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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Martynski, Tomasz , Hertmanowski, Robert and Bauman, Danuta(2011) 'Molecular organization in two-dimensional films of liquid II. Langmuir and Langmuir-Blodgett films of a perylene-like dye mixed with liquid crystals having a terminal cyano group crystalline mixtures', *Liquid Crystals*, 28: 3, 445 – 450

To link to this Article: DOI: 10.1080/02678290010010103

URL: <http://dx.doi.org/10.1080/02678290010010103>

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Molecular organization in two-dimensional films of liquid crystalline mixtures

II. Langmuir and Langmuir–Blodgett films of a perylene-like dye mixed with liquid crystals having a terminal cyano group†

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(Received 11 August 2000; accepted 14 September 2000)

Langmuir and Langmuir–Blodgett (LB) films of a perylene-like compound 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–area isotherms, the molecular organization on the air–water interface has been estimated. Information about the miscibility or the phase separation of components in the binary mixtures has been obtained. The spectroscopic study of the LB films has allowed conclusions to be drawn about the arrangement of the molecules on the quartz slides. The fluorescence spectra of the LB films of the perylene-like compound have revealed the formation of self-aggregates.

1. Introduction

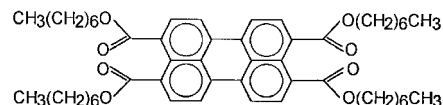
As is well known, amphiphilic molecules, i.e. molecules having hydrophilic and hydrophobic groups, are able to form stable floating monolayers at the air–water interface (Langmuir films) that may be easily transferred onto solid substrates (Langmuir–Blodgett films) [1]. There are also liquid crystals which behave similarly and some information about Langmuir (L) and Langmuir–Blodgett (LB) films formed from mesogenic molecules possessing strongly polar hydrophilic head groups and hydrophobic alkyl chains can be found in literature [2–10]. In a preceding paper [11] we also investigated two liquid crystal materials with a cyano terminal group: 4-octyl-4'-cyanobiphenyl (8CB) and 4-pentyl-4''-cyano-*p*-terphenyl (5CT) and their mixtures at the air–water interface. On the basis of the surface pressure–area isotherms and analysis of the Brewster angle microscope images we ascertained that these two liquid crystals are not miscible in an ultrathin layer and drew conclusions about the molecular packing in L films.

It is also well established that there are other molecules, namely porphyrins [12], phthalocyanines [13], quinones [14], oligothiophenes [15, 16], perylene derivatives [17] and others which, despite being non-amphiphilic, can form stable L and LB films.

In this work we have attempted to make L and LB layers from a derivative of perylene-3,4,9,10-tetra-carboxylic acid (**1**). This compound is a dichroic dye with excellent fluorescent properties [18] which can be applied in organic light emitting diodes [19] on the one hand and in guest–host liquid crystal displays [18] on the other. The latter possibility required that we study not only the pure compound **1**, but also its binary mixtures with the liquid crystals 8CB and 5CT at various concentrations. The aim of our investigations was to check the miscibility of the components, as well as to determine the molecular alignment and spectral properties of **1** with and without the liquid crystals in ultrathin films.

2. Experimental

The derivative of 3,4,9,10-perylenetetracarboxylic acid (**1**) was the heptyl ester with the following chemical structure:



This was synthesized and chromatographically purified in the Institute of Dyes at Łódź University of Technology, Poland.

The liquid crystals 4-octyl-4'-cyanobiphenyl (8CB) and 4-pentyl-4''-cyano-*p*-terphenyl (5CT) were purchased

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 † For part I see [11].

from E. Merck (Germany) and were used without further purification; their phase transition temperatures were in substantial agreement with the data given in the literature [20–22].

Pure compound **1** and **1**/8CB and **1**/5CT mixtures were spread from chloroform solutions onto the deionized water subphase and surface pressure–area isotherms were measured by a Wilhelmy plate balance in a Minitrough (KSV Instruments Ltd, Finland). Further experimental details about L film preparation are given elsewhere [11].

Polished quartz plates ($35 \times 10 \times 1 \text{ mm}^3$) were used as the solid substrates with a hydrophilic surface. The substrates were dipped and raised through the floating layer vertically at a speed of 5 mm min^{-1} at different surface pressures (before and after collapse point of the film). The dipping stroke was 25 mm. Successful deposition of the film on the quartz took place only on raising the substrate. In the case of 8CB, repeated attempts to transfer a floating layer onto quartz slides failed. Therefore, for **1** and its mixtures with both liquid crystals only one dipping and one raising were made. The transfer ratio was estimated by calculating the ratio of the actual decrease in the subphase area to the actual area on the substrate coated by the floating layer. Values between 1.0 and 1.5 were obtained.

Absorption spectra of the LB films were recorded using a double beam spectrophotometer SPECORD M40 (Carl Zeiss Jena), while the fluorescence measurements were carried out by using a home-made photon counting fluorimeter. The exciting light was the 436 nm line from a high pressure mercury lamp. Both in the absorption and fluorescence measurements the incident light beam was normal to the substrate surface.

3. Results and discussion

3.1. Surface pressure–area isotherms

3.1.1. Pure compound **1**

Figure 1 shows the surface pressure–isotherm for the Langmuir film of pure compound **1**. We can see that **1** is able to form a stable and compressible floating layer at the air–water interface. The increase in the surface pressure π begins at a mean molecular area (Mma) equal to 96 \AA^2 , indicating the formation of a homogeneous monolayer which collapses at $\text{Mma} = 82 \text{ \AA}^2$. A cross-sectional area of the perylene skeleton with four -C=O groups per molecule of **1** was estimated to be *c.* 80 \AA^2 . This value suggests that in the monolayer the rigid cores of the molecules lie flat on the water surface, whereas the four hydrophobic alkoxy chains are turned upwards. As the Mma decreases, a plateau region is observed in the isotherm; this can probably be ascribed to the transition from the flat to a tilted alignment of the

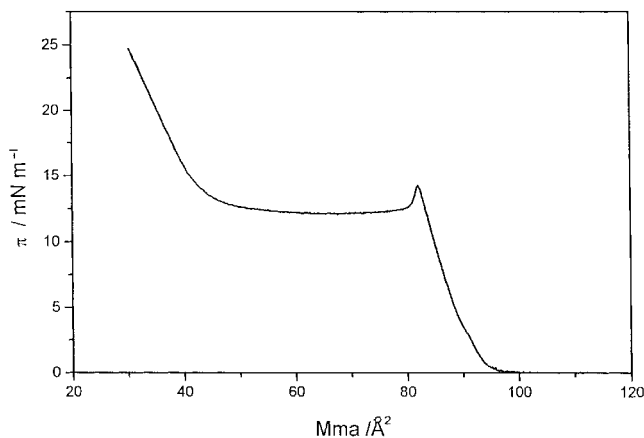


Figure 1. Surface pressure–area isotherm of the monolayer of **1** at the air–water interface at 25°C.

molecules under compression. When the Mma reaches a value of about 45 \AA^2 , a rapid rise in π occurs leading to the conclusion that a rigid condensed layer is formed, in which the molecules are densely packed in tilted ‘stacks’. For some discotic mesogens a model was previously [3] proposed in which an ‘edge-on’ arrangement of the aromatic cores with two hydrocarbon chains submerged in water and two hydrophilic groups lifted away from the water surface was assumed. Recently it was found [19] that some derivatives of 3,4,9,10-perylenetetracarboxylic acid are able to form liquid crystalline columnar phases over an elevated temperature range. It is possible then that a similar molecular arrangement may also occur in a strongly compressed L film. In order to resolve this problem, further investigations of L films formed from other perylene-like compounds, probably with different substituents with various chain lengths, will be needed.

3.1.2. Mixtures of **1** with liquid crystal material

The surface pressure–area isotherms for L films of binary mixtures of **1** in 8CB at various molar fractions (MF) of **1** are presented in figure 2; in table 1 the values of Mma and π at the first collapse point are gathered. The data are average values obtained in five independent runs. It is seen that with increase in the content of 8CB in the film the tilt angle of the isotherm decreases, indicating that the monolayer becomes less stable and rigid. We should keep in mind that as a result of strong repulsive interactions between the electric dipoles of the cyano groups, the monolayer formed from pure 8CB is fragile and the molecules are not densely packed. Moreover, the molecules are tilted with respect to the air–water interface and it has been found that the average angle between the hydrophilic polar group of 8CB and the normal to the interface is 62° [5]. This influences the arrangement and packing of the molecules in mixed films.

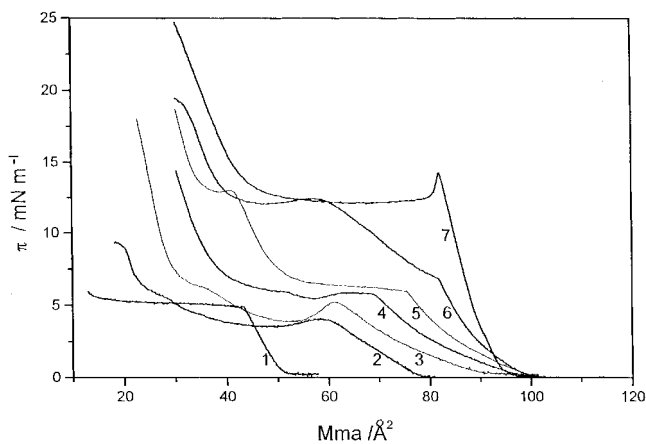


Figure 2. Surface pressure–area isotherms of Langmuir films of 1/5CT mixtures; the molar fractions MF of **1** = 0.0 (1), 0.2 (2), 0.4 (3), 0.5 (4), 0.6 (5), 0.8 (6) and 1.0 (7).

Table 1. Mean molecular area Mma and surface pressure π_c at the first collapse point for 1/8CB Langmuir films.

MF of 1	Mma/Å ²	π_c /mN m ⁻¹
0.0	43.11	4.77
0.2	57.50	4.06
0.4	62.39	5.11
0.5	68.37	5.69
0.6	73.55	5.88
0.8	80.86	6.79
1.0	80.98	14.01

In order to establish the miscibility of the two components in the monolayer, the average area per molecule and the collapse pressure need to be analysed against the monolayer composition. If the components are not miscible, the monolayer will exist as patches of one monolayer in the other. In this case the average area per molecule will follow the additivity rule [1]:

$$A_{12} = x_1 A_1 + x_2 A_2 \quad (1)$$

where A_{12} is the Mma of the mixed monolayer, A_i are Mma values of the single component monolayers at the same π , and x_i are the molar fractions of the components.

Figure 3 shows the excess of the average area per molecule, $A_E = A_{12} - (x_1 A_1 + x_2 A_2)$ versus the MF of **1** in mixed films of 1/8CB at the air–water interface, corresponding to the pressure $\pi = 3$ mN m⁻¹. It is evident from this figure that Mma varies with MF and displays a positive deviation from the additivity rule. This means that the area occupied by the mixed films at $\pi = 3$ mN m⁻¹ is greater than the area of the same amount of the separate pure components, which suggests the existence of a repulsive interaction between **1** and the 8CB molecules. This observation, in conjunction with the additional

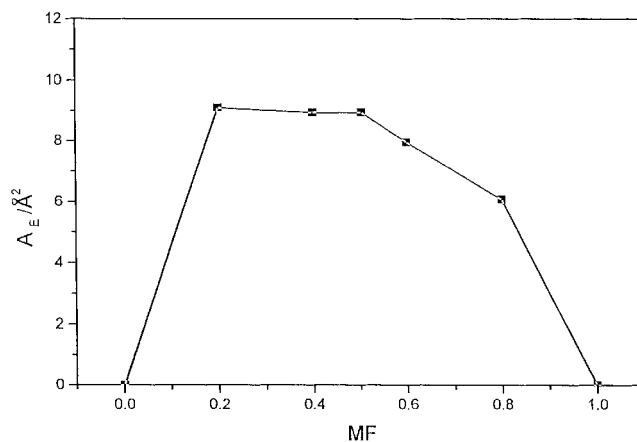


Figure 3. Plot of the deviation of the average area per molecule, A_E of 1/8CB in Langmuir films versus the molar fraction of **1** at a surface pressure $\pi = 3$ mN m⁻¹.

criterion, i.e. a monotonic decrease of π_c when the MF of **1** grows smaller (table 1), gives strong evidence for the miscibility of both components in the 1/8CB system.

Langmuir films of binary mixtures of **1** in 5CT behave very differently from those of the 1/8CB mixtures. Figure 4 presents the surface pressure–area isotherms for 1/5CT mixtures at the air–water interface at various MF of **1**. It is seen that the tilt angle of the isotherms is significantly greater than in the case of the 1/8CB mixtures and increases with increase in the content of 5CT. This is probably a consequence of the fact that the monolayer formed from pure 5CT is more stable and rigid than the 8CB monolayer, and the molecules are aligned perpendicular to the water surface [2, 4, 11]. Table 2 contains the Mma and π data for the first collapse point, while figure 5 shows the concentration dependence of the excess of Mma, A_E at a surface pressure $\pi = 7$ mN m⁻¹ for 1/5CT mixtures. It is evident

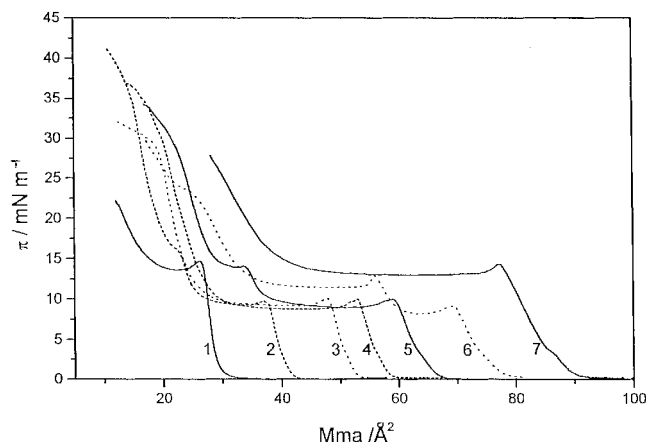


Figure 4. Surface pressure–area isotherms of Langmuir films of 1/8CB mixtures; the molar fractions MF of **1** = 0.0 (1), 0.2 (2), 0.4 (3), 0.5 (4), 0.6 (5), 0.8 (6) and 1.0 (7).

Table 2. Mean molecular area M_{ma} and surface pressure π_c at the first collapse point for 1/5CT Langmuir films.

MF of 1	$M_{ma}/\text{\AA}^2$	$\pi_c/\text{mN m}^{-1}$
0.0	26.25	15.24
0.2	37.18	9.83
0.4	48.84	10.06
0.5	53.16	10.09
0.6	59.95	10.09
0.8	70.49	9.92
1.0	77.10	14.29

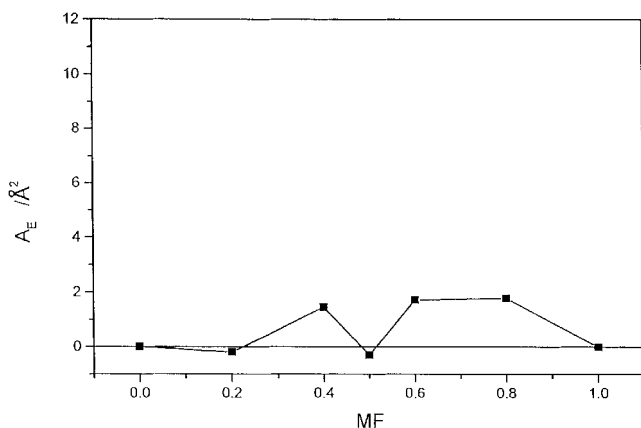


Figure 5. Plot of the deviation of the average area per molecule, A_E of 1/5CT in Langmuir films versus the molar fraction of **1** at a surface pressure $\pi = 7 \text{ mN m}^{-1}$.

that the values of π_c remain almost constant in the mixed films, although they are smaller than those for the pure components. This observation, together with the small deviation of the A_E values from additivity rule, indicates immiscibility or very small partial miscibility in the 1/5CT system.

3.2. Spectroscopic studies

The absorption and emission spectra of compound **1** in ethanol solution ($1 \times 10^{-4} \text{ M}$) at room temperature were obtained. The absorption bands show a fine structure with two peaks at 449 and 472 nm and one shoulder. Mirror symmetry between the absorption and emission spectra is observed with the fluorescence peaks at 490 and 518 nm. Similar spectra were obtained previously for diluted solutions of **1** in dioxan and acetone [18]. It is worth noting that in the solvents investigated compound **1** shows a bright green–yellow fluorescence with a high quantum yield [18].

3.2.1. Pure compound **1**

Pure compound **1** was transferred from a floating layer onto quartz slides at three different surface pressures: 6.5, 12 and 17 mN m^{-1} . Figure 6 presents the absorption spectra of the LB films of **1** at these three values of π .

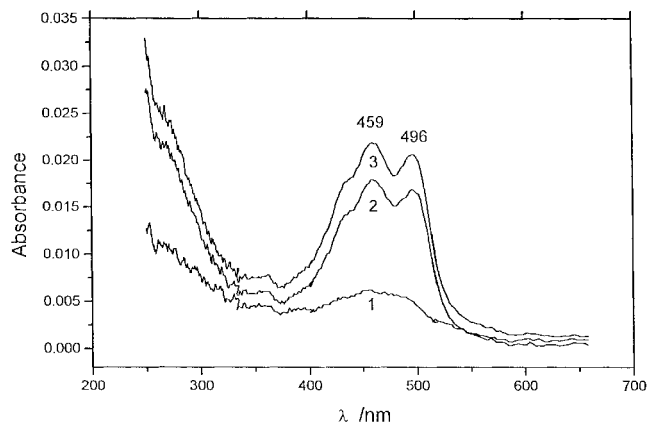


Figure 6. Absorption spectra of **1** in Langmuir–Blodgett films deposited on quartz slides at the surface pressure $\pi = 6.5$ (1), 12.0 (2) and 17.0 mN m^{-1} (3).

As can be seen from figure 1, $\pi = 6.5 \text{ mN m}^{-1}$ corresponds to the homogeneous monolayer. The transfer ratio (TR) was equal to 1.0. In this case the absorbance is relatively weak and two peaks cannot be distinguished in the absorption spectrum. At higher surface pressure, TR was equal to 1.3, which means that more than one layer was transferred onto the quartz slides. Moreover, the molecules of **1** are now densely packed as was ascertained on the basis of the analysis of the surface pressure–area isotherm. This is reflected in the increase in the absorbance, and the absorption spectra reveal two peaks which are red shifted (459, 496 nm) in comparison with the absorption peaks of **1** in ethanol. Moreover, the absorbance ratio of the first peak to the second peak is now reversed, suggesting the formation of aggregates of molecules of **1**.

The emission spectra of **1** in LB films are quite different from the solution spectrum. Figure 7 shows the emission spectra of films obtained at the same surface

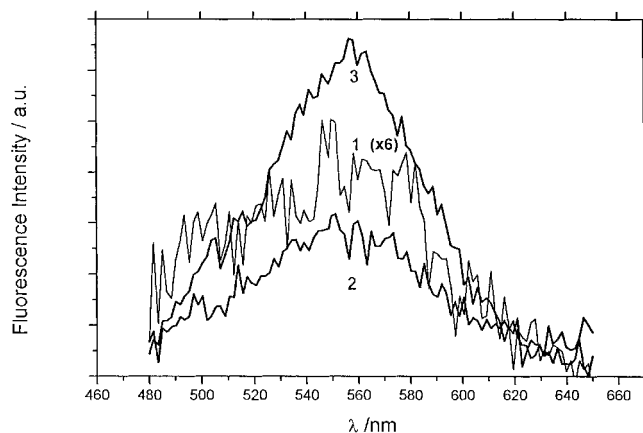


Figure 7. Fluorescence spectra of **1** in Langmuir–Blodgett films deposited on quartz slides at the surface pressure $\pi = 6.5$ (1), 12.0 (2) and 17.0 mN m^{-1} (3).

pressures as in the case of the absorption measurements. They show a single band with its maximum at 556 nm, which may support our thesis concerning the formation of aggregates. Recently, Benning *et al.* [19] reported that pure derivatives of 3,4,9,10-perylenetetracarboxylic acid show an orange fluorescence with one peak (between 582 and 606 nm, depending on the chain length) and ascribed the strong red shift, with respect to the fluorescence of the solutions, to the formation of excimers which originate from an interaction of neighbouring molecules after one is excited. In the case of **1** in a LB film, the red shift is only somewhat smaller, therefore it is very probable that we too observe the excimer fluorescence. However, the lack of coincidence between the absorption spectrum in ethanol and that in the film means that interaction also in the ground state cannot be excluded.

3.2.2. Mixtures of **1** with liquid crystal material

The **1**/8CB and **1**/5CT mixtures were transferred onto quartz slides at the surface pressure corresponding to the value of π before the collapse point on the surface pressure–area isotherm (homogeneous monolayer). Figure 8 presents the absorption spectrum of the **1**/8CB LB film for a MF of **1** equal to 0.5 as an example. In this spectrum two bands are seen: the long wavelength band belonging to **1** and the band in the UV region with maximum at 283 nm which corresponds to 8CB. The presence of the latter band shows that the 8CB molecules are tilted with respect to the quartz surface similarly to those at the air–water interface.

For various MF of **1** in 8CB, values of TR between 1.3 and 1.5 were obtained. We have found that with increase in MF, the absorbance of the band corresponding to 8CB decreases almost proportionally to MF (after normalization to an equal value of TR), whereas the absorbance of **1** remains constant within the experimental uncertainties. This is a rather unexpected result

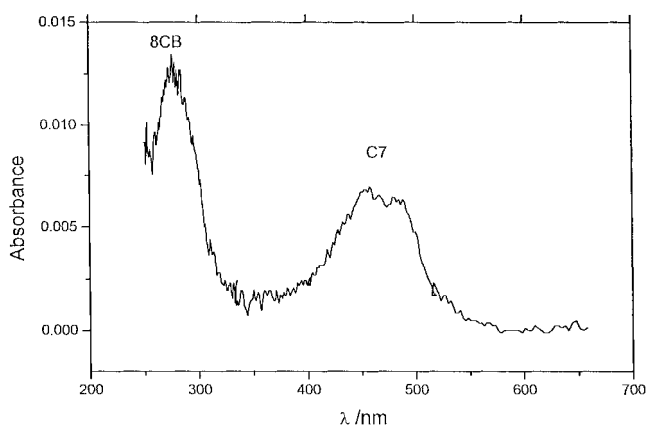


Figure 8. Absorption spectra of a **1**/5CB mixture in a Langmuir–Blodgett film; molar fraction of **1**, MF = 0.5, deposited onto quartz slides at $\pi = 3 \text{ mN m}^{-1}$.

and indicates that the arrangement of the molecules of **1** on the quartz slides is quite different from that in the L film. The almost constant absorbance of **1** over a five-fold increase of its concentration (from 0.2 to 1.0) would suggest a change in the arrangement of the molecules of **1** from a flat adhesion of the perylene skeleton in the case of small concentrations (large amount of 8CB) to the orientation with the relatively large tilt angle found in the case of the pure compound. Meanwhile, the considerations in §3.1 have led to the conclusion that when the molecules of **1** form the homogeneous film monolayer their rigid cores lie flat at the air–water interface.

A similar arrangement to that for **1**/8CB mixtures in the LB film can be supposed for **1**/5CT mixtures on the basis of the spectroscopic studies. In this case, however, the absorption band corresponding to 5CT is not present, which means that as in the L film the molecules of this liquid crystal probably stand vertically to the quartz slides. This is in agreement with a previous report [4]. The absorbance of the band belonging to **1** (after normalization to an equal value of TR, which was now 1.0 to 1.3) changes only a little with change in the film composition, showing just a small tendency to decrease as the MF of **1** rises.

The emission spectra of LB films of **1**/5CT mixtures are shown in figure 9. It is evident that the fluorescence intensity changes only slightly and irregularly with increase in the MF of **1**. Very similar spectra were obtained for **1**/8CB mixtures. Although the fluorescence in both kinds of mixture is very weak, two indistinct maxima at 550 and 585 nm can be distinguished, in contrast to only one maximum for pure **1**. This may indicate the possible formation of different types of aggregate.

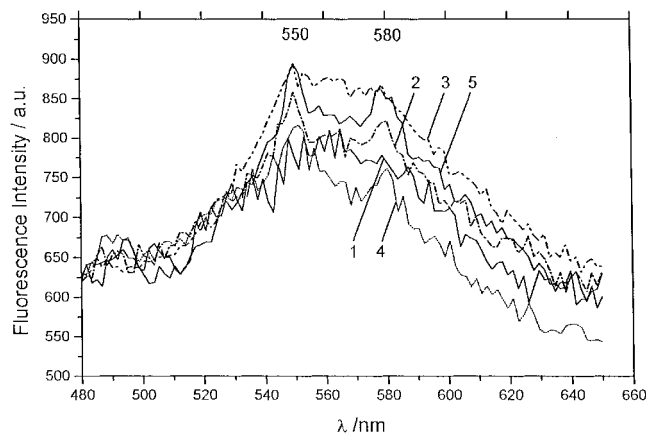


Figure 9. Fluorescence spectra of **1**/5CT mixtures in Langmuir–Blodgett films at molar fractions of **1**, MF = 0.2 (1), 0.4 (2), 0.5 (3), 0.6 (4) and 0.8 (5), deposited onto quartz slides at $\pi = 5 \text{ mN m}^{-1}$.

4. Conclusions

A derivative of 3,4,9,10-perylenetetracarboxylic acid (**1**) and its binary mixtures with liquid crystals with a terminal cyano group, 8CB and 5CT, have been investigated as Langmuir and Langmuir–Blodgett films. It was found that **1**, when spread on the water subphase, forms a stable monolayer at the air–water interface. The surface pressure–area isotherm suggests that in the monolayer the rigid cores of **1** (perylene skeleton with $\text{C}=\text{O}$ groups) lie flat on the water surface and change to a tilted arrangement under compression. Mixtures of **1** with 8CB are miscible over the whole range of MF of **1**, whereas for **1**/5CT mixtures, immiscibility or only very small partial miscibility of **1** with 5CT is observed. Both the pure compound **1** and the mixtures **1**/8CB and **1**/5CT can be transferred onto quartz slides forming LB films. In mixed LB films the liquid crystal molecules are arranged in the same way as in L films, i.e. the 8CB molecules are tilted with respect to the quartz surfaces, while the 5CT molecules are aligned perpendicular to the film plane. The molecules of **1** in LB films are aligned quite differently from those in L films: their cores lie flat on the surface only at small MF and assume a more and more vertical arrangement as the MF rises. The emission spectra of **1**, pure and mixed with liquid crystal, indicate the formation of aggregates of the molecules of **1**.

Finally, it is worth noting that the concentrations of **1** in the liquid crystals used in our investigations are relatively high. For application in liquid crystal displays, perylene-like dyes are dissolved in a liquid crystal at a concentration of the order to 10^{-3} – 10^{-2} M. At such concentrations, both the absorption and emission spectra are similar to those in typical isotropic solvents [18, 23], indicating the presence of only the monomers.

This work was supported by Polish Research Project No 2 P03B 027 16 coordinated by the Committee of Scientific Research (KBN).

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