB	0.4	63		0.4	82
	0.6	62	**8**/7CB	0.6	71
	0.8	64		1.0	61
	0.2	67		0.2	70
	0.4	65		0.4	71
3/7CB	0.6	61	**9**/7CB	0.6	75
	0.8	64		0.8	66
	1.0	63		1.0	66
	0.2	–[a]		0.2	63
4/7CB	0.4	–[a]	**10**/7CB	0.4	78
	0.6	–[a]		0.6	75
				0.2	71
5/7CB	0.2	76	**11**/7CB	0.4	71
	0.4	70		0.6	66
				0.2	75
	0.2	65		0.4	66
6/7CB	0.4	66	**12**/7CB	0.6	79
	0.6	67		0.8	68
	0.8	66		1.0	61

[a] impossible to determine

substituted in R position. As the dyes with the piperidine ring (dyes **1** and **7**) are able to form the monolayer on the water surface, it seems that the presence of the oxygen atom in the ring is responsible for the hindering of the molecules compression. Such effect was observed also for derivative of naphthoyle-nebenzimidazole with the morpholine ring as substituent [18]. The steepness of the isotherms is different for various dyes, which means that the rigidity of the monolayer strongly depends on substituents. 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 [19], is 0.63 nm^2, while cross-sectional area estimated from edge-on configuration (assuming free rotation) is 0.47 nm^2. Thus, the values of the area at the collapse point A_C show that in compressed monolayers the molecules neither lie flat at the water surface nor assume the edge-on configuration with the possibility of free rotation. It is rather reasonable to assume that the rigid cores of the molecules are tilted with respect to the water surface. The detailed discussion of the molecular arrangement of the derivatives of 4-aminonaphthalimide and of their mixtures with 7CB in the monolayer on the water surface is presented elsewhere [10,20].

The absorption spectra of 4-aminonaphthalimides in 7CB measured in the sandwich cell, in the most cases, reveal some spectral broadening in comparison with those in chloroform, and the position of the maximum of the absorption band shifts towards longer wavelengths but no more than 7 nm. However, in the LB films, a distinct bathochromic shift (up to 24 nm for pure dye **10**) is observed. The molecular structure of the substituents, especially that of R, has a quite large effect on both the wavelength of the maximum and the width of the band. For various dyes, the shift of the absorption maximum position of the LB films with respect to that in chloroform is also different.

The shift and the broadening of the absorption band of dyes **1**-**12** mixed with 7CB can suggest the tendency of the dye molecules to aggregation. Indeed neither an additional peak, nor a shoulder, which would directly indicate on the dimers formation in the ground state, is observed, but the dye/7CB mixtures in the LB films do not follow Beer's law (the absorbance does not vary proportional to X_M). For example, the content of dye **9** in 7CB in the LB films, which absorption spectra are shown in Fig. 5, decreases by a factor of 5, and the absorbance of the long wavelength band related to dye **9** decreases no more than 3.5-fold. The lack of the proportionality between the dye content in the mixture and the absorbance value occurs for all the dyes. The reasons of such an effect may be, of course, different. However, as the experimental conditions for all the mixtures of the given dye with 7CB were identical, the components were good miscible [10,20], and the LB films were deposited below the collapse point, *i.e.*, before the phase transition, we can suppose that the slower increase in the absorbance confirms the suggestion on creation of some fraction of aggregates of dyes **1**-**12** in the LB films, already in the ground electronic state.

It is well established that if in molecules sufficiently strong electronic transitions exist, the exciton splitting of excited states may be observed in molecular aggregates [21,22]. The molar extinction coefficient of dyes **1**-**12** is quite large over 10 000 [9,10], thus the exciton coupling is most likely to occur in the LB films. It follows from exciton coupling model [21,22] that the dipole-dipole interactions result 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. The change in energy of these two levels is called Davydov splitting. Assuming the parallel configuration of dyes **1**-**12** molecules in the simplest aggregate consisted of two molecules (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 antiparallel alignment of dipole moments, is forbidden, while the energy difference between the excited monomer level and the exciton level ΔE is given by [21]

$$\Delta E = \frac{\left|\vec{M}\right|^2}{r^3}(1 - 3\cos^2\theta), \qquad (3)$$

where $\vec{M}$ is the dipole moment vector, θ is the angle between the dipole transition moment of the molecule and $\vec{r}$ vector, and r is the length of the vector joining the centres of two dipoles.

When $0° < \theta < 54.7°$, the exciton band is energetically located below the monomer band causing a red shift in the electronic absorption spectrum, and creating aggregates are called J-aggregates [23]. For $54.7° < \theta < 90°$, the exciton band is located energetically above the monomer band causing a blue shift, and corresponding aggregates are termed H-aggregates [18]. When $\theta = 54.7°$, no shift in the absorption spectrum is observed, and the aggregates are then called I-aggregates [23].

Broadening of the absorption band with the red shift of the maximum position in the case of derivatives of 4-aminonaphthalimide can be due to the formation of J-aggregates between dye molecules in the LB films. Small fraction of aggregates can appear also at the higher dye concentrations used in the sandwich cells.

In the case of the fluorescence spectra, for all the dyes in the LB films, not only significant broadening of the fluorescence band, but also strong red shift of the maximum position (> 60 nm for pure dye **9**) with respect to the appropriate values in the solution can be seen. Both the half-bandwidth and the red shift of the maximum increase with the dye content and this effect is observed already at the concentrations used for spectral measurements in the sandwich cells. It follows from comparison of the results obtained from the fluorescence and absorption measurements (Tables 1–3) that so 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 states. The excimer forma-

tion is often observed in the solid phase of flat aromatic molecules and at their high concentrations in solutions [25,26]. In these case, the exciton is delocalized over several molecules due to the large intermolecular interactions. Therefore the excimer creation was observed also in the LB films, where the high dye concentration and molecular ordering favour the aggregation process [12,18,27–31]. The excimer states decay with a much smaller radiative efficiency as compared to monomer states and this effect is referred as to "dye self-quenching" [25,26]. For dyes **1-12** in the LB films, in spite of the absorbance growth with the dye content (although not proportional to X_M, see Fig. 5 for example), observed for all the dye/7CB mixtures, the fluorescence intensity behaves differently for various dyes. In the case of some dyes, the fluorescence increases in intensity to maximum at some X_M and then it decreases. For dyes **3**, **6**, and **9** we observed first a decrease in the fluorescence intensity and at the higher concentrations small increase. The intensity of dyes **1**, **5**, **7**, and **11** increases up to the maximal concentrations used, but considerably slower than the rise of X_M. The influence of the dye concentration on the efficiency of emission is observed already in the sandwich cells. For the most dyes, the fluorescence intensity grows up to $X_M = 1.7 \times 10^{-2}$ (see dye **10** in Fig. 7 as an example) and next starts to diminish. In the case of dyes **1**, **5**, and **11** the intensity increases up to the maximal concentration, but not proportional to X_M, for dye **7** it remains almost constant, and for dye **3** the continuous decrease in the intensity with the rise of X_M is seen. The changes of the fluorescence intensity with the dye concentration observed for the derivatives of 4-aminonaphthalimide can be some confirmation that we are dealing here with the emission of at least some fraction of excimers. The next confirmation are the excitation spectra of dyes **1-12** in the LB films, which are almost

identical as the absorption spectra, independent by of the monitoring wavelength. Thus, in the fluorescence spectrum we should expect the contributions from monomer and excimer emissions only. For this reason, an attempt was made to separate the fluorescence spectra of the LB films of 4-aminonaphthalimides under investigation into two bands, corresponding to the both emitters. It was supposed that at the smallest concentration used in the sandwich cells ($X_M = 7.3 \times 10^{-3}$), the dye molecules occur only in the monomeric form. So, the values of λ and δ for the monomer (M) absorption band were taken from these measurements and were used as fixed parameters in the decomposition procedure. Next, one additional band related to the excimer (E) emission was assumed, which should appear at the longer wavelengths with respect to the peak position of the monomer. A sum of normalized Gaussians was used as a model function for the experimentally obtained fluorescence band of dyes **1-12** in the LB films.

In Figs. 9(a) and 10(a), the exemplary decomposition of the fluorescence band into Gaussian-type components for the LB films of dyes **3** and **7**, resulting from the best fit, is shown. Similar results for other dyes which can be themselves transferred onto quartz slides (dyes **8**, **9**, **12**) were also obtained. It is seen that in the case of pure dyes, the excimer emission dominates the fluorescence spectrum. For dye/7CB mixtures, the contribution from this emission decreases when the liquid crystal content increases, suggesting the diminishing excimer fraction. This effect is observed both in the LB films and in the sandwich cell and for dyes **3** and **7** mixed with 7CB at $X_M = 5 \times 10^{-2}$ is demonstrated in Figs. 9(b) and 10(b). The results obtained clearly indicate that with the rise of the dye concentration, the excimer formation occurs more and more effectively.
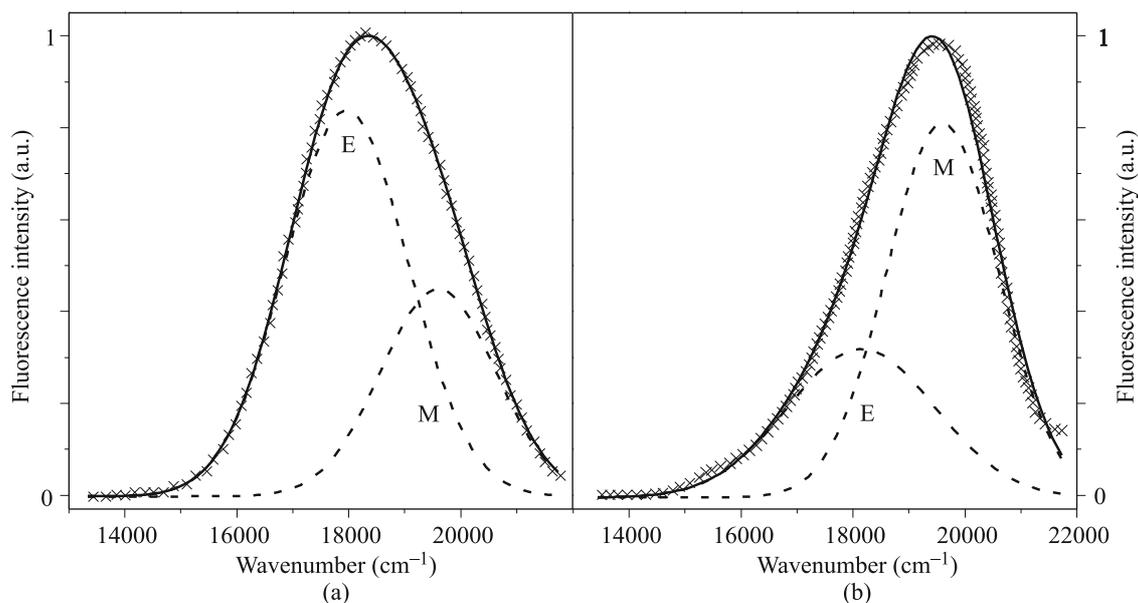

Fig. 9. Decomposition of the fluorescence spectrum of dye **3** in the LB film (a) and dye **3** mixed with 7CB at $X_M = 5 \times 10^{-2}$ in the sandwich cell (b) into two Gaussian-type fluorescence bands. Crosses are experimental points, dashed curves represent resolved components, whereas the solid curve is the sum of these components.
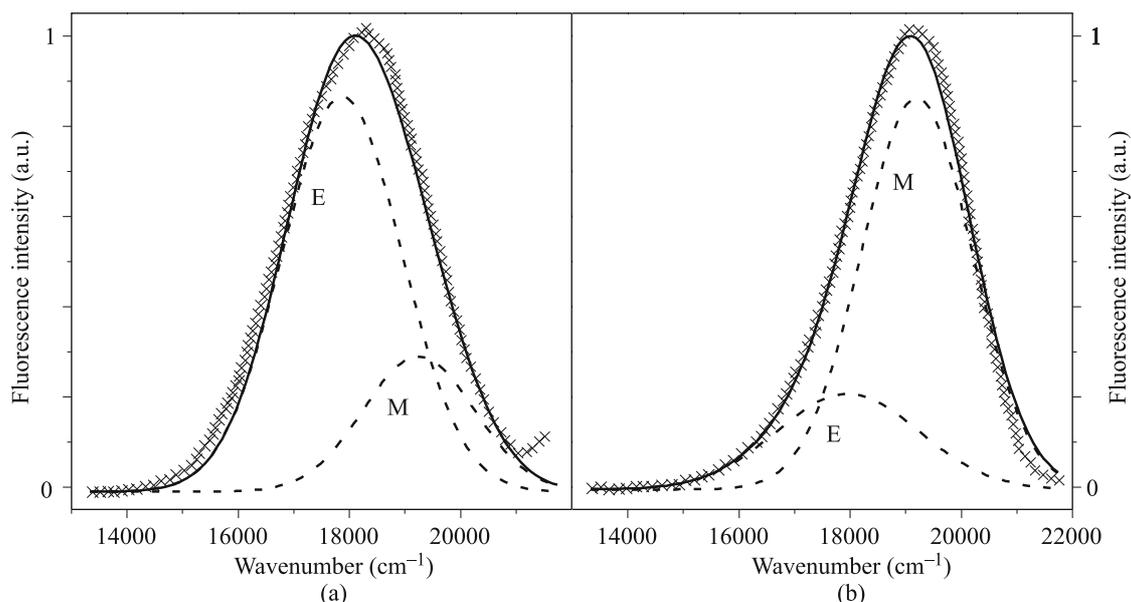
Fig. 10. Decomposition of the fluorescence spectrum of dye **7** in the LB film (a) and dye **7** mixed with 7CB at $X_M = 5 \times 10^{-2}$ in the sandwich cell (b) into two Gaussian-type fluorescence bands. Crosses are experimental points, dashed curves represent resolved components, whereas the solid curve is the sum of these components.

The angles β gathered in Table 4 give some information about the orientation of the liquid crystal 7CB and dyes **1-12** molecules with respect to the quartz slides. However, only for 7CB, the angle β reflects directly the arrangement of the molecules in the LB films as in this case one can assume, in the first approximation, that the angle between the transition moment direction and the long molecular axis is equal to zero [32]. For dyes **1-12**, the long wavelength absorption band oscillator, resulting from $\pi \rightarrow \pi^*$ transition, is directed at some angle (different for various dyes, Ref. 8) with respect to the long axis of the molecule. Thus, the data given in Table 4 for derivatives of 4-aminonaphthalimide can be treated only as informative ones. It can be seen that the rigid molecular cores of the dyes are significantly tilted toward the quartz surface. The addition of the liquid crystal has no large influence on the arrangement of the dye molecules in the LB films, but for the most dyes some tendency to the increase of the tilt angle with the rise of 7CB content is seen. Similar observation was made for dyes **1-12** mixed with 7CB in the Langmuir films [10,20], although the molecules were aligned more vertically with respect to the water surface than to the quartz surface. This indicates that during the transfer of the floating monolayer from the air-water interface onto the solid substrate the molecular rearrangement can take place, as it was also previously reported for other compounds [12,28,30,34].

5. Conclusions

The creation of the stable Langmuir and Langmuir-Blodgett films from derivatives of 4-aminonaphthalimide depends strongly on the molecular structure of the substituent to the main core of the molecule. Except of dyes **5** and **11**, having

morpholine ring in the substituent R, all other dyes under investigation 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 dyes **3**, **7**, **8**, **9** and **12**. Other dyes could make the LB films after they were mixed with 7CB at a definite molar fraction X_M. The maximal values of X_M were different for various dyes confirming the influence of the nature of the substituents on the formation of stable monolayers at interfaces.

The shape of the absorption spectra of dyes **1-12** 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 us to conclude that in the excited state at enough high concentration, derivatives of 4-aminomnaphthalimide can create molecular configurations giving the excimer emission. The fraction of excimers strongly depends on the dye content 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**, **5**, **7** and **11**. This indicates that the presence of the piperidine or morpholine ring in the substituent R hinders the interactions between dye molecules. Thus, the LB films formed of these dyes could be considered as promising products to use as active layers in OLEDs, but they have to be first embedded in a stabilizing matrix, e.g., in one of thermotropic liquid crystals.

Acknowledgements

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