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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.

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)-perylenes 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 ^{1}H 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 $CDCl_3$.

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.

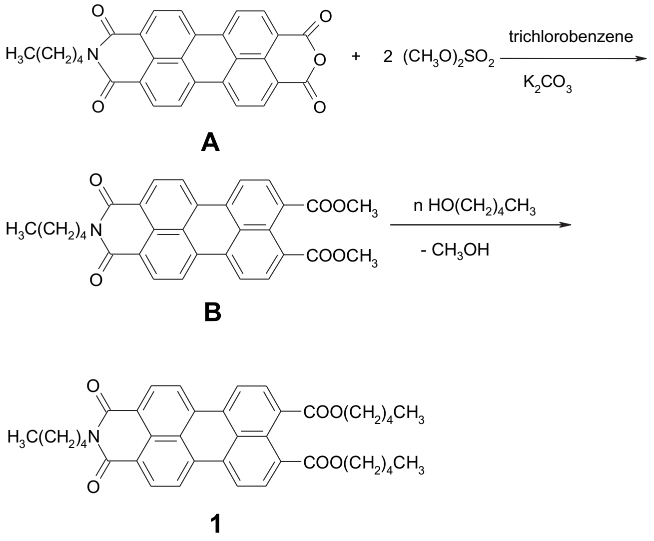
The absorption spectra of Langmuir and Langmuir–Blodgett films were recorded in the visible spectral region using a spectrophotometer CARY 400. For *in situ* measurements a spectrophotometer was equipped with fiber optic accessory supplied by Varian. The details of the equipment are described in reference [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

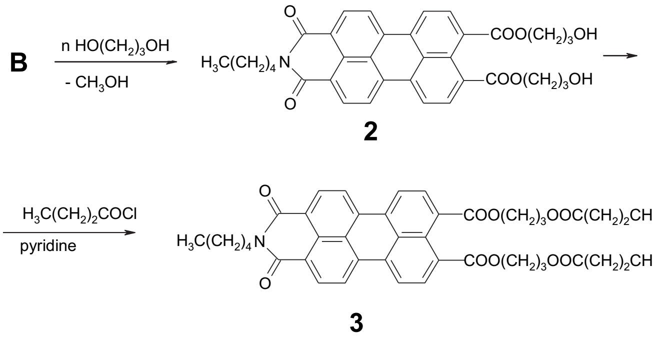
Scheme 1 presents the synthetic route for dye **1** which is an intermediate product for dyes **2** and **3**, prepared in the way illustrated by Scheme 2. N-(*n*-pentylo)monoimide perylene-3,4,9,10-tetracarboxylic acid anhydride (**A**) was synthesized by Troester method [26].

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

6.5 g of **A**, 30.0 g of potassium carbonate anhydrous, 60 cm^3 of trichlorobenzene and 10 cm^3 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 cm^3 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: $\delta = 8.07$–8.49 (d, q, d, 8H, perylene ring); $\delta = 4.20$ (t, 2H, $-CH_2CN(CO_2)_2{=}$); $\delta = 3.99$ (s, 6H, 2× $-OCOCH_3$); $\delta = 1.79$ (q, 2H, $-H_2CH_2CH_2C-$); $\delta = 1.46$ (k, 4H, $H_3CH_2CH_2CH_2C-$); $\delta = 0.96$ (t, 3H, H_3CH_2C-).



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



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

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

5.1 g of compound **B** was added to 100 cm^3 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 cm^3 of the solvent under reduced pressure and precipitated by addition of 50 cm^3 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: $\delta = 8.01$–8.48 (d, q, d, 8H, perylene ring); $\delta = 4.35$ (t, 4H, 2× $-OCOCH_2CH_2-$); $\delta = 4.18$ (t, 2H, $CH_2CN(CO_2)_2{=}$); $\delta = 1.71$–1.89 (m, 6H, $-H_2CH_2CH_2C-$ + 2× $CH_2CH_2CH_2-$); $\delta = 1.41$–1.48 (m, 12H, $H_3CCH_2CH_2C-$ + 2× $-CH_2CH_2CH_2CH_3$); $\delta = 0.92$–0.98 (m, 9H, H_3CCH_2- + 2× $-CH_2CH_3$).

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

0.1 g sodium was added to 60 cm^3 of anhydrous propane-1,3-diole 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 cm^3 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: $\delta = 8.10$–8.67 (d, q, d, 8H, perylene ring); $\delta = 4.58$ (t, 4H, $H_2CH_2C\ N(CO_2)_2{=}$); $\delta = 4.21$ (t, 2H, 2× $-OCOCH_2CH_2-$); $\delta = 3.84$ (t, 4H, 2× $-CH2CH2OH$); $\delta = 2.07$ (q, 4H, 2× $-CH_2CH_2CH_2$); $\delta = 1.45$ (m, 6H, $H_3CH_2CH_2CH_2CH_2C-$); $\delta = 0.94$ (t, 3H, H_3CH_2C-).

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

0.5 g of dye **2**, 1 cm^3 of butyryl chloride and 20 cm^3 of pyridine anhydrous was heated to 60 °C and stirred for 12 h at this temperature. The product was precipitated by adding 80 cm^3 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: $\delta = 8.01$–8.64 (d, q, d, 8H, perylene ring); $\delta = 4.44$ (t, 4H, 2× $-OCOCH_2CH_2-$); $\delta = 4.28$ (t, 4H, 2× $-CH_2CH_2OCO-$); $\delta = 4.20$ (t, 4H, $-H_2CH_2C\ N(CO_2)_2{=}$); $\delta = 2.30$ (t, 4H, 2× $-OCOCH_2CH_2-$); $\delta = 2.12$ (t, 4H, 2× $-CH_2CH_2CH_2-$); $\delta = 1.56$–1.70

(m, 6H, $-CH_2CH_2CH_2-$ + 2× $CH_2CH_2CH_3$); $\delta = 1.43$ (s, 4H, $H_3CH_2CH_2CH_2C-$); $\delta = 0.95$ (m, 9H, H_3CH_2C- + 2× $-CH_2CH_3$).

2.3. Langmuir and LB films fabrication

Freshly prepared solutions of pure dyes in chloroform were spread drop by drop from a microliter syringe (Hamilton, England). The chloroform was allowed to evaporate for 15 min after spreading. Next, the monolayer was compressed at a barrier motion speed of 5 mm/min (approximately 2×10^{-7} nm^2 molecule^{-1} s^{-1}), while the surface pressure π was monitored by a Wilhelmy plate balance with an accuracy of ±0.1 mN/m. All measurements were repeated 3–5 times to confirm reproducibility. Standard trough cleaning procedure was adopted between measurements.

Polished quartz plates (35 × 10 × 1 mm^3) were used as solid substrates with hydrophilic surface for LB film fabrication. The vertical dipping method was used and dipping rate was 5 mm/min. Langmuir films were transferred onto quartz plates at various surface pressures. The dipping stroke was 25 mm. Successful deposition of the dyes took place only on the first up-stroke of the substrate. In all the cases, the transfer ratio was near unity.

3. Results and discussion

3.1. Surface pressure–mean molecular area isotherm

A plot of the change in the surface pressure as a function of the average area available for one molecule on the water surface (π–A isotherm) is basic and widely used technique to characterize a Langmuir film. Fig. 1 presents π–A isotherms of Langmuir films formed of dyes **1**–**3**. The increase of the surface pressure at reducing area is observed for all three dyes, which means that they, despite non-amphiphilic molecular structure, are able to form themselves a compressible floating monolayer at the air–water interface. However, for each dye the π–A isotherm has different shape. Both for dyes **1** and **2** the pressure onset at a molecular area close to 0.4 nm^2 is observed, but the slope of isotherm is different. As a result, in the case of dye **1** up to A = 0.1 nm^2 no collapse point on the isotherm is observed, whereas monolayer of dye **2** collapses at $\pi \approx 65$ mN/m, indicating greater rigidity of the film. In both cases, the area per molecule at the pressure onset is smaller than that for flat-on configuration of molecules at the air–water interface. This is clear by inspecting the molecular structure and dimensions of dyes **1** and **2** (Fig. 2) and assuming that the average area in the Langmuir film is dominated by the rigid core (perylene skeleton with four >C=O groups) of dye molecules. Thus, it is rather reasonable to assume that as the pressure starts to increase the rigid cores of the molecules are already tilted with respect to the water surface, similarly as it was found for 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes in Langmuir films [15,16]. The shape of π–A isotherm of dye **3** is totally different. The surface pressure starts to rise already at A = 1.5 nm^2 and first collapse point is observed at $A_C = 1.28$ nm^2 with $\pi_C = 4.1$ mN/m. The collapse point is followed by a plateau region and at A = 0.92 nm^2 the peak at approximately 15 mN/m appears. With reducing the surface area below 0.7 nm^2, the increase of π can be noticed, similarly as in the case of other dyes under investigation. Taking into account the dimensions of dye **3** molecule (Fig. 2), it can be supposed that at the first pressure onset the molecules lie flat on the surface, probably with the ester (–COO–) groups in the chains anchored to the water. By further compression the molecules assume tilted arrangement, but the ester groups are still the steric hindrance for molecules to be close to each other.

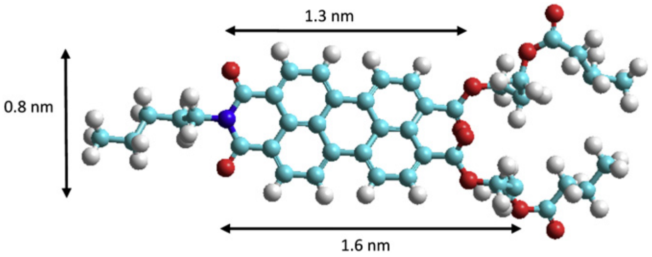


Fig. 2. Model of molecular structure of dye **3**.

3.2. Spectroscopic study

Fig. 3 shows normalized long-wavelength absorption and fluorescence spectra of the dyes under investigation, dissolved in chloroform at c = 10^{-5} mol/dm^3. The spectra are characteristic for the monomeric form of the dyes. They reveal in the visible spectral region the intense absorption band (the half-bandwidth $\delta = 2300$ cm^{-1}) with vibronic structure and two main maxima at 474 nm and 505 nm. This band is reminiscent of the absorption band of pure perylene and corresponds to the $S_0 \rightarrow S_p$ transition,

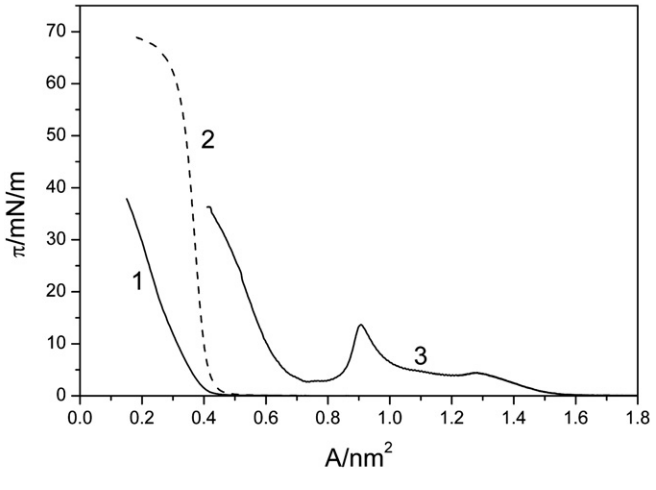


Fig. 1. Surface pressure–area isotherms for Langmuir films of dyes **1** (1), **2** (2) and **3** (3).

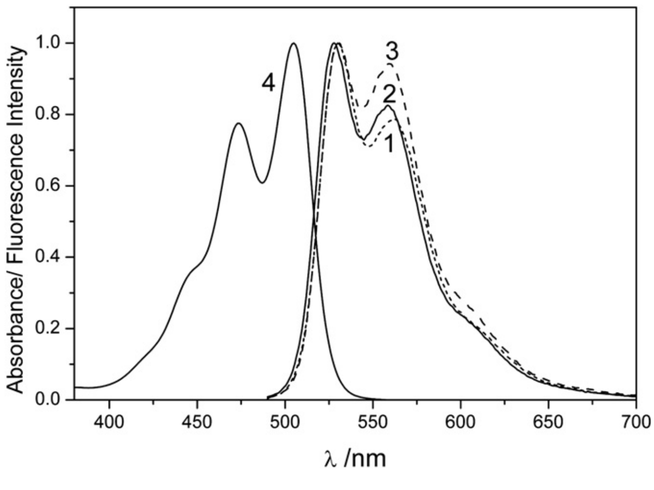


Fig. 3. Normalized fluorescence spectra of dyes **1** (1), **2** (2) and **3** (3) and long-wavelength absorption spectrum (4) of these dyes in chloroform at c = 10^{-5} mol/dm^3.

the dipole moment of which is directed parallel to the long axis of the molecule [27–29]. Two other absorption bands, one parallel ($S_0 \rightarrow S_\beta$) and one perpendicular ($S_0 \rightarrow S_\alpha$) to the molecular long axis, are observed for perylene and its derivatives in UV region [28,29] and were not recorded in our experiment. The position of the maxima and the shape of the band in the visible region do not depend on the substituents. The fluorescence band is almost mirror image of that of absorption and corresponds to the $S_p \rightarrow S_0$ transition of pure perylene. The maxima positions of the band for dyes **1**–**3** differ slightly being observed at about 530 and 560 nm, the half-bandwidth $\delta = 2000$–$2100\ \mathrm{cm}^{-1}$, and the relative intensity of the fluorescence peaks is different than that of the absorption peaks and also different for various dyes. The dilute solutions of perylene-like dyes show a bright green–yellow fluorescence with the quantum yield decreasing from 0.64 for dye **1** through 0.53 for dye **2** to 0.40 for dye **3**. This indicates on the strong dependence of the emission efficiency of perylene-like dyes on the substituent molecular structure, which can be caused by different interaction of fluorescent molecules with environment.

The long-wavelength absorption spectra of dyes **1**, **2** and **3** in Langmuir films, recorded *in situ* at various surface pressures, are presented in Fig. 4a, b and c, respectively. The transfer of the Langmuir film of the dyes took place at various surface pressures and Fig. 4d, e and f illustrate the absorption spectra of dyes **1**–**3** in LB films obtained. In the case of dye **3** the measurements at $\pi = 10$ mN/m were made at $A \approx 0.95\ \mathrm{nm}^2$. It is seen that the shape of the absorption band in both kinds of films is very similar, but the absorbance values for LB films are always greater than those for corresponding Langmuir films. As the absorption intensity is related to the projection of the absorption transition moment on the water or quartz slide surface, the smaller absorbance of Langmuir films means that the average angle between the long axes of molecules and the normal to the surface is smaller than that in LB

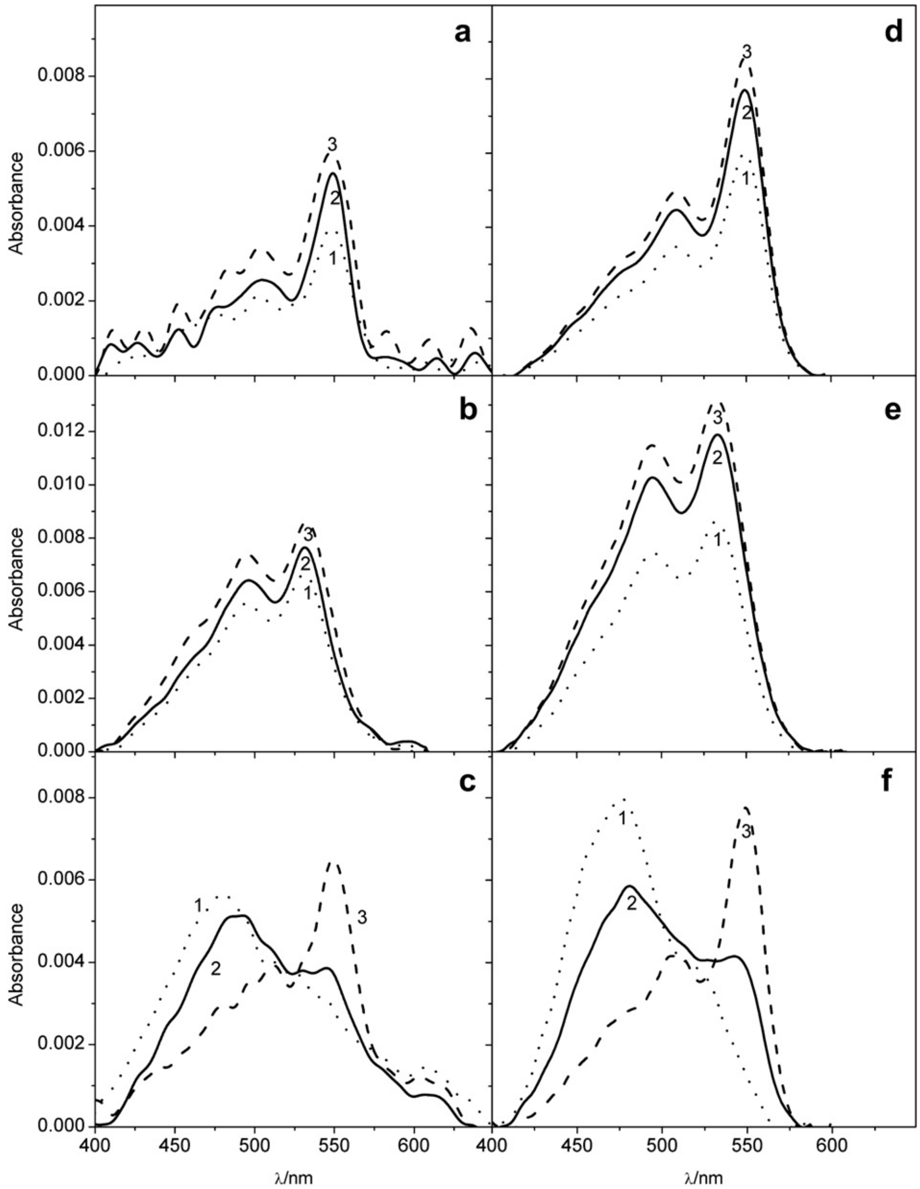


Fig. 4. Absorption spectra of perylene-like dyes in Langmuir (a, b, c) and LB (d, e, f) films for various surface pressure: a, d) dye **1**, $\pi = 1.5$ (1), 6.5 (2) and 12 mN/m; b, e) dye **2**, $\pi = 10$ (1), 20 (2) and 40 (3) mN/m; c, f) dye **3**, $\pi = 3$ (1), 6 (2) and 10 mN/m.

films. This indicates that at the transfer of the monolayer from the water surface to the quartz plate the molecules experience some shock, causing a rearrangement of the molecular organization. It can be connected with the different surface interaction of dye molecules with the quartz with respect to that with the water. Such effect was previously observed for other compounds [7,16,24,30,31].

The absorption spectra recorded for dyes **1**–**3** in Langmuir and LB films are different as compared with the spectra of diluted solution. In the case of dyes **1** and **2** for each pressure the same shape of the absorption band, similar to that in diluted solution, is observed in both kinds of films. However, the maxima positions shift up to $\lambda_{\max} = 510$, 550 nm for dye **1** and 495, 530 nm for dye **2**. Moreover, the ratio of the absorption peaks is changed and the band is strongly broadened. For dye **3** one notices the strong dependence of the absorption band shape on the surface pressure. At low surface pressures the shape of the band is quite different than that for other dyes in monolayers. The most intensive maximum occurs at $\lambda_{\max} = 480$ nm, with small shoulder at $\lambda \approx 515$ nm for $\pi = 3$ mN/m and more distinct shoulder at $\lambda \approx 550$ nm for $\pi = 6$ mN/m. In both cases the strong band broadening is observed. When the absorption *in situ* is measured at $\pi = 10$ mN/m and at the same point the transfer on the quartz takes place, the shape of the recorded spectra changes and is almost identical as that for dye **1**.

The shift and the broadening of the absorption bands are usually indicative for the creation of some types of self-aggregates of dye molecules. Up to now, the best description of the aggregation phenomenon of aromatic dye molecules is based on the molecular exciton model [32]. From this model follows that in the simplest case, *i.e.* a binary system composed of two identical molecules or chromophores (dimer), strong interactions between molecules can cause the splitting of the electronic excited state, which appears as a spectral shift of the absorption band and/or its splitting, known in literature as the Davydov splitting [33]. Then, the perturbation theory yields the following energy values of the two excited molecular states, E' and E'', arising from the exciton splitting of the undisturbed localized transition $0 \rightarrow a$ in both molecules [32]:

$$E' = E_{0a} - \epsilon, \quad E'' = E_{0a} + \epsilon, \tag{1}$$

where E_{0a} is the excitation energy from the ground (0) to the excited (a) state of molecules and ε is dipole–dipole interaction energy between the two transition moments. $\Delta\varepsilon = 2\varepsilon$ is the exciton splitting energy (Davydov splitting).

ε can be calculated in the point-dipole approximation by:

$$\epsilon = \frac{\overrightarrow{\mu}_{u0a} - \overrightarrow{\mu}_{v0a}}{R_{uv}^3} - \frac{3(\overrightarrow{\mu}_{uoa} \cdot \overrightarrow{R_{uv}})(\overrightarrow{\mu}_{v0a} \cdot \overrightarrow{R_{uv}})}{R_{uv}^5}, \tag{2}$$

where $\overrightarrow{\mu}_{u0a}$ and $\overrightarrow{\mu}_{v0a}$ are the electric transition moment of molecules u and v, respectively, and R_{uv} is the distance between centers of two molecules.

The exciton band placed at higher energies (E'') is defined as the H-band, while that at lower energies (E') is defined as J-band. The corresponding aggregates are called, respectively, H- and J-aggregates [20].

Assuming a sandwich dimer configuration of perylene-like molecules, the co-planar arrangement of the absorption transition moments can be considered. In such a case the transition to one of the state is forbidden due to the zero value of the resultant transition moment for antiparallel dipoles arrangement. Then $\Delta\varepsilon$ is dependent on the angle θ between the dipole moment of the molecule and the line connecting the molecules' centers and is given by the formula [32]:

$$\varDelta\epsilon = \frac{2|\overrightarrow{\mu}_{u0a} \cdot \overrightarrow{\mu}_{v0a}|^2}{R_{uv}^3}\left(1 - 3\cos^2\theta\right). \tag{3}$$

When $0^\circ < \theta < 54.7^\circ$, the transition to the J-band occurs, while for $54.7^\circ < \theta < 90^\circ$, the transition to H-band is observed.

For the oblique configuration of two dipole transition moments, their vector sum and difference are always different from zero, giving in the absorption spectrum the band with two maxima, corresponding to the transitions to both the H-band and J-band.

The distinct broadening of the absorption band of dyes **1** and **2** in Langmuir and LB films (compared to that characteristic of monomers) with distinct red shift of the absorption maxima positions, implies that we are dealing here with formation of J-aggregates by the dye molecules in the ground electronic state. In the case of dye **3** the situation is more complicated. Only when the surface pressure at which the monolayers were formed (both on the water and quartz surfaces) is about 10 mN/m, the absorption spectrum reveals the creation of aggregates of J-type. The absorption spectra of Langmuir and LB films of dye **3** obtained at lower π indicate that the aggregates of various geometries can be created. It seems that loose packing of this dye molecules at the low surface pressure favors the formation of a broad distribution of structurally different aggregates. As a result a simultaneous presence of a blue- and red-shifted absorption can be observed.

Fig. 5 presents fluorescence spectra of the dyes under investigation. The spectra were recorded for various wavelengths of the excitation light and always the same shape of them was obtained. Fig. 5a shows the spectra of dyes **1** and **2** in LB films deposited at $\pi = 20$ mN/m and 12 mN/m, respectively, whereas in Fig. 5b the spectra of dye **3** in LB films deposited at $\pi = 3$, 6 and 10 mN/m are illustrated. It is seen that, similarly, as in the case of absorption, the fluorescence spectra of the dyes in the monolayer at the quartz surface are very different as compared with the spectra of diluted solution. Further, for dye **3** one observes again the strong dependence of the shape of the fluorescence band on the surface pressure at which the film was deposited, while in the case of dyes **1** and **2** the shape of the fluorescence band is almost the same for each pressure. For dye **2** a broad ($\delta = 2400$ cm^{-1}) structureless fluorescence band with the peak at $\lambda = 610$ nm is observed. As this band has no mirror band in the absorption spectrum, and its shape and position are similar to perylene excimer fluorescence band, observed by Ferguson [22] as well as for α-perylene crystal [21], it can be doubtlessly attributed to the excimer created in the LB film by two dye **2** molecules from which one is in the excited state. Likewise, as it was mentioned in introduction, the excimer emission for 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes in LB films was found [14–19]. However, for these dyes the genuine excimer emission (E-type emission) appeared distinctly not before the multilayers were formed and/or the deposition took place at high surface pressure (behind the collapse point). For the monolayer mainly the emission of excimer precursors (Y-type emission) was found, and only a small shoulder in the red side of the fluorescence band indicated the creation of some fraction of genuine excimers. In the fluorescence spectrum of dye **1** in the LB film, very broad ($\delta = 3300$ cm^{-1}) band with two separated maxima is observed, indicating the presence of at least two kinds of emitters. The long-wavelength peak can be assigned to the emission of the genuine excimer, whereas the short-wavelength one is probably connected with the emission of the excimer precursors. Other possibilities of the origin of the latter peak should be rather excluded. The short-wavelength peak cannot be related with the monomeric fluorescence because it is shifted with respect to the monomer band of about 40 nm. It may also not originate from the dimer emission, as the excitation spectra monitored at $\lambda = 575$ nm and 620 nm were identical and almost the same as the absorption spectrum.

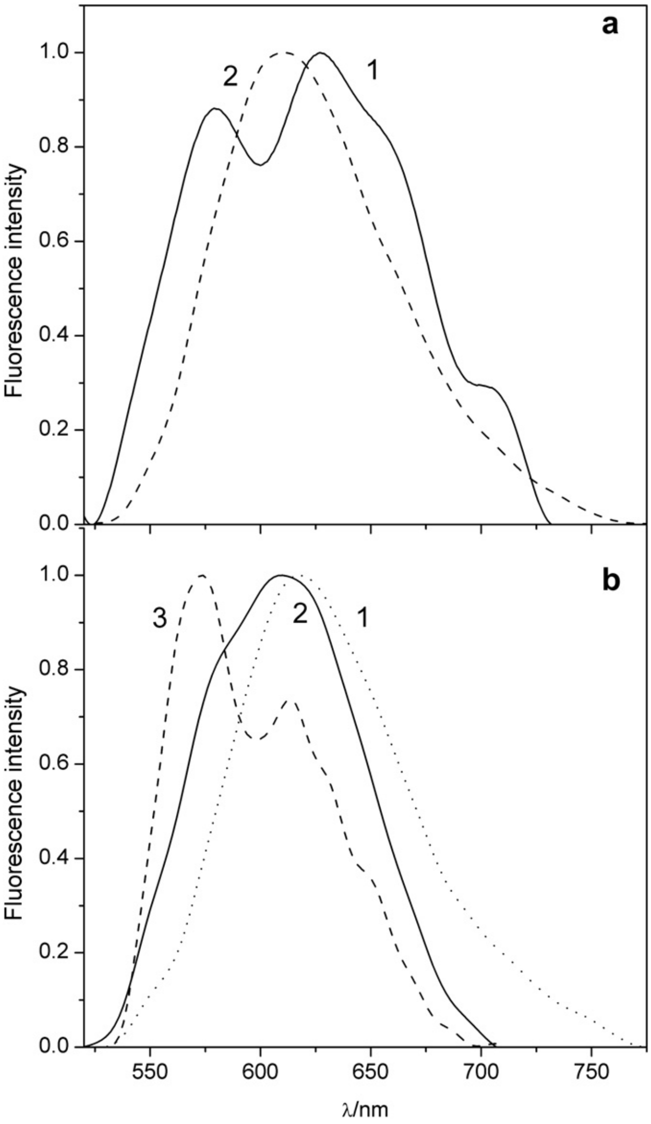


Fig. 5. Fluorescence spectra of perylene-like dyes in LB films: a) dye **1**, $\pi = 12$ mN/m (1) and dye **2**, $\pi = 20$ mN/m; b) dye **3**, $\pi = 3$ (1), 6 (2) and 10 (3) mN/m.

However, the existence of two kinds of excimers with different degree of aromatic ring overlapping in the LB film was found previously not only for 3,4,9,10-tetra-(*n*-alkoxy-carbonyl)-perylenes, but also for other perylene derivatives [9,11] and is characteristic for α-perylene crystal [21]. Thus, it can be observed in the fluorescence spectrum of dye **1** in the monolayer at the solid surface. The emission of the excimer precursors is probably seen also in the fluorescence spectrum of dye **3** in the LB film deposited at $\pi = 10$ mN/m. The presence of other types of emitters is rather impossible for the same reasons as in the case of dye **1**. However, looking at the fluorescence spectra of dye **3** in the monolayer transferred on the solid surface at various surface pressures (Fig. 5b) it should be assumed that at low π the genuine excimers are created. The excimer precursors, giving Y-type emission, become apparent only when the surface pressure rises. For $\pi = 10$ mN/m this type of emission is dominant, while emission of E-type is a residual. This is unlike to dye **1** fluorescence spectrum, which is independent of π and in which the emission of E-type predominates. It seems that reduction of the area available for dye **3** molecules in the Langmuir and next in the LB films hinders the creation of such configurations of molecules that emit genuine excimer emission. This effect can be due to the steric interaction of the long terminal chains and causes that the molecules in the excited dimer are only partially overlapped. As a result the fluorescence spectrum is dominated by Y-type emission.

4. Conclusions

Three novel perylene-like dyes were synthesized and investigated in the monolayers formed at air–water and air–solid substrate interfaces. The dyes differ in the length and molecular structure of chains substituted to the main perylene core. The substituents do not affect the monomer absorption spectrum, and their influence on the monomer fluorescence spectrum is very small. However, the aggregation properties of the dyes under investigation strongly depend on the molecular structure of the substituted chains. The replacement of the $-C_2H_5$ group by the $-OH$ group causes a small change in aggregation behavior of molecules in the ground state, but considerably affects the formation of aggregates in the excited state – is conducive to effective formation of genuine excimers. The long chains with the ester group occurring in dye **3** molecules are responsible for the different molecular organization in the monolayer on the water surface as compared with that of dyes **1** and **2**. As a result the kind of the aggregates created strongly depend on the surface pressure in the Langmuir film as well as in the LB film after the monolayer transfer. When the surface pressure increases, which means that the average area for one molecule decreases, more and more J-type aggregates in the ground electronic state appear. The emission of these aggregates is, however, not observed in the fluorescence spectrum. In the excited state mostly the excimer precursors, giving emission with higher energy compared to that of genuine excimers, are created.

Acknowledgments

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