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Aggregation properties of tetrachloroperylene-tetracarboxylic acid in binary Langmuir and Langmuir–Blodgett films

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ABSTRACT

The Langmuir and Langmuir–Blodgett films formed of tetra-*n*-butyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylate and its binary mixtures with 4-octyl-4'-cyanobiphenyl and arachidic acid have been studied. The Langmuir films were characterized by surface pressure versus mean molecular area isotherms and the films morphology observations were made by means of a Brewster angle microscope. The miscibility of the compounds was determined. Subsequently, the Langmuir films were transferred onto hydrophilic quartz substrates forming the monolayer Langmuir–Blodgett films. The electronic absorption and fluorescence spectra reveal aggregation of the chromophores in ground state driven by π - π molecular orbitals interactions. Perylene-like dye aggregation depends upon the dye concentration in the dye/liquid crystal mixed films and is concentration-independent in dye/arachidic acid one.

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1. Introduction

Over the last two decades perylene derivatives have attracted much attention due to their potential applications in organic molecular electronics. These dyes combine strong absorption in the visible region with high fluorescence quantum yield and long fluorescence lifetime [1]. Moreover, they exhibit excellent high thermal and photochemical stability [2,3]. Depending on which type of electric current through the molecular layer is mostly effective, organic semiconductors are classified into two groups of hole-conductive (p-type) and electron-conductive (n-type). Stable organic p-type semiconductors are more commonly used in diverse applications. N-type organic materials are much less developed. Recently, perylene derivatives are of increasing interest as active semiconducting materials which can be applied as active layers in organic molecules electronic devices [4], such as optical discs [5,6], photovoltaic elements [7,8], dye lasers [9], organic light emitting diodes [10–12] or organic field effect transistors [13,14].

It is well known that the number of perylene-like dyes with good n-type semiconductivity is still limited. One of the ways for utilization of this type of organic compounds is the substitution of strong electron-withdrawing atoms or groups such as F, Cl, CN or perfluoroalkyl chains [15] in the bay position. It causes a change in

conformational structure, i.e. twist of perylene core. In the case of chlorinated perylene core, the molecule is no longer flat but becomes strongly twisted and the torsion angle is about 37° [16,17]. Moreover, it also changes the electronic and optical properties of the dye. Generally, electron-withdrawing substituents incorporated into perylene-based materials decrease the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The lower LUMO level allows electron injection by lowering the charge injection barrier and makes electrons less susceptible to ambient oxidation [1]. Additionally, molecules with substituted halogen atoms in the bay positions to the perylene core are expected to have the molecular degree of motional freedom efficiently reduced. It may have a positive impact on the arrangement of these molecules in thin films and therefore improves the transport of charge carriers in organic systems.

To assess the effect of the bay-substituted of halogens on molecular organization, the tetrachloroperylene derivative was synthesized. In such compounds self-organization, which corresponds to an aggregation, appears. These processes are accompanied by characteristic changes of the electronic absorption and emission spectra. The control of aggregate formation is limited to certain concentration of chromophores in solutions [18,19]. A very simple system in which molecular alignment can be easily investigated is the molecular monolayer formed at gas–liquid (Langmuir film) and gas–solid substrate (Langmuir–Blodgett (LB) film) interfaces. Typical compounds forming the Langmuir and LB

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films are amphiphilic molecules such as phospholipids and long chain fatty acids. Additionally, some liquid crystals with strong dipole moments are able to form stable monolayers at the water surface. These compounds can be used to create mixed monolayers in which investigated dye molecules can be used in extremely high concentration. A great advantage of these films is the fact that molecules are located in highly oriented environment, similarly as it takes place in solid matrices and can be successfully transferred from water onto a solid support (LB film). Thereafter, the latter can be easily characterized by spectroscopic methods. Some problems resulting from the component miscibility in such two-dimensional solution systems can appear.

In this paper we have studied the properties of the Langmuir and Langmuir–Blodgett films formed of binary mixtures of newly synthesized dye tetra-*n*-butyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylate (**PC4**) with 4-octyl-4'-cyanobiphenyl (**8CB**) and arachidic acid (**AA**). The aim of our investigations is to obtain information about organization and intermolecular interactions in ultrathin ordered layers of the perylene derivative and its binary mixtures. We used two different compounds **8CB** and **AA** as a “solvent” for the dye because the miscibility of the dye with them is different. Usually perylene-like dyes are soluble in **8CB** matrix but components separation appears in mixtures with **AA**.

2. Materials and methods

The molecular structure of compounds under investigation is given in Fig. 1. The dye tetra-*n*-butyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylate (**PC4**) was 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. Dąbrowski Laboratory at the Institute of Chemistry, Military University of Technology, Poland. Its phase transitions were in excellent agreement with literature data [20,21]. Arachidic acid (**AA**) with a quoted purity of >99% was purchased from Sigma-Aldrich and used as received.

A commercially available Minitrough 2 manufactured by KSV Instruments Ltd., Finland, was used for the formation of the Langmuir and Langmuir–Blodgett films. Pure water used as a subphase was deionized and purified to a final resistivity of 18.2 MΩ cm by a Milli-Q system (Millipore Corporation, Austria). A constant subphase temperature (21 °C) was maintained by a cooling circulator. 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 achieve appropriate molar fraction (X_p) of **PC4** in **8CB** and **AA** matrix. The pure and mixed compound were spread on the clean air–water interface with using a glass microlitre syringe (Hamilton, Great Britain). After 10 min for the solvent

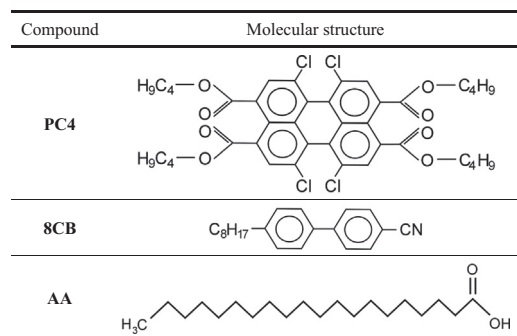


Fig. 1. Molecular structure of perylene-like dye **PC4**, liquid crystal **8CB** and arachidic acid **AA**.

evaporation, the monolayer was compressed at a barrier motion speed of 5 mm min⁻¹ and the surface pressure was monitored by a platinum Wilhelmy plate hanged on a balance with an accuracy of ±0.1 mN m⁻¹. All measurements were repeated on the fresh subphase three times to confirm reproducibility.

The morphology of the films at the air–water interface was visualized by means of a Brewster angle microscope (BAM). The BAM images and the compression isotherms were recorded simultaneously. The instrument we used is based on the Höniß and Möbius setup [22] and was built in our laboratory. The image features were observed with a lateral resolution of ≈ 2 μm.

Polished quartz plates (35 × 15 × 1 mm³) were used as the solid substrate with hydrophobic surface for LB films preparation. The hydrophobic state of the quartz was obtained by silanization using hexamethyldisilazane (Fluka). The vertical dipping method (Langmuir–Blodgett technique) was used with dipping rate of 5 mm min⁻¹ and dipping stroke of 20 mm. The transfer ratio was near unity.

The absorption spectra of the LB films were recorded in the UV–vis spectral region by means of a spectrophotometer CARY 400 (Bruker), while the fluorescence measurements were carried out by using a photon-counting spectrofluorimeter constructed in our laboratory and described in detail elsewhere [23]. 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. Additionally, some fluorescence spectra were recorded by means of Hitachi F-4500 spectrofluorimeter with a Xenon lamp. The

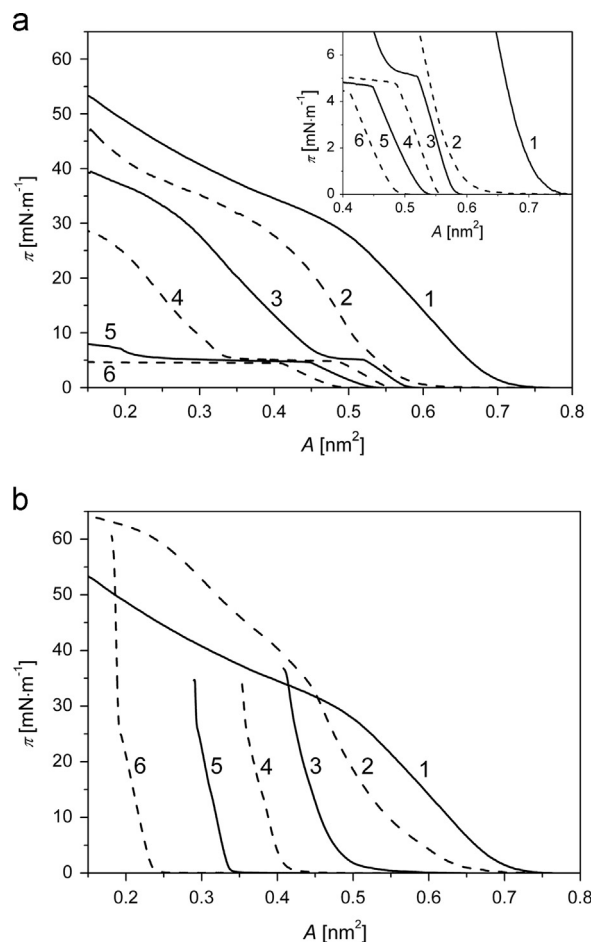


Fig. 2. Surface pressure–mean molecular area isotherm of the Langmuir films of **8CB** (6), **PC4** (1), and **PC4/8CB** mixtures (a) and of **AA** (6), **PC4** (1), and **PC4/AA** mixtures (b) at X_p of the dye: 0.8 (2), 0.6 (3), 0.4 (4), and 0.2 (5).

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