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Self-aggregates formation of 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes in Langmuir–Blodgett films

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Abstract

Langmuir–Blodgett (LB) films formed of some 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes and of their binary mixtures with the liquid crystal 4-octyl-4′-cyanobiphenyl (8CB) have been studied. Absorption and fluorescence studies were carried out. Both absorption and fluorescence spectra have revealed the formation of self-aggregates of dye molecules in monomolecular layers. Moreover, information about the molecular organization at the air–solid substrate interface has been obtained.

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Keywords: Perylene-like dye; Langmuir–Blodgett film; Absorption spectrum; Fluorescence spectrum; Dimer

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1. Introduction

Perylene and its derivatives are well-known organic dyes which have attracted considerable attention both from scientific and technological points of view. Because of excellent fluorescent properties [1], good defined direction of absorption and emission oscillators [2,3] and high photostability, perylene itself can be used as a probe to study orientational order in oriented systems, such as polymers, lipid membranes, thermotropic and lyotropic liquid crystals [4–6]. It does not, however, find technological application. Instead, most of perylene derivatives are promising compounds for application in electronic devices as molecular semiconductors and are useful materials for electrophotographic photoreceptors [7], optical disks [8], photovoltaic elements [9] and organic light-emitting diodes [10]. They can be also applied as guest species in ‘‘guest–host’’ liquid crystal displays working both in passive and active modes [11,12]. Depending on the substituents, perylene derivatives can exist in a wide range of hues; they provide yellow, orange, red, bordeaux, brown and even black shades. Therefore, they offer high tinctorial strength and most of them are used in high grade industrial paints, especially in original automotive finishes and in automotive refinishes [13]. From the scientific point of view perylene-like dyes pay attention because of their fascinating aggregation properties. These properties depend on the substituents attached to the main perylene skeleton, on the temperature and on the matrix in which dyes are embedded [14–28].

Langmuir–Blodgett (LB) films (see for example: [29]) are very interesting two-dimensional systems where aggregation properties of perylene and its derivatives have been observed [17–25,28]. Although these dyes are non-amphiphilic, they can form stable LB films, but usually when they are mixed with fatty acids [17,18,20–25]. Only a very little is known about perylene derivatives properties in LB films formed without stabilizing action of fatty acids [19,21,28]. Depending on the molecular structure of the perylene-like dye, a concentration (in the case of mixtures with fatty acids) and temperature, LB films show different spectral properties, indicating the formation of various kinds of aggregates among dye molecules.

Vitukhnovsky et al. [17] investigated properties of perylene mixed with tricosanoic acid in various molar

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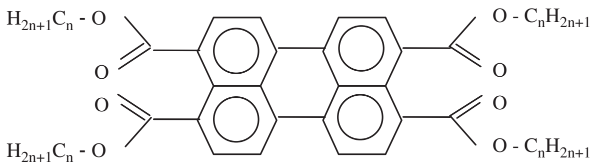
ratios in multilayers fabricated by using LB technique. They found that at some molar fraction of perylene, in absorption spectrum appeared broad band with maximum at 380 nm, very similar to that described by Ferguson [15] and attributed to dimer formation in the ground state. With the increase of the molar fraction varied also the shape and the position of the fluorescence band: it broadened, lost its vibronic structure and maximum was shifted towards longer wavelength (≈ 550 nm). This band was ascribed to the ground state dimer emission. However, the study carried out for these same mixtures at 110 K [18] showed the existence of three emitters in LB films, which gave different contributions to the fluorescence spectrum depending on the molar ratio. In spite of the monomer and dimer fluorescence, observed at room temperature, an additional band with distinct maximum at 600 nm appeared. Because this band had no mirror band in the absorption spectrum, and its shape and position were similar to perylene excimer fluorescence band, observed by Ferguson [15] as well as for α-perylene crystal [14], it was attributed to the excimer created in the LB film by two perylene molecules from which one is in the excited state. Further investigations carried out by Sluch et al. [21] showed that if long alkyl chain was attached to the perylene skeleton, the excimer fluorescence disappeared. Even then, when the LB film was created from pure compounds, without a fatty acid, in the fluorescence spectrum only the contributions from monomer and ground state dimer were observed. Johnson et al. [19] first reported about formation of LB films from pure derivative of perylene. The absorption spectrum of the LB film indicated on the formation of aggregates among dye molecules, which was explained by molecular exciton model [30,31]. However, in the fluorescence spectrum recorded at room temperature, very broad band with two separated maxima was found. The authors supposed the creation of two kinds of excimers with different degree of aromatic ring overlapping. Similar suggestion about occurrence of two kinds of excimers in LB films of perylene-like dyes was given by Akimoto et al. [24]. Willig et al. [20,22] made the detailed analysis of the temperature effect on the fluorescence and its lifetime for the LB film of one of perylene derivatives mixed with arachid acid. They ascribed the bands appearing in the fluorescence spectrum with maxima at about 550 and 630 nm (at 2 K) to, respectively, Y-type and E-type emissions, which are characteristic also for α-perylene crystal [32–34]. Y-type emission originates from a partially relaxed excited molecular pair, while E-type emission is related to the fully relaxed excimer. Other perylene-like dye, namely perylene derivative of dicarboximide, mixed with stearic acid in LB films was studied by Dutta et al. [23]. They observed the broadening of the absorption band in the visible spectral region with respect to this band in solution, the change of the intensity ratio of the absorption maxima and their bathochromic shift, giving indication on the J-type aggregation [35]. The fluorescence spectrum of the LB film showed unstructured profile with maximum at about 545 nm and very intensive, broad band with its maximum at 590 nm, attributed to the excimer emission. LB films formed of derivatives of 3,4,9,10-tetracarboxylic acid with various length of bis(*n*-alkylimido)-perylene chains were investigated by Antunes et al. [28]. They found in the absorption spectra of LB films the bands which were shifted towards shorter and longer wavelengths, suggesting the creation of both H-type [36] and J-type [35] aggregates. However, in the fluorescence spectrum only the band ascribed to the excimer were observed.

Some years ago in our laboratory we obtained stable Langmuir and LB films formed of 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes [37,38] and observed the creation of self-aggregates, which are revealed especially in the fluorescence spectrum. However, some questions remained still open. Therefore, in this work, we have investigated in detail absorption and fluorescence spectra of five members of 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylene homologous series (n = 4–8) as LB films obtained during the transfer of the monolayer from the water surface on the solid substrate at various stages of the Langmuir film formation. The aim of our study was to answer the question, which kind of aggregates can be created by perylene-like dyes in LB films when they are compressed in a cage with significantly high pressure. The influence of the alkyl chain length substituted to the perylene core on the aggregates formation should be also recognized.

2. Experimental

The compounds 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes (**1–5**) (see Fig. 1) were synthesized and chromatographically purified in the Institute of Dyes at Łódź



Dye Code	n
1	4
2	5
3	6
4	7
5	8

Fig. 1. Molecular structure of 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes.