

Floating layer structure of mesogenic phthalocyanine of A₃B-type

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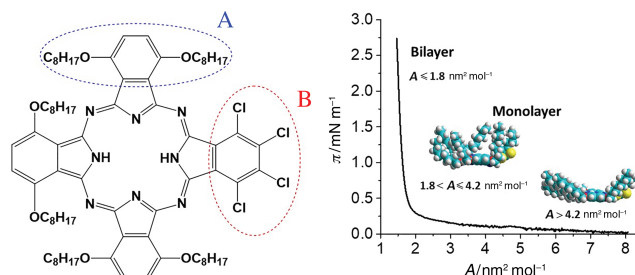
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To design efficient thin-film materials for low cost organic nanoelectronic devices, the Langmuir floating layer structure of the mesogenic 1,4,8,11,15,18-hexaethoxy-22,23,24,25-tetrachlorophthalocyanine (A₃B-type) was characterized by Brewster angle microscopy, grazing incidence diffraction, and reflectometry. Starting from the area per one molecule of 7.6 nm², a single two-dimensional ordered structure with the period of 2.3 nm was formed. When the area reaches the value of 2.5 nm², a stable bilayer structure with imperceptible number of 3D aggregates was detected, in which each monolayer preserved organization of the preceding monolayer.



Keywords: mix-substituted phthalocyanine, floating layers, structure, Brewster angle microscopy, grazing incidence diffraction, X-ray reflectivity.

In recent years, thin film materials based on mesogenic macroheterocyclic compounds have aroused a great interest in both the scientific community and industry.^{1–3} In contrast to well-studied symmetric phthalocyanine derivatives,^{4–6} their asymmetric analogues are not widely explored. Meantime, the latter are among the most promising representatives of discotic compounds for nanoelectronics element applications such as photovoltaic devices,^{7–9} gas sensors,¹⁰ semiconductors,¹¹ nonlinear optics,¹² and other organic electronic devices.^{13–15} The uniqueness of these objects is associated with an absorption in the long-wavelength spectral region, as well as with the presence of both electron-donating and electron-withdrawing groups in one phthalocyanine molecule. These compounds are capable of forming liquid crystalline phases containing a columnar packing of molecules and upon cooling, they ensure a vitrification of thin films preserving the structure of preceding columnar phase.^{16,17}

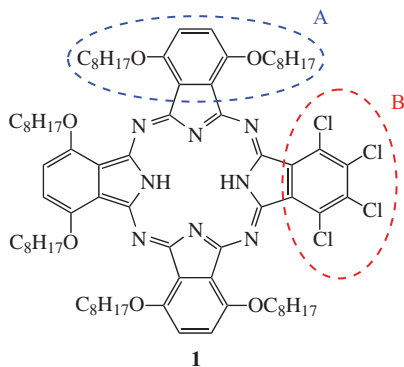
In classic photovoltaic cells, the active light absorbing layer is a multicomponent composition, where each of the components is separately responsible for the light absorption, vitrification, electron transfer, and one-dimensional conductivity, *viz.* the required properties for successful functioning of such devices. A replacement of the multicomponent composition by a single nanostructured material, which combines all these features, is a promising way in the development of modern organic photovoltaic elements.¹⁸ In this work, we consider an asymmetric phthalocyanine

derivative as such an expectant material. At the same time, it is important to know structural peculiarities of the obtained thin films in order to improve the efficiency of nanoelectronic devices. This knowledge allows one to correct the required physicochemical properties of thin films by controlling conditions of the active layer formation.¹⁹

In our previous reports on the structure and physicochemical properties of asymmetric phthalocyanine derivatives of A₃B-type, it was shown that the number of acceptor substituents (two or four chlorine atoms) introduced to the molecule significantly affects electronic absorption spectra (both in solutions and thin films), energy of boundary orbitals (HOMO/LUMO), values of the dipole moment, and mesomorphic properties of those compounds.^{16,18} A difference in photoelectric properties of heterophase systems based on phthalocyanines of this type in combination with fullerene C₆₀ was also observed.¹⁶

In the present work, we continued our ongoing research and comprehensively examined the floating layer structure formed by asymmetric 1,4,8,11,15,18-hexaethoxy-22,23,24,25-tetrachlorophthalocyanine **1**.

Synthesis of compound **1** was reported earlier.²⁰ As was previously shown,¹⁷ this compound possesses liquid crystalline properties, exhibiting columnar two-dimensional ordered mesophase with a characteristic texture (Figure 1) in the temperature range of 100–200 °C. Above 200 °C, compound **1** starts to decompose without any transition into the isotropic state.



Upon cooling below 100 °C, it undergoes the glass transition (*i.e.*, vitrifies) with a preservation of the mesophase texture.

Once the floating layer was formed,[†] its images were recorded by a CCD camera of the Brewster microscope every 5 s. The speed rate of Langmuir trough the barrier (ν) was 6 cm² min⁻¹. Figure 2 depicts the compression isotherm.

Figure 3 shows six images corresponding to the different points (a)–(f) on the compression isotherm (see Figure 2). These images indicate that at $A_{\text{mol}} = 7.6$ nm², a monolayer is formed on the surface of water subphase [see Figure 3(a)]. A compression of the monolayer to $A_{\text{mol}} = 4.2$ nm² does not change the image [see Figures 3(a)–(c)]. According to the simulation data, we assume that this compression leads to the displacement of lateral substituents out of the phthalocyanine macrocycle plane into the air phase. The further compression results in breaking the monolayer [see Figure 3(d)], and the formation of bilayer structures with the local 3D aggregates occurs [see Figures 3(e), (f)].

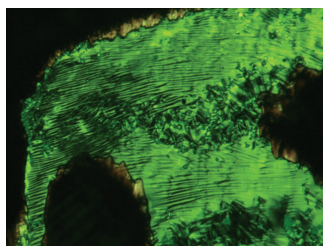


Figure 1 Columnar mesophase texture of compound **1** recorded upon cooling (at $T = 323$ K and magnification of 250 times).

[†] To determine the type of possible molecular packing in the floating layers formed on the water surface, the models of phthalocyanine and its monomolecular layer were simulated using the HyperChem software (version 8.0, MM+ calculation method), which also revealed the geometric characteristics for both of them.

Experimental floating (Langmuir) layers were prepared from a CHCl₃ solution (the mass fraction of dissolved compound **1** was 0.013 wt%) using Nima 601A, KSV 5000 and KSV 2000 units (Finland). Water (with the resistivity of 18 MΩ·cm) used as a subphase was purified by Millipore Elix 3 and Millipore Simplicity 158 systems. The initial coverage degree of water surface with the phthalocyanine molecules was calculated according to the known method.²¹ The layer formation process at the water/air interface was investigated *in situ* by the Brewster angle microscopy using an Optrel 3000 microscope (KSV Instruments, Finland). The structural organization of floating layers was studied by diffraction in the sliding geometry (GID, grazing incidence diffraction) and reflectometry (XRR, X-ray reflectivity) methods.

GID experiments were carried out at the 'Langmuir' station at the Kurchatov synchrotron radiation source. The radiation of a rotary magnet with an energy of 6.95 keV ($\lambda = 1.78$ Å) was used. All the measurements were performed in a humid helium atmosphere. XRR measurements were performed at the LISA station (PETRA III, DESY, Germany).²² The size of focused X-ray beam (18 keV) was 500×8 μm at the sample location.

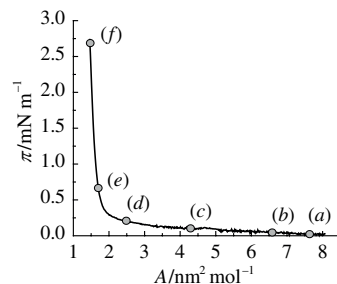


Figure 2 Compression isotherm of floating (Langmuir) layer for compound **1**. Dots indicate positions, where the images were taken by BAM.

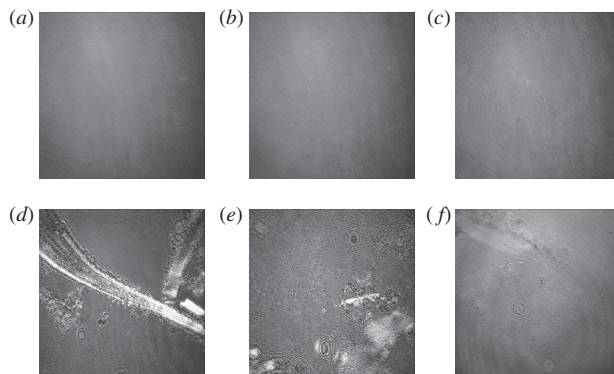


Figure 3 BAM images of the floating layer formed on the water surface and taken at various area values per one molecule, A_{mol} : (a) 7.6, (b) 6.7, (c) 4.2, (d) 2.5, (e) 1.8 and (f) 1.5 nm².

The results acquired by Brewster angle microscopy (BAM) method were confirmed by the grazing incidence X-ray diffraction (GID) data (Figure 4) and the X-ray reflectivity (XRR) experiment (Table 1). The visual observation showed that the speed of 3D aggregates was low upon approaching to the barrier. This indicates the formation of a sufficiently stable layer. As A_{mol} decreases, the surface pressure begins to grow faster (see Figure 2), and fragments of bilayer structures become larger. Therefore, it was confirmed that such an additional pressure in the layer arises due to the displacement of aliphatic substituents from the macrocycle plane of phthalocyanine into the air phase, which is in agreement with the simulation results.

Figure 4 shows the *in-plane* diffraction curve recorded for the floating layer of the studied phthalocyanine. This layer was formed on the water surface at the surface pressure π of 2.94 mN m⁻¹. The GID pattern measured in the angular range from 0.17 to 1 Å⁻¹ shows the presence of only one diffraction peak at ~ 0.27 Å⁻¹. The absence of any additional diffraction peaks in a wide measurement range indicates the existence of a single crystalline phase with the interplanar spacing d of 2.3 nm. The formation of additional crystalline phases does not occur probably due to the presence of long aliphatic substituents in the studied phthalocyanine. The substituents sterically disrupt the interaction of phthalocyanine

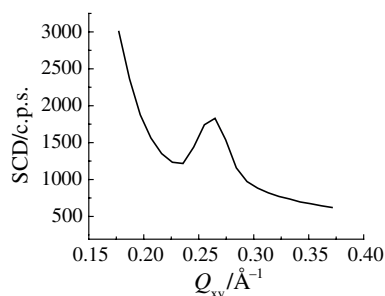


Figure 4 GID curve for the floating layer.

Table 1 Parameters of the layer model at $\chi^2 = 2.56$.

Layer	χ_{0r} and χ_{0i}	χ_{0r} and χ_{0i} error (%)	Thickness/ nm	σ_z /nm
layer 1	-1.46×10^{-6} , 2.15×10^{-9}	± 5.3	0.6 ± 0.01	0.26 ± 0.02
layer 2	-2.21×10^{-7} , 3.7×10^{-9}	± 1	1.1 ± 0.03	0.22 ± 0.03
H ₂ O	–	–	–	0.31 ± 0.01

macrocycles and thereby prevent the formation of any crystalline phase, other than the one with a planar location of the macrocycle on the water surface.

Based on analysis of the XRR data, the electron density profile over the layer depth was obtained. The procedure of the profile restoring was carried out in several steps. At the first step, taking into account the results of molecular modeling, the floating layer was represented as a layered model (*i.e.*, the phthalocyanine is on the water layer). It was done for monolayer as well as for bi- or poly-layer. Each of these floating layer models was described by a theoretical stepwise electron density profile over depth (each layer was given by the thickness and averaged value of the electron density along the surface). To consider the non-ideality of interfaces (capillary waves or possible film inhomogeneity in the lateral plane), we used the known approach²³ to approximate the smearing of interlayer boundaries by transition layers described by function:

$$F(z) = \frac{1}{1 + e^{\left(\frac{z - z_0}{L}\right)}},$$

where z_0 is the boundary depth, L is the parameter of transition layer associated with the mean-square roughness (σ_z) by the equation $\sigma_z = 1.67L$. Taking into account the assignment of transition layers with the initial widths corresponding to $\sigma_z = 0.3$ nm, a smoothed electron density profile was constructed.

At the second step, the smoothed profile was broken up on the lamellae with a step of 0.1 nm, and the theoretical reflectometry calculation based on Parratt's recurrent relations²⁴ was performed. By minimizing the discrepancy between the calculated and experimental reflectometry (χ^2 function) using the least squares method, the parameters for the layer model (thickness, electron density, and root-mean-square roughness) were found as providing the best fit to the experimental data. Table 1 shows the obtained values of parameters for the layer model and their errors. The value of chi square (χ^2) is 2.56 for the range of angles from 0.2 to 0.85 E⁻¹. The best agreement was obtained for the model of bilayer film (see Table 1), where 3D aggregates are additionally present. Layer 1 and layer 2 (see Table 1) are elements of the layered model of a bilayer film.

In conclusion, it has been revealed that during the formation of floating layer, the aliphatic substituents of 1,4,8,11,15,18-hexaoctyloxy-22,23,24,25-tetrachlorophthalocyanine are smoothly displaced from the plane of phthalocyanine macrocycle into the air phase. Moreover, a stable bilayer structure with imperceptible number of included 3D aggregates was formed, the interplanar spacing in its crystal lattice being $d = 2.3$ nm. The acquired data open up a possibility for efficient applications of developed thin film materials in organic photovoltaic devices, which is based on the studied behaviour of floating layers.

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