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Spectroscopic studies of Langmuir-Blodgett films of 3,4,9,10-tetra(heptyloxycarbonyl)perylene and its mixtures with a liquid crystal

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Spectroscopic studies of Langmuir–Blodgett films of 3,4,9,10-tetra(heptyloxycarbonyl)perylene and its mixtures with a liquid crystal

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Langmuir (L) and Langmuir–Blodgett (LB) films of 3,4,9,10-tetra(heptyloxycarbonyl)perylene and its binary mixtures with 4-octyl-4'-cyanobiphenyl (8CB) and 4-pentyl-4'-cyano-*p*-terphenyl (5CT) have been studied. On the basis of the surface pressure–mean molecular area isotherms of L films, the alignment of the molecules on the air–water interface has been estimated. The L films were transferred onto quartz plates at surface pressures below the collapse point. The absorption and fluorescence spectra of LB films, obtained using unpolarized and linearly polarized light, were recorded. The results obtained have led to conclusions on the arrangement of the dye and liquid crystal molecules on the air–solid substrate interface. The fluorescence spectra revealed the formation of excited dimers in LB films.

1. Introduction

It is well documented [1, 2] that some perylene-like dyes have good dichroic and excellent fluorescent properties, and can therefore be successfully employed in liquid crystal display devices using the ‘guest–host’ effect (GH LCDs) [3]. 3,4,9,10-tetra(*n*-Alkoxy carbonyl)perylene were first synthesized by Stolarski and Fiksiński [4] and it was found [2] that these dyes have a brilliant yellow colour and emit fluorescent light in a spectral region advantageous for the human eye with a significantly high quantum yield. Furthermore, they can orient well in liquid crystals, are stable to sunlight and do not significantly destabilize the mesomorphic phase of the host. Such features make these perylene-derivatives very interesting for use in GH LCDs working both in passive and active modes. Recently, Benning *et al.* [5] found that some homologues of the 3,4,9,10-tetra(*n*-alkoxy carbonyl)perylene series form discotic liquid crystalline phases over an elevated temperature range which, combined with their fluorescent properties, gives the opportunity to apply these dyes in organic light emitting diodes (OLEDs) [6, 7]. In both these applications the interfacial molecular orientation plays an important role. The

Langmuir–Blodgett (LB) technique [8–10] offers a unique method for fabricating ultrathin ordered layers, in which the molecular organization and interfacial interactions can be identified with ease. Moreover Stapff *et al.* previously proposed the use of this technique to obtain active layers in OLEDs [11].

The first step required for the successful fabrication of a LB film is the creation of a compressible monolayer at the air–water interface (Langmuir film) [8–10, 12]. Previously it was found that perylene and some perylene derivatives can form Langmuir (L) films, which can be transferred onto solid substrates (LB films), but not before they are mixed with (usually) fatty acids [13–19]. Fatty acids, may however induce a different arrangement of the molecules dispersed in their matrices, and in order to determine the orientation of the perylene-like molecules themselves it is necessary to fabricate L and LB films from a pure compound. We have shown that it is possible to obtain a stable and compressible monolayer at the air–water interface from pure 3,4,9,10-tetra(heptyloxycarbonyl)perylene and to deposit this layer onto a quartz slide [20]. Somewhat later Antunes *et al.* reported that it was possible to obtain L and LB films from some pure perylene tetracarboxylic acid derivatives [21]. Recently, we have been successful in obtaining both kinds of film from

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other homologues of the 3,4,9,10-tetra(*n*-alkoxy-carbonyl)perylene series [22].

It is also well established that many thermotropic liquid crystal molecules are amphiphilic and insoluble in water, therefore they are good candidates to form mono- or multi-layers at air–water or air–solid substrate interfaces. Much information about L and LB films fabricated from mesogenic molecules possessing strongly polar hydrophilic head group and hydrophobic alkyl chain can be found in the literature [23–30]. Previously [20] we mixed 3,4,9,10-tetra(heptyloxycarbonyl)perylene with two liquid crystals—4-octyl-4'-cyanobiphenyl (8CB) and 4-pentyl-4''-cyano-*p*-terphenyl (5CT)—and obtained preliminary results on the interfacial organization of molecules in mixed L and LB films.

In this paper we report the detailed study of LB films formed of pure 3,4,9,10-tetra(heptyloxycarbonyl)perylene and its mixture with 8CB and 5CT by means of optical spectroscopic methods using natural and linearly polarized light. Our aims were to determine the spectral characteristics and to obtain information about the alignment of molecules with respect to the solid substrate in ultrathin ordered layers of the perylene derivative and of binary dye–liquid crystal mixtures.

2. Experimental

The compound 3,4,9,10-tetra(heptyloxycarbonyl)perylene (**1**) (see figure 1) was synthesized and purified chromatographically in the Institute of Dyes at Łódź University of Technology. The details of the synthesis are described in [4]. The liquid crystal materials 4-octyl-4'-cyanobiphenyl (8CB) and 4-pentyl-4''-cyano-*p*-terphenyl (5CT) were purchased from E. Merck (Germany) and used without further purification: their phase transition temperatures were in excellent agreement with literature data [31–33].

The L and LB films were formed in a Minitrough (KSV Instruments Ltd., Finland). Pure compound **1** and 1/8CB and 1/5CT mixtures were spread from chloroform solutions onto the deionized water sub-phase; a Wilhelmy plate balance at both the compression and expansion processes measured the surface pressure as a function of the average molecular area. The LB film fabrication was performed using Z-type

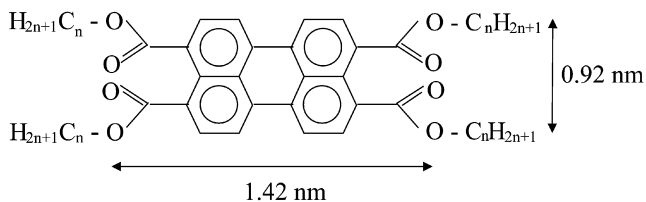


Figure 1. Molecular structure of 3,4,9,10-tetra(heptyloxycarbonyl)perylene.

deposition [8–10] and with the floating monolayer kept under constant pressure. The solid substrates with a hydrophilic surface were polished quartz plates. The monolayers were transferred onto these substrates with a transfer ratio of around 1. Successful deposition of 8CB took place only on first raising the substrate. Therefore, for **1** and its mixtures with both liquid crystals one dipping and one raising operation were made. Further experimental details on L and LB film preparation are given elsewhere [20, 22, 29].

The absorption spectra of LB films were recorded in the UV-Vis region by means of a CARY 400 spectrophotometer, while the fluorescence measurements were carried out using a home-made photon-counting spectrofluorimeter. The experimental set-up of the spectrofluorimeter makes investigations of different samples possible, both isotropic and anisotropic, and is schematically represented in figure 2. All the components of the optical system are fixed to a steel honeycombed breadboard with mounting holes (Thorlabs, Inc.). This gives a high flexibility of the mutual displacement of the basic parts of the system and in the arrangement of a particular experiment. As a source of exciting light, a xenon or mercury lamp can be used. The exciting light, after crossing the water filter which cuts part of the infrared irradiation, falls onto the entrance slit of the TRIAX 180 monochromator (S.A. Instruments, Inc., Jobin Yvon/Spex Division). After passing the monochromator, the light enters the relatively large housing ($380 \times 380 \times 250 \text{ mm}^3$), where it falls onto the properly placed polarizer, and then is directed by the mirror system onto the sample at a given angle ϕ . The fluorescent light emitted from the sample in a given direction with respect to the surface (the angle α), passes the second polarizer, and subsequently falls onto the entrance slit of the second TRIAX 180 monochromator. Behind the exit slit of the monochromator, the integrated H6240-02 photon counting head (Hamamatsu Photonics K.K.) is mounted; this incorporates a photon-counting tube, high voltage power supply, high speed amplifier, discriminator, and TTL signal-forming circuit. The head operates in the photon-counting mode, and thus the detection of even very weak fluorescence in the photomultiplier spectral sensitivity range (185–900 nm) is possible. The TTL signal from the head output is analysed by a pulse counter (a PC computer card) and thus, the overall counting linearity of the head is about 10^5 s^{-1} . A special program working under the DOS operating system on a PC controls the spectrofluorimeter. This program allows the adjustment of the operating parameters of the monochromators and the PC counter card, and also the control of the registration of fluorescence spectra. The spectra are

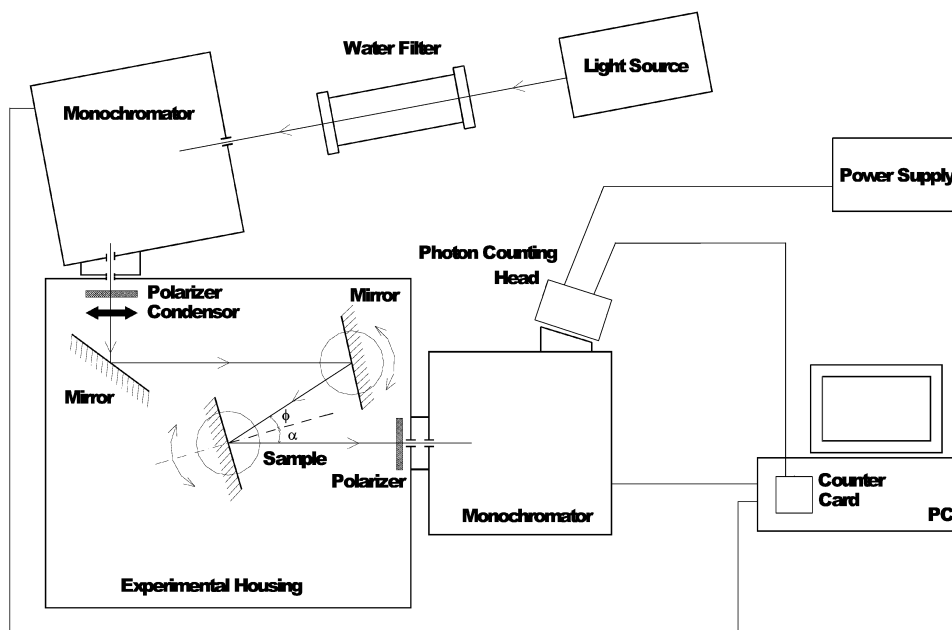


Figure 2. The experimental set-up for fluorescence measurements.

stored on a computer disk using a format accepted by programs designed for data analysis. In our experiment the exciting light was the 436-nm line from a high pressure mercury lamp.

Both in the absorption and fluorescence measurements using polarized light, Glan-Thomson polarizers and an angular sample holder were used. The measurements were performed in the geometry shown in figure 3; α is the angle between the normal to the quartz slides and the direction of the incident or emitted light.

3. Results and discussion

3.1. Langmuir films

Figures 4 and 5 show the surface pressure–mean molecular area (π – A) isotherms for Langmuir films of

pure compounds **1**, 8CB, 5CT and of **1**/8CB and **1**/5CT mixtures at various mole fractions of the dye. The isotherms were recorded for various compression speeds, and no significant differences in the isotherm runs were found. The curves obtained by the compression process were very similar to those obtained by the expansion process. This shows that the isotherms were recorded under equilibrium conditions.

From the isotherm for pure **1**, it is seen that the increase in the surface pressure begins at a mean molecular area $A_0 = 0.92 \text{ nm}^2$, indicating the formation of a homogeneous monolayer which collapses at $A_C = 0.78 \text{ nm}^2$ and $\pi_C = 14 \text{ mN m}^{-1}$. A cross-sectional area of the perylene skeleton with four $-\text{C}=\text{O}$ groups per molecule of **1**, calculated on the basis of the space-filling model (including van der Waals radii of the

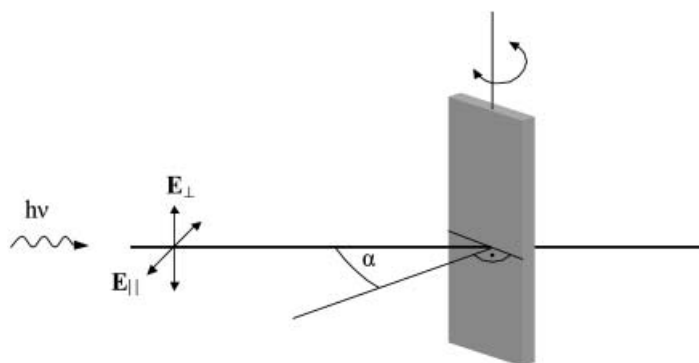


Figure 3. Geometry for the polarized absorption and fluorescence measurements. \mathbf{E}_{\parallel} and \mathbf{E}_{\perp} are the electric vectors of the incident (absorption measurement) or emitted (fluorescence measurement) light polarized, respectively, parallel and perpendicularly to the plane of incidence or emission; α is the incidence angle.

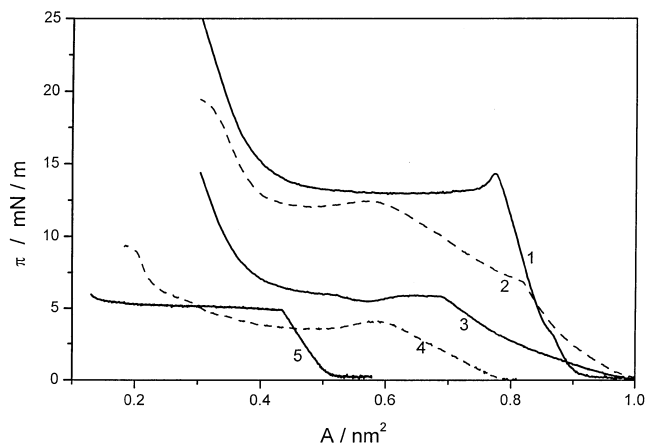


Figure 4. Surface pressure–mean molecular area isotherms of L films of **1** (1), 8CB (5) and 1/8CB mixtures with mole fraction of dye: 0.8 (2), 0.5 (3) and 0.2 (4).

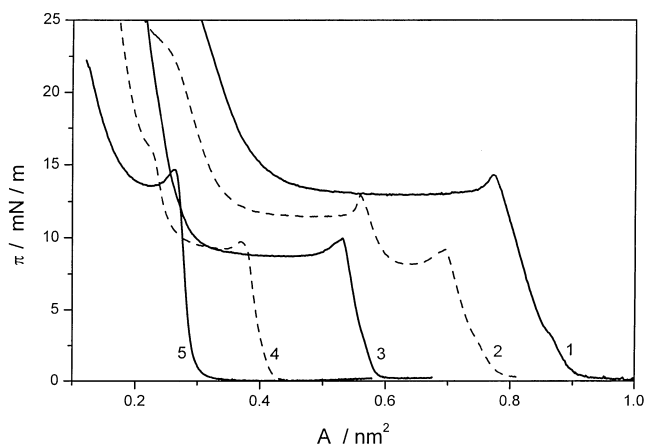


Figure 5. Surface pressure–mean molecular area isotherms of L films of **1** (1), 5CT (5) and 1/5CT mixtures with mole fraction of dye: 0.8 (2), 0.5 (3) and 0.2 (4).

terminal atoms [34]), is 1.31 nm² (figure 1 shows dimensions of the rigid core of **1**). However, cross-sectional areas estimated from the longer and shorter edge-on configurations (assuming free rotation) are 1.58 and 0.66 nm², respectively. Therefore, it is evident that the molecules of **1** neither lie flat at the water surface nor assume the edge-on configurations. The values of A_0 and A_C suggest that in the monolayer, the rigid cores of the molecules must be tilted with respect to the water surface. This angle was estimated to be 48° [22].

Compression of the L film of **1** beyond the collapse point results in a broad plateau region, in which π remains constant with a decreasing A . When A reaches a value of about 0.40 nm² a second rapid rise in π occurs. Neither detailed analysis of π – A isotherms for **1** and other homologues of 3,4,9,10-tetra

(*n*-alkoxycarbonyl)perylene, nor Brewster angle microscopy observations made previously [22], allow us to determine unambiguously the alignment of the molecules in the plateau region and at higher surface pressure values in L films. Two possibilities were considered [22]. As the molecules of 3,4,9,10-tetra (*n*-alkoxycarbonyl)perylene are able to form a liquid crystalline hexagonal phase [5] it is possible that they also have a tendency in L films to form parallel columns which can ‘jump out’ above the monolayer surface when the available area on the water decreases (the second rise in π would then indicate the creation of the next layer). Another possibility is that with a decreasing A , the molecules assume increasingly vertical arrangements, which do not cause a change in the surface pressure. A rise of π then does not occur before the formation of a rigid condensed layer in which the molecules cannot undergo free rotation. The problem of the molecular arrangement of **1** in L films needs further investigation, perhaps using other experimental techniques.

The π – A isotherms for pure 8CB and 5CT as two-dimensional layers at the air–water interface (curve 5 in figures 4 and 5, respectively), are similar to those given in the literature [23–29]. A significant difference in the shape of these two isotherms is seen, despite the similar molecular structures of 8CB and 5CT. The collapse point for 8CB occurs at 0.42 nm², which is almost twice the theoretical molecular cross-section. Xue *et al.* [25] and de Mul and Mann [28] explained this effect in terms of strong repulsive interactions between the electric dipoles of the cyano groups. As a result of such interactions, the 8CB monolayer is fragile and the molecules are not densely packed. It has been found [35] that the average angle between the molecular long axes of 8CB and the normal to the water surface is approximately 60°. However, the collapse point at the π – A isotherm of 5CT appears at 0.27 nm², which approximately corresponds to the 5CT molecular cross-section. This leads to the conclusion that repulsive forces between the electric dipoles are compensated by attractive interactions between the three phenyl rings, and suggests that the 5CT molecules can locate very close to each other. As a result the L film of 5CT has a higher packing factor than that of 8CB and the molecules are aligned almost perpendicularly to the interface.

The isotherms for L films of binary mixtures of 1/8CB and 1/5CT at various mole fractions of the dye are shown as curves 2–4 in figures 4 and 5, respectively. It is seen that with increasing 8CB content of the mixed L films, the tilt of the isotherm decreases, indicating that the monolayer becomes less stable and rigid. A monotonic decrease of the collapse pressure is observed

when the mole fraction of **1** decreases, providing evidence for the good miscibility of both components of **1**/8CB mixtures [12], which was also found previously [20]. The L films of binary mixtures of **1** with 5CT behave very differently. The tilt angle of the isotherms is significantly greater than in the case of **1**/8CB mixtures, and increases with an increasing content of the liquid crystal. This is probably connected with the fact (as mentioned above) that the monolayer formed from pure 5CT is more stable and rigid than the 8CB monolayer [29]. The values of the collapse pressure remain constant in mixed films, although they are smaller than those for pure components. This observation indicates immiscibility or very small partial miscibility of **1** and 5CT molecules [12, 20].

3.2. Langmuir–Blodgett films

3.2.1. Absorption and emission of **1** in solution

Figure 6 shows long wavelength absorption and emission spectra of **1** dissolved in ethanol at mole fraction = 5×10^{-7} (curves 1 and 4) and in 8CB at mole fraction = 2.5×10^{-3} in ‘sandwich’ cells of 20 μm in thickness (curves 2 and 5). In both solvents the absorption spectra of **1** show two peaks with vibronic structure. The emission spectra show mirror symmetry with respect to the absorption spectra, although the relative intensity of the fluorescence peaks is slightly different from that of the absorption peaks. Both absorption and emission spectra of **1** in 8CB are somewhat red-shifted in comparison with the spectra in ethanol, which may be attributed to the differing values of the refractive index and dielectric constant of these two solvents. The absorption and emission bands are reminiscent of those of pure perylene and correspond to

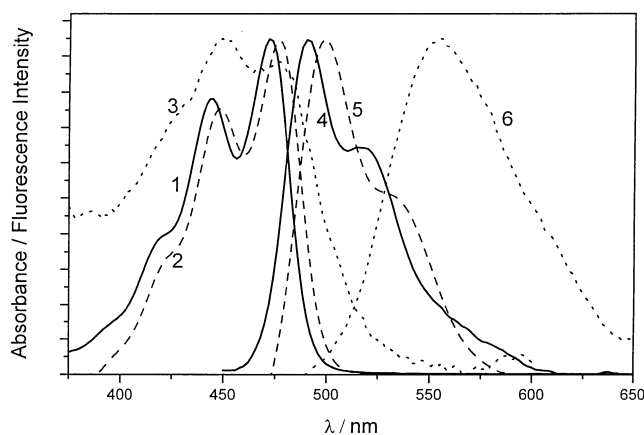


Figure 6. Normalized absorption, curves (1–3), and emission (4–6) spectra; **1** in ethanol, mole fraction = 5×10^{-7} (1,4); **1** in 8CB, mole fraction = 2.5×10^{-3} (2,5); **1** in 8CB as LB film at mole fraction = 0.5 (3,6).

the S_1 – S_0 transition, the dipole moment of which is directed parallel to the long axis of the molecule [36, 37]. Although the spectra of **1** are similar to those of the parent compound perylene, the observed shift in the band positions may be attributed to the substituent chains attached. Both curves 1 and 4, as well as 2 and 5, are characteristic of monomer absorption and fluorescence [36, 38], despite a 5000-fold concentration change.

For comparison, the absorption and emission spectra for **1** mixed with 8CB (mole fraction = 0.5) in a LB film are shown in figure 6 (curves 3 and 6). The change in shape of the spectra is seen very distinctly, and suggests the formation of self-aggregates of molecules of **1**. This will be discussed in the next section.

3.2.2. Electronic absorption of **1** mixed with liquid crystals in LB films

The pure compounds and the mixtures of **1** with 8CB or 5CT were transferred onto quartz slides at a surface pressure corresponding to the value of π before the collapse point at the π – A isotherm (homogeneous monolayer). Figure 7 presents the absorption spectra in the UV and visible regions for pure **1** (curve 1), pure 8CB (curve 6) and **1**/8CB mixtures in LB films obtained at $\pi = 2 \text{ mN m}^{-1}$. The presence of the band at 280 nm, which is related to the absorption of 8CB, shows that 8CB molecules are tilted with respect to the quartz surfaces in similar fashion as on the air–water interface.

The absorption spectra of pure 5CT and **1**/5CT mixtures also reveal the existence of the band at about 285 nm (see later, figure 9). Thus 5CT molecules in LB films must also be tilted with respect to the quartz surfaces, unlike their alignment in L films. This finding is in contrast with that made by Sakuhara *et al.* [24] who ascertained, on the basis of the absorption spectra

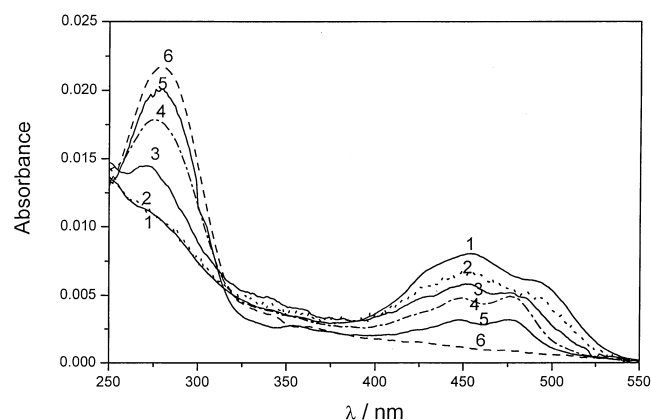


Figure 7. Absorption spectra of LB films formed of pure **1** (1), 8CB (6) and **1**/8CB mixtures at mole fractions of dye: 0.8 (2), 0.5 (3), 0.2 (4) and 0.1 (5).

of 5CT in LB films, that at the air–solid interface the molecules of this liquid crystal are aligned vertically to the substrates. However, the tilted alignment has also been found for 5CT mixed with other dyes [39].

The absorption spectrum of pure **1** in the LB film (curve 1 in figure 7) in comparison with that in dilute solutions (curves 1 and 2 in figure 6), reveals a slight bathochromic shift and a large spectral broadening. Moreover, two peaks are now not clearly distinguished. Instead, a broad band is observed, with a maximum at the wavelength corresponding to the first peak and a shoulder related to the second peak. As the liquid crystal content in the mixture increases (curves 2–5 in figure 7) the absorption band related to the dye becomes similar to that in solutions, and at a mole fraction of dye equal to 0.2 the absorbance of the second peak is again greater than that of the second peak. Similar results were obtained for 1/5CT mixtures in LB films.

The shapes of the absorption spectra of LB films formed from the dye and its mixtures with liquid crystals at higher concentrations are indicative of a dipole–dipole interaction between the molecules. According to Ferguson [38] and Vitukhnovsky *et al.* [13] the dimer absorption band of the parent compound perylene is structureless and occurs at about 380 nm. Weiss *et al.* [15] found, in the absorption spectrum of a LB film of a perylene-like compound, an additional shoulder to the red in the long wavelength band, and attributed it to the forbidden transition to the lowest singlet dimer state. However, Struijk *et al.* [40] observed the change in shape of the absorption spectra for some perylene diimides in evaporated films, when compared with the spectra of these compounds in solutions as well as the additional red-shifted absorption band. Meanwhile, in the case of **1** as a LB film, neither an additional peak nor a shoulder, which could suggest the formation of dimers in the ground state, is observed. On the other hand, the dye content in the liquid crystal in the LB films, whose absorption spectra are shown in figure 7, decreases 10-fold. The absorbance of the band related to the liquid crystal changes in an almost proportional fashion to its concentration, whereas the absorbance of the band related to **1** varies only less than threefold (compare curves 1 and 5 in figure 7). This effect may be connected with the creation of some type of self-aggregates of **1**. It is, however, also possible that a change of orientation of the dye molecules with composition takes place. Further insight may be gained by looking at the polarized absorption spectra as well as the emission spectra.

The measurements of absorption spectra using linearly polarized light, for **1** and its mixtures with liquid crystals in LB films, were made in the geometry

shown in figure 3. The spectra were run at an incidence angle α of 0° , 30° and 60° . On the basis of the polarized absorption spectra, the linear dichroism (LD) was determined. Following N'soukpoé-Kossi *et al.* [41] we define LD by:

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

where A_P and A_S are the absorbance values at the band maximum for light polarized parallel and perpendicularly to the plane of incidence, respectively. LD can be related to the angle of incidence α using [41]:

$$LD_\alpha = \frac{2 - \tan^2 \beta}{\tan^2 \beta \frac{1 + \cos^2 \alpha}{\sin^2 \alpha} + 2} \quad (2)$$

where β is the angle between the transition dipole moment vector and the normal to the plane of the LB film. Equation (2) is valid if the molecules in the monolayer are distributed on a cone, uniformly on the slide surface, with their transition moment tilted at an angle β with respect to the normal. In this case LD for $\alpha = 0^\circ$ should be equal to zero.

Figure 8 shows the polarized absorption spectra recorded at $\alpha = 0^\circ$ for **1** as a LB film. It is seen that for this compound the value of the linear dichroism for light incident perpendicularly to the quartz surface ($LD_{\alpha=0}$) is different from zero and positive. This means that vertical movement of the quartz slide during deposition disturbed the homogeneity of the molecular alignment. In this case some modification to the formulation of the linear dichroism with respect to the angle α must be applied. N'soukpoé-Kossi *et al.* [41] showed that:

$$LD_\alpha = \frac{2 + LD_{\alpha=0} \tan^2 \beta \left(\frac{1 + \cos^2 \alpha}{\sin^2 \alpha} \right) - \tan^2 \beta}{2 + \tan^2 \beta \left(\frac{1 + \cos^2 \alpha}{\sin^2 \alpha} \right) - LD_{\alpha=0} \tan^2 \beta} \quad (3)$$

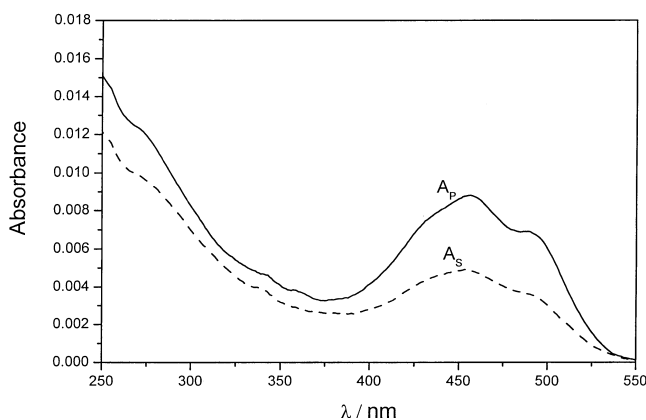


Figure 8. Polarized absorption spectra of **1** in LB film, recorded at $\alpha = 0^\circ$.

in which LD_α is the linear dichroism calculated for an appropriate angle α , and $LD_{\alpha=0}$ is the linear dichroism measured for normal incidence.

A positive $LD_{\alpha=0}$ value for the band related to the dye was also found for all the 1/5CT mixtures. The band corresponding to 5CT revealed a small positive value of $LD_{\alpha=0}$ for the LB film of pure liquid crystal, whereas in the mixtures it becomes negative. An example for **1** mixed with 5CT at mole fraction=0.2 can be seen in figure 9. However, in the case of 1/8CB mixtures the values of $LD_{\alpha=0}$ were always zero for both bands, indicating a homogeneous distribution of the transition moment vectors of the dye and liquid crystal molecules at the air–solid substrate interface. Such a difference in behaviour between 8CB and 5CT molecules seems to be related to the different molecular arrangement of these two liquid crystals in L films, resulting in varying properties of the monolayers formed on water or on a quartz surface. The values of the angle β for **1** in LB films created from pure dye and its mixtures with 8CB and 5CT are listed in the table. These are the mean values of results obtained at incidence angles $\alpha=30^\circ$ and 60° for at least three

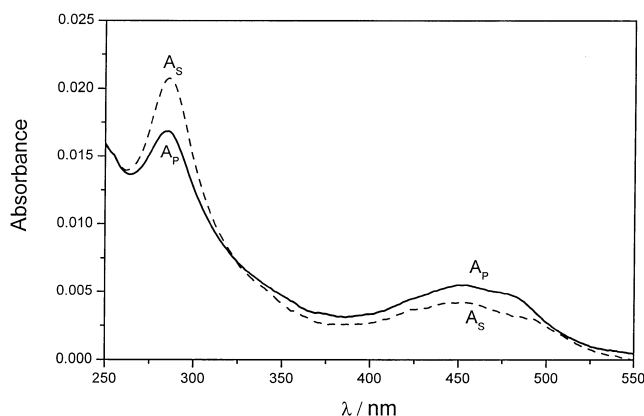


Figure 9. Polarized absorption spectra of LB film of 1/5CT mixture with mole fraction of dye of 0.2, recorded at $\alpha=0^\circ$.

Table. Values of the angle (β) between the molecular long axis and the normal to the quartz slide, in LB films of **1** and its mixtures with liquid crystal.

Mole fraction of 1	$\beta/^\circ$	
	1/8CB	1/5CT
1.0	59.5	59.5
0.9	63.2	59.5
0.8	67.1	60.2
0.5	69.3	60.9
0.2	73.0	64.5
0.1	75.7	62.8

independently prepared samples. LD_α values for these two incidence angles differ no more than 1.5° .

From the angle between the absorption oscillator and the long molecular axis of the dye we can obtain information about the orientation of the molecules with respect to the quartz slides. It was found previously that, as for perylene, the absorption transition moment of **1** in the visible spectral region is directed parallel to the longer edge of the molecule [37]. On the basis of the π - A isotherm of the L film of **1** it was determined that the rigid molecular cores create an angle $90^\circ - 48^\circ = 42^\circ$ with the normal to the water surface (see §3.1). From the A_0 value it was, however, impossible to decide whether the molecules assume a shorter or longer edge-on configuration. Meanwhile, we have seen already that the non-zero value of $LD_{\alpha=0}$ for pure **1** in the LB film, and its change observed on varying the incidence angle, suggest that most of the dye molecules are aligned with the shorter edge to the quartz slide. Moreover, the results listed in the table indicate that the rigid molecular cores are significantly more tilted toward the solid surface in LB films than toward the water in L films.

In LB films formed from 1/8CB and 1/5CT mixtures the tilt angle of **1** molecules with respect to the normal to the quartz surface increases with increasing liquid crystal content, indicating rearrangement of the molecular alignment in the mixed films. The changes of the angle β are, however, too small to explain the behaviour of the absorbance of the band related to **1** for various compositions. Therefore it is expected that some kind of dipole–dipole interaction in the ground state occurs.

The increase of β with increasing mole fraction of liquid crystal in LB films is slower for mixtures with 5CT than for those with 8CB, which may be related to the somewhat different arrangement of the liquid crystal molecules in LB films of pure 8CB and 5CT. For both liquid crystals we can assume that the absorption oscillator of the band at ≈ 280 nm is parallel to the long axis of molecules. Therefore, the values of angle β obtained on the basis of the polarized absorption spectra of LB films of pure 8CB and 5CT allow us to determine directly the alignment of the liquid crystal molecules at the air–solid substrate interface. It was calculated that the molecules of 8CB are tilted at $\beta=63^\circ$ with respect to the normal of the quartz slide. This value is in agreement with that obtained previously [42] and very similar to the tilt angle of 8CB molecules at the air–water interface. However, for 5CT as a LB film, a value of $\beta=55^\circ$ was obtained. Bearing in the mind that the π - A isotherm shape of the L film of 5CT indicates a very small angle between the molecular long axes of this liquid crystal

with the water surface, it is clear that during the transfer of the monolayer from the air–water interface onto the solid substrate a molecular rearrangement takes place. Similar observations were also made previously [39, 43].

For the mixed LB films it is very difficult to calculate the angle β for the liquid crystal molecules because the absorption band at 280 nm is strongly overlapped by the UV absorption associated with **1** (see figures 7 and 8). However, the proportionality between the absorbance and concentration also changes, as the estimation made for LB films with a small content of **1** (mole fraction = 0.2) allow us to suppose that the alignment of the liquid crystal molecules does not vary in the presence of the dye.

3.2.3. Fluorescence of **1** in LB films

Figure 10 shows the fluorescence spectra obtained by excitation with unpolarized light for LB films of pure **1** and its mixtures with 8CB at various mole fractions. The spectra for LB films of **1**/5CT mixtures are very similar to those for **1**/8CB mixtures. All the films were obtained at the same surface pressure ($\pi = 2 \text{ mN m}^{-1}$) as in the case of absorption measurements (figure 7). Curve 1 in figure 10 indicates that the emission spectrum of **1** in the LB film is quite different from the solution spectrum. An unstructured broad fluorescence band with maximum around 550 nm is seen. A

detailed discussion of the emission spectra of **1** and its homologues in LB films has been given elsewhere [22]. Previously, Benning *et al.* [5, 7] reported that 3,4,9,10-tetra(*n*-alkoxycarbonyl)perylene in the crystalline state show an orange fluorescence with one peak (582–600 nm, depending on the alkyl chain length) and the loss of fine structure, and attributed the spectral changes in the emission spectrum with respect to that in dilute solutions, to the formation of excimers. Since the excimers (which originate from an interaction of neighbouring molecules after one is excited) do not exist in the ground state, it is clear that they cannot be seen in the absorption spectrum. The hypsochromic shift of the fluorescence band maximum of **1** in the LB film, with respect to the position of the band in the solid state ($\approx 40 \text{ nm}$), can be connected related to the existence of either of two emitters, monomers and excimers (the fluorescence spectrum is then the superposition of the spectra of both emitters), or with a smaller degree of overlapping between molecules in the film at the quartz surface [5, 19]. As was determined in [22] on the basis of the spectral study of LB films transferred from water at various π , both possibilities can occur.

The fluorescence intensity of LB films of binary mixtures of **1** with the liquid crystal decreases as the content of **1** decreases, but not in a proportional manner to the dye concentration. However, the shape of the emission band is similar to that of pure **1**, despite the changes in the shape of the absorption spectra (figure 7). This would suggest that even if some kind of aggregates appear in the ground state at higher dye concentration in LB films, they do not contribute to the fluorescence.

For LB films of pure **1** and its mixtures with 8CB or 5CT, the polarized components of the fluorescence spectra were also recorded. For excitation natural light was used. Figure 11 shows, as an example, the fluorescence spectra of **1** in the LB film recorded at angle $\alpha = 0^\circ$ (see figure 2) for two positions of the polarizer placed in the path of the emitted light beam. It is seen that, as in the case of absorption, the two polarized components have differing intensity, and the parallel component has greater intensity than the perpendicular ($F_P > F_S$). The measurements indicated that the intensities of the components of the polarized fluorescence spectra for mixed films differ in a similar way as the absorbances. This confirms the conclusions drawn from the absorption spectra concerning the alignment of dye molecules and its changes in the presence of the liquid crystal at the air–solid substrate interface.

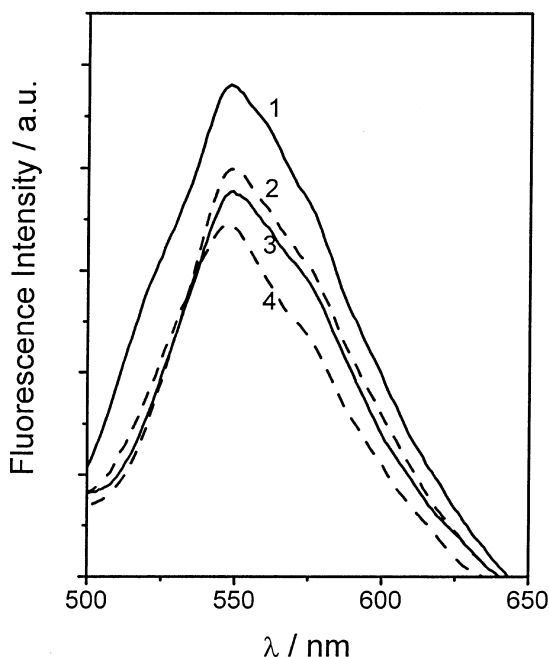


Figure 10. Fluorescence spectra of LB films formed of pure **1** (1) and its mixture with 8CB at mole fractions of dye: 0.8 (2), 0.5 (3) and 0.2 (4).

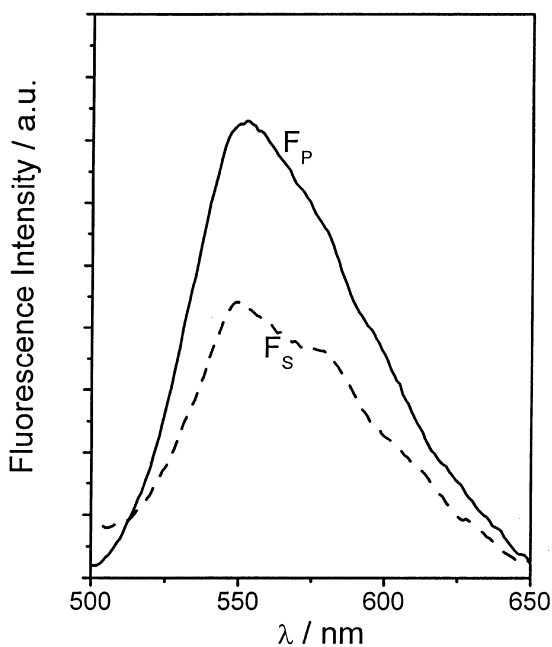


Figure 11. Polarized fluorescence spectra of **1** in a LB film recorded at $\alpha = 0^\circ$.

4. Summary

A 3,4,9,10-tetra(heptyloxycarbonyl)perylene (**1**) and its binary mixtures with liquid crystals 8CB and 5CT have been investigated as Langmuir and Langmuir–Blodgett films. The surface pressure–mean molecular area isotherm of the L film suggests that in the monolayer the rigid cores of the dye (perylene skeleton with $-\text{C}=\text{O}$ groups) are tilted with respect to the normal to the water surface at an angle of 42° . The analysis of the isotherm shape does not allow us to determine unambiguously the alignment of the molecules in the plateau region and at higher surface pressure values. Mixtures of **1** with 8CB are miscible over the whole range of mole fraction of **1**, whereas for **1**/5CT mixtures, immiscibility or only a very small partial miscibility of **1** with 5CT is observed.

L films of the pure compound **1** and the mixtures **1**/8CB and **1**/5CT can be transferred onto quartz slides forming LB films. The 8CB molecules in LB films are arranged in the same way as in L films, i.e. they are tilted with respect to the quartz slides. The 5CT molecules are also tilted in LB films, in contrast to L films where they are aligned almost perpendicularly to the film plane. The molecules of **1** show a significantly greater tilt angle ($\approx 60^\circ$) with the normal to the solid surface than with the normal to the air–water interface. On increasing the liquid crystal concentration the tilt angle increases. These observations indicate that both during transfer of the monolayer from water to the

quartz slide, as well as in LB films formed from binary mixtures, rearrangement of the molecules takes place.

The shape and band position of the absorption and emission spectra of **1**, pure and mixed with liquid crystals, indicate the formation of various kinds of aggregates between the **1** molecules. However, only excimers are revealed in the fluorescence spectrum of the LB films.

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