



The synthesis of novel perylene-like dyes and their aggregation properties in Langmuir and Langmuir–Blodgett films

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ABSTRACT

The synthesis of novel perylene-like dyes with different length and molecular structure of terminal chains substituted to the main perylene core is described. The dyes are able to form compressible and stable monolayers at the air–water interface (Langmuir films), which can be easily transferred onto solid substrates (Langmuir–Blodgett films). In the Langmuir and Langmuir–Blodgett films, the dye molecules show tendency to creation of self-aggregates, both in the ground and excited electronic states. The influence of the molecular structure of the substituents on the aggregation properties is observed and discussed.

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1. Introduction

In recent years, the development of experimental research in the field of molecular electronics [1,2] and molecular organized systems [3–5] concerned with dimers, trimers and higher order aggregates, is observed. Intermolecular interactions responsible for self-aggregation can cause the dramatic change of the optical, electrical and photophysical properties of molecules. Therefore, systems in which aggregation phenomena occur, may be used as new functional materials for application in molecular electronics, photonics and nonlinear optics [6]. For rational design of novel materials a thorough understanding of the types of intermolecular interactions is needed. Very simple systems in which such interactions can be easily determined are well-ordered layer structures formed at gas–liquid (Langmuir films) and gas–solid substrate (Langmuir–Blodgett films) interfaces [3–5].

Perylene and its derivatives are well known dyes which are able to create self-aggregates in ultrathin films fabricated by using Langmuir–Blodgett (LB) technique [7–13]. In our previous study of 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylene in Langmuir and LB films [14–19] we found that molecules of these dyes can form J-type

aggregates [20] in the ground electronic state and excimers giving Y-type and E-type emissions [9,11,21–23] in the excited state.

In this paper we report the synthesis of three perylene-like dyes that differ in the length and molecular structure of chains substituted to the main perylene core. Next, we present the results of the investigation of the dyes in Langmuir and LB films by means of optical spectroscopy methods: electronic absorption and fluorescence. Newly synthesized perylene-like dyes show interesting variant aggregation properties in ultrathin ordered layers.

2. Experimental

2.1. Characterization of products and equipment

All reagents and chemicals were used as received from Aldrich. All solvents were dried according to standard procedures. The melting point of finally synthesized compounds was determined with Boethius PHMK-05 apparatus, and the values were corrected. The structure of the final products were confirmed by ¹H NMR analysis with Bruker DPX-250 Avance spectrometer at a frequency of 250 MHz. Chemical shifts are reported in ppm (δ) downfield from TMS, in CDCl₃.

A commercially available Minitrough 2 manufactured by KSV Instruments Ltd., Finland, was used for the Langmuir films

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formation and deposition of the mono- and multilayers on solid substrates. The subphase was deionized water, purified to a final resistivity of 18.2 MΩ cm by a Milli-Q system (Millipore Corporation, Austria). A constant subphase temperature was maintained by a cooling circulator and kept constant at 20 °C. Chloroform Uvasol with spectroscopic quality (Merck, Germany) was used as a spreading solvent.

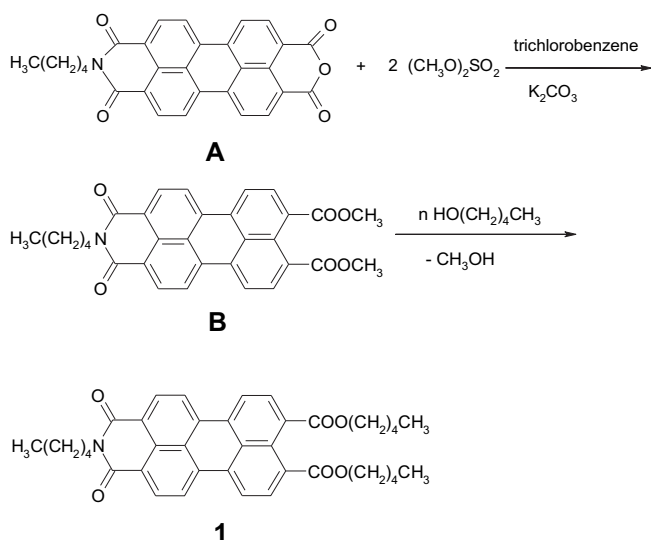
The absorption spectra of Langmuir and Langmuir–Blodgett films were recorded in the visible spectral region using a spectrophotometer CARY 400. For *in situ* measurements a spectrophotometer was equipped with fiber optic accessory supplied by Varian. The details of the equipment are described in reference [24]. The fluorescence was measured with a photon-counting spectrofluorimeter built in our laboratory and described in detail in reference [15]. The exciting light was the 436 nm line from high-pressure mercury lamp. Additionally, some fluorescence spectra as well as excitation spectra were recorded by means of a spectrofluorimeter Hitachi F-4500 with Xenon lamp. The quantum fluorescence yield was determined according to fluorescein in 10⁻⁶ N NaOH using the method described in [25].

2.2. Synthesis

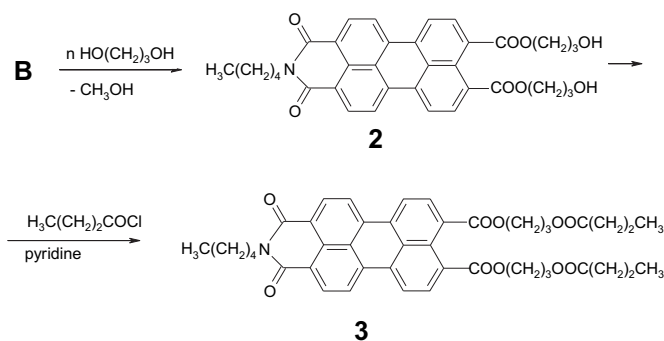
Scheme 1 presents the synthetic route for dye **1** which is an intermediate product for dyes **2** and **3**, prepared in the way illustrated by Scheme 2. *N*-(*n*-pentyl)monoimide perylene-3,4,9,10-tetracarboxylic acid anhydride (**A**) was synthesized by Troester method [26].

2.2.1. Preparation of 3,4-bis-methyl ester of 9,10-*N*-(*n*-pentylimide)-perylene-tetracarboxylic acid (**B**)

6.5 g of **A**, 30.0 g of potassium carbonate anhydrous, 60 cm³ of trichlorobenzene and 10 cm³ of dimethyl sulfate were heated to 165–170 °C and stirred at this temperature for 6 h. The half of the solvent was evaporated under reduced pressure and dye was separated by adding 100 cm³ of hexane. The dye was next filtered off, thoroughly washed by hexane and dispersed in water after drying. The precipitated product was filtered, washed by water and dried to give 6.4 g (yield 90%) of compound **A** as the dark red solid. After crystallization from butanol, the product's melting point was 310–311 °C. The structure was confirmed by ¹H NMR spectra: δ = 8.07–8.49 (d, q, d, 8H, perylene ring); δ = 4.20



Scheme 1. Synthetic route to dye **1**.



Scheme 2. Synthetic route to dyes **2** and **3**.

(t, 2H, –CH₂CN(CO₂)₂–); δ = 3.99 (s, 6H, 2 × –OCOCH₃); δ = 1.79 (q, 2H, –H₂CH₂CH₂C–); δ = 1.46 (k, 4H, H₃CH₂CH₂CH₂C–); δ = 0.96 (t, 3H, H₃CH₂C–).

2.2.2. Preparation of 3,4-bis-pentyl ester of 9,10-*N*-(*n*-pentylimide)-perylene-tetracarboxylic acid (dye **1**)

5.1 g of compound **B** was added to 100 cm³ of 1-pentanol, in which 0.1 g of metallic sodium was previously dissolved. The mixture was stirred and refluxed under nitrogen for 36 h. 0.5 g of sodium 1-pentanolate was added two times, after 12 and 24 h. The dye was separated by evaporation of 70 cm³ of the solvent under reduced pressure and precipitated by addition of 50 cm³ of hexane. Next it was left overnight, filtered off, washed by hexane and dried. After crystallization (ethanol) 3.8 g (61.1%) of dye **1** was obtained in red crystal form. Melting point of the dye in cyclohexane was 210–211 °C. ¹H NMR: δ = 8.01–8.48 (d, q, d, 8H, perylene ring); δ = 4.35 (t, 4H, 2 × –OCOCH₂CH₂–); δ = 4.18 (t, 2H, CH₂CN(CO₂)₂–); δ = 1.71–1.89 (m, 6H, –H₂CH₂CH₂C– + 2 × CH₂CH₂CH₂–); δ = 1.41–1.48 (m, 12H, H₃CCH₂CH₂C– + 2 × –CH₂CH₂CH₂CH₃); δ = 0.92–0.98 (m, 9H, H₃CCH₂– + 2 × –CH₂CH₃).

2.2.3. Preparation of 3,4-bis-(3-hydroxypropyl) ester of 9,10-*N*-(*n*-pentylimide) perylene-tetracarboxylic acid (dye **2**)

0.1 g sodium was added to 60 cm³ of anhydrous propane-1,3-diol and when it was dissolved 1.92 g of **B** was added. The mixture was heated for 60 h under slightly reduced pressure. After this time 80% of solvent was evaporated under vacuum, next 30 cm³ of water was added and left overnight. The precipitated was filtered, washed with water and dried. After crystallization (first from butanol, and next from methanol), 0.9 g (yield 37.9%) of dye **2** was obtained as yellow crystals. Melting point of the dye in methanol was 221–222 °C. ¹H NMR: δ = 8.10–8.67 (d, q, d, 8H, perylene ring); δ = 4.58 (t, 4H, H₂CH₂C N(CO₂)₂–); δ = 4.21 (t, 2H, 2 × –OCOCH₂CH₂–); δ = 3.84 (t, 4H, 2 × –CH₂CH₂OH); δ = 2.07 (q, 4H, 2 × –CH₂CH₂CH₂–); δ = 1.45 (m, 6H, H₃CH₂CH₂CH₂CH₂C–); δ = 0.94 (t, 3H, H₃CH₂C–).

2.2.4. Preparation of 3,4-bis-(butyryloxy-3-hydroxypropyl) ester of 9,10-*N*-(*n*-pentylimide)-perylene-tetracarboxylic acid (dye **3**)

0.5 g of dye **2**, 1 cm³ of butyryl chloride and 20 cm³ of pyridine anhydrous was heated to 60 °C and stirred for 12 h at this temperature. The product was precipitated by adding 80 cm³ of 50% ethanol, filtered, washed with water and dried. After crystallization (twice from butanol) 165 mg of dye **3** (yield 28%) was obtained as dark red crystals. Melting point of the dye was 164–165 °C. ¹H NMR: δ = 8.01–8.64 (d, q, d, 8H, perylene ring); δ = 4.44 (t, 4H, 2 × –OCOCH₂CH₂–); δ = 4.28 (t, 4H, 2 × –CH₂CH₂OCO–); δ = 4.20 (t, 4H, –H₂CH₂C N(CO₂)₂–); δ = 2.30 (t, 4H, 2 × –OCOCH₂CH₂–); δ = 2.12 (t, 4H, 2 × –CH₂CH₂CH₂–); δ = 1.56–1.70

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