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Spectral properties of some fluorescent dyes in two-dimensional films formed by means of Langmuir–Blodgett technique

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Abstract

Langmuir and Langmuir–Blodgett (LB) films formed of some fluorescent dyes, namely three derivatives of naphthalenebicarboxylic acid and one derivative of naphthoylenebenzimidazole as well as of their mixtures with arachid acid and liquid crystal 4-octyl-4′-cyanobiphenyl (8CB) have been studied. Surface pressure and surface potential versus mean molecular area isotherms for Langmuir films were recorded and information about intermolecular interactions at the air–liquid interface were obtained. Absorption spectra in situ for Langmuir films and both absorption and fluorescence spectra for LB films were recorded. Additionally, in order to analyze the spectra in wide range of a dye concentration some absorption and fluorescence measurements of dyes dissolved in 8CB were performed in sandwich cells. The results obtained from spectroscopic studies have led to conclusions about the formation of self-aggregates by dye molecules.

Keywords: Langmuir and Langmuir–Blodgett films; Surface pressure–area isotherm; Surface potential–area isotherm; Absorption and fluorescence spectra; Self-aggregate

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1. Introduction

Some derivatives of naphthalenebicarboxylic acid and of naphthoylenebenzimidazole have brilliant yellow to red colour, good dichroic properties, and, when dissolved in liquid crystalline matrices, emit light with a high efficiency in a spectral region advantageous for the human eye [1–3]. Therefore, they can be used as guest species in guest–host liquid crystal displays (GH LCDs) working both in passive and active modes [4,5]. Because of the excellent fluorescent properties and the structure of molecules these dyes are also good candidates for application as active layers in organic light emitting diodes (OLEDs) [6]. One of the basic requirements for the organic layer used in OLEDs is that it should be a good charge transporter. The transport of charge carriers in organic compounds will be favoured by increasing molecular order. Highly ordered environment for molecules can be provided by two-dimensional films formed by using Langmuir–Blodgett (LB) technique [7–9]. This technique is a unique method which gives the possibility 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 of the field of molecular electronics [7]. Some years ago Stapff et al. [10] proposed to use LB technique to obtain organic layer for OLEDs.

Recently, it was found in our laboratory that some derivatives of naphthalenebicarboxylic acid and of naphthoylenebenzimidazole are able to create stable and compressible Langmuir films which can be easily transferred onto the solid substrates forming LB films [11–14]. The molecular organization in Langmuir and LB films was determined and spectroscopic study of LB films was carried out. The creation of self-aggregates, which are revealed especially in the fluorescence spectrum, was observed. However, some questions remained still open. Therefore, in this work, we have

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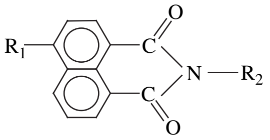
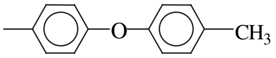
investigated in detail, absorption and fluorescence spectra of Langmuir and LB films of selected derivatives of naphthalenebicarboxylic acid and of naphthoylenebenzimidazole as well as of their mixtures with arachid acid and liquid crystal 4-octyl-4′-cyanobiphenyl (8CB). The aim of our study was to answer the question, which kind of aggregates can be created by molecules of dyes under investigation when they are ordered in two-dimensional layers at the air–liquid and air–solid substrate interfaces.

2. Materials and methods

The following dyes were studied:

1. Derivatives of naphthalenebicarboxylic acid



Dye code	R_1	R_2
1	$—NH(CH_2)_4CH_3$	$—CH_2CH_3$
2	$—NH(CH_2)_{11}CH_3$	$—CH_2CH_3$
3	$—N\,(C_8H_{17})_2$	

2. Derivative of naphthoylenebenzimidazole

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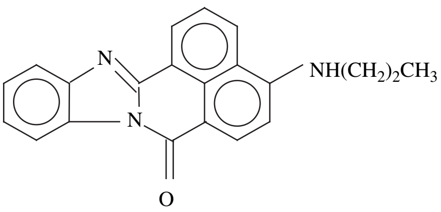

All the dyes were synthesized and chromatographically purified at the Institute of Polymer Technology and Dyes, Łódź University of Technology, Poland. Arachid acid (AA) with a quoted purity of >99% was obtained from Sigma–Aldrich, and liquid crystal 4-octyl-4′-cyanobiphenyl (8CB) was purchased from Merck, Germany. Both compounds were used without further purification.

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. We used pure water or calcium-containing buffer solution as the subphase. The water was deionized and purified to a final resistivity of 18.2 MΩ cm by a Milli-Q system (Millipore Corporation, Austria). The buffer was composed of 1.8×10^{-3} mol/dm^3 $CaCl_2$ dissolved in purified water. A constant subphase temperature was maintained by a cooling circulator and was kept constant at 20 °C. Chloroform Uvasol with spectroscopic quality (Merck, Germany) was used as a spreading solvent. Pure dyes **1–4** and their mixtures with AA or 8CB in chloroform solution were spread drop by drop from a microlitre syringe (Hamilton, England). The chloroform was allowed to evaporate for 15 min after spreading.

The most basic characterization of Langmuir films is the measurement of the surface pressure versus the average area available for one molecule isotherm (π–A isotherm) [7–9,15]. 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 monolayer was compressed, symmetrically from both sides at a barrier motion speed of 5 mm min^{-1} (approximately 2×10^{-7} nm^2 molecule^{-1} s^{-1}), while the surface pressure was monitored by a Wilhelmy plate balance with an accuracy of ±0.1 mN/m. Additionally, the surface potential (ΔV) of the monolayer as a function of the mean molecular area (ΔV–A isotherm) was measured using the vibrating plate method by means of a SPOT 1 head from KSV. Accuracy of this method was ±1.0 mV. ΔV is defined as the difference in potential between a monolayer-covered surface and a clean subphase surface. All measurements were repeated on fresh subphases three to five times to confirm reproducibility. Standard trough cleaning procedure was adopted between measurements.

Absorption spectra of spread monolayers on the water surface were recorded in situ by means of a spectrophotometer CARY 400 equipped with fiber optic accessory supplied by Varian. The quartz fiber bundle delivered UV and vis radiation from appropriate lamps in the spectrophotometer to the Langmuir film on a trough with a quartz window at the center. Another bundle collected the light transmitted through the film and led it back to the spectrophotometer (detector) sample compartment. Both fiber bundles were fixed in the holder, which enabled to position the end of the bundle vertically to the water surface on both sides of the trough. The fiber bundles were precisely focused on the film to maximize the transmitted light level. The reference light beam of the spectrophotometer was properly attenuated to reduce a level of noise.

Polished quartz plates ($35 \times 10 \times 1$ mm^3) were used as solid substrates with hydrophilic surface for LB film fabrication. The vertical dipping method was used and the dipping rate was 5 mm/min. Langmuir films were transferred onto quartz plates at surface pressure 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 dyes **1–4** and their mixtures with AA and 8CB took place only on the first up-stroke of the substrate, when pure water was used as a subphase. The floating layers of pure dyes and of dye/AA mixtures could be transferred onto quartz surface at repeated dipping, but the calcium-containing buffer had to be used as a subphase. The multilayers of dye/8CB mixtures were not possible to obtain.

The absorption spectra of LB films were recorded in the UV–vis region by means of a spectrophotometer CARY 400, and the fluorescence measurements were carried out with a photon-counting spectrofluorimeter built in our laboratory and described in detail in Ref. [16]. The exciting light was the 436 nm line from high-pressure mercury lamp. Both in absorption and fluorescence measurements the incident light beam was normal to the substrate surface. The spectra were recorded for various molar fractions (MF) of a dye, ranging from 1.0 to 0.2. In order to analyze the spectra in wide range of dye concentrations some additional absorption and fluorescence measurements of dyes **1–4** dissolved in 8CB 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/8CB mixtures at MF ranging from 1.5×10^{-3} to 7×10^{-2}.

3. Results and discussion

3.1. Surface pressure and surface potential versus mean molecular area

Fig. 1 shows surface pressure–mean molecular area (π–A) isotherms for Langmuir films of dyes investigated. It is seen that all the dyes are able to form stable and compressible floating monolayer at an air–water interface, although the shape of isotherms is different for various dyes. As it was discussed in detail in Ref. [11] it depends strongly on the molecular structure of the side groups attached to the main skeleton of the molecule. We have also recorded π–A isotherms for Langmuir films of dyes **1–4** mixed with AA and 8CB. The examples of isotherms of such films formed on a pure water surface are presented in Fig. 2. In this figure, apart from π–A isotherms for dyes **1** and **4** and their mixtures with AA or 8CB (MF = 0.5), the surface potential–mean molecular area (ΔV–A) isotherms are also shown. The isotherms of pure AA and 8CB, given here, are very similar to those reported in literature [8,17–19].

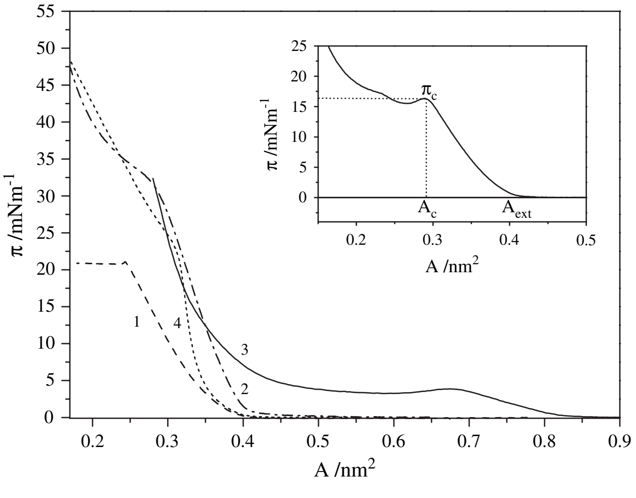

Fig. 1. Surface pressure–mean molecular area isotherms for Langmuir films of dyes **1–4** on pure water: **1** (1), **2** (2), **3** (3) and **4** (4).

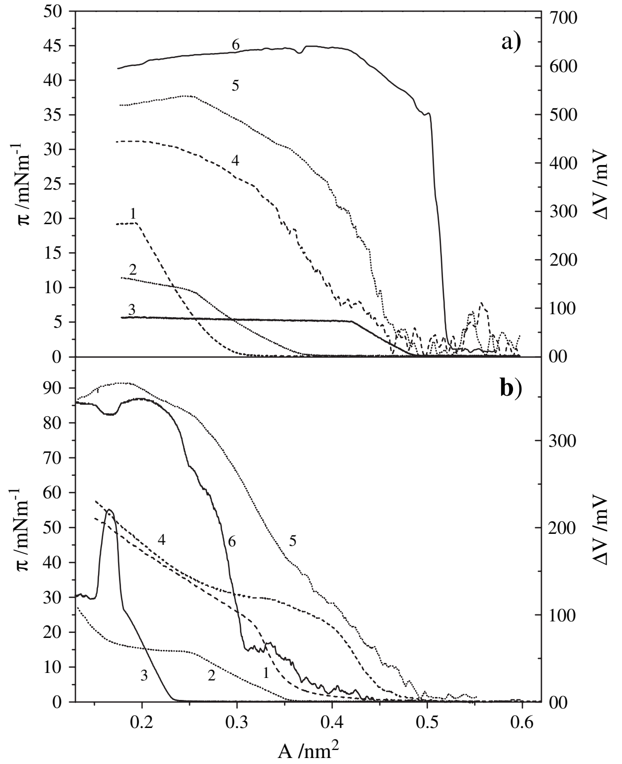

Fig. 2. Surface pressure and surface potential versus mean molecular area isotherms for Langmuir films of: (a) pure **1** (1,4), **1**/8CB mixture at MF = 0.5 (2,5) and pure 8CB (3,6), (b) pure **4** (1,4), **4**/AA mixture at MF = 0.5 (2,5) and pure AA (3,6).

Table 1 contains the characteristic values of π–A and ΔV–A isotherms for Langmuir films of pure dyes **1–4**, AA, 8CB and their binary mixtures of three different MF of a dye. The following data are presented: A_{ext} – the value of the area obtained by extrapolating the tangent of the tilt angle of the π–A or ΔV–A plots to π or ΔV equal to zero (see: inset in Fig. 1), A_{C} – the value of the collapse area, π_{C} – the value of the collapse pressure (the collapse point is recognized as the point in the π–A isotherm where the ratio $\partial\pi/\partial A$ begins to decrease due to the next phase transition) and ΔV^{max} – the maximal value of the surface potential.

From the analysis of the shapes of the isotherms and the data given in Table 1 for Langmuir films formed from binary mixtures of dyes **1–4** with AA and 8CB it 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 both components but also on the film composition. The addition of the dye to AA or 8CB affects considerably the surface potential. Although the dye molecules are only weakly polar, they influence the organization of strongly polar AA and 8CB molecules in the monolayer at the water surface and as a result the resultant polar ordering changes.

In order to establish whether in Langmuir films formed of binary mixtures the miscibility or the phase separation occurs, the mean molecular area and the collapse pressure versus the film composition were analyzed. Fig. 3 presents values of the excess of the average area per molecule,

Table 1
Features of π–A and ΔV–A isotherms for Langmuir films of dyes **1**–**4** with AA and 8CB on a pure water

Compound	MF of dye	A^{π}_{ext} (nm^2)	A_C(nm^2)	π_C(mN/m)	$A^{\Delta V}_{\mathrm{ext}}$(nm^2)	$\Delta V^{\max}$ (mV)
AA	–	0.23	0.19	25.8	0.32	350
8CB	–	0.50	0.42	5.0	0.52	630
1/AA	1.0	0.35	0.20	21.0	0.46	440
	0.8	0.34	0.21	19.6	0.54	430
	0.5	0.27	0.17	19.8	0.37	370
	0.2	0.21	0.15	26.0	0.29	340
1/8CB	0.8	0.38	0.24	17.0	0.58	520
	0.5	0.41	0.26	10.7	0.48	530
	0.2	0.49	0.36	6.7	0.58	580
2/AA	1.0	0.31	0.23	40.3	–	–
	0.8	0.25	0.20	54.4	–	–
	0.5	0.22	0.18	53.5	–	–
	0.2	0.23	0.19	27.6	–	–
2/8CB	0.8	0.36	0.33	13.3	–	–
	0.5	0.43	0.37	8.1	–	–
	0.2	0.52	0.43	6.6	–	–
3/AA	1.0	0.91	0.75	4.5	–	–
	0.8	0.80	0.59	4.8	–	–
	0.5	0.56	0.43	4.6	–	–
	0.2	0.40	0.34	5.1	–	–
3/8CB	0.8	0.84	0.74	2.2	–	–
	0.5	0.70	0.50	7.4	–	–
	0.2	0.65	0.47	7.1	–	–
4/AA	1.0	0.34	0.31	22.3	0.46	130
	0.8	0.44	0.29	12.5	0.51	360
	0.5	0.35	0.25	14.3	0.50	390
	0.2	0.26	0.20	15.6	0.40	350
4/8CB	0.8	0.38	0.32	13.0	0.51	370
	0.5	0.35	0.25	20.1	0.53	560
	0.2	0.37	0.31	7.6	0.52	660

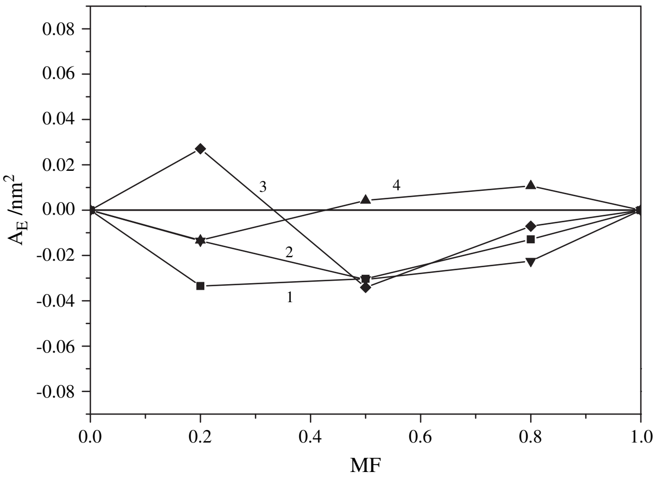

Fig. 3. Plot of the excess of the mean molecular area per molecule, A_E of dyes **1**–**4** mixed with AA versus the molar fraction of a dye: **1** at $\pi = 13.4$ mN/m (1), **2** at $\pi = 19.4$ mN/m (2), **3** at $\pi = 2.8$ mN/m (3) and **4** at $\pi = 10.0$ mN/m (4).

$A_E = A_{12} - (x_1A_1 + x_2A_2)$, as a function of MF of a dye for dye/AA mixtures. A_{12} here is the average molecular area in the two-component film, x_1 and x_2 are the mole fractions of the components, and A_1 and A_2 are the single component areas at the same π. All the dyes under investigation mixed with AA show $A_E \neq 0$. The negative deviation from additivity rule, which is distinctly observed for dyes **1** and **2** mixed with AA, means a contraction of the two-component films due to attractive interactions between dye and liquid crystal molecules [15]. The positive deviations are characteristic for miscible components with repulsive intermolecular interactions [15] and they occur here in **3**/AA mixture at small dye concentration. A_E values for **4**/AA systems indicate that the interactions between dye and AA molecules are not very strong and their kind changes with the mixture composition. The nature of interactions between dyes **1**–**4** and AA molecules in Langmuir films is quite different than that in dye/8CB films, which can be followed from Fig. 4. This is probably because the monolayer that formed from pure 8CB is less stable and rigid than AA monolayer [17]. In general, the deviation from the additivity rule for dye/AA mixtures is significantly smaller than that for dye/8CB mixtures (except **1**). Joining this fact with changes in π_C values (see: Table 1) we can conclude that the dyes under investigation have good miscibility with 8CB, whereas in their mixtures with AA only partial miscibility occurs.

3.2. Electronic absorption spectra

Table 2 lists the positions of the maximum (λ) and the half-bandwidths (δ) of the longwavelength absorption band for dyes **1**–**4** in chloroform and ethanol. Additionally, the data for dyes **1** and **4** in 8CB measured in sandwich cell at three MF in the isotropic phase ($T = 46$ °C) are given. The differences observed in λ and δ values in dilute solutions may originate from the different refractive index and the dielectric constant of various solvents. With the rise of the dye concentration in dye/8CB mixtures δ values rise systematically,

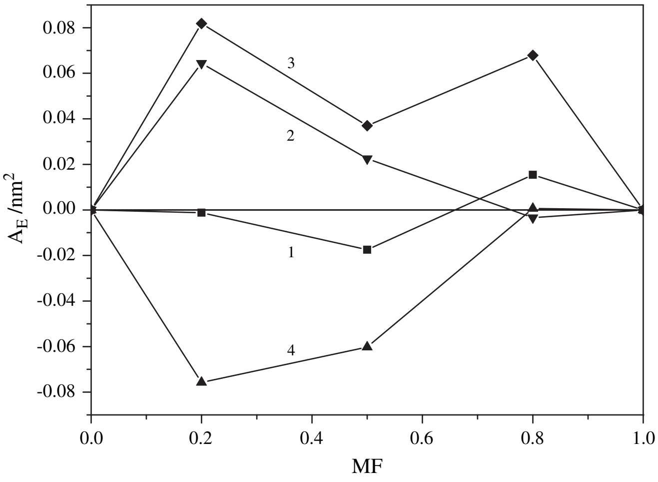

Fig. 4. Plot of the excess of the mean molecular area per molecule, A_E of dyes **1**–**4** mixed with 8CB versus the molar fraction of a dye at $\pi = 4$ mN/m: **1** (1), **2** (2), **3** (3) and **4** (4).

Table 2
The position of the absorption maximum (λ) and the half-bandwidth of the absorption band (δ) for dyes **1–4** in chloroform, ethanol and 8CB

Dye code	Chloroform, MF = 8.2×10^{-7}		Ethanol, MF = 5.7×10^{-7}		8CB ($T = 46$ °C)					
					MF = 1.5×10^{-3}		MF = 1.4×10^{-2}		MF = 3×10^{-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}), $\Delta\delta = \pm 10$ cm^{-1}	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}), $\Delta\delta = \pm 10$ cm^{-1}	λ_{max}(nm), $\Delta\lambda = \pm 1$ nm	δ(cm^{-1}), $\Delta\delta = \pm 10$ cm^{-1}
1	428	3690	450	3520	433	3460	432	3640	432	3850
2	428	3710	447	3510	–	–	–	–	–	–
3	430	3750	446	3580	–	–	–	–	–	–
4	435, 457	3080	452, 466	3120	440, 460	3130	440, 459	3330	440, 459	3390

whereas the position of the maxima does not vary (see later: Figs. 7 and 8). Fig. 5a presents longwavelength absorption spectra of pure dye **3** and its mixtures with AA, as examples, in Langmuir films on pure water before the collapse point, whereas in Table 3 the values of λ and δ for Langmuir films of all the dyes under investigation and their mixtures with AA at MF = 0.5 are given. It is seen that in the spread monolayers on the water the absorption band of dyes **1–4** is distinctly broadened in comparison with that in solutions. This observation could suggest that with the rise of the dye content some fractions of self-aggregates by dye molecules are created. Indeed, neither an additional peak, nor a shoulder, which would indicate the dimer-creation in the ground state, is observed, but the dye absorbance in Langmuir films does not vary proportional to its concentration. For example, the content of dye **3** in AA, whose absorption spectra are shown in Fig. 5a, decreases by a factor of 5, while the absorbance of dye **3** decreases about 3-fold. For other dyes similar behaviour was found. The same observation can be made for LB films of dyes **1–4**. Fig. 5b shows the longwavelength absorption band of pure dye **3** and its mixtures with AA as LB films, while the values of λ and δ for dyes **1–4**, pure and mixed with AA or 8CB at MF = 0.5, are listed in Table 3. The results obtained indicate both the spectral broadening of the longwavelength absorption band and the lack of the proportionality between the dye content in the mixture and the absorbance value. This seems to confirm the suggestion about the occurrence of the small fraction of dye **1–4** aggregates in Langmuir and LB films already in the ground state.

The creation of dimers without spectral shift is a peculiar phenomenon, but it is predicted by the molecular exciton model proposed by Kasha et al. [20]. According to this model, if sufficiently strong electronic transitions exist, dipole–dipole interactions in molecular aggregates 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.

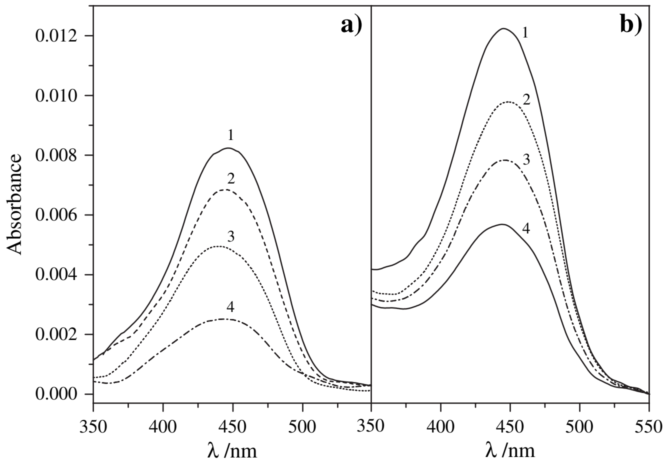

Fig. 5. Absorption spectra of monolayers of pure **3** (1) and **3**/AA mixtures at MF of dye: 0.8 (2), 0.5 (3) and 0.2 (4); (a) on the water surface at π below the collapse point, (b) in LB films.

Table 3
The position of the absorption maximum (λ) and the half-bandwidth of the absorption band (δ) for dyes **1–4**, pure and mixed with AA and 8CB in Langmuir and LB films

Dye code	Langmuir films				LB films					
	Pure dye		Dye/AA, MF = 0.5		Pure dye		Dye/AA, MF = 0.5		Dye/8CB, MF = 0.5	
	λ_{max}(nm), $\Delta\lambda = \pm1$ nm	δ(cm^{-1}), $\Delta\delta = \pm50$ cm^{-1}	λ_{max}(nm), $\Delta\lambda = \pm1$ nm	δ(cm^{-1}), $\Delta\delta = \pm50$ cm^{-1}	λ_{max}(nm), $\Delta\lambda = \pm1$ nm	δ(cm^{-1}), $\Delta\delta = \pm50$ cm^{-1}	λ_{max}(nm), $\Delta\lambda = \pm1$ nm	δ(cm^{-1}), $\Delta\delta = \pm50$ cm^{-1}	λ_{max}(nm), $\Delta\lambda = \pm1$ nm	δ(cm^{-1}), $\Delta\delta = \pm50$ cm^{-1}
1	450	4000	444	3800	448	4050	448	3850	451	3750
2	445	4000	450	3650	447	4150	440	4210	445	4210
3	447	3850	440	3900	449	3900	446	4000	444	4150
4	451	3850	445	4000	450	4100	446	3950	450	3650

Table 4
The position of the fluorescence maximum (λ) and the half-bandwidth of the fluorescence band (δ) for dyes **1–4** in chloroform, ethanol and in microcrystal

Dye code	Chloroform, MF = 8.2×10^{-7}		Ethanol, MF = 5.7×10^{-7}		Microcrystal	
	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}), $\Delta\delta = \pm10$ cm^{-1}	λ_{max}(nm), $\Delta\lambda = \pm1$ nm	δ(cm^{-1}), $\Delta\delta = \pm10$ cm^{-1}
1	502	2570	531	2830	545	3140
2	503	2580	532	2830	548	3150
3	502	2600	535	2970	550	3170
4	488	2080	508	2220	590	3060

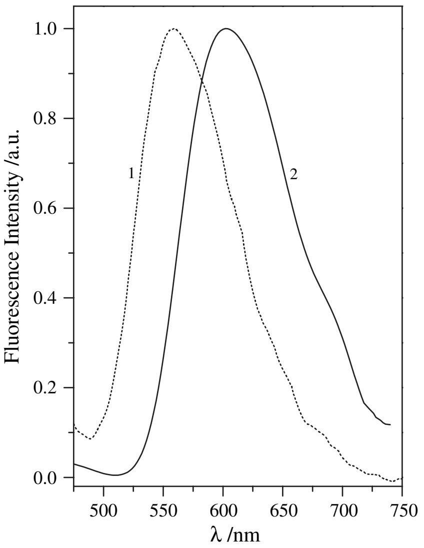

Fig. 6. Fluorescence spectra of dyes **1** (1) and **4** (2) as LB films are transferred from a pure water surface.

The molar extinction coefficient of dyes **1–4** is quite large, over 15 000 [1–3], thus the exciton coupling is most likely to occur in compressed monolayers. Assuming the parallel configuration of dye **1–4** molecules in dimer, the co-planar arrangement of the absorption transition moments can be considered. This leads to the exciton band splitting given by the formula [20]:

$$\Delta E_{\mathrm{NK}} = \frac{2|\mathbf{M}|^2}{\mathbf{R}^3}\left(1 - 3\cos^2\Theta\right) \qquad (1)$$

where **M** is the electric dipole transition moment of the molecule, **R** is the intermolecular distance vector connecting the centers of two molecules in dimer, and Θ is the angle between **M** and **R**.

For Θ equal to 54.7° the exciton splitting is zero, irrespective of the intermolecular distance, and thus no shift of absorption band position is observed. Aggregates corresponding to Θ having values between 54.7° and 60° are referred to as the intermediate or I-type aggregates [21] and were observed previously for spiropyrans [21], dioctadecylrhodamine [22] and pyrene [23]. The distinct broadening of the absorption band of dyes **1–4** in Langmuir and LB films (compared to that characteristic of monomers) with no shift in the absorption maximum position, implies that, in the case of derivatives of naphthalenebicarboxylic acid and of naphthoylenebenzimidazole, we are dealing predominantly with I-aggregates in the ground electronic state.

From Fig. 5, it follows that the absorbance values of the dye at the same MF are different in Langmuir and LB films. This observation seems to confirm the fact, found previously for derivatives of naphthalenebicarboxylic acid and of naphthoylenebenzimidazole as well as for their mixtures with liquid crystals [14] that at the transfer of the monolayer from the water surface to the quartz plate, a rearrangement of the molecular organization takes place. The angle between the long

Table 5
The position of the fluorescence maximum (λ) and the half-bandwidth of the fluorescence band (δ) for **1–4**, pure and mixed with AA and 8CB in LB films

Dye code	Pure dye		Dye/AA				Dye/8CB			
			MF = 0.5		MF = 0.2		MF = 0.5		MF = 0.2	
	$\lambda_{\max}$ (nm), $\Delta\lambda = \pm 1$ nm	δ (cm^{-1}) $\Delta\delta = \pm 50$ cm^{-1}	$\lambda_{\max}$ (nm), $\Delta\lambda = \pm 1$ nm	δ (cm^{-1}), $\Delta\delta = \pm 50$ cm^{-1}	$\lambda_{\max}$ (nm), $\Delta\lambda = \pm 1$ nm	δ (cm^{-1}), $\Delta\delta = \pm 50$ cm^{-1}	$\lambda_{\max}$ (nm), $\Delta\lambda = \pm 1$ nm	δ (cm^{-1}), $\Delta\delta = \pm 50$ cm^{-1}	$\lambda_{\max}$ (nm), $\Delta\lambda = \pm 1$ nm	δ (cm^{-1}), $\Delta\delta = \pm 50$ cm^{-1}
1	559	3050	547	3100	–[a]	–[a]	552	2750	539	2950
2	557	3200	553	3100	545	2850	553	3100	542	3050
3	554	3250	547	2900	547	2850	548	3300	548	3000
4	601	3000	603	2850	605	3150	602	2900	589	3100

[a] Fluorescence is not measurable.

Table 6
The position maximum (λ) and the half-bandwidth of the fluorescence band (δ) for **1** and **4** in 8CB measured in sandwich cell ($T = 46$ °C)

1 in 8CB			**4** in 8CB		
MF of dye	λ_{max} (nm), $\Delta\lambda = \pm 1$ nm	δ (cm^{-1}), $\Delta\delta = \pm 10$ cm^{-1}	MF of dye	λ_{max} (nm), $\Delta\lambda = \pm 1$ nm	δ (cm^{-1}), $\Delta\delta = \pm 10$ cm^{-1}
$1.5 \cong 10^{-3}$	505	2610	$1.5 \cong 10^{-3}$	496	2340
$9.0 \cong 10^{-3}$	508	2640	$1.4 \cong 10^{-2}$	504	2340
$1.7 \cong 10^{-2}$	509	2650	$3.0 \cong 10^{-2}$	504	2360
$3.0 \cong 10^{-2}$	512	2650	$3.5 \cong 10^{-2}$	505	2480
$7.0 \cong 10^{-2}$	516	2700	$4.0 \cong 10^{-2}$	507	2560

molecular axis and the normal to the surface is significantly smaller in Langmuir films than that in LB films, which is reflected in the absorption intensity because the projection of the absorption transition moment on the surface changes.

3.3. Fluorescence spectra

Table 4 shows the positions of the maximum and the half-bandwidths of the fluorescence band for dyes **1–4** in chloroform and ethanol solutions as well as in microcrystal for comparison. The strong bathochromic shift of the maximum position as well as the broadening of the band of the dyes in ethanol with respect to chloroform, especially for derivatives of naphthalenebicarboxylic acid, are observed. Because the concentration of dyes in both solvents is very small, it cannot be supposed that the aggregates in ethanol are created. The differences in λ and δ for solutions are rather connected with various polarity of the solvents. In the crystalline state the maximum position for derivatives of naphthalenebicarboxylic acid is shifted towards longer wavelengths of ≈15 nm and for derivative of naphthoylenebenzimidazole of ≈80 nm with respect to that in ethanol. Additionally, in the case of dye **4** the distinct broadening of the fluorescence band occurs. Fig. 6 shows the fluorescence spectra of dyes **1** and **4** as LB films are transferred onto the solid substrate from the pure water at surface pressure below the collapse point, while in Table 5 the values of λ and δ for LB films of all dyes under investigation as well as of their mixtures with AA and 8CB at MF = 0.5 and 0.2 are summarised. Similarly as in microcrystal, the red shift of maximum positions for all the dyes and the broadening of the fluorescence band (especially for dye **4**) with respect to appropriate values in solutions are seen.

From comparison of the results obtained from the fluorescence (Tables 4 and 5) and absorption measurements (Tables 2 and 3), it follows that a distinct bathochromic shift of the fluorescence peak for dyes in LB films with respect to that in diluted solutions has no reflection in absorption spectra. Therefore, we can speculate that we are dealing here with the fluorescence of excimers which originate from an interaction between the ground and excited state molecules and are often observed in the solid state of flat aromatic molecules [24]. In order to check whether the red shift of the fluorescence peak is really due to the formation of the excimer we measured the fluorescence of dyes **1–4** in 8CB at various concentrations in sandwich cells. The results for dyes **1** and **4** are given in Table 6 and it indicates that with the rise of the dye content the maximum position of the fluorescence band shifts systematically towards longer and longer wavelengths and the half-bandwidth increases. Simultaneously, at sufficiently high concentration the fluorescence intensity starts to decrease, although the absorbance rises almost proportional to increasing MF, which is seen in Figs. 7 and 8. Thus we can conclude that the interaction between two molecules in dimers created in the electronic ground state is very weak and the overall shape of the absorption spectrum of dyes **1–4** in 8CB is monomer-like. However, the decrease of the fluorescence intensity with the rise of a dye concentration would indicate on 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 [24,25]. The maximum shift and the band broadening are confirmation of tendency to the aggregates formation.

In LB films when the dye concentration in 8CB or AA is several times higher than in the sandwich cell, the fluorescence band maximum shifts rapidly to the longer wavelengths, and the half-bandwidth increases, indicating that more and more molecules come together and form excimer configurations. For pure dyes in LB films the δ values are comparable with those in microcrystal, whereas the fluorescence peak in monolayers is slightly red-shifted compared to that of the solid state. This would suggest that in LB films the overlap between two molecules forming excimer is larger than in microcrystal. This is rather an unexpected result, but could be understood if one takes

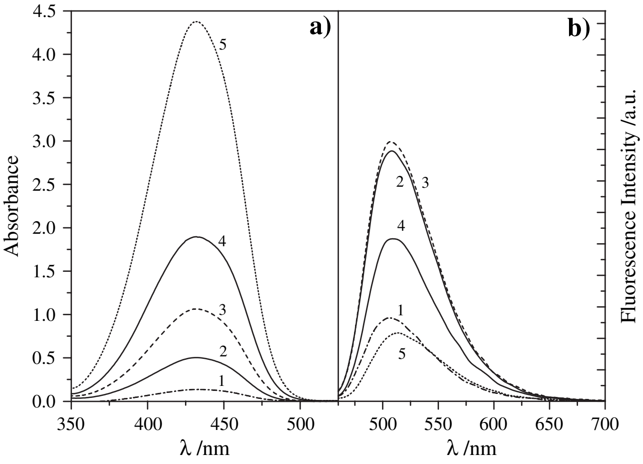

Fig. 7. Absorption (a) and fluorescence (b) spectra of **1** in 8CB at MF of dye: 1.5×10^{-3} (1), 9×10^{-3} (2), 1.7×10^{-2} (3), 3×10^{-2} (4) and 7×10^{-2} (5) measured in sandwich cell in the isotropic phase ($T = 46$ °C).

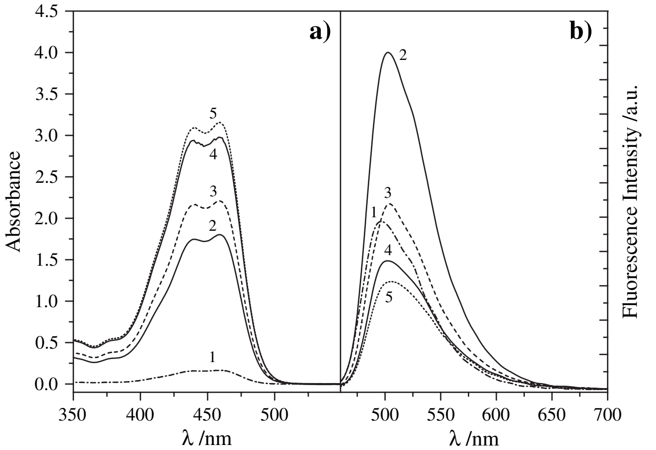

Fig. 8. Absorption (a) and fluorescence (b) spectra of **4** in 8CB at MF of dye: 1.5×10^{-3} (1), 1.4×10^{-2} (2), 3×10^{-2} (3), 3.5×10^{-2} (4) and 4×10^{-2} (5) measured in sandwich cell in the isotropic phase ($T = 46$ °C).

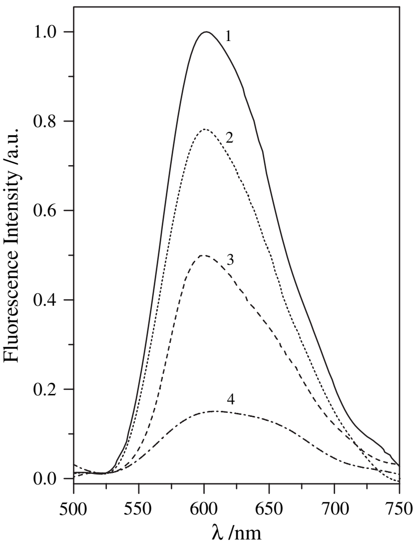

Fig. 9. Fluorescence spectra of pure dye **4** (1) and **4**/AA mixtures at MF of a dye: 0.8 (2), 0.5 (3) and 0.2 (4) in LB films transferred from water/$CaCl_2$ buffer.

into account that in LB films the distance between molecules is less well defined than in the solid state. As a result some molecules may transitorily be closer to each other causing the fluorescence spectrum to be dominated by the low energy emission.

Looking at the data given in Table 5 it is seen that there are small differences between the fluorescence maximum of LB films of dye/AA and dye/8CB at the same mixture composition, which is probably due to various molecular packing of AA and 8CB molecules first in Langmuir, and next in LB films. Therefore the differences are more distinct at smaller dye content.

In order to check whether the influence of the number of layers in the LB film on the fluorescence spectra occurs, we fabricate LB films of **1**/AA and **4**/AA after 1 and 4-fold dipping of the quartz substrate in the monolayer on the water with $CaCl_2$ at the surface pressure just below the collapse point. The fluorescence spectra obtained for such LB films do not reveal noticeable changes in the maximum position and half-bandwidth values with respect to those presented in Table 5. This means that already in the monolayer formed on the quartz substrate the molecules of derivatives of naphthalenebicarboxylic acid and of naphthoylenebenzimidazole have sufficiently good conditions to overlap in the way enabling the genuine excimers creation. Such observation is unlike to that made for 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes, which were previously investigated by some of us in LB films [26]. For perylene-like compounds the excimer emission appeared distinctly for multilayers, whereas for the monolayer the emission of excimer precursors was mainly observed, and only a small shoulder in the red side of the fluorescence band indicated the creation of some fraction of genuine excimers.

Fig. 9 shows the fluorescence spectra of dye **4** and its mixtures with AA in LB films transferred onto the quartz plates from the buffer with $CaCl_2$ at one dipping. The fluorescence intensity is almost proportional to the dye content, which can be additional confirmation of the fact that in the case of the dyes under investigation already in a single monolayer and at MF $\gtrsim 0.2$ the molecular organization is high enough for excimer creation and therefore the emission spectrum does not change when the number of layers and/or dye concentration increases.

4. Conclusions

Three derivatives of naphthalenebicarboxylic acid (**1**–**3**) and a derivative of naphthoylenebenzimidazole (**4**), together with their binary mixtures with arachid acid and liquid crystal 8CB have been investigated as Langmuir and Langmuir–Blodgett films. The analysis of π–A and ΔV–A isotherms of Langmuir films reveals that the properties of the monolayer on the subphase surface (packing density, stability and rigidity) depend strongly on the structure of dye molecules as well as on the mixture composition. Mixtures of the dyes with 8CB are miscible over the whole range of MF, while for dye/AA systems only partial miscibility of components is observed.

For Langmuir films the absorption spectra in situ and both the absorption and fluorescence spectra for LB films were recorded. In order to resolve the problem of dye aggregation the mixtures of dyes with 8CB in sandwich cells have been studied additionally as a function of a dye concentration. The shape of the absorption spectra of dyes **1**–**4**, pure and mixed with the liquid crystal or arachid acid, suggests a tendency of formation of aggregates between dye molecules already in the ground electronic state. The detailed analysis of the fluorescence spectra allows to conclude that derivatives of naphthalenebicarboxylic acid and derivatives of naphthoylenebenzimidazole can create molecular configurations giving excimer emission. The energy and intensity of this emission strongly depend on the dye concentration in the range investigated in sandwich cell (up to MF $\approx 4 \times 10^{-2}$ for derivative of naphthalenebicarboxylic acid and 7×10^{-2} for derivative of naphthoylenebenzimidazole). In LB films at MF $\gtrsim 0.2$

no influence of the dye content and of the number of layers on the shape and the position of the fluorescence band is observed, which indicates the genuine excimers' creation.

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