BAM and GID structural investigation of 1,4,8,11,15,18-hexahexyloxy-22,23,24,25-tetrachlorophthalocyanine floating layers

A Smirnova¹, A Kazak¹,²,³, M Kovaleva¹, M Marchenkov¹,², D N Chausov³, E Glukhovskoy⁶, N Usol'tseva¹

¹Nanomaterials Research Institute, Ivanovo State University, Ermak St. 39, 153025 Ivanovo, Russia
²Shubnikov Institute of Crystallography of Federal Scientific Research Center “Crystallography and Photonics” of Russian Academy of Sciences, Leninskii pr. 59, 119333 Moscow, Russia
³Moscow Region State University, Very Voloshinoy str., 24, 141014, Mytishi, Russia
⁴National Research Center “Kurchatov Institute”, Academician Kurchatov Sq. 1, 123182, Moscow, Russia
⁵Moscow Institute of Electronics and Mathematics National Research University Higher School of Economics, Tallinskaya St. 34, 123458 Moscow, Russia
⁶Saratov State University, Astrakhanskaya St. 83, 410012 Saratov, Russia

E-mail: alexkazak86@gmail.com

Abstract. The article presents a comprehensive study of the supramolecular organization of floating layers of the mix-substituted phthalocyanine of A₃B-type (1,4,8,11,15,18-hexahexyloxy-22,23,24,25-tetrachlorophthalocyanine). Molecular packing modeling of the studied compound in monolayer structures on the water surface was simulated, and the parameters of the unit cell of the monolayer were calculated. On the base of these data, the supramolecular organization of the floating layers was proposed. Using Brewster microscopy (BAM) and grazing incidence X-ray diffraction (GID), it was shown that at the water/air interface the studied phthalocyanine forms a stable bilayer crystalline structure with an imperceptible number of 3D-aggregates. Interplanar spacing of the crystalline bilayer is 1.93 nm.

1. Introduction
The tasks of upgrading the element base for nanoelectronic devices require an increasingly targeted search and scrupulous study of new materials whose functional properties, on the one hand, provide high performance in resolution, sensitivity, contrast, speed, conductivity, photoconductivity, etc., and on the other hand, allow to withstand intense light irradiation, high mechanical loads, significant temperature differences, etc. [1–8]. Liquid crystals are very interesting materials that form condensed phases. They combine such properties as mobility and fluidity with long-range positional order. Today, liquid crystals are widely known for their successful use in display technologies. Besides, these materials possess a number of another unique properties that determine their enormous potential both for the development of fundamental science and for innovative applications far beyond the limits of display technologies [9–16]. Discotic mesogens are of great interest due to their special columnar supramolecular organization in the mesophase [17–21]. Their disk-shaped molecules possessing
macroheterocyclic core have a strong tendency to associate due to \( \pi-\pi \) interactions and due to that form columnar aggregates. Among these mesogens, asymmetrically substituted phthalocyanine derivatives are the least studied and exceptionally interesting compounds. The presence of both electron-donating and electron-withdrawing substituents in one molecule leads to a polarized electronic structure [22] and these compounds are quite promising for practical applications in optics [23]. In addition, phthalocyanines with asymmetric structure, containing extended alkyl or alkoxy substituents, often possess liquid crystalline properties [24–28], including thermostable columnar mesophase [27]. The molecular and electronic structure peculiarities of asymmetrically substituted phthalocyanines determine the possibility of their use as highly efficient functional materials [29]. One of the most important steps in creating new high-performance functional materials based on nanoscale phthalocyanine thin films is to control their structure, including the evaluation of film homogeneity [30–34]. Considering the above mentioned, the aim of this work was a comprehensive study of the structure of the floating layers of 1,4,8,11,15,18-hexahexyloxy-22,23,24,25-tetrachlorophthalocyanine (Fig. 1).

![Figure 1. Structural formula of the studied mix-substituted phthalocyanine derivative.](image)

2. Materials and methods
Synthesis of the studied 1,4,8,11,15,18-hexahexyloxy-22,23,24,25-tetrachlorophthalocyanine was carried out by Prof. N.E. Galanin (Ivanovo State University of Chemistry and Technology) according to the method described in [35]. Models of the phthalocyanine molecule and its monomolecular layer on the water surface, as well as the calculation of their geometric characteristics, were performed using HyperChem 8.0 software (MM+ method), as it was described earlier [36]. These data were used to determine the type of molecular packing in floating layers. Floating (Langmuir) layers were formed from a chloroform solution (\( C = 0.013 \text{ wt. \%} \), where \( C \) is the mass fraction of the dissolved phthalocyanine) utilising Nima 601A, KSV 5000 and KSV 2000 units (Finland). Water (with resistivity \( \rho = 18 \text{ M}\Omega \cdot \text{cm} \)) used as a subphase was purified by Millipore Elix 3 and Millipore Simplicity 158 systems. The initial coverage degree \( (c) \) of the water surface with phthalocyanine molecules was calculated according to the method published in [37]. Layer formation at the water/air interface was studied in situ by Brewster microscopy method (BAM Optrel 3000 microscope, KSV Instruments, Finland). The HeNe laser with a radiation wavelength of 633 nm and a power of 10 mW was used as a light source in this setup. The goniometer of the microscope set the angle of laser incidence beam in the range from 45 to 75° with an accuracy of 0.01°. To obtain polarized light and contrast image, high-precision polarizers with a polarization ratio of \( 10^{-8} \) were used. The image was enlarged using interchangeable lenses \((\times5, \times10, \times20)\) and recorded by a computer-controlled high-quality camera with a resolution of 768 \( \times 72 \) pixels, the spatial resolution was 2 \( \mu\text{m} \).
Structural organization of floating layers was studied by diffraction in sliding geometry method (GID – grazing incidence diffraction). GID experiments were carried out at the “Langmuir” station of the Kurchatov synchrotron radiation source. Radiation from a bending magnet with an energy of 6.95 keV \((\lambda = 1.78 \text{ Å})\) was used for the experiments. The pair of flat mirrors was used to incline beam to water surface and the incidence angle was 0.8 of critical angle of the total external reflection for water. The intensity of diffraction reflection was collected by a point detector in a plane parallel to the sample surface. For horizontal collimation of diffracted beam, the Soller slots with an angular aperture of 2 mrad were used. To reduce scattering in air, as well as evaporation of liquid from the Langmuir trough, all measurements were carried out in the humid helium atmosphere. Since at room temperature monolayers are actually 2D-“powder”, i.e. superposition of two-dimensional crystallites randomly oriented on the water surface, the diffraction pattern was scanned only at an angle of 2\(\theta\) in the film plane \((q_{xy} – \text{scanning})\). The qualitative analysis of diffraction pattern was carried out according to the standard (three-dimensional) powder diffraction scheme, when the angular positions of the Bragg peaks 2\(\theta_{hk}\), corresponding to the vectors of the two-dimensional reciprocal lattice, determine the distances between the chains of molecules \(d_{hk}\).

3. Results and discussion

3.1. Modeling of floating layers

A model of a monomolecular floating layer placed on the water surface was obtained after optimization by the molecular mechanics method (Fig. 2). When simulating the floating layer, phthalocyanine molecules were situated in one plane. Such location corresponds to a monolayer package. The formed monolayer was placed on the preliminary modeled water surface. According to the data obtained, the model area of the elementary cell of the monolayer was calculated. If the structure of the phthalocyanine molecule is assumed to be flat, the area per one molecule in the densest face-on monomolecular packing is 4.5 nm\(^2\). When lateral substituents are displaced from the phthalocyanine macrocycle plane, the area per one molecule in the densest face-on monolayer can be reduced to 1.6 nm\(^2\). The calculated area size was then compared with the areas obtained in the experiment, and on the basis of these results, a conclusion about the layer structure was drawn.

Figure 2. Model of floating monolayer packing of 1,4,8,11,15,18-hexahexyloxy-22,23,24,25-tetrachlorophthalocyanine placed on the water surface before the lateral substituents were displaced from the macrocycle plane: a) top view, b) side view.
3.2. Supramolecular organization of floating layers

During floating layer formation (when the barrier of the Langmuir trough approached with the rate \( \nu = 6 \text{ cm}^2/\text{min} \)) its images were recorded by the CCD camera of the Brewster microscope with a period of 5 seconds. Four of the obtained images, which correspond to different points (a–d) of the compression isotherm (Fig. 3) are shown in Fig. 4.

![Isotherm graph](image)

**Figure 3.** Compression isotherm of floating layer of the studied compound. Dots indicate where BAM images were taken.

![BAM images](image)

**Figure 4.** BAM images of the floating layer of the studied compound on the water surface during its formation at various area values per one molecule \( A_{\text{mol}} \):

a) \( A_{\text{mol}} = 6.9 \text{ nm}^2 \); b) \( A_{\text{mol}} = 3.9 \text{ nm}^2 \); c) \( A_{\text{mol}} = 2.1 \text{ nm}^2 \); d) \( A_{\text{mol}} = 1.6 \text{ nm}^2 \)

The image of a low-density monolayer (Fig. 4a) was obtained at a very large area per molecule \( A_{\text{mol}} \) and at zero surface pressure. The image shows a gray area on a dark background. The dark background corresponds the gas phase, whereas the gray area is the low-density phase of the monolayer at the water/air interface. As \( A_{\text{mol}} \) decreases, the dark background disappears and a uniform gray area is registered (Fig. 4b). According to the simulation data (described above), we assume that in this case a dense *face-on* floating monolayer with lateral substituents displaced from the macrocycle plane is
formed. The intensity of BAM images depends on the floating film thickness and the surface density of molecules [38]. Upon further compression, a large number of bright domains appear on a gray background (Fig. 4c). This image corresponds to a monolayer breaking with the formation of local 3D aggregates. As $A_{\text{mol}}$ decreases, the surface pressure grows rapidly (according to Fig. 3) and a stable bilayer with imperceptible number of 3D aggregates is formed (Fig. 4d). Such additional pressure in the layer probably appears due to the displacement of aliphatic substituents from the macrocycle plane into the air phase. The results obtained by BAM are in good agreement with the GID (Fig. 5) and simulation (Fig. 2) data.

![Figure 5. GID curve of the obtained floating layer (taken at the point d, Fig. 3)](image)

Fig. 5 shows the in-plane diffraction curve registered from the floating layer formed on the water surface at surface pressure of $\pi = 4.5$ mN/m. Only one diffraction peak at $\sim 0.33$ Å$^{-1}$ was detected in the angle range from 0.17 to 1 Å$^{-1}$. The absence of additional diffraction peaks in a wide measurement range indicates the existence of a single crystalline phase with interplanar spacing $d = 1.93$ nm. The formation of additional crystalline phases does not occur, possibly due to sufficiently long aliphatic substituents ($\text{-OC}_6\text{H}_{13}$) in the structure of the studied phthalocyanine, which hinder the interaction of macrocycles. Thus, the formation of any additional crystalline phase, different from the phase with the planar macrocycle location on the water surface, becomes impossible.

4. Conclusion
Models of the 1,4,8,11,15,18-hexa(hexyloxy)-22,23,24,25-tetrachlorophthalocyanine molecule and its monomolecular floating layer were built and their geometric characteristics were calculated. In the densest face-on monomolecular packing, when aliphatic substituents are coplanar to macrocycle plane, $A_{\text{mol}}$ is 4.5 nm$^2$. When the substituents displaced from the macrocycle plane, the area per molecule in the densest face-on monolayer decreases and equal to 1.6 nm$^2$. As a result of the comprehensive study, it was confirmed that during formation of floating layer, the aliphatic substituents are displaced from the macrocycle plane into the air phase and a stable bilayer crystalline structure with imperceptible number of 3D aggregates forms. Interplanar spacing of the crystalline bilayer is 1.93 nm. The results obtained in this work open up the opportunity of the effective use of thin film materials formed on the basis of the floating layers. They can be utilized in organic nanoelectronics devices due to reduction of defects of film structures.
Acknowledgments
The authors are grateful to Prof. N.E. Galanin and Prof. G.P. Shaposhnikov (Ivanovo State University of Chemistry and Technology) for kind providing of the phthalocyanine derivative.

The work was supported by the Ministry of Education and Science of the Russian Federation in the framework of the state task for Ivanovo State University (Grant No 16.1037.2017/4.6) and partially supported by the RFBR (Grants No 19-03-00763, 19-57-04002, 19-32-50019) and Program of the President of the Russian Federation (Grant No. MK-3767.2019.9).

References
[1] Kamanina N V, Vaganov V E 2010 Liq. Cryst. and their Appl. 2 5.
[2] Dadivanyan A K, Pashchina Y M, Chausov D N, Belyaev V V, Solomatin A S 2011 Mol. Cryst. Liq. Cryst. 545 159. DOI 10.1080/15421406.2011.571998.
[3] Dadivanyan A K, Pashchina Y M, Belyaev V V, Chausov D N, Noah O V, Chigrinov V G 2012 Mol. Cryst. Liq. Cryst. 560 108. DOI 10.1080/15421406.2012.663185.
[4] Shhtykov N M, Palto S P, Umanskii B A, Geivandov A R 2018 Crystallography Reports 63 633. DOI 10.1134/S1063774518040259.
[5] Ong L-K, Ha S-T, Yeap G-Y Lin H-C 2018 Liquid Crystals 45 1574. DOI 10.1080/02678292.2018.1455225.
[6] Lagerwall J P F, Scalia G 2012 Current Applied Physics 12 1387. DOI 10.1016/j.cap.2012.03.019.
[7] Dadivanyan A K, Belyaev V V, Chausov D N, Stepanov A A, Smirnov A G, Tsybin A G, Osipov M A 2015 Mol. Cryst. Liq. Cryst. 611 117. DOI 10.1080/15421406.2015.1030196.
[8] Usol'tseva N, Bykova V, Zharnikova N, Alexandrov A, Semeikin A, Kazak A 2010 Mol. Cryst. Liq. Cryst. 525 184. DOI 10.1080/15421401003799557.
[9] Chausov D N, Kurilov A D, Belyaev V V, Kumar S 2018 Opto-Electronics Review 26 (1) 44. DOI 10.1016/j.opere.2017.12.001.
[10] Chausov D N, Kurilov A D, Kazak A V, Smirnova A I, Velichko V K, Gevorkyan E V, Rozhkova N N, Usol'tseva N V 2019 Liquid Crystals DOI 10.1080/02678292.2019.1566503.
[11] Kazak A V, Usol'tseva N V, Smirnova A I, Bodnarchuk V V, Sul'yanov S N Yablonskii S V 2016 Crystallography Reports 61 (3) 493. DOI 10.1134/S1063774516030159.
[12] Usol'tseva N V, Smirnova A I, Kazak A V, Giricheva N I, Galanin N E, Shaposhnikov G P, Bodnarchuk V V, Yablonskii S V 2017 Opto-Electronics Review 25 127. DOI 10.1016/j.opere.2017.03.003.
[13] Chumakov A S, Al-Alwani A J, Gorbachev A I, Kletsov A A, Glukhovsky E G, Shtykov S N, Ermakov A V, Kazak A V, Usol'tseva N V 2017 BioNanoScience 7 666. DOI 10.1007/s12668-017-0449-4.
[14] Kazak A V, Usol'tseva N V, Smirnova A I, Dyakova Yu A, Marchenko M A, Nabatov B V, Tereshchenko E Yu, Kholodkov I V 2015 Macrobicycles 8 (3) 284. DOI 10.6060/mhc150972k.
[15] Usol'tseva N V, Smirnova M V, Kazak A V, Smirnova A I, Bumbina N V, Ilyin S O, Rozhkova N N 2015 J. Friction and Wear 36 (5) 380. DOI 10.3103/S1068366615050165.
[16] Usol'tseva N V, Bykova V V, Anan'eva G A, Alexandrov A I, Pashkova T V, Kazak A V, Semeikin A S, Glazunov A V, Lyubimova T V, Yudin S G, Palto S P 2009 Liq. Cryst. and their Appl. 4 37.
[17] Kazak A V, Usol'tseva N V, Bykova V V, Semeikin A S, Yudin S G 2011 Mol. Cryst. Liq. Cryst. 541 28 DOI 10.1080/15421406.2011.569529.
[18] Kazak A V, Usol'tseva N V, Sotsky V V, Yudin S G, Semeikin A S 2012 Langmuir 28 16951. DOI 10.1021/la303958q.
[19] Kazak A V, Usol'tseva N V, Yudin S G, Bykova V V, Semeikin A S 2011 Liq. Cryst. and their Appl 2 52.
[20] Kazak A V, Usol'tseva N V, Smirnova A I, Kashitsyn A S, Kovaleva M I 2014 Liq. Cryst. and
[21] Kazak A V, Usol'tseva N V, Yudin S G, Alpatova A V, Semeikin A S, Bykova V V 2011 *Liq. Cryst. and their Appl* **14** (4) 85.

[22] De la Torre G, Torres T 1997 *J. Porphyrs Phthalocyanines* **1** 221. DOI 10.1002/(SICI)1099-1409(199707)1:3<221.

[23] Lawrence D S, Whitten D G 1996 *Photochemistry and Photobiology* **64** (6) 923. DOI 10.1111/j.1751-1097.1996.tb01857.x.

[24] Galanin N E, Shaposhnikov G P, Smirnova A I, Kazak A V, Usol’tseva N V 2014 *Liq. Cryst. and their Appl* **14** (4) 74.

[25] 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 2014 *Phase Transitions: A Multinational Journal* **87** (8) 801. DOI 10.1080/01411594.2014.893343.

[26] Eichhorn H 2000 *Journal of Porphyrs and Phthalocyanines* **4** (1) 88. DOI 10.1002/(SICI)1099-1409(200001/02)4<1:88::AID-JPP208>3.0.CO;2-6.

[27] Lawrence D S, Whitten D G 1996 *Photochemistry and Photobiology* **64** (6) 923. DOI 10.1111/j.1751-1097.1996.tb01857.x.

[28] De la Escosura A, Martinez-Diaz V M, Thordarson P, Rowan A E, Nolte R J M, Torres T 2003 *J. Am. Chem. Soc.* **125** (40) 12300. DOI 10.1021/ja030038m.

[29] Dyakova Yu A, Marchenko M A, Seregin A Yu, Imamova L R, Tereschenko E Yu, Klechkovskaya V V, Alekseev A S, Kovalchuk M V 2016 *Mendeleev Communications* **26** 149. DOI 10.1016/j.mencom.2016.03.023.

[30] Alg-Alwani A J, Chumakov A, Shinkarenko O, Qassime M, Begletsova N, Gorbachev I, Venig S, Kazak A, Glukhovskoy E 2018 *Journal of Physics: Conference Series* **1135** (1) 012029. DOI 10.1088/1742-6596/1135/1/012029.

[31] Dyakova Y A, Ilina K B, Konarev P V, Kryukova A E, Marchenko M A, Blagov A E, Volkov V V, Pisarevsky Y V, Kovalchuk M V 2017 *Crystallography Reports* **62** (3) 364. DOI 10.1016/j.crystrep.2017.04.014.

[32] Kazak A V, Usol'tseva N V 2011 *Functional Materials* **18** (1) 24.

[33] Galanin N E, Shaposhnikov G P 2012 *Russian Journal of General Chemistry* **82** 1734. DOI 10.1134/S1070363212010179.

[34] Kazak A V, Usol'tseva N V, Bykova V V, Semeikin A S, Yudin S G 2010 *Liq. Cryst. and their Appl* **4** 90.

[35] Kazak A V, Zhukova L N, Kovaleva M I, Chausov D N, Kuznetso M M, Gabdulsadykova G F 2018 *Liq. Cryst. and their Appl* **18** (3) 74. DOI 10.18083/LCAppl.2018.3.74.

[36] Gupta R K, Suresh K A, Kumar S, Lopatina L M, Selinger R L B, Selinger J V 2008 *Phys Rev E.* **78** 041703. DOI 10.1103/PhysRevE.78.041703.