

Optical Properties and Supramolecular Organization of Mix-Substituted Phthalocyanine Holmium Complex in Langmuir-Schaefer Films

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The structural and functional properties of new mix-substituted phthalocyanine holmium complex thin films (1,4,8,11,15,18-hexaoctyloxy-23,24-dichlorophthalocyaninate hydroxyholmium) (A₃B-Ho type) obtained under different initial conditions, were studied by optical methods and atomic force microscopy. The surface morphology of thin film samples was determined by atomic force microscopy using the tapping mode. Analysis of the internal structure homogeneity of the films via the spatial distribution of the fluorescent signal was fulfilled by confocal microscopy. We have studied the conditions of the floating layers formation and transferring them onto a solid substrate by Langmuir-Schaefer technique. The optical properties of the films were studied by spectrophotometry and spectrofluorometry. Selection of conditions of floating layers formation and their transfer onto the solid substrate under the constant control of the supramolecular organization in the films has allowed us to solve the problem of displaying the fluorescent properties in the films of the holmium complex with mix-substituted phthalocyanine (A₃B-Ho type), in contrast to previously investigated phthalocyanine derivatives of A₃B, ABAB or AABBB types, which have not indicated the fluorescence in films.

Keywords: Mix-substituted phthalocyanine derivatives, metal complexes, Langmuir-Schaefer films, optical properties, fluorescence, atomic force microscopy.

Оптические свойства и надмолекулярная организация гольмиевого комплекса смешанно-замещенного фталоцианина в пленках Ленгмюра-Шеффера

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В работе изучены структурные и функциональные свойства тонких пленок нового фоточувствительного соединения – гольмиевого комплекса смешанно-замещенного фталоцианина (1,4,8,11,15,18-гексаоктилокси-

23,24-дихлор-фталоцианината гидроксигольмия) типа A_3B-Ho с применением оптических методов и атомно-силовой микроскопии. С помощью атомно-силовой микроскопии полуконтактным методом определен рельеф поверхности пленок. Анализ однородности внутренней структуры пленок по пространственному распределению флуоресцентного сигнала выполнен методом конфокальной микроскопии. Исследовано влияние условий формирования плавающих слоев и их переноса методом Ленгмюра-Шеффера на надмолекулярную организацию данного соединения в пленках. Оптические свойства пленок изучены методами спектрофотометрии и спектрофлуориметрии. Подбор условий формирования плавающих слоев и условий переноса на твердую подложку позволил решить задачу проявления флуоресцентных свойств в пленках гольмиевого комплекса смешанно-замещенного производного фталоцианина типа A_3B-Ho , в отличие от ранее исследованных нами производных фталоцианина типов A_3B , $ABAB$ и $AABB$, которые в виде пленок не проявляли флуоресценцию.

Ключевые слова: Смешанно-замещенные производные фталоцианина, металлокомплексы, пленки Ленгмюра-Шеффера, оптические свойства, флуоресценция, атомно-силовая микроскопия.

Introduction

Thin-film technologies using organic dyes are one of the most promising for creation of photovoltaic and sensor devices.^[1,2] Discotic mesogens are currently considered a new generation of organic semiconductors with unique properties that are destined to replace conjugated polymers commonly used for these purposes.^[3]

In our work aimed at the creation of materials for photovoltaic and sensor devices, we set a task to replace the compositions where each component is individually responsible for glass formation, absorption of light, electron transport and one-dimensional conductivity necessary for the operation of these devices^[4,5] by a material combining all these properties. Based on the fact that, while having a certain structure, discotic mesogens – phthalocyanine derivatives (Pc) and their metal complexes can fulfill all the above mentioned requirements, we have synthesized Pc glass-forming symmetrically substituted derivatives in peripheral positions that have maximum absorption in the visible region and satisfactory current-voltage characteristics.^[6] Scientific literature analysis has made it possible to state that the substitution of Pc by alkoxy-groups at non-peripheral positions helps to shift the maximum of absorption bands into the far visible light region, which is most favorable for practical use in photovoltaic devices. However, the described compounds were non-mesomorphic.^[7] Based on the data obtained from scientific literature and our own results, we have constructed mix-substituted Pc derivatives and their metal complexes that have donor and acceptor groups in a molecule of the A_3B , $AABB$ and $ABAB$ types, where **A** – the Pc fragments with alkoxy substituents possessing donor properties, and **B** – the fragments containing Cl substituents as electron acceptors (4 Cl and 2 Cl).^[8]

As a result, both ligands and metal complexes of these mix-substituted phthalocyanines have obtained all the necessary physical and physico-chemical characteristics:^[8]

- they form columnar mesophases;
- they undergo glass transition from mesophase on cooling;
- their absorption maximum is located at the visible part of the spectrum of about 600–750 nm;
- one and the same molecule contains both donor and acceptor substituents, which should increase electrical conductivity and eliminate the question of the system's

heterogeneity and temperature differences at the phase transitions that lead to bad losses during light scattering at the domains boundaries represented by crystals of various system components;

- in solutions they show fluorescent properties.

However, these compounds showed no fluorescence in Langmuir-Blodgett films.^[8]

Experimental

In order to achieve the manifestation of the fluorescent properties by the mix-substituted phthalocyanine thin films, Langmuir-Schaefer (LS) films of 1,4,8,11,15,18-hexaalkoxy-23,24-dichlorophthalocyaninate of hydroxyholmium of the A_3B-Ho type were prepared (Figure 1). The dependence of the optical properties of the obtained films on their structure was studied. The synthesis of this compound was carried out according to the previously described method.^[9]

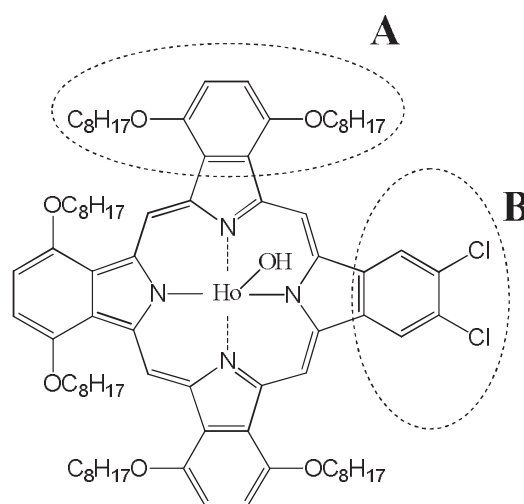


Figure 1. Mix-substituted phthalocyanine holmium complex: 1,4,8,11,15,18-hexaalkoxy-23,24-dichlorophthalocyaninate of hydroxyholmium.

The molecular model construction of the studied compound and the calculation of its geometrical characteristics were made by the method described previously.^[10] These data were used to determine the packing type of the molecules in the films.

Langmuir layers were formed from a chloroform solution of the studied compound on Langmuir-Blodgett Deposition Troughs NT-MDT (Russia) and the KSV 5000 (Finland). The Water purification systems were Millipore Elix 3 and Millipore Simplicity 185. The resistivity of water was $\rho = 18 \text{ M}\Omega \cdot \text{cm}$. The thin films were prepared by layers transfer from the water surface onto the quartz or oriented glass substrates at room temperature (293–295 K) and surface pressure $\pi = 0\text{--}0.4 \text{ mN/m}$ (Table 1).

The layers transfer from the water surface was made by Langmuir-Schaefer technique (horizontal lift) for $n = 1\text{--}4$ layers. The orientation of the glass substrates was made by rubbing with an abrasive material.

The surface morphology of the thin films was studied with the help of the atomic force microscope (AFM) Solver 47 Pro. The tapping mode was applied as it has a higher resolution capacity in investigation of organic materials and does not damage the studied surface by the probe during scanning. One of the most important factors determining the resolution of this method is the presence of static charge on the surface of a sample. For this reason the oriented glass substrates with a conductive ITO-coating, which allows to perform scanning with zero potential difference between the surface and the probe, have been used.

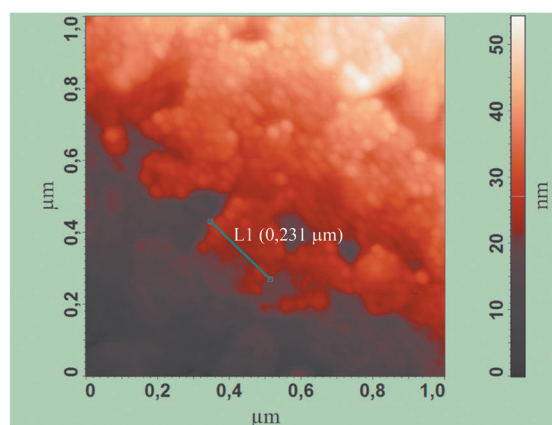


Figure 2. AFM image of the film of the compound $A_3B\text{-Ho}$ (Sample No 1, Table 1) on the glass substrate with the ITO-coating (compression speed of barriers – $90 \text{ cm}^2/\text{min}$, area per one molecule – 0.97 nm^2).

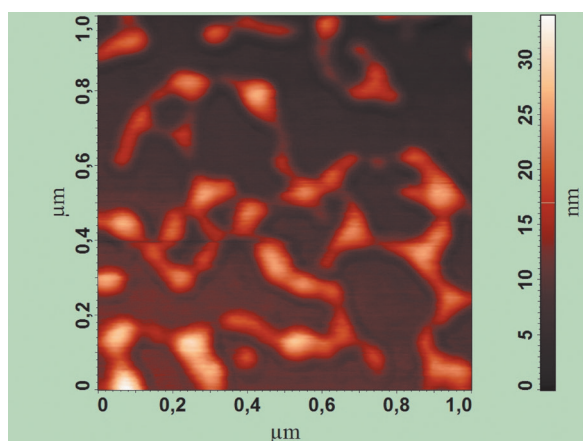
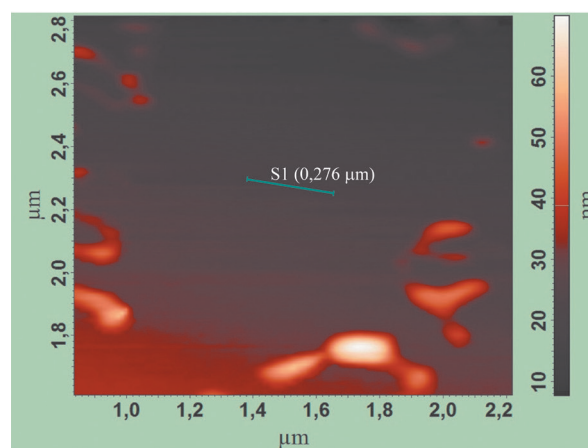


Figure 3. AFM image of the film of the compound $A_3B\text{-Ho}$ (Sample No 4) transferred onto the glass substrate with ITO-coating.

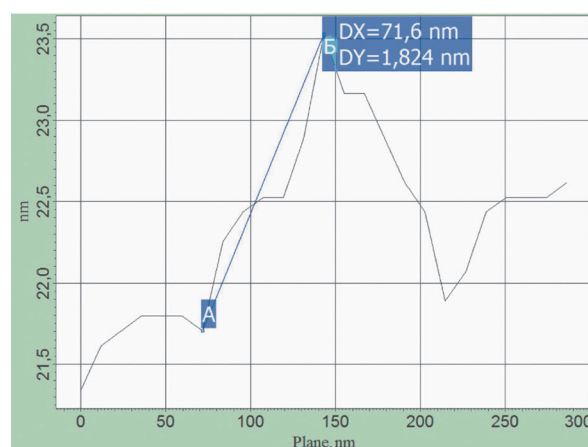
Recording of the absorption spectra of the films was carried out on Cary 5000 (Varian) spectrophotometer at the wavelength range of 200–1000 nm, with the spectral band width (SBW) of 2 nm. The fluorescence spectra of the films were recorded on Cary Eclipse (Varian) spectrofluorimeter at the wavelength range of 220–850 nm with the SBW of 5 nm. The analysis of the film morphology with regard to the lateral distribution of fluorescence was made on the confocal microscope Leica TCS SPE, with the fluorescence excitation wavelength at 405 nm.

Results and Discussion

Aiming to obtain fluorescent films, we have varied the compression speed and the area per one molecule, thereby achieving different structures of floating layers. In order to control the supramolecular organization in LS-films and compare the structure of the floating layers with that of the transferred films, the surface relief of the thin film samples obtained under different initial conditions (Table 1) was investigated.



a



b

Figure 4. a) AFM image of the film of $A_3B\text{-Ho}$ compound (Sample No 5) deposited on the glass substrate with the ITO-coating; b) linear measuring of the film thickness of Sample No 5 deposited on the glass substrate with the ITO-coating (on the area marked by the segment in Figure 4a).

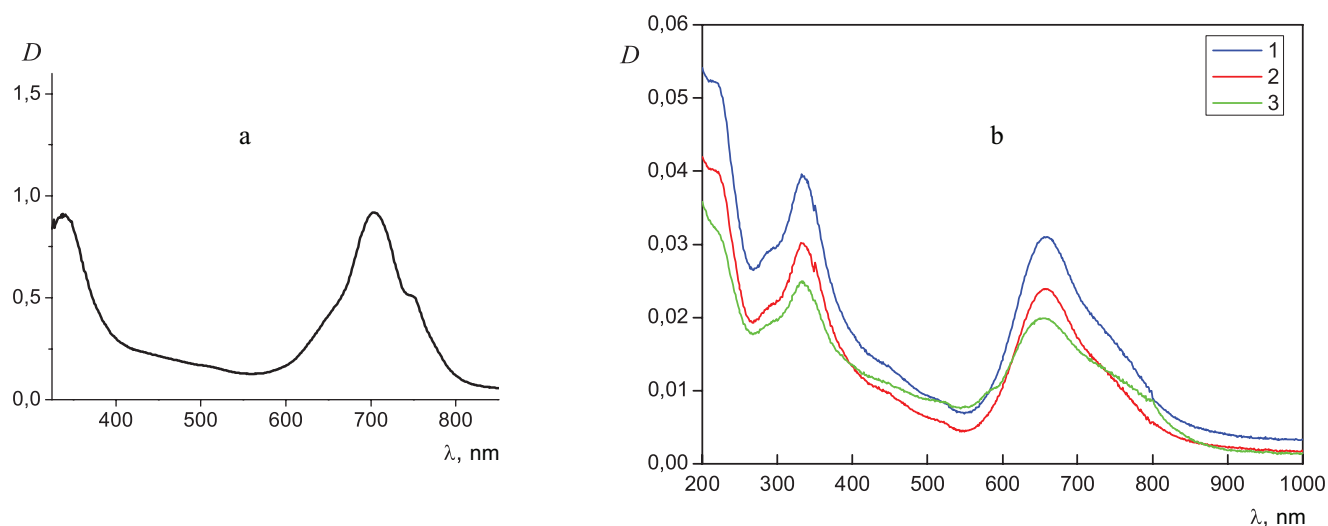


Figure 5. a) The electronic absorption spectrum of A_3B-Ho compound in chloroform;^[9] b) the absorption spectra of the transferred layers of the A_3B-Ho compound on the substrate (Samples No 1–3, Table 1).

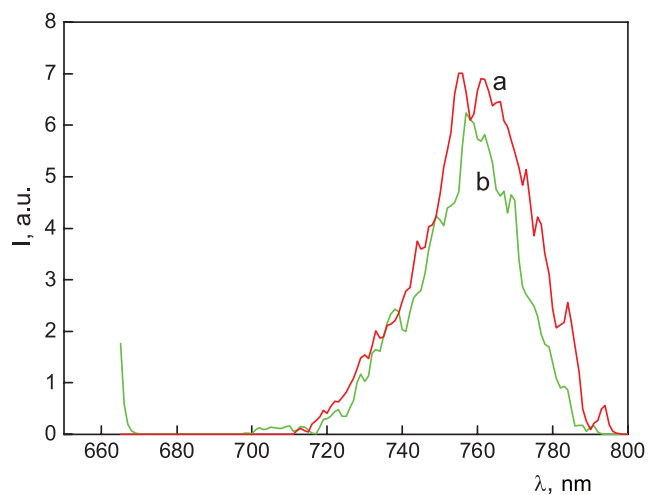


Figure 6. The fluorescence spectra of chloroform solution of the compound A_3B-Ho at different excitation wavelengths: a) 340 nm, b) 660 nm.^[9]

When the floating layers were transferred by Langmuir-Schaefer method onto the oriented glass substrate with ITO-coating at the maximum of the investigated compression speed of barriers and the minimum area per one molecule (Sample No 1, Table 1), the obtained film was not uniform (the thickness was about 20–40 nm with the formation of 3D aggregates (Figure 2)).

According to our previous study,^[11] these high speeds can lead to the layer fracture and formation of polylayer structures in the floating layers. Thus, we can say that the floating layers of the investigated phthalocyanine derivative are transferred onto the solid substrate preserving their structure (the transfer was carried out from the bilayer containing polylayer formations, the model thickness of Sample No 1 in the bilayer region was about 20 nm, 4 transfers).

In order to obtain homogeneous films with fluorescent properties, we have reduced the compression speed of the barriers to 45–30 cm²/min and increased the area per one

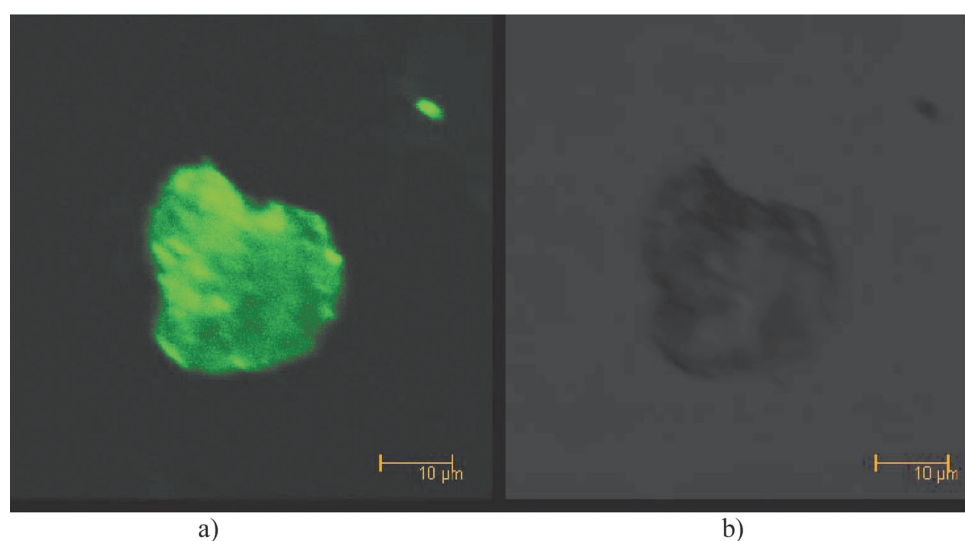


Figure 7. The confocal microscopy image of the film morphology for Sample No 3 of the compound A_3B-Ho : a) fluorescence mode, b) transmission mode.

Table 1. Parameters of transfer of the A_3B-Ho complex layers on the quartz substrates by Langmuir-Schaefer method. Langmuir-Blodgett troughs: KSV 5000, $S=750\text{ cm}^2$ and NT-MDT, $S=293\text{ cm}^2$.

No sample	C , mg/ml	M , g/mol	V , μl	π , mN/m	ν , cm^2/min	Area per molecule, nm^2	Sub-phase	Substrate	Number of transfers	Type of layer structure
1				0.4	90	0.97		Quartz glass (for spectrophotometry	4	Bilayer
2			200	0.4	45	0.97		and confocal microscopy),	4	Bilayer
3	0.19	1514		0.2	45	2.4	water	glass with ITO coating	4	Monolayer
4			150	0	30	5.9		(for AFM)	3	Monolayer
5			150	0	15	5.9			1	Monolayer

molecule to 2.4 and 5.9 nm^2 under the transfer conditions. The films were transferred from monolayers (e.g. Sample No 4, Table 1). However, the formation of polylayer structures was clearly visible under these conditions (Figure 3), although in general the films are fairly uniform.

By reducing the compression rate to 15 cm^2/min we have succeeded in obtaining a substantially uniform monolayer film (Figure 4). Based on the simulation data of the supramolecular organization of the mix-substituted phthalocyanine holmium complex in the thin films,^[11] and synchrotron study,^[12] we can claim that the molecules form a rarefied layer on the water surface under the conditions of Sample No 5 preparation.

These results are confirmed by the relief study of the LS-film of Sample No 5 (Figure 4a,b). The thickness of the transferred film (Figure 4b) is equal to 1.82 nm, which corresponds to the monolayer packing with the location of the molecules macrocycle plane parallel to the substrate. Moreover, considering that the film thickness corresponds to the macrocycle thickness we can assume that the lateral substituents are located in the plane of the molecule.

In order to determine the effect of the film formation conditions and the supramolecular organization on the optical properties of the prepared films, the absorption and fluorescence spectra of various samples of LS-films of the A_3B-Ho compound were obtained (Figure 5).

The study of the optical properties of LS-films of the mix-substituted phthalocyanine derivative has showed (Figure 5b) that the film samples are characterized by a hypsochromic shift of the Q band maximum in comparison with the spectrum in chloroform solution. Such changes can be explained by the amplification of the associative processes in the plane-plane type film.

The previously studied LS-films of the holmium complexes of mix-substituted phthalocyanine derivatives ($\text{Pc-Ho}-(\text{OC}_8\text{H}_{17})_2-\text{Cl}_4$) prepared from the bilayer with 30–50 transfers did not exhibit fluorescent properties, although the chloroform solutions of these compounds possessed such properties.^[8] Hence, we set a task to achieve the appearance of fluorescence in the films by adjusting the conditions of the floating layers formation and transfer onto the solid substrate. It is proved that the holmium complex of the mix-substituted phthalocyanine A_3B-Ho exhibits fluorescent properties in LS-films if the transfer is performed from a monolayer strictly. The optimal conditions for the layer formation are the following: the preload barriers speed is 15–45 cm^2/min ,

and the surface pressure is 0–0.2 mN/m. A weak band of the film fluorescence was observed in the range of 700–800 nm. The film emission maximum wavelength of $\sim 750\text{ nm}$ is close to the corresponding one of the compound A_3B-Ho in chloroform solution (Figure 6).

To visualize the fluorescent properties the confocal microscopy method was additionally used (the excitation wavelength was 405 nm) (Figure 7). The mosaic appearance of the fluorescent areas under the microscopy conditions is associated with a narrow range of the excitation wavelength. However, this method confirms the presence of the fluorescent properties in the studied samples.

Conclusions

The supramolecular organization in Langmuir-Schaefer films of the new holmium complex of the mix-substituted phthalocyanine containing donor and acceptor substituents in the structure of a single molecule was determined. The influence of the conditions of the floating layers formation and transfer on the supramolecular organization in LS-films was determined. It is shown that an uniform monomolecular film is formed when the compression speed of the barriers equals 15 cm^2/min , the area per one molecule is 5.9 nm^2 and the transfer number is 1. It means that, when transferred onto the solid substrate, the films of the compound A_3B-Ho preserve the floating layers structure. The spectra of the film samples of the A_3B-Ho compound are characterized by a hypsochromic shift of the Q band maximum in comparison with the spectrum of the chloroform solution. Such changes can be explained by the amplification of the associative processes in the plane-plane type film. For the first time, the fluorescent films of the holmium complex of mix-substituted phthalocyanine were obtained (under the partial compression and $n=1-4$) by means of selecting the conditions of the floating layers formation and their transfer onto the solid substrate (under the constant control of the transferred monolayer structure).

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References

1. Wöhrle D., Schnurpfeil G., Makarov S.G., Kazarin A., Suvorova O.N. *Macroheterocycles* **2012**, *5*, 191–202.
2. Pochekailov S., Nozar J., Nespurek S., Rakusan J., Karasikova M. *Sensors Actuators B* **2012**, *169*, 1–9.
3. Cupere V. De., Tant J., Viville P., Lazzaroni R., Osikowicz W., Salaner W., Geerts Y.H. *Langmuir* **2006**, *22*, 7798–7806.
4. Sergeev S., Pouzet E., Debever O., Levin J., Gierschner J., Cornil J., Fspre R.G., Gteerts Y.H. *J. Mater. Chem.* **2007**, *17*, 1777–1784.
5. De la Torre G., Bottary G., Hahn U., Torres T. *Struct. Bond.* **2010**, *135*, 1–44.
6. Usol'tseva N.V., Bykova V.V., Zharnikova N.V. New Glassing Mesogens. In: *Advances in Study of Liquid Crystal Materials*, (Usol'tseva N.V., Ed.), Ivanovo: Iv. State Univers., **2007**. pp. 4–26 (in Russ.) [Усольтцева Н.В., Быкова В.В., Жарникова Н.В. Новые стеклюющиеся мезогены. В кн.: *Успехи в изучении жидкокристаллических материалов* (Усольтцева Н.В., ред.), Иваново: Ив. гос.ун-т, **2007**. с. 4–26].
8. Nyokony T. *Struct. Bond.* **2010**, *135*, 45–88.
9. Usol'tseva N.V., Kazak A.V., Luk'yanov I.Yu., Sotsky V.V., Smirnova A.I., Yudin S.G., Shaposhnikov G.P., Galanin N.E. *Phase Transitions* **2014**, *87*, 801–813.
10. Galanin N.E., Shaposhnikov G.P., Smirnova A.I., Kazak A.V., Usol'tseva N.V. *Liquid Crystals and Their Application* **2014**, *14(4)*, 74–84 (in Russ.).
11. Kazak A.V., Usol'tseva N.V., Bykova V.V., Semeykin A.S., Yudin S.G. *Liquid Crystals and Their Application* **2010**, *10*, 90–97 (in Russ.).
12. Kazak A.V., Usol'tseva N.V., Smirnova A.I., Kashitsyn A.S., Kovaleva M.I. *Liquid Crystals and Their Application* **2014**, *14*, 85–90 (in Russ.).
13. Kazak A.V., Usol'tseva N.V., Smirnova A.I., Yakunin S.N., Rogachev A.V., Dyakova Yu.A., Marchenkova M.A., Terechenko E.Yu. Supramolecular Organization of Mix-substituted Phthalocyanine Holmium Complex in Floating Layers according to the Data of Synchrotron Study. In: *25th Int. Crimean Conference "Microwave & Telecommunication Technology" (CriMiCo'2015)*, Sevastopol, Crimea, **2015**. pp. 687–688 (in Russ.).

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