Self-aggregates formation of tetrachloroperylene acid esters in Langmuir and Langmuir-Blodgett films

A. Modlińska, E. Chrzumnicka, T. Martyński*

Faculty of Technical Physics, Poznan University of Technology, Pl. Marii Skłodowskiej-Curie 5,60-965 Poznan, Poland

A B S T R A C T

Using Langmuir and Langmuir-Blodgett techniques molecular films of chlorinated perylene derivatives, namely tetra-n-butyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylate (**PCn** for n = 1, 5, 9) have been studied. The Langmuir films of pure compounds and mixed with liquid crystalline 4-octyl-4′-cyanobiphenyl (**8CB**) were characterized by surface pressure-mean molecular area isotherms. An additive rule reveals miscibility of all the dyes with 8CB but shows different types of intermolecular interaction forces. The pure and mixed Langmuir films were transferred onto quartz plates and characterized spectroscopically. Absorption and fluorescence spectra were recorded for the samples in form of diluted chloroform solution, the dye with **8CB** mixtures in monomolecular Langmuir-Blodgett films and in liquid crystal cells. Different tendency to aggregation of the dye with short and long alkyl chains was observed. It is shown that the dye molecule stacking and aggregation of the chlorinated perylene dyes depend on the dye concentration and are related to the torsion of the perylene core.

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1. Introduction

Organic electronic devices based on low molecular mass compounds have been developed rapidly during last decade. High performance of such molecular devices depend on suitable optical end electronic parameters of individual molecules and their organization in bulk and ultra-thin layers. Technological development and improvement of the devices is possible when new materials with desired properties are synthesized and precisely characterized. In case of chromophores a high absorption coefficient, fluorescence and electroluminescence quantum yield, fluorescence lifetime, charge carrier conductivity and type of semi-conductivity with respect to the tendency to self-organization are the most important. All this properties have to be examined using complementary techniques. Optical and electric properties depend strongly on molecular orientation and aggregation. Intermolecular interaction is reflected in electronic absorbance and emission band structure position and intensity. Also the charge mobility is governed by molecular mutual relation when organization of the molecules form not only dimers, excimers but other types of molecular order in form of columnar stacking or mesogenic phases. Such effects have been observed in numbers of compounds which form
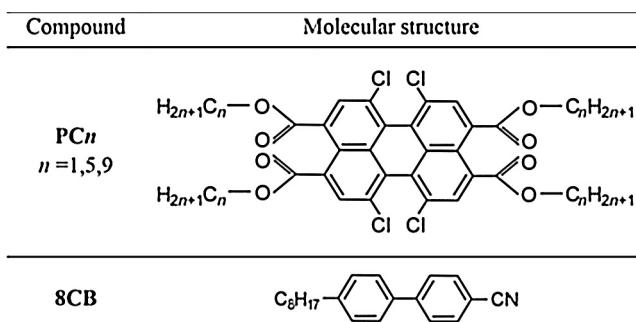
ordered systems like cyanine [1], phthalocyanine [2,3], porfirine, perylene derivatives [4–6] and others [7,8].

Investigation of properties' changes caused by molecular aggregation is difficult to evaluate by quantum-mechanics computer simulation even now [9,10]. Therefore, experimental techniques are almost only way to get a deep knowledge about properties of organized complex systems. One of the best systems to investigate all of mentioned above properties, which simplified molecular order up to two-dimension is a monomolecular film created at the air–water interface and transferred onto a solid support by using well developed Langmuir-Blodgett technique. This technique is one among others in the fields of molecular nanoscience and nanotechnology where it is possible to manipulate the individual molecules in building ordered two-dimensional systems.

Perylene derivatives have been attracting much interest because of their high absorption coefficient, excellent bluish-green fluorescence with extremely high quantum yield [11] and electrical properties which depend on the molecular structure. These dyes have a tendency to aggregate because of strong π-π^* electrons interactions just in concentrated solutions, monomolecular films. Types of aggregates created in the films depend on the structure of peripheral substituents [12–16]. In condensed form like thermally evaporated thin layers, drop-casted or spin-coated films and Langmuir-Blodgett films the dyes reveal semiconducting properties. Typically perylene derivatives exhibit p-type of conductivity as other organic compounds [17–19]. In the case of the derivatives

Fig. 1. Molecular structure of the compounds investigated.

with chlorine atoms attached in the bay position to the perylene core the dyes in the films reveals n-type of semiconductivity [18].

Chlorinated perylene derivatives possess strongly deformed plane of the core. This deformationhas a major influence on the spectral properties of the dye in condensed phases because of changes in aggregation tendency [16]. Also the elementary cell, in correctly formed molecular crystals, is different from the non-chlorine substituted dyes. From X-ray analysis, the distance between molecules within the cell is significantly larger (3.5 Å and 4.5 Å in non-chlorinated and chlorinated, respectively) [16,20]. These changes are caused by strong repulsion and dimension of chlorine atoms. Chlorinated perylene derivatives with alkyl chains attached to the carboxylic group show ability to form stable Langmuir films at the air–water interface that depends on the number of carbon atoms. To investigate the aggregation process of such systems the Langmuir technique is an appropriate method in particular, that it is possible to form pure dye films, as well as mixed with monolayer builder molecules to obtain two-dimensional concentrated mixtures [12,13,15,16,21].

Taking into account the above, we studied molecular alignment of recently synthesized promising dye materials at air–water and air–solid interfaces using Langmuir-Blodgett (LB) technique which is very suitable for identifying molecular alignment and phase transitions in thin films. In our previous paper [15] we reported organization of perylene-like dye tetra-n-butyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylate (**PCn** for n = 1, 4, 5, 6, 9). We have shown that almost all **PCn** investigated are able to create stable and compressible monolayers which can be successfully transferred onto the solid substrates forming LB films. However, some questions concerning molecular interactions remained still opened. Therefore, in this work, we study three most intriguing dyes with different length of terminal alkyl chains – **PC1**, **PC5** and **PC9** – in mixtures with liquid crystal 4-octyl-4′-cyanobiphenyl (**8CB**) in Langmuir and LB films. This research along with previous results reveals extended analysis of behaviour of these perlene-like dyes at air–water and air–solid interfaces.

2. Materials and methods

The molecular structure of compounds under investigation is given in Fig. 1. The dyes tetrachloroperylene acid esters (**PCn**) for n = 1, 5, 9 were synthesized and chromatographically purified at the Institute of Polymer Technology and Dyes, Lodz University of Technology, Poland. The liquid crystal 4-octyl-4′-cyanobiphenyl (**8CB**) was received from prof. R. Dabrowski Laboratory at the Institute of Chemistry, Military University of Technology, Poland. Its phase transitions were in excellent agreement with literature data [22].

A commercially available Minitrough 2 manufactured by KSV Instruments Ltd., Finland, was used for the formation of Langmuir and Langmuir-Blodgett films. The subphase was deionized and purified water to a final resistivity of 18.2 MΩ cm by a Milli-

Q system (Millipore Corporation, Austria). The temperature of the subphase was kept constant at 21 °C by a cooling circulator F12-ED (Julabo, Germany). The compounds were dissolved in spectroscopically pure chloroform (POCH, Poland) at a concentration of 0.1 mM in order to obtain stock solutions which were subsequently mixed to receive appropriate molar fraction (*MF*) of the dyes in the **8CB** matrix. The sample material was spread on the clean air–water interface with using a glass microlitre syringe (Hamilton, Great Britain) and left for 10 min for the solvent evaporation and the film relaxation. Next, the monolayer was symmetrically compressed at a barrier motion speed of 5 mm min⁻¹ and the surface pressure was monitored by a platinum Wilhelmy plate hanged on an electronic balance with an accuracy of ±0.1 mN m⁻¹. All measurements were repeated on the fresh subphase three times to confirm reproducibility. Standard trough cleaning procedure was adopted between measurements.

For LB film deposition polished plates of fused quartz (35 × 15 × 1 mm) were used. The vertical dipping method was used with dipping rate of 5 mm min⁻¹ and dipping stroke of 20 mm. The quantity and the quality of the deposited monolayer on a solid substrate is given by transfer ratio, *TR*, which was calculated as the ratio of the decrease in the monolayer area during the deposition to the area on the substrate coated by the layer. For all LB films the transfer ratio was near unity what means that the Langmuir films have been transferred without structural changes.

The absorption spectra of the LB films were recorded in the UV–vis spectral region using a spectrophotometer CARY 400 (Varian, Austria). The fluorescence measurements were carried out with a computer-controlled photon-counting spectrofluorimeter build in our laboratory. The exciting light was the 436 nm line from the high-pressure arc mercury lamp. In both absorption and fluorescence measurements the incident light beam was directed normally to the substrate surface.

In order to analyse the absorption and fluorescence spectra over a wide range of dye concentrations, some additional measurements for **PC1** 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 the absorption and emission spectra of **PC1/8CB** mixtures at *MF* from 7.3·10⁻⁴ to 1.4·10⁻².
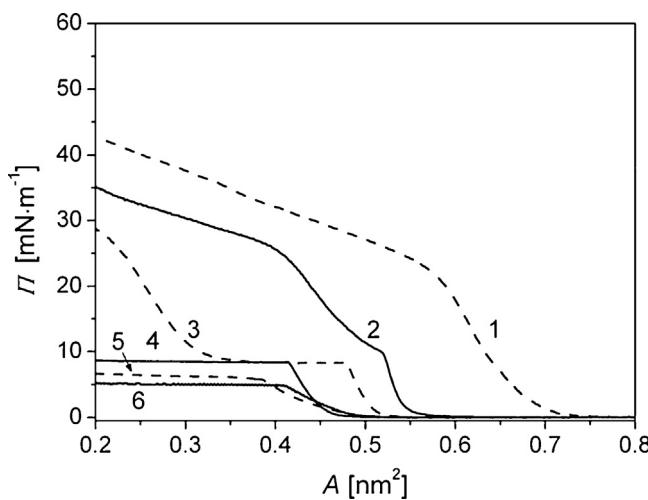
3. Results and discussion

3.1. Surface pressure-mean molecular area isotherms of Langmuir films

As the first stage of our research we have recorded π–A isotherms for Langmuir films of dyes **PC1**, **PC5** and **PC9** mixed with **8CB**. The exemplary isotherms for such films of **PC5/8CB** mixtures prepared for various molar fraction of the dye, *MF*, are shown in Fig. 2 whereas in Table 1 characteristic data for all mixtures investigated are gathered. The following data are presented: A_{ext} – area obtained from the tangent to the slope of linear part the π–A curve extrapolated to π equal to zero, A_C and π_C – values of collapse area and pressure. The collapse point is recognized as the point in the π–A isotherm where the ratio $\partial\pi/\partial A$ starts to decrease due to phase transition and indicates the formation of the condensed monolayer. For better characterization of compounds investigated in this table additionally are seen: C_S^{-1} – compressional modulus calculated from the following equation:

$$C_S^{-1} = \frac{1}{A}\left(\frac{\partial A}{\partial \pi}\right)_T,\tag{1}$$

where A is the molecular area and $\left(\frac{\partial A}{\partial \pi}\right)_T$ is the inverse of the slope of the isotherm through the given phase and φ – average angle between the normal to the water surface and rigid molecular core of

Fig. 2. Surface pressure-mean molecular area isotherm of Langmuir films of **PC5** (1), **8CB** (6) and **PC5/8CB** mixtures at *MF* of the dye: 0.2 (2), 0.4 (3), 0.6 (4), and 0.8 (5).

Table 1
Characteristic parameters of π–A isotherms of Langmuir films of **PC*n*/8CB** mixtures and **8CB** on the water at various molar fractures *MF* of the dye.
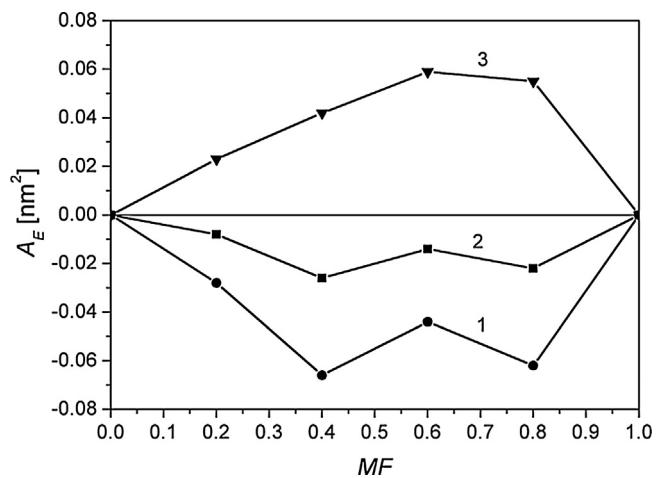
Compound	MF	A_{ext} [nm²]	A_C [nm²]	π_C [mN m⁻¹]	C_S^{-1} [m N⁻¹]	φ [°]
PC1	1.0	0.56	0.35	47.8	107.2	24
PC1/8CB	0.8	0.46	0.34	18.6	128.9	25
	0.6	0.42	0.39	5.2	66.8	33
	0.4	0.47	0.43	4.8	51.1	43
	0.2	0.49	0.43	4.8	37.9	51
PC5	1.0	0.67	0.57	22.1	126.6	41
PC5/8CB	0.8	0.54	0.52	9.7	253.4	41
	0.6	0.51	0.48	8.4	160.9	42
	0.4	0.45	0.41	8.4	96.5	40
	0.2	0.49	0.38	5.8	32.5	43
PC9	1.0	–	–	–	–	–
PC9/8CB	0.8	1.39	1.27	2.3	22.0	–[a]
	0.6	1.17	1.05	2.9	29.3	–[a]
	0.4	0.92	0.84	3.4	29.9	–[a]
	0.2	0.73	0.62	4.2	30.2	–[a]
8CB	1.0	0.24	0.19	26.5	7.6	60

$\Delta A_{ext} = \Delta A_C = \pm0.01$ nm², $\Delta \pi_C = \pm0.01$ mN m⁻¹, $\Delta C_S^{-1} = \pm0.1$ m N⁻¹, $\Delta\varphi = \pm5°$.
[a] Impossible to calculate.

the dyes mixed with **8CB** calculated from the average area occupied by the dye molecule with respect to the area of the rigid part of the dye and cross-section of **8CB** molecules.

From the run of the π–A isotherms and data gathered in Table 1 for **PC1**, **PC5** and **PC9** dyes follows that the stability and rigidity of the Langmuir films formed of the dyes depends on the length of the terminal alkyl chains. The highest surface pressure is observed for **PC1** what clearly demonstrates that this dye forms the most stable and rigid monolayer. For **PC5** the value of surface pressure of the collapse point is two times smaller whereas **PC9** is not able to form Langmuir film. That means that excessively long hydrocarbon chains in **PC9** separate –COO– group from the water surface and screen interactions between perylene cores of the dye molecules. Interestingly, for **PC1** and **PC5** the mean molecular area of at the collapse point A_C is lower than the cross-sectional area of perylene rigid core of the dyes. The cross-sectional area of the perylene core with incorporated chlorine atoms in the bay positions and four ester groups of the dyes obtained from single crystal XRD is approximately 0.87 nm² [15]. Far less values of A_C imply that molecules do not lie at the air–water interface but are arranged in head-on configuration with relatively small angle. The significant difference in shape of the π–A isotherms is seen for the liquid crystal **8CB**. Due

to strong repulsive interactions between cyano groups in the two dimensional film postulated by Xue et al. [23], the **8CB** monolayer is fragile and not densely packed.
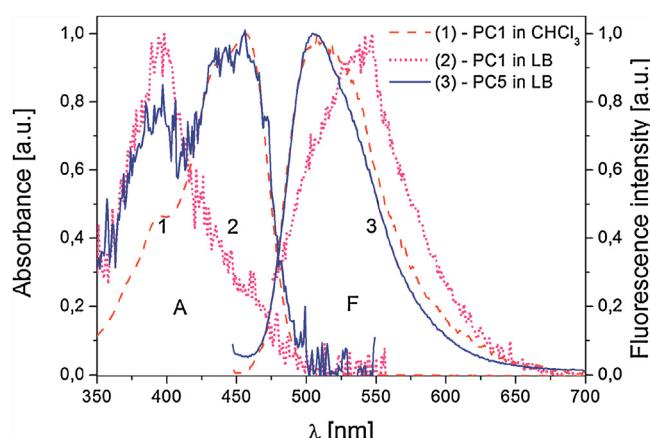
The analysis of the Langmuir films formed of the perylene-derivatives with liquid crystal shows that properties of the film depends not only on the molecular structure of the dye but also on the mixture composition. With increasing **8CB** content the slope of the isotherms decreases what suggests that monolayers become less stable and rigid. Decrease of both surface pressure at collapse point and compressional modulus also confirm this conclusion. Moreover, bigger values of the average tilt angle φ indicate that molecules occupy bigger area at the interface and by consequence the interactions between them are weaker. The only exception is mixture of **PC9** (the dye which alone is not able to form Langmuir film) with **8CB**. Here, all the dependences are inverted indicating that liquid crystal plays a role of the stabilizing matrix.

To study quantitatively the molecular organization of the mixed monolayers at the air–water interface, excess of the average area per molecule, A_E, at given surface pressure was calculated from the following formula:

$$A_E = A_{12} - (MF_1 A_1 + MF_2 A_2), \qquad (2)$$

where A_{12} is the average molecular area in the two-component film, MF_1 and MF_2 are the molar fractions of two components, and A_1 and A_2 are the molecular areas of two single-component films at the same π. If A_E is equal to zero, the average area per molecule follows the additivity rule, $A_{12} = MF_1 A_1 + MF_2 A_2$, what means that the two components are completely miscible (ideal mixture) or immiscible. Deviation from zero, either positive or negative, indicates miscibility and non-ideal behaviour [24].

Plots of the excess area A_E vs. molar fracture *MF* of the dyes investigated mixed with **8CB** for Langmuir films formed on water subphase are presented in Fig. 3. For **PC1** and **PC5** negative values of A_E are observed what means the constriction of area occupied by molecules in mixed films with respect to films formed by only one component. That suggests the attractive interactions between dyes and liquid crystal molecules and improvement of the stability of the monolayers. Reversely, for **PC9** repulsive interactions are postulated due to positive values of excess area A_E. One can notice that for some *MF* of **PC5/8CB** mixture the values of excess area deviate within experimental uncertainty ($\Delta A_E = \pm0.02$ nm²). Therefore, it is necessary to take into account surface phase rule which claims that two ingredients are miscible if π_C changes with the mixture composition. The data gathered in Table 1 confirm good miscibility of all tetrachloroperylene acid esters investigated with **8CB**.

Fig. 3. Excess area as a function of the molar fraction *MF* of the dyes **PC1** (1), **PC5** (2) and **PC9** (3) at $\pi = 4$ mN m⁻¹ (1, 2) and at $\pi = 1.5$ mN m⁻¹ (3).

Fig. 4. Normalised absorption (A) and fluorescence (F) spectra of **PC1** in chloroform at $MF = 2 \cdot 10^{-6}$ (1—red dashed curves) as well as **PC1** (2—pink doted curves) and **PC5** (3—blue solid curves) in LB film deposited at $\pi = 4\,mN\,m^{-1}$.

Table 2

The maximum positions ($\lambda_1 - \lambda_3$), the half–bandwidth (δ) of the absorption band of a monomeric form of **PC5** in chloroform, in LB films formed of the dyes investigated mixed with liquid crystal **8CB** and in sandwich cells formed of **PC1** mixed with liquid crystal **8CB**.

Compound	MF	λ_1 [nm]	λ_2 [nm]	λ_3 [nm]	δ [cm^{-1}]
chloroform					
PC5	$2 \cdot 10^{-6}$	395	437	456	3460
LB film					
PC1	1.0	396	–	–	3650
PC1/8CB	0.8	396	–	–	3850
	0.6	399	–	–	4450
	0.4	396	–	–	5200
	0.2	395	–	–	5800
PC5	1.0	397	435	456	5200
PC5/8CB	0.8	397	433	455	4950
	0.6	397	446	457	4350
	0.4	397	435	456	4200
	0.2	397	435	455	3800
PC9	1.0	–	–	–	–
PC9/8CB	0.8	–	436	459	2750
	0.6	–	437	459	2850
	0.4	–	437	457	3300
	0.2	–	438	456	3300
Sandwich cell					
PC1/8CB	$7.3 \cdot 10^{-4}$	381	439	457	–[a]
	$4.3 \cdot 10^{-3}$	384	439	457	–[a]
	$1.4 \cdot 10^{-2}$	380	439	457	–[a]

$\Delta\lambda_{1,2,3} = \pm 1\,nm$, $\Delta\delta = \pm 10\,cm^{-1}$ (for chloroform and sandwich cell), $\Delta\delta = \pm 50\,cm^{-1}$ (for LB film).

[a] Impossible to calculate.

3.2. Spectroscopic properties of LB films

The monolayers transferred on the quartz substrates at surface pressures below collapse point of the π–A isotherms were spectrophotometrically analyzed. The absorption and fluorescence spectra of the dyes (Fig. 4) are compared to monomeric form (diluted in chloroform at low MF of $2 \cdot 10^{-6}$). Characteristic spectral parameters of dyes in chloroform as well as in LB films are gathered in Tables 2 and 3. The absorption spectrum of monomeric form reveals three peaks associated with the π–π transition of the perylene chromophore with 0-0 band at 456 nm followed by 0-1 transition at 437 nm and 0-3 at 395 nm. Whereas the fluorescence shows structure-less band with maximum at 508 nm characterized by brilliant yellow colour being very close to the maximum spectral sensitivity of the human eye. The absorption and fluorescence spectra of LB films are more noisy due to its lower intensity resulting from monomolecular structure of the samples and ori-

Table 3

The maximum positions (λ), the half–bandwidth (δ) of the fluorescence band of a monomeric form of **PC5** in chloroform and in LB films formed of the dyes investigated mixed with liquid crystal **8CB** and in sandwich cells formed of **PC1** mixed with liquid crystal **8CB**.
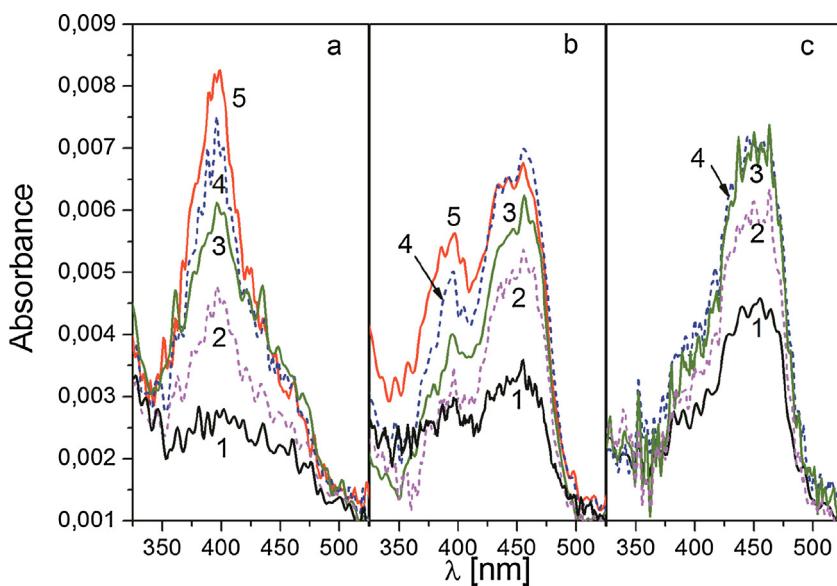
Compound	MF	λ [nm]	δ [cm^{-1}]
chloroform			
PC5	$2 \cdot 10^{-6}$	508	2680
LB film			
PC1	1.0	538	3000
PC1/8CB	0.8	538	2650
	0.6	536	2550
	0.4	534	2650
	0.2	533	2550
PC5	1.0	505	2500
PC5/8CB	0.8	505	2500
	0.6	506	2450
	0.4	507	2400
	0.2	504	2450
PC9	1.0	–	–
PC9/8CB	0.8	536	2450
	0.6	536	2350
	0.4	535	2550
	0.2	529	2750
Sandwich cell			
PC1/8CB	$7.3 \cdot 10^{-4}$	502	2410
	$4.3 \cdot 10^{-3}$	501	2600
	$1.4 \cdot 10^{-2}$	501	2400

$\Delta\lambda = \pm 1\,nm$, $\Delta\delta = \pm 10\,cm^{-1}$ (for chloroform and sandwich cell), $\Delta\delta = \pm 50\,cm^{-1}$ (for LB film).
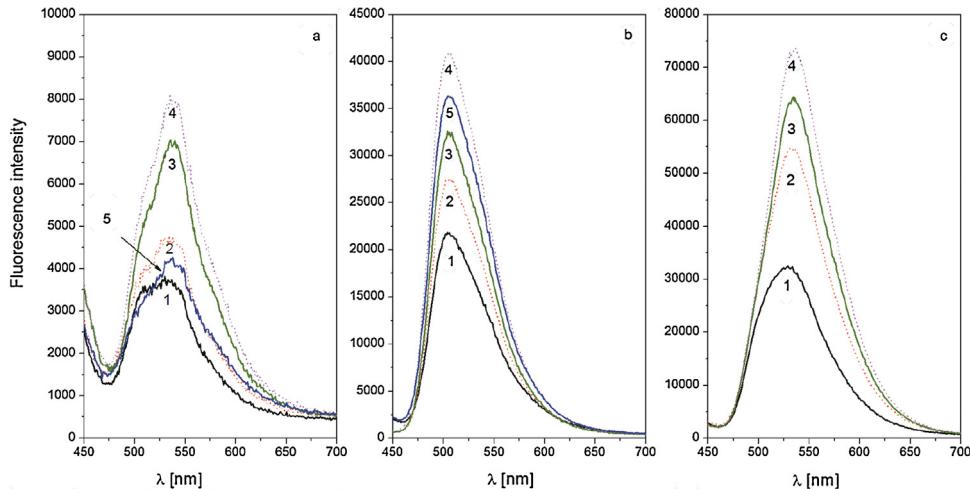
entation of the perylene core with respect to the normal to the quartz substrate surface. For **PC5** in LB film both spectra resemble monomeric form. However, some change of the intensity of the structured band in the absorption spectrum and half-bandwidth of the fluorescence band is seen. In contrast, for **PC1** in LB film both spectra are structure-less and shifted with respect to chloroform. Additionally, absorption spectra in LB films of both **PC1** and **PC5** are characterized by a bigger half-bandwidth than in chloroform. These differences in the shape of the spectroscopic bands of the dyes in the LB films with respect to monomeric form suggest the creation of self-aggregates between the dye molecules in LB films, in the ground state.

To shed more light on molecular interaction and aggregation process, LB films of **PC1**, **PC5** and **PC9** mixed with **8CB** were formed. Both, absorption and fluorescence spectra as a function of molar fraction (MF) of the dye were recorded and are presented in Figs. 5 and 6, respectively whereas characteristic spectral parameters of LB films are gathered in Tables 2 and 3. In absorption bands of the **PC1/8CB** mixtures as well as for **PC1** dye the vibronic structure disappears — it possesses only one maximum located around $\lambda_1 = 396$ nm. The intensity of the absorption peaks rise proportionally with the increase of the dye content. Simultaneously, the distinct narrowing of the absorption peaks is observed. For the **PC5/8CB** mixtures the absorption bands show vibronic structure with characteristic three bands. However, with rise of the content of the dye, proportions between intensities of the bans are changing causing the change in half-bandwidth. In case of **PC9/8CB** the band corresponding to the shortest wavelengths seems to be quenched. Both, for **PC5/8CB** and **PC9/8CB** mixtures absorption intensity do not vary proportional to MF of the dye.

The changes of the absorbance with the mixture composition and in a function the molar fraction of the dye show the influence of the terminal alkyl chains on the intermolecular interactions. The other reason of these changes is the projection of the absorption transition moment on the surface of the quartz plates. In case of **PC1** dye, which possesses the shortest terminal alkyl chains, molecules may strongly interact with each other in the condensed phase what leads to their almost vertical orientation in LB film. As

Fig. 5. Absorption spectra of Langmuir-Blodgett films of **PC1/8CB** (a), **PC5/8CB** (b) and **PC9/8CB** (c) mixtures at MF = 0.2 (1—black), 0.4 (2—purple), 0.6 (3—green), 0.8 (4—blue) of the dye deposited at π = 4 mN m^{-1} (a, b) and π = 1.5 mN m^{-1} (c). The curves (5—red) for (a, b) correspond to absorption spectrum of the pure dye PC1 and PC5, respectively.
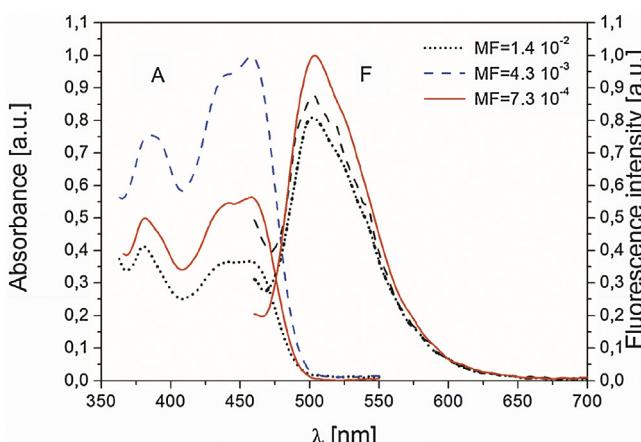

Fig. 6. Fluorescence spectra of Langmuir-Blodgett films of **PC1/8CB** (a), **PC5/8CB** (b) and **PC9/8CB** (c) mixtures at MF = 0.2 (1—black), 0.4 (2— red), 0.6 (3—green), 0.8 (4—purple) of the dye deposited at π = 4 mN m^{-1} (a, b) and π = 1.5 mN m^{-1} (c). The curves (5—blue) for (a, b) correspond to fluorescence spectrum of the pure dye **PC1** and **PC5**, respectively.

a consequence, only the transition dipole moment directed parallel to the short molecular axis may interact with the electronic vector of incident light. The interactions between **PC1** molecules are strong enough that the addition of the liquid crystal did not disturb them causing only absorption decrease proportional to MF of the dye in **PC1/8CB** mixtures. Additionally, the hypsochromic shift of absorption spectrum confirm our interpretation that due molecules interaction formation of H-aggregates of PC1 in the LB film is also possible in the ground state. For **PC5/8CB** mixture bigger contribution of the transition dipole moment directed parallel to the long molecular axis is seen. However, due to the torsion of the perylene core the absorption band at λ_1 = 396 nm is also present in recorded spectra. The lack of shift of the absorption spectra with respect to the monomeric form may indicate creation of I-aggregates. Interestingly, for **PC9/8CB** quenching of the band at λ_1 = 396 nm is observed. Because **PC9** alone is not able to form the Langmuir and LB film and addition of **8CB** as a stabilizing matrix was necessary, it is reasonable to conclude that molecules of **PC9** (such as **8CB**) are strongly tilted with respect to the interface. Therefore, the bands resulting from interaction of the light with the dipole

moment directed parallel to the long molecular axis is seen. Moreover, changes of the absorption not proportional to MF of the dye suggest creation of I-aggregates of **PC9** in LB film.

In order to get more information about molecular interaction of the dyes investigated additional spectroscopic research of **PCn** mixed with **8CB** in sandwich cells were carried out. Unfortunately, only **PC1** shows good miscibility in liquid crystal what allowed us to obtain reliable data. The absorbance and fluorescence spectra of **PC1/8CB** mixtures at three concentrations are presented in Fig. 7. The characteristic parameters of the spectra are gathered in Tables 2 and 3. The lack of the proportional changes of the absorption intensity to MF of the dye and no significant shift of the maximum positions was observed (Table 2). However, the fine structured absorption spectra is seen for the lowest concentrations whereas for MF = 7.3·10^{-4} absorbance is diminished and structural information is declined. This observation reveals formation of the **PC1** aggregates in **8CB** matrix at high concentration (higher than MF = 1.5·10^{-2}), it means that **PC1** has a strong tendency to aggregate in a bulk, not only in two-dimensional film.

Fig. 7. Normalised absorption (A) and fluorescence (F) spectra of **PC1**/**8CB** mixtures at MF of a dye: $7.3 \cdot 10^{-4}$ (red solid curves), $4.3 \cdot 10^{-3}$ (blue dashed curves) and $1.4 \cdot 10^{-2}$ (black doted curves) in a sandwich cell at the temperature of T = 25 °C.

The fluorescence spectra of the dyes investigated also differ with the length of terminal alkyl chains. According to Fig. 6 and Table 3, in case of **PC1** and its mixtures with **8CB** significant batochromic shift is observed. According to Ref. [25] this band is strongly related to Y–type excimers interpreted as the metastable parallel perylene dimer. Presence of the excimer band results from formation of well organized stacked molecules with overlapping perylene cores of the dye in LB films. Moreover, for **PC1** dye in the LB films very strong fluorescence quenching is detected – the emission intensity for pure dye is lower than **PC1**/**8CB** mixture at $MF = 0.4$. This fact expressively confirm our assumption of creation of H-aggregates among **PC1** dye molecules. Interestingly, with a decrease of the dye molar fraction in the mixture, the additional band around $\lambda_1 = 510$ nm corresponding to fluorescence of the monomeric form is more clearly seen. The fluorescence spectra of **PC5**, **PC5**/**8CB** and **PC9**/**8CB** mixtures show the unstructured broad emission bands with the maximum depending on number of carbon atoms in the terminal alkyl chains. For **PC5**/**8CB** mixtures both maximum positions and half-bandwidth are very similar to the monomeric form confirming formation of I-aggregates. Again, due to the aggregation process, the fluorescence of the dye molecules is lower than for **PC5**/**8CB** mixture although the quenching is not so strong as for **PC1** molecules. In all likelihood, it is related to different orientation of the molecules with respect to the solid substrate in the LB films. Bigger tilt angle results in displacement of the perylene cores and creation of I-aggregates. In case of **PC9**/**8CB** mixtures we observed very strong fluorescence – almost two times higher than for **PC5**/**8CB**. In our opinion it is related to the longest terminal alkyl chains in **PC9** dye. The weakest interactions between the dye forced by liquid crystal results in the biggest tilt angle of the **PC9** molecules in the LB film what allows to obtain molecular arrangement similar to these observed in J-aggregates.

In the liquid crystalline sandwich cells the shape of the **PC1** fluorescence spectra are similar to the monomeric emission. There is no correlation between the fluorescence and absorption changes with the increase of the dye content. However, the decrease of the fluorescence intensity with the rise of the dye concentration indicates the aggregation formation. In the **PC1**/**8CB** LB films when the dye concentration is several times higher than in the sandwich cell, the maximum of the fluorescence band shifts rapidly to the longer wavelengths, and the half-bandwidth increases. This indicate that more and more molecules are gathered forming excimers (see Table 2).

4. Conclusions

In the present work we have demonstrated the molecular organization and spectral properties of three chlorinated perylene derivatives – tetra-*n*-butyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylate (**PC*n*** for *n* = 1, 5, 9) mixed with liquid crystal 4-octyl-4′-cyanobiphenyl (**8CB**) in Langmuir and Langmuir-Blodgett films with comparison to their absorption and fluorescence spectra in diluted chloroform solutions and dye-liquid crystalline matrix. The perylene derivatives with short alkyl chains **PC1** and **PC5** are able to form stable Langmuir monolayer contrary to the **PC9**. The components mixing of the dyes with **8CB** in the Langmuir films were observed. The attractive forces dominate in mixtures of **PC1**/**8CB** and **PC5**/**8CB**, although repulsive in **PC9**/**8CB** in the LB films. In the liquid crystal cell, only **PC1** was examined because of a low **PC5** and **PC9** solubility in **8CB**. **PC1** molecules starts to aggregate in **PC1**/**8CB** mixtures above concentration of $MF = 1.4 \cdot 10^{-2}$. Similar behaviour of **PC1** is observed in pure and mixed LB films where formation of the H-aggregates is postulated. The **PC9**/**8CB** LB films show absorption and emission spectra depending on the dye concentrations typical for J-aggregates what can be interpreted as a result of molecular stacking. Spectral characteristics of **PC5**/**8CB** mixtures in LB films show an intermediate state between H- and J-aggregates in the LB films. Spectroscopic analysis of two-dimensional LB films created by dyes investigated suggest presence of an aggregates in form of stacked columns rather than dimers or trimmers which are observed in bulk concentrated solutions.

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