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Research Article

AGGREGATION BEHAVIOR AND SPECTRAL PROPERTIES OF BODIPY LUMINOPHORS IN LANGMUIR-SCHAEFER AND POLY(METHYL METHACRYLATE) THIN FILMS

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ABSTRACT

It is known that boron-dipyrromethene (BODIPY) dyes have a remarkable combination of photophysical and photochemical properties in solutions. Unfortunately, these properties are lost in thin films due to aggregation quenching effect (ACQ) and internal filter effect, limiting BODIPY application in optical devices. The introduction of bulky substituents into dye molecule should affect the supramolecular organization of BODIPY in thin films. Therefore, using the example of β-benzyl-substituted complex (**1**) and bis(BODIPY) dimer (**2**), we study the influence of bulky substituents at the β, β′-positions of these BODIPY molecules on their aggregation behavior in mono- and multilayer Langmuir-Schaefer (LS) films. A comparative analysis of BODIPY spectral properties in LS and poly(methyl methacrylate) (PMMA) films has been carried out. It was shown that the presence of bulky benzyl-substituents in β-positions of pyrrole rings promotes the formation of H- and J-type aggregates in multilayer LS-films of the dye **1** and BODIPY dimer **2**. The dye **1** predominantly forms H-type aggregates, while for the dye **2**, the equilibrium is shifted towards the formation of J-type aggregates. The studied BODIPYs with a low content of up to 1 wt. % exhibit intense fluorescence being included in PMMA films. The results obtained give the possibility to use more efficiently thin-film structures based on the studied BODIPY thin films in optoelectronics.

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АГРЕГАЦИОННОЕ ПОВЕДЕНИЕ И СПЕКТРАЛЬНЫЕ СВОЙСТВА BODIPY ЛЮМИНОФОРОВ В ТОНКИХ ПЛЕНКАХ ЛЕНГМЮРА-ШЕФФЕРА И ПОЛИМЕТИЛМЕТАКРИЛАТА

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АННОТАЦИЯ

Как известно, бор(III) дипиррометеновые красители (BODIPY) обладают удачным сочетанием фотофизических и фотохимических свойств в растворах органических растворителей. К сожалению, эти свойства теряются в составе тонких пленок из-за интенсивной агрегации молекул (ACQ) и эффекта внутреннего фильтра, что ограничивает их применение в оптических устройствах. Введение объемных заместителей в структуру молекул красителей позволяет целенаправленно управлять надмолекулярной организацией BODIPY в тонких пленках. В связи с этим, на примере β-бензилзамещенного комплекса (**1**) и димера бис(BODIPY) (**2**), изучено влияние объемных заместителей в β, β′-позициях молекул BODIPY на их агрегационное поведение в моно- и мультислойных пленках Ленгмюра-Шеффера (ЛШ). Проведен сравнительный анализ спектральных свойств BODIPY красителей в пленках ЛШ и полиметилметакрилата (ПММА). Показано, что как введение объемных бензильных заместителей в β-позиции пиррольных колец соединения **1**, так и присоединение второго BODIPY домена в случае димера **2**, приводят к формированию агрегатов как H-, так и J-типа в мультислойных ЛШ пленках. Краситель **1** преимущественно образует агрегаты H-типа, тогда как для люминофора **2** равновесие смещено в сторону образования агрегатов J-типа. Изученные BODIPY демонстрируют интенсивную флуоресценцию в составе ПММА пленок с низким содержанием красителя до 1 мас. %. Полученные результаты позволят расширить возможности более эффективного использования тонких пленок BODIPY в оптоэлектронике.

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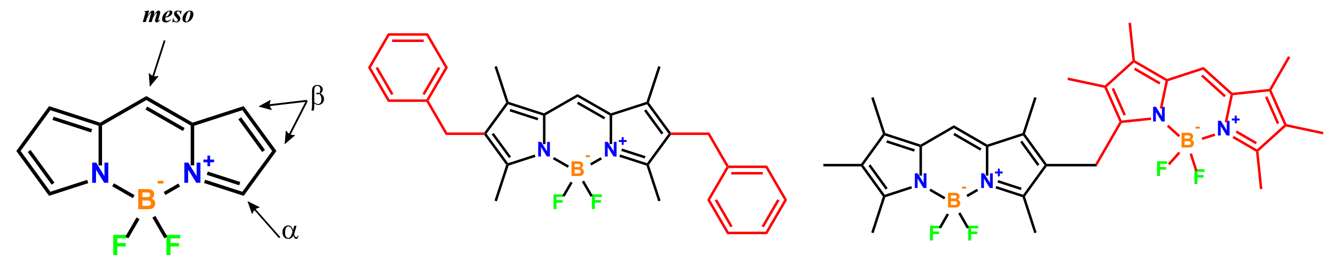
Introduction

Recently, research in the development of highly efficient materials for nanoelectronics and photovoltaic devices based on thin-film organic dyes has been actively investigated [1–5]. The main task is to improve methods for controlling the processes of organic dyes aggregation in solid state, which has a dramatic effect on their spectral properties [6]. An important fundamental assignment of great practical importance is to control the structure of such materials [7–9]. This makes it possible to create thin-film nanomaterials with optimal physico-chemical properties, which is necessary for creating modern efficient nanoelectronic devices. Among a wide variety of organic dyes (porphyrins, rhodamines, cyanine dyes), BODIPY luminophores have already become very promising luminescent components of new materials with a wide action spectrum due to their unique physical and chemical properties (intense absorption and fluorescence in the visible region of the spectrum, biocompatibility and non-toxicity, good photo- and thermal stability) [10–20]. The extended π-system of indacene core gives BODIPY molecules the ability of efficient π-stacking, intensive association and formation of large aggregates within solid monolayers and crystal structures [21]. Various methods have been proposed for controlling the processes of dye aggregation and imparting attractive optical properties to solid samples. The main group of methods is based on structural modification of BODIPY by the introduction of aggregation-controlling specific substituents. In most cases, bulky substituents [22–26] or extended alkyl groups [22, 26–31] are introduced into the *meso*-position of BODIPY compounds Fig. 1.



BODIPY

Benzyl-BODIPY (**1**)

Bis(BODIPY) (**2**)

Fig. 1. The structure formulas of BODIPYs

At the same time, a large number of dyes modified with rather simple aryl or alkyl substituents on the pyrrole rings of BODIPY molecules are known, which demonstrate excellent optical properties in organic solvents [13, 14, 19]. It seems relevant to study their aggregation behavior in condensed media and select optimal conditions to reduce aggregation processes in the design of dye thin films. Langmuir-Schaefer (LS) technology is considered as the best method for forming uniform film structures [32]. This technology makes it possible to obtain regular layers with controlled thickness and to create supramolecular structures with a given combination of various material properties under mild condition. There is a large number of works on the preparation of thin-film structures based on porphyrin or phthalocyanine complexes [33–43]. A small number of studies associated with the development of practically attractive monomolecular layers of BODIPY dyes obtained by LS technology has been published [22, 23, 27, 44, 45]. It is known that the ordinary hexamethyl-substituted BODIPY dye is characterized by undesirable intense aggregation with the formation of H-aggregates both in water-organic mixtures and in thin films. In our previous study, we showed that in the form of LS films and in the composition of PMMA films, the BODIPY dyes with simple *meso*-positioned phenyl substituent show intense background fluorescence [22]. The formation of J-type aggregates was found in multilayer LS films of such dyes. This makes them attractive for the development of optical devices. Previously, we have studied in organic solvents the properties of the BODIPY dye **1** with two bulky benzyl groups at the β, β′-positions of the pyrrole rings [19] and BODIPY dimer **2** (Fig. 1) [46–48]. It was shown that the dye **1** has a high (about 100 %) quantum yield of fluorescence in solvents of different nature.

The attachment of second BODIPY domain through the CH_2 spacer leads to a deviation of the molecule from planarity due to rotation of BODIPY domains relative to the CH_2 spacer. This prevents parallel alignment of molecules in layers and decreases the formation rate of H-type aggregates in solid state. In addition, it was previously shown that BODIPY **2** is characterized by exciton splitting of the intense band in electronic absorption spectra. In contrast to the medium-insensitive fluorescence characteristics of monomeric BODIPY **1**, the fluorescence quantum yield (Φf) of dimeric luminophor **2** in non-polar saturated (cyclohexane, heptane) and aromatic (benzene, toluene) organic solvents is almost 100 % and decreases by almost by one or two orders of magnitude in polar proton- or electron-donating solvents (alcohols, DMF, DMSO). Practical application prospects of bis(BODIPY) **2** are proposed for the analysis of polarity and proton-donor properties of the medium [46–48]. In this regard, the aim of this work was to develop and optimize conditions for obtaining thin films based on BODIPY dyes **1** and **2** having attractive spectral properties. Two types of thin films were obtained: *i*) mono- and multilayer Langmuir-Schaefer films, *ii*) PMMA films with different quantitative content of BODIPYs. Their morphology and spectral properties are analyzed.

Experiment

3,3′,5,5′-tetramethyl-4,4′-di-benzyl dipyrrolyl-methene-2,2 difluoroborate **1** and *bis(1,2,3,7,9-penta-methyl-2,2′-dipyrrolylmeten-8-yl)-(1,2,3,7,8-pentame-thyl-2,2′-dipyrrolylmeten-9-yl)methane bis(difluoro-borate)* **2** were synthesized according to the previously described methods [35, 46, 47]. The composition of the compounds was confirmed by FTIR, ^{1}H NMR, mass spectroscopy.

Most solvents employed for the measurements were of spectroscopic grade. The reagents for the synthesis of dyes were purchased from *Sigma-Aldrich* and used without any purifications. *Poly(methyl methacrylate)* (PMMA) ($M_n = 43800$ M, $M_w/M_n = 1.54$) was obtained by suspension polymerization.

The floating layers of BODIPYs were formed with the use of the NT-MDT Langmuir trough (*Zelenograd, Russia*) from chloroform solutions of **1** (C_l is $1.0{\cdot}10^{-4}$ M) and **2** (C_l is $1.86{\cdot}10^{-4}$ M). The chloroform solutions were spreaded onto the surface of bi-distilled water (20±1 °C) with a microliter syringe (*Hamilton, Sweden*) to form the air/water interfacial assemblies. The volume of the solutions to be applied was determined according to the required initial surface coverage degree, i.e. the ratio of the area occupied by the molecules to the total area of water surface available to the molecules. Two percentage values of the initial surface coverage degree were calculated for two extreme orientations of BODIPY molecules: the c_{face}, assuming that planes of all molecules are parallel to water surface (“face-on” orientation), and the c_{edge}, assuming that the molecular planes are orthogonal to water surface (“edge-on” orientation). Herein, these two values are provided using a slash (in the form c_{face}/c_{edge}) when specifying surface coverage degree at large c_{face} values. The floating layers of BODIPYs **1** and **2** were created at c_{face}/c_{edge} values 35/28 % and 34/19 %, correspondingly. The initial degree of surface coating (*c*) was calculated in accordance with the technique described in [48]. After allowing the solvent to evaporate for 20 min, the floating layer formed on the water surface was compressed at a rate of $v = 55$ cm^2/min. The surface pressure was measured by a Wilhelmy sensor with an accuracy of 0.02 mN/m.

The floating layers of BODIPYs were transferred onto quartz or silicon substrates by the horizontal lifting method at 20±1 °C and surface pressure $\pi = 0.2$–0.3 mN/m. The transfer of a monolayer was carried out in the densest packing in a “face-on” arrangement of molecules for each compound. The number *n* of transfers from 1 to 50 was chosen to accumulate an optical density optimal for spectral studies, while *n* was equal 1 and 5 to investigate surface morphology of films by atomic force microscopy. The states of floating layers transferred onto a quartz substrates were estimated by the value of the area per molecule in the layer (A). PMMA films with coating thickness of 25 μm were prepared from 2.5 mL toluene solution of PMMA (10 mg) and BODIPYs by using a drop-casting method. The spectral properties were shown to be homogeneous over each individual film.

The absorption spectra were measured for at least four positions on each film and show a variation of only within 0.03 for the absorption optical density and 1 nm for the spectra maximum. The absorption and fluorescence spectra of BODIPYs in solution and PMMA films were measured on SM 2203 spectrometer (SOLAR) at resolution of 1.0 nm. The electron absorption spectra of BODIPY LS-films were measured with a Cary 100 (*Varian-Agilent, US-Australia*) spectrophotometer.

The fluorescence microscopy of films was performed with Micromed 3 LYUM microscope (*Russia*) under the x40 magnification in mode B filter (the excitation wavelength λ_{ex} = 410–490 nm).

The surface morphology of thin film samples was studied by atomic force microscopy in semi-contact mode using the Solver 47 Pro microscope (*NT-MDT, Russia*). The semi-contact mode was used, since it has a higher resolution in the study of organic materials and does not damage the test surface during scanning.

Results and discussion

Spectral characteristics of BODIPY LS films

In our previous works [35], it was found that benzyl-BODIPY **1** intensively absorbs (lgε = 4.84÷4.96, λ_{abs} = 526÷533 nm) and fluoresces (λ_{fl} = 538÷547 nm) in solutions of organic solvents in the visible region of the spectrum. The fluorescence quantum yield weakly depends on solvent nature and varies from 0.82 to 0.91 in non-polar and polar media. This makes BODIPY **1** a promising dye for the production of thin-film optical materials.

In contrast to monomeric BODIPY **1**, the sensitivity of dimeric complexes to the polarity of medium can be determined by the features of their electronic structure. The absorption spectra of dimer **2** show the splitting of more intensive band (S_0-S_1) into two: one blue shifted low-intense band and the other red shifted high-intense band (Fig. 2). In comparison with monomeric dye **1**, dimer **2** is characterized by higher value of extinction coefficient (lgε = 5.06÷5.18), its most intense absorption band S_0-S_1 (λ_{abs} = 546÷553 nm) as well as the emission band (λ_{fl} = 551÷5.18 569 nm) are red shifted [46, 47].

LS films of BODIPYs **1** and **2** with the number of layers *n* from 1 to 50 were obtained and their spectral properties were analyzed. In contrast to the previously studied hexamethyl and *meso*-phenyl-substituted BODIPY dyes [22], which form only H- or J-aggregates respectively, a different aggregation behavior was found for compounds **1** and **2** in LS films.

The absorption spectra of benzyl-BODIPY **1** have a significantly broadened profile (Fig. 2, *a*). With an increase in the number of layers, the absorption maximum shifts to the blue region of the spectrum up to 26 nm, relatively to the initial monomer solution. This indicates the predominant formation of H-type aggregates. Decomposition of the long-wavelength broadened absorption band of the dye film with *n* = 50 into Gaussian components gives a three-band spectrum (Fig. 2, *b*) with λ_{abs} = 526, 488 and 579 nm, corresponding to the monomeric, H- and J-aggregated dye forms. An increase in the background signal indicates the formation of solid particles, which strongly scatter light.

Dimeric dye **2** is also characterized by the formation of a mixture of H- and J-aggregates. At the same time, based on the absorption spectra (Fig. 2, *c*), the equilibrium is shifted towards the formation of J-type aggregates. For bis(BODIPY) **2**, a broadening and splitting of the absorption band of the LS films is observed: a band with a maximum at 564 nm is clearly recorded, apparently corresponding to J-type aggregates. A shoulder is observed on the left slope of the intense band. Decomposition of the long-wavelength broadened absorption band of the dye film with *n* = 50 into Gaussian components gives a three-band spectrum (Fig. 2, *d*) with λ_{abs} = 540, 564 and 524 nm, corresponding to the monomeric, J- and H-aggregated dye forms.

The fluorescence spectra of LS films of BODIPYs **1** and **2** couldn't be recorded.

Probably, the reason of it in the case of BODIPY **1** was a strong light scattering due to the presence of crystalline structures and weak fluorescence. The results of fluorescence microscopy of LS film with *n*=50 confirm the heterogeneous surface with a large accumulation of globular aggregates on the substrate surfaces (Fig. 3). The most uniform surface and intense green fluorescence were observed for the film with *n*=10. An increase in the number of transfers from 1 to 50 leads to an increase in the size of crystal structures in LS films.

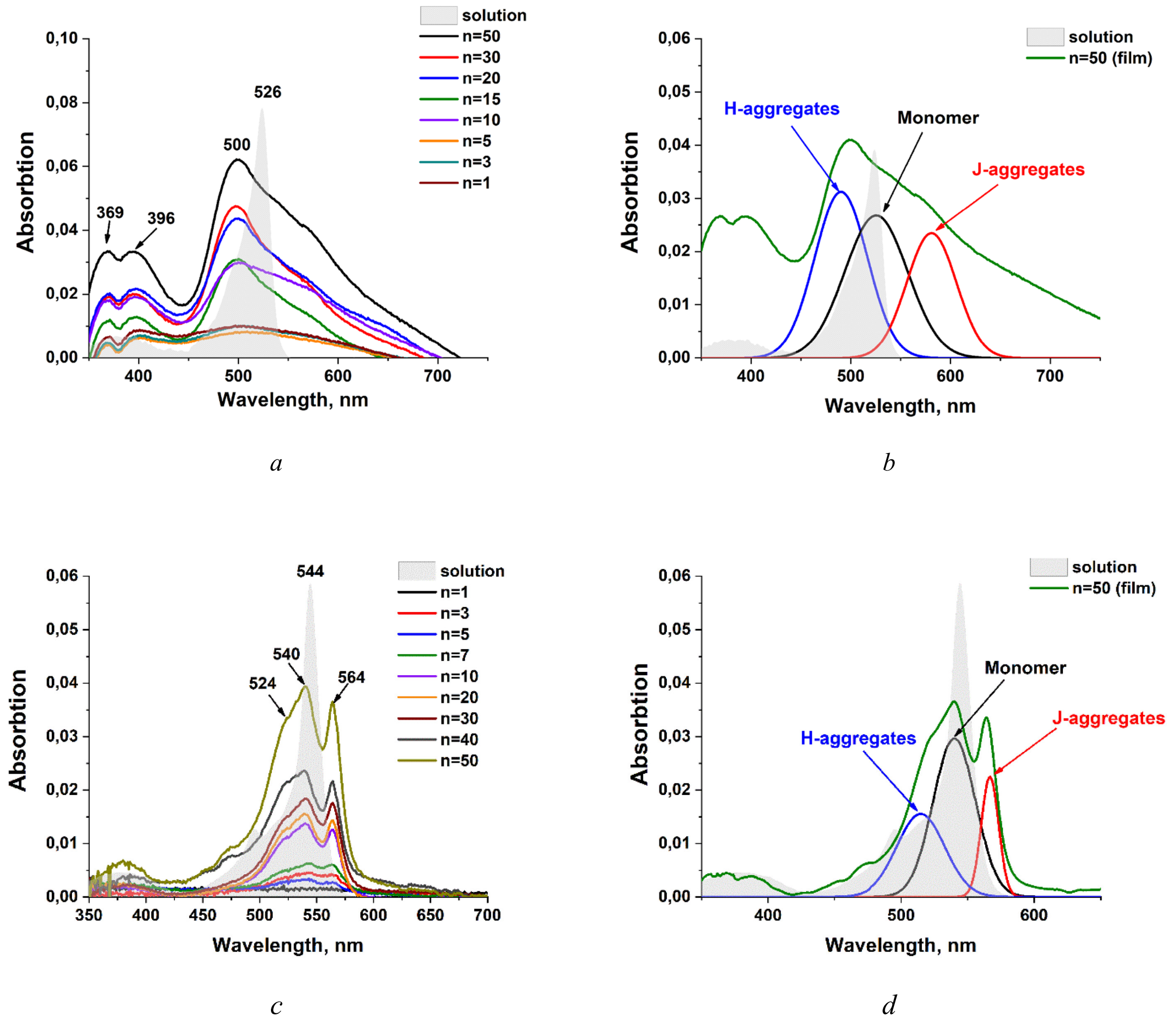
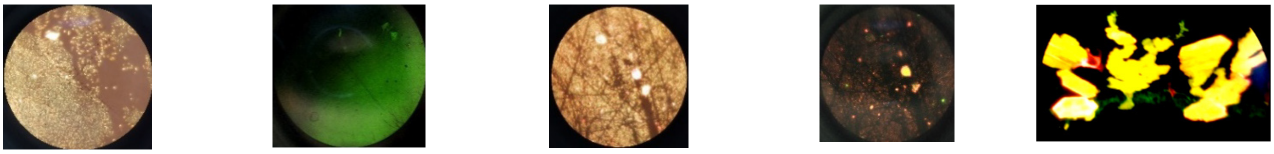


Fig. 2. The absorption spectra of **1** (*a*) and **2** (*c*) in solution (CHCl$_3$) and LS films; absorption spectra of **1** (*b*) and **2** (*d*) LS film fitted with Gaussian functions, $n = 50$



$n = 10$, daylight LS film of **1**

$n = 10$, UV light LS film of **1**

$n = 50$, daylight LS film of **1**

$n = 50$, UV light LS film of **1**

UV light drop-cast film of **2**

Fig. 3. The microscope images of LS-films of BODIPY **1** (*n* is the number of transfers) and drop-cast film of bis(BODIPY) **2**

In the case of bis(BODIPY) **2**, the fluorescence quenching apparently caused not only by aggregation processes, but also by penetration of water molecules from subphase into film structure. In our previous studies [47, 48], it was shown that bis(BODIPY) **2** have a high fluorescence sensitivity to the polarity of medium. In media with high polarity, proton and electron donor abilities (ethanol, DMF, DMSO), almost complete quenching of fluorescence intensity occurs. Apparently, this is the main reason for the absence of fluorescence in LS films of **2**, since the fluorescent photographs of drop-cast films obtained from a chloroform solution clearly show brightly fluorescent large particles of this dye (Fig. 3).

Analysis of the surface relief of a monolayer LS film of **1** showed that the film is formed rather uniformly and its thickness is 1.0 nm. However, film contains conical 3D aggregates. The sizes of these aggregates reach 65 nm in diameter and up to 1.2 nm height (Fig. 4). An increase in the number of transfers to *n* = 5 leads to a thickening of film to 7.0 nm and partial accretion of conical structures with the formation of three-dimensional agglomerates (Fig. 4). The size of the aggregates reaches 170 nm with a height of about 4.96 nm.

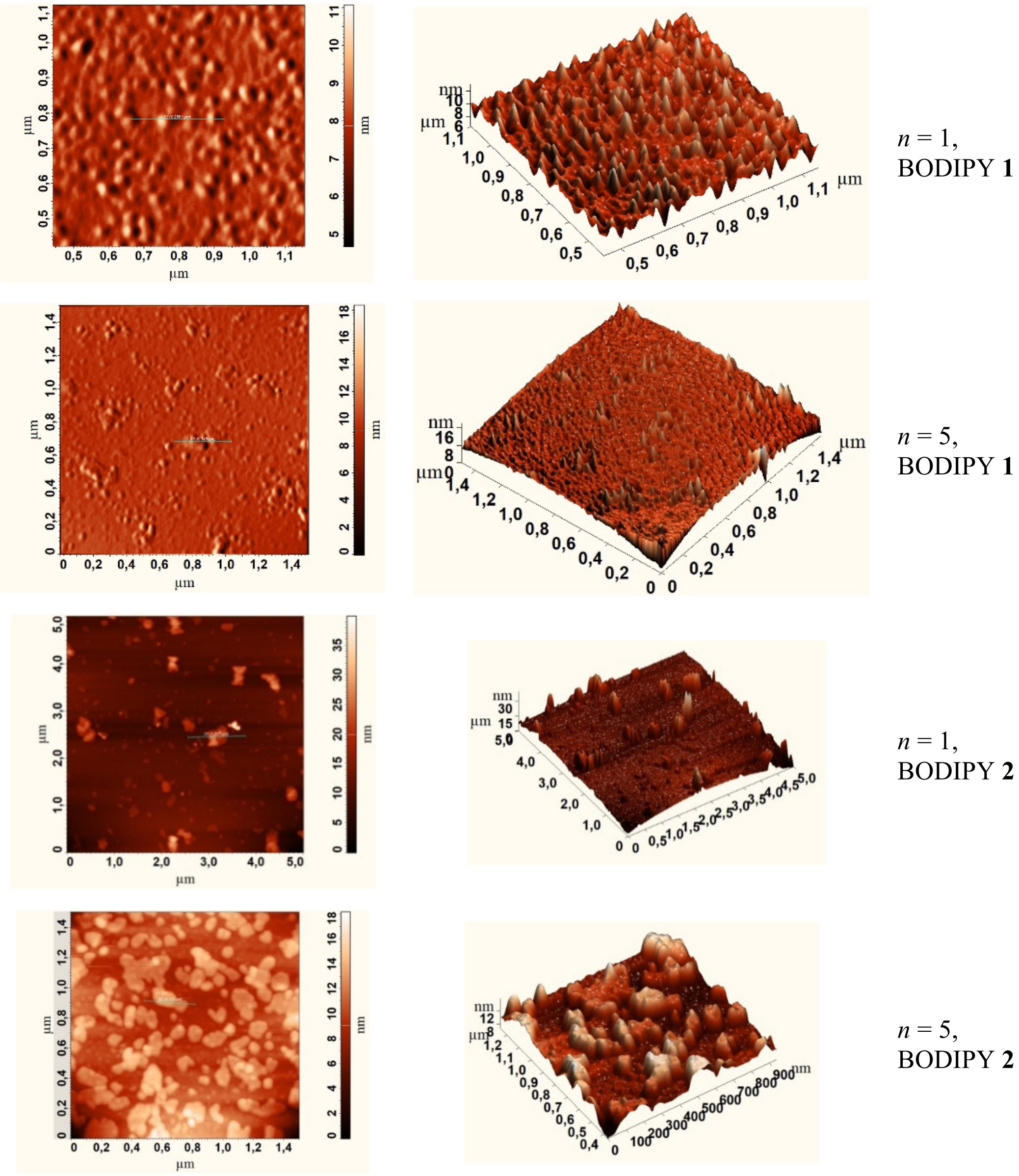


Fig. 4. The AFM images of BODIPY LS films on silica substrates with the number of transfers *n* = 1 and *n* = 5

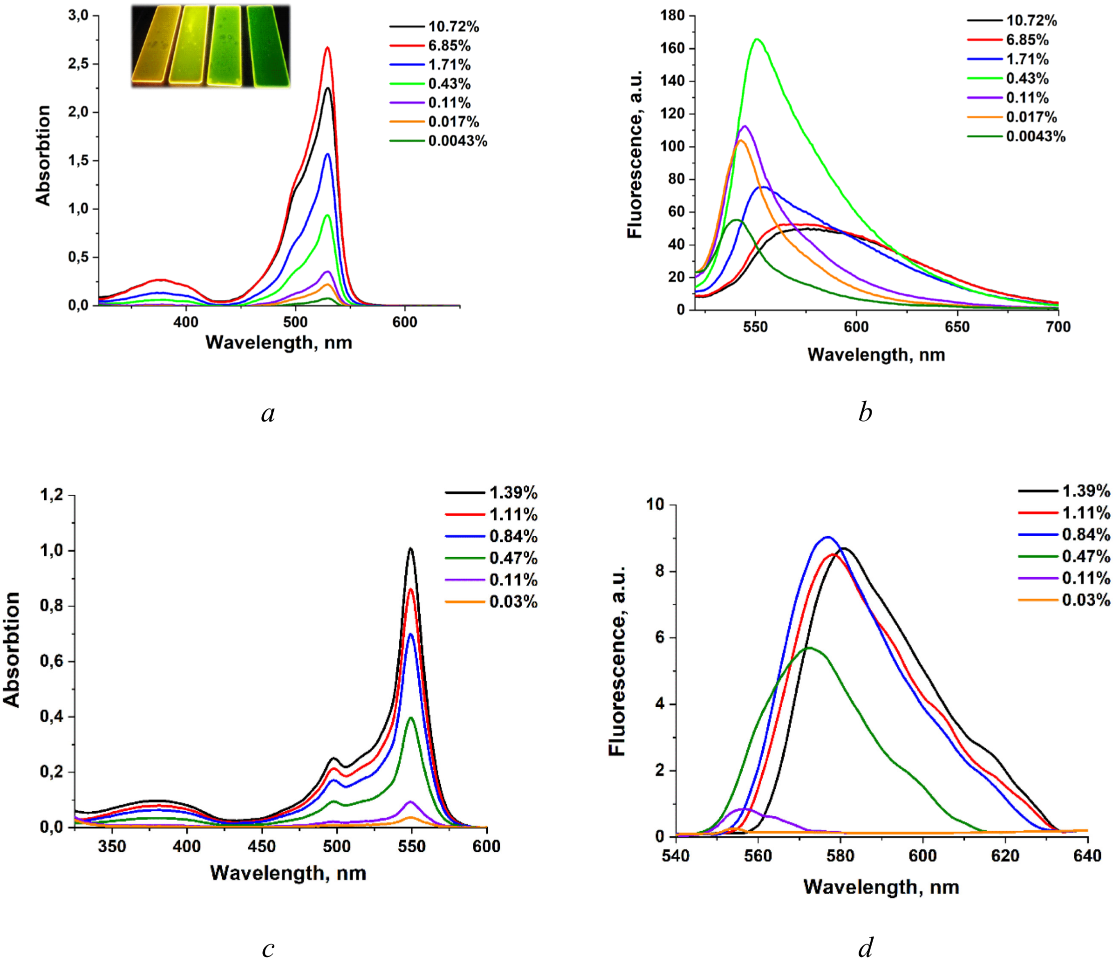
The AFM results of the monolayer 8 nm thick LS film of **2** showed that there are some cone-shaped particles with an average size of 490 nm and a height of up to 11 nm on its surface (Fig. 5). An increase in transfers to 5 leads to an increase in the number of particles on the film surface and their merge into larger 3D agglomerates up to 250 nm in size and up to 15 nm in height, with an average film thickness of 10 nm.

The data obtained prove the tendency of the studied BODIPY compounds to strong aggregation in the condensed phase.

Spectral properties and aggregation behavior of BODIPYs in PMMA films

Impregnation of dyes into neutral amorphous polymer, such as PMMA, is a good way to limit the aggregation of luminophore and introduce additional functional properties of the obtained materials for specific practical applications. PMMA films with different contents of dyes (from 0.04 to 11 wt. % for compound **1** and from 0.03 to 1.4 wt. % for compound **2**) were obtained.

For **2**, it was not possible to obtain a higher dye content in the film due to its low solubility in the initial toluene solution. In all cases, the films showed intense fluorescence (Fig. 5). The position of band maxima and the type of absorption spectrum remained unchanged in all range of the dye content in the polymer film (Fig. 5, *a*). This indicates the absence of noticeable dye aggregation in the film composition. However, when the dye content is above 1 wt. %, a decrease in the fluorescence intensity is observed (Fig. 5), which also leads to a red shift of the emission band maximum from 540 to 580 nm due to the effect of internal filter.



a *b*

c *d*

Fig. 5. The UV-Vis absorption and emission spectra of BODIPY **1** (*a, b*) and BODIPY **2** (*c, d*) in PMMA films with different wt. % of dyes. Inserts: intensity of benzyl-BODIPY emission of dyes vs. wt. %

Conclusion

The spectral properties of mono- and multilayer Langmuir-Schaefer films and PMMA films of benzyl-BODIPY **1** and bis(BODIPY) **2** dyes have been studied. In multilayer LS films, in addition to the monomeric form, there are both H- and J-type aggregates. Moreover, due to the intense π-π stacking of benzyl-BODIPY molecules, the equilibrium is shifted towards H-aggregates, which leads to significant fluorescence quenching and the formation of large agglomerates on the surface of LS films. For bis(BODIPY), the formation of a mixture of aggregates of various types was also found, but the formation of predominantly J-type aggregates occurs. It is necessary to introduce surfactants or other agents into the composition of the film that prevent the aggregation of dye molecules and allow to obtain more uniform surface. The introduction of dyes into PMMA films avoids aggregation processes and preserves the characteristics of absorption and fluorescence spectra. The optimal range of dyes content (from 0.8 to 1 wt. %) in PMMA films was estimated, which allows avoiding the fluorescence quenching due to the effect of internal filter.

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