Influence of 2,3-naphthalocyanines structure on their supramolecular organization in floating layers

A V Kazak1,2,3, M A Marchenko2, T V Dubinina4,5, D N Chausov3,6

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
4Department of Chemistry, Lomonosov Moscow State University, GSP-1, Leninskie Gory, 119991, Moscow, Russian Federation.
5Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432, Chernogolovka, Russia.
6National University of Science and Technology «MISIS», Leninskii pr. 4, 119049, Moscow, Russia

E-mail: alexkazak86@gmail.com

Abstract. Herein, we present a study of the floating layers morphology for 2-naphthyl- and 2-naphthoxy-substituted zinc 2,3-naphthalocyaninates. The packing of molecules in the monolayer structures at the air-water interface were simulated, and the unit-cell parameters of face-on and edge-on monolayers were calculated. Using these data, the supramolecular organization of the floating layers of the substituted 2,3-naphthalocyanine complexes was determined. It was shown that these compounds form stable layers with edge-on packing of molecules at the air-water interface. The results obtained give the possibility to use more efficiently thin-film structures based on the obtained Langmuir layers in optoelectronics.

1. Introduction

The relevance of the topic of this work is conditioned by the urgent need to obtain new cheap and highly efficient materials for nanoelectronics devices [1–7], including elements of photovoltaic devices based on thin-film organic nanomaterials [8–11]. An important fundamental task of great practical importance is to control the structure of such materials [12–18]. The control of structure results in direct creation of thin-film nanomaterials with optimal physico-chemical properties, which is necessary for creating modern efficient nanoelectronic devices [19, 20].

In contrast to expensive and difficult in preparation silicon nanoelectronic elements, organic materials can be deposited by cheaper wet techniques and show controlled absorption in a wide optical range. Derivatives of porphyrins [21–24] and phthalocyanines [25–28] are promising organic materials. They demonstrate the combination of properties necessary for their effective application in photovoltaic devices, organic light emitting diodes (OLED) and other organic electronic devices. Disk-shaped molecules with a macroheterocyclic core have a strong tendency to associate due to π-π interactions and the formation of columnar aggregates. Among the phthalocyanine derivatives, the most interesting
compounds are naphthalocyanine derivatives because of the ability to absorb light in the near infrared region \cite{29, 30}. It allows effective coverage of solar spectrum and corresponding enhancement of conversion of sunlight into electricity. Introduction of \(\pi\)-extended peripheral functional groups can lead to bathochromic shift of absorption maximum in comparison with phenyl-substituted analogues. The aim of this work was to study the morphology of Langmuir monolayers of 3,4,12,13,21,22,30,31-octa-(2-naphthyl)-2,3-naphthalocyaninato zinc and 3,4,12,13,21,22,30,31-octa-(2-naphthoxy)-2,3-naphthalocyaninato zinc (Fig. 1) for the subsequent production of effective thin-film nanomaterials based on them. Their synthesis was carried out according to the previously described methods \cite{31, 32}.

![Fig. 1. Structural formulas of the studied substituted 2,3-naphthalocyanines.](image)

2. Materials and methods
The construction of models of naphthalocyanine molecules and monomolecular layers at the air-water interface, as well as the calculation of their geometric characteristics, were performed in the HyperChem program version 8.0 (calculation method MM +) according to the mentioned earlier method \cite{33}. These data were used to determine the type of molecules packing in floating layers. Langmuir layers were formed from solutions of the studied compounds in chloroform (\(C = 0.013\) wt.\%), where \(C\) is the mass fraction of the solute. The monolayers formed in KSV miniTrough (Finland), using ultrapure water (\(\rho = 18.2\) M\(\Omega\)*cm, Millipore Simplicity 185). The initial coverage degree of the water surface with naphthalocyanine molecules was calculated according to the method published in literature \cite{34}. The monolayers formation of the naphthalocyanine derivatives at the air-water phase separation was studied in situ by Brewster microscopy (BAM Optrel 3000 microscope from 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. The goniometer of the microscope allows to set the incident angle of the laser beam in the range from 45 ° to 75 ° with an accuracy of 0.01 °. To obtain polarized light and a contrast image high-precision polarizer with a polarization ratio of \(10^{-8}\) were used. The image was enlarged using different lenses (\(\times 5, \times 10, \times 20\)) and captured by a computer-controlled high-quality camera with a resolution of 768 \(\times\) 72 pixels, the spatial resolution was 2 \(\mu\)m.

3. Results and discussion

3.1. Modelling of floating layers
To simulate floating layers, the molecules of the studied naphthalocyanine complexes were located in one plane in two ways (face-on and edge-on of the molecules arrangement), which correspond to monolayer packaging. The formed monolayer was placed on the surface of the previously simulated volume of water. After optimization by the method of molecular mechanics, we obtained a model of a monomolecular layer at the air-water interface (Fig. 2). Based on the obtained data, the area of the unit
The area per molecule in the densest face-on monomolecular package ($A_{mol}$) is 507 Å$^2$ for compound I and 474 Å$^2$ for compound II. For the edge-on monomolecular package, the area per molecule is 124 Å$^2$ and 149 Å$^2$ for compound I and II correspondingly. After that, the calculated area size was compared with the areas obtained in the experiment, and on the basis of the obtained results a conclusion about the structure of the layer was made.

Air

Monolayer

Water

Fig. 2. Edge-on model of monolayer packing of 3,4,12,13,21,22,30,31-octa-(2-naphthyl)-2,3-naphthalocyaninato zinc at the water surface (side view). The inset in the upper left corner shows the relative position of two nearby molecules.

3.2. Supramolecular organization of floating layers

To study the morphology of the formed floating layers, $\pi$-A isotherms and Brewster images were obtained. The $\pi$-A isotherms of the I and the II compounds are shown in fig. 3.

Fig. 3. The $\pi$-A isotherm of the floating layer of compound I (left) and compound II (right) with corresponding Brewster images.

The molecule area dependence of surface pressure for both compounds is similar to that one obtained for 3,4,12,13,21,22,30,31-octa-phenyl-2,3-naphthalocyaninato zinc ($^{6}$NcZn) [27]. The initial molecule
area in our experiments was $A_{\text{mol}} = 510 \text{ Å}^2$ and $A_{\text{mol}} = 540 \text{ Å}^2$ for the I and the II compounds, respectively. The area occupied by one molecule in the formed monolayer was determined by extrapolating the tangent to the $\pi$-$A$ isotherm in the linear interval corresponding to the formation of the liquid crystal (Langmuir) phase onto the abscissa. The determined area per molecule was $A_{\text{mol}} = 120 \text{ Å}^2$ and $A_{\text{mol}} = 140 \text{ Å}^2$ for the I and II compounds, respectively. For PhNcZn, $A_{\text{mol}} = 150 \text{ Å}^2$. The isotherms of both materials are characterized by a continuous increase in surface pressure during film compression.

To determine the morphology of the floating layers of the studied compounds forming during the compression, the images of the floating layer were recorded with a Brewster microscope CCD camera with a period of 10 sec. The compression rate was $\nu = 2 \text{ cm}^2/\text{min}$.

Figures 4 and 5 show images of the floating layers of compounds I and II corresponding to different points on the $\pi$-$A$ isotherms (Fig. 3, a-f). The obtained micrographs clearly demonstrate fairly homogeneity of the monolayers. However, during the formation of the films, an aggregation process is present, leading to the formation of three-dimensional structures at the air-water interface, which are recognized by the presence of Newton rings on the images. With an increase of surface pressure up to 20 mN/m, the number of three-dimensional aggregates increases slightly, since the reflectivity of the monolayer almost does not change. Taking into account the simulation data, it can be assumed that a monolayer is formed in which naphthalocyanine molecules are oriented at an angle of 90° to the surface of the water, i.e. edge-on monomolecular layer. A slight decrease in the molecular area in the layer compared to the model area in the densest edge-on package of the monolayer is associated with the local formation of 3D aggregates.

Fig. 4. Brewster images of the floating layer for various compression ratios of the floating layer for compound I: a) $A_{\text{mol}} = 510 \text{ Å}^2$, b) $A_{\text{mol}} = 200 \text{ Å}^2$, c) $A_{\text{mol}} = 120 \text{ Å}^2$, d) $A_{\text{mol}} = 105 \text{ Å}^2$, e) $A_{\text{mol}} = 97 \text{ Å}^2$, f) $A_{\text{mol}} = 92 \text{ Å}^2$. Image width is 267 μm.
4. Conclusion

The models of molecules and monomolecular layers 3,4,12,13,21,22,30,31-octa-(2-naphthyl)-2,3-naphthalocyaninato zinc (compound I) and 3,4,12,13,21,22,30,31-octa-(2-naphthoxy)-2,3-naphthalocyaninato zinc (compound II) were built, their geometric characteristics were calculated. In the densest face-on monomolecular package, $A_{mol}$ is 507 Å$^2$ for the compound I and $A_{mol}$ is equal to 474 Å$^2$ for compound II; in the densest edge-on monomolecular packing, $A_{mol}$ is 124 Å$^2$ for compound I and $A_{mol}$ is equal to 149 Å$^2$ for compound II. As a result of morphology study of the floating layers of these naphthalocyanine complexes, it was firstly found that floating layers with edge-on packing of molecules in the layer are formed on the air-water interface. In this case, insignificant inclusions of 3D aggregates are observed in the layers. The results obtained in the work discover the possibility of efficient employment of thin-film materials formed on the basis of the studied floating layers in organic nanoelectronics devices by reducing the defectiveness of film structures.

Acknowledgments

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 (Application No. FZZM-2020-0006), the Ministry of Science and Higher Education within the framework of State assignment to the Federal Scientific Research Center ‘Crystallography and Photonics’ of the Russian Academy of Sciences and partially supported by the RFBR (Grants No. 19-03-00763a, 19-57-04002bel_mol_a, 20-07-00181a) and Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (Grant No. MK-3767.2019.9). Synthesis of zinc naphthalocyaninates was performed under the support of Russian Science Foundation Grant № 19-73-00099.

References

[1] 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.

[2] Usoltseva N, Bykova V, Zharnikova N, Alexandrov A, Semeikin A, Kazak A 2010 Mol. Cryst.
[3] Chausov D N, Kurilov A D, Kazak A V, Smirnova A I, Velichko V K, Belyaev V V, Gevorkyan E V, Rozhkova N N, Usol’tseva N V 2019 *Liquid Crystals* 46 1345. DOI 10.1080/02678292.2019.1566503.

[4] Kazak A V, Usol’tseva N V, Smirnova A I, Dyakova Yu A, Marchenko M A, Nabatov B V, Tereschenko E Yu, Kholodkov I V 2015 *Macromolecules* 8 (3) 284. DOI 10.6060/mhc150972k.

[5] Chausov D N, Kurilov A D, Kazak A V, Smirnova A I, Belyaev V V, Gevorkyan E V, Usol’tseva N V 2019 *J. Mol. Liq.* 291 111259. DOI: 10.1016/j.molliq.2019.111259.

[6] Al-Alwani A J, Chumakov A, Shinkarenko O, Gorbachev I, Pozharov M, Venig S, Glukhovskoy E 2017 *Applied Surface Science* 424 222. DOI 10.1016/j.apsusc.2017.03.235.

[7] Chausov D N, Kurilov A D, Belyaev V V, Kumar S 2018 *Opto-Electronics Review* 26 (1) 44. DOI 10.1016/j.opelre.2017.12.001.

[8] Williams G, Sutty S, Klenkler R, Aziz H 2014 *Sol. Energy Mater. Sol. Cells* 124 217. DOI 10.1016/j.solmat.2014.02.013.

[9] 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.

[10] Luisb Y, Louisb H, Oparab T O 2019 *Advanced Journal of Chemistry-Section A* 2 (1) 21. DOI 10.29088/sami/AJCA.2019.2.2144.

[11] Kazak A V, Usol’tseva N V, Yudin S G, Alpatova Y A, Marchenko M A, Nabatov B V, Tereschenko E Yu, Kholodkov I V 2015 *Liquid Crystals and their Application* 3 47.

[12] Opecyma O M, Louisb H, Opurab C I, Funmilayod O O, Magu T O 2019 *Nano Res. Lett.* 9 537. DOI 10.1186/1556-276X-9-537.

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

[14] Kazak A V, Usol’tseva N V, Yudin S G, Alpatova A V, Semeikin A S, Bykova V V 2011 *Liquid Crystals and their Application* 3 47.
[25] Urbani M, Ragoussi M-E, Nazeeruddin M K, Torres T 2019 *Coordination Chemistry Reviews* 381 1. DOI 10.1016/j.ccr.2018.10.007.

[26] Galanin N E, Shaposnikov G P, Smirnova A I, Kazak A V, Usol’tseva N V 2014 *Liquid Crystals and their Application* 14 (4) 74.

[27] Kazak A V, Marchenkova M A, Smirnova A I, Seregin A Yu, Rogachev A V, Warias J, Murphy B, Tereschenko E Yu, Usol’tseva N V 2020 *Mendelev Commun.* 30, 52. DOI 10.1016/j.mencom.2020.01.017.

[28] 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.

[29] Hirao A, Akiyama T, Okujima T, Yamada H, Uno H, Sakai Y, Aramaki S, Ono N 2008 *Chem Commun.* 39 4714. DOI 10.1039/B811674A.

[30] Kazak A V, Marchenkov M A, Dubinina T V, Smirnova A I, Tomilova L G, Rogachev A V, Chausov D N, Sistiapanau A A, Usol’tseva N V 2020 *New J. Chem.* DOI 10.1039/C9NJ06041C.

[31] Dubinina T V, Paramonova K V, Trashin S A, Borisova N E, Tomilova L G, Zefirov N S 2014 *Dalton Trans.* 43 2799. DOI 10.1039/C3DT52726C.

[32] Dubinina T V, Piskovoi R A, Tolbin A Y, Pushkarev V E, Vagin M Y, Tomilova L G, Zefirov N S 2008 *Russ. Chem. Bull.* 57 1912. DOI 10.1007/s11172-008-0258-6.

[33] Kazak A V, Usol’tseva N V, Bykova V V, Semeikin A S, Yudin S G 2010 *Liquid Crystals and their Application* 4 90.

[34] Kazak A V, Zhukova L N, Kovaleva M I, Chausov D N, Kuznetsov M M, Gabdulsadykova G F 2018 *Liquid Crystals and their Application* 18 (3) 74. DOI 10.18083/LCAppl.2018.3.74.