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# Two–Dimensional Aggregation of Crown–Phthalocyanine Ligand at Air–Water Interface

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*Physico-chemical properties of monolayers of tetra-15-crown-5-phthalocyanine ligand were studied using Langmuir-Blodgett technique and fiber optic spectroscopy. Dependences between concentration of monolayer forming solution and phthalocyanine ligand aggregation degree in monolayer were established. True stable monolayers of tetra-15-crown-5-phthalocyanine ligand at the air/water interface were formed with orientation of phthalocyanine macrocycle planes parallel to the subphase surface. It was proven that absence of aggregates in solution does not guarantee absence of aggregation in the monolayer upon its formation. It was shown that studied substance generates columnar aggregates upon compression even in monolayer formed from extremely diluted solutions. Using special IR-spectroscopy techniques, it was shown that orientation of molecules relative to the substrate surface remains the same upon formation of solid ultrathin films by Langmuir-Blodgett technique.*

**Keywords:** Langmuir monolayer, phthalocyanines, aggregation degree, molecule orientation, fiber optic spectroscopy.

# Двумерная агрегация краун–фталоцианинового лиганда на поверхности раздела воздух/вода

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*Физико-химические свойства монослоев тетра-15-краун-5-фталоцианинового лиганда изучены с помощью методов монослоев Ленгмюра и оптоволоконной электронной спектроскопии. Установлена взаимосвязь между концентрацией раствора, из которого сформирован монослой, и степенью агрегации фталоцианинового лиганда на поверхности субфазы. На поверхности раздела воздух/вода получены стабильные истинные монослои тетра-15-краун-5-фталоцинаинового лиганда, в которых плоскости фталоцианиновых макроциклов ориентированы параллельно поверхности субфазы. Доказано, что отсутствие агрегатов в формирующем растворе не гарантирует отсутствия агрегации в монослое при его формировании. Показано, что при сжатии исследуемое вещество образует колончатые агрегаты даже в монослоях, сформированных из сильно разбавленных растворов. С помощью ИК-спектроскопии в поляризованном свете показано, что ориентация молекул относительно поверхности подложки не изменяется при формировании из монослоя тетра-15-краун-5-фталоцианинового лиганда пленок Ленгмюра-Блоджетт.*

**Ключевые слова:** Монослои Ленгмюра, фталоцианины, степень агрегации, молекулярная ориентация, оптоволоконная спектроскопия.

## Introduction

Unique properties of phthalocyanine macrocycles as ligands in various complexes draw attention of specialists in various fields of science due to both theoretical and practical significance of such compounds. Lability of the electronic system, Red/Ox multistablity, possibility to easily change physico-chemical properties of the complex via introduction of substituents and metal ions, ability of self-assembling of molecules into associates of various forms are the properties that make phthalocyanine ligands attractive from the standpoint of practical application in design of molecular machines and electronic devices, photovoltaic cells and field effect transistors, sensors and so on.[1-5] Abovementioned ability to self-assemble is of critical importance for practical application, as phthalocyanine nanotubes formed this way possess properties favorable for usage in electronics due to efficient electron transport over the conducting channels. But in order to employ these properties one should be able to transfer these phthalocyanine columns onto a solid substrate, for example, working electrode of the molecular electronic device. One of the most promising methods for doing so is the Langmuir-Blodgett technique, as it allows such assembly to form at the air/water interface, and then, to transfer them onto solid surface. In most cases, however, transition of such associates leads to the case, where these tubes are parallel to the solid surface because such orientation was prevalent in the monolayer, thus, ensuring the high lateral conductivity but lowering or neglecting the usefulness of electron transfer properties that are observed in normal direction (interlayer electron transfer). With this being said, successful application of these discotic compounds in electronic devices requires development of the technique that could allow one to arrange phthalocyanine tubes along the axis perpendicular to the substrate surface, *i.e.* with planes of phthalocyanine macrocycles parallel to the surface.

This problem is well known, and urgently requires development of methods that could solve it. Chemical modification of the phthalocyanine macrocycle with peripheral substituents that would enhance the spreading of the molecules in the monolayer, such as hydroxyalkyl,[6-12] alkoxycarbonyl,[13,14] and other[15-19] groups is one of the prime methods to enable planar orientation of phthalocyanine molecules in precursor monolayer. However, in our view, peripheral substitution with crown ether fragments seems most promising due to the fact that substituents of this type affect the properties of the whole phthalocyanine ligand in a way that facilitates the planar arrangement of discotic molecules in the monolayer and aggregation of them into columns on the substrate afterwards via Langmuir-Blodgett or Langmuir-Schaffer deposition technique.

In our previous work[20] we used so-called "spreaders", amphiphilic compounds that form stable monolayers at air/water interface, to improve the distribution of crown-substituted phthalocyanine ligand over water subphase. But this method introduces new substance into the monolayer, and could lead to interaction between spreader and studied compound, decrease effective amount of columnar structures on the working surfaces and change optical behavior of LB films obtained from such mixed monolayer. Thus, in this work we synthesised and studied physico-chemical properties of monolayers of tetra-15-crown-5-phthalocyanine ligand $H_2R_4Pc$ ($R_4Pc^{2-}$ is 4,5,4′,5′,4′′,5′′,4′′′,5′′′-tetrakis (1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninate ion), studying effects of extreme dilution of monolayer forming solution on aggregation behaviour in monolayer by means of non-invasive fiber optic spectroscopic *in situ* measurement technique.

## Experimental

Dicyanobenzo-15-crown-5 was synthesized according to a previously described procedure.[21] Tetra-15-crown-5-phthalocyanine $H_2R_4Pc$ was synthesized according to a known procedure[22] by melting of dicyanobenzo-15-crown-5 with hydroquinone in an evacuated tube at 180 °C for 12 h. The subsequent chromatographic purification on a column with neutral alumina (chloroform-methanol (96:4) as eluent) gave $H_2(R_4Pc)$ in 60 % yield. UV-vis ($CHCl_3$) $\lambda_{max}$ nm (lg ε): 701 (5.10), 661 (5.01), 644 (4.66), 601 (4.38), 420 (4.48), 348 (4.88). $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta_H$ ppm: 3.93 (m, 32 H, $C(3)H_2$, $C(4)H_2$); 4.22 (m, 16 H, $C(2)H_2$); 4.77 (m, 16 H, $C(1)H_2$); 8.91 (s, 8 H, HAr). MS (MALDI-TOF) *m/z*: 1275.3 $[H_2(R_4Pc)]H^+$.

Monolayers of $H_2(R_4Pc)$ were formed from chloroform solution (analytical grade). Compression isotherms of monolayers were obtained using KSV mini automated Langmuir trough maximum area between the barriers of which was 283 $cm^2$. The surface pressure was determined by the Wilhelmy method using a platinum measuring plate. Solutions of crown-phthalocyanines were deposited onto the subphase surface (deionized water (Vodolei)) using a micropipette (Distriman Gilson). Volume of deposited solution varied with varying concentrations in such a way, that total number of ligand molecules remained the same. The time of solvent evaporation was 15 minutes, and the rate of monolayer compression was 0.1 $mm\cdot s^{-1}$ (0.1 $cm^2\cdot s^{-1}$).

Electronic absorption spectra of solutions in a wavelength interval of 200-900 nm were recorded on a UV 2450 PC "Shimadzu" spectrophotometer. For studing solutions, quartz cells with a thickness of 1 and 10 mm (in the case of a dilute solution) were used.

Differential reflection-absorption spectra (DRAS) of the monolayers on the water subphase surface in the wavelength range of 240-750 nm were recorded using an Avantes 2048×64 fiber optic spectrophotometer according to the method described by D. Möbius[23,24] and upgraded by us.[25,26] The UV-vis reflectometric probe with a fiber optic cable with diameter of 400 μm, combined with a 6 fiber irradiating cables, was placed perpendicularly to the studied surface at a distance of 2-3 mm from the monolayer. The signal reflected from the surface of the subphase prior to the deposition of the monolayer was used as a baseline.

Infra-red (IR) spectra were recorded in the range of 400 $cm^{-1}$ - 4000 $cm^{-1}$ using Perkin-Elmer 2000 (GX) IR-Fourier spectrometer. For estimation of molecular orientation in Langmuir-Blodgett films the two modifications of IR measurement techniques were used in this work. In the first method, VeeMAXtm 11 mirror reflection attachment with variable light incidence angle, which operates in the range from 80 to 30° with step of 1°. In the second method, registration of spectra in transmission mode was carried out with variable polarization angles of incident light. This spectrometer allows measurements in the range of polarization angles from 0 to 180° with step of 1°. Further computer processing of the spectra was carried out using standard "Spectrum" software integrated into spectrometer.[27-29]

## Results and Discussion

Stacking-type aggregation typical for studied compounds is beneficial for practical application in electronics, as was noted above, but in many cases this kind of structure is only required on a surface of a solid substrate when it is perpendicular to the substrate surface. In precursor monolayers, however, non-associated form is required, as stacking in monolayers upon spreading results in island-like structure of it, hinders formation of true monolayer, and leads to transfer of columnar structures of aggregated phthalocyanines onto solid substrate in undesired arrangement parallel to the substrate surface. Besides, even use of solutions free of aggregates can lead to formation of aggregates on subphase surface, as was shown by us previously.[20] Thus, in present work, we developed the way to form true monolayers of $H_2R_4Pc$ ligand at the air/water interface using extremely diluted solutions of studied substance for monolayer formation.

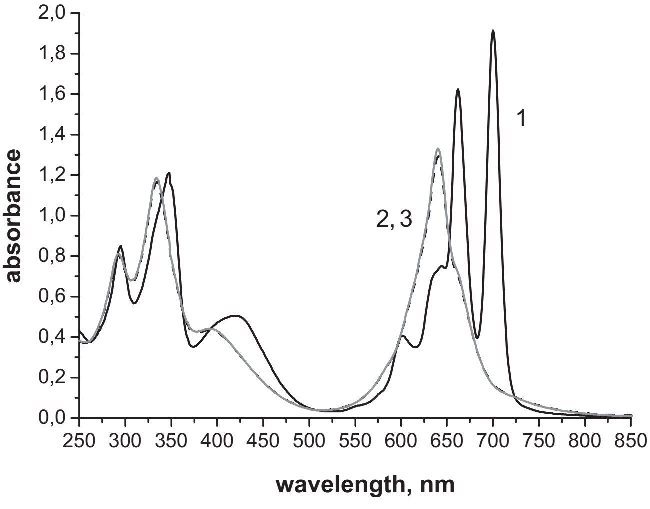

**Figure 1.** UV-vis absorption spectra of chloroform solution of $H_2R_4Pc$ (1), with additions of 2 equivalents (2), and 4 equivalents of KOAc (3).

First step of our work was to study aggregation behavior of this compound in solutions. It is well-known that crown-ethers can form complexes with alkaline metals in organic solvents, and potassium ion, ionic radius of which is larger than cavity size of 15-crown-5-fragment, can form sandwich complexes. Thereby, using spectrophotometric titration we found that addition of 2 equivalents of potassium acetate (so there are two crown-ether-fragments for each cation) leads to peculiar spectral changes. UV-vis absorption spectra of dilute $H_2R_4Pc$ solution (Figure 1, curve 1) and $H_2R_4Pc$ solution with addition of potassium acetate (Figure 1, curve 2) show significant differences in positions and intensity of several absorption bands, and addition of more $K^+$ ions does not lead to further spectral changes (Figure 1, curve 3). Implying that addition of $K^+$ ions to solution leads to aggregation of crown-phthalocyaninate molecules we can see that monomer form of the ligand (as in diluted solutions without any additions) is mainly characterized by splitted *Q* band at 660 and 700 nm, and spectrum of aggregated form lacks these bands, and is characterized by intensive peak at 645 nm. These results are in a good agreement with literature data.[30]

Thus, using these data we can discriminate between monomeric and aggregated forms of ligand in monolayer on the water subphase by employing fiber optic spectroscopy technique for measuring differential reflection-absorption spectra (DRAS) of studied monolayer upon deposition of solution onto subphase, evaporation of solvent, subsequent formation of monolayer, and its further compression. So, in order to fully understand the aggregation process in such two-dimensional environment as Langmuir monolayer, we began our investigation with monolayer formed from previously studied solution, *i.e.* solution with concentration of $1\cdot10^{-4}$ M. And as can be seen from Figure 2, as expected, DRAS of the monolayer corresponds to that of aggregated form (apart from red shift by ~10 nm typical for an environmental polarity change that occurs due to transition from chloroform solution to aqueous subphase surface), and further compression of the monolayer, which can lead to further aggregation, does not cause any further spectral changes, apart from increase of overall intensity associated with growing of the monolayer surface density. This phenomenon, as was explained above, is associated with the fact that molecules in monolayer formed from a solution with such concentration are prone to association into aggregates with planes close to the normal to the subphase surface.

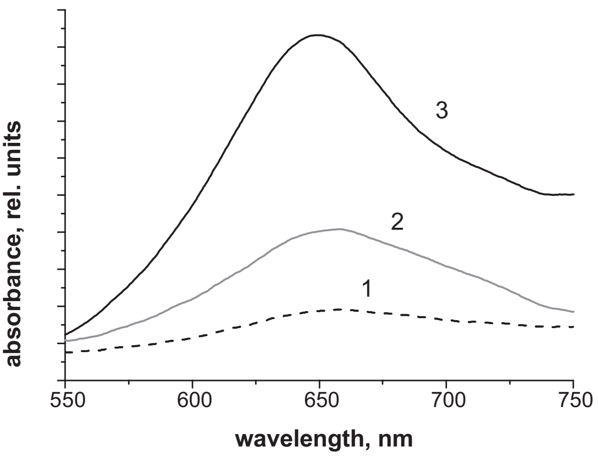

**Figure 2.** Differential reflection-absorption spectra of monolayer of $H_2R_4Pc$ formed from solution with concentration of $10^{-4}$ M at surface pressure of 0 (1), 2 (2), and 14 (3) mN/m.

However, dilution of forming solution by 10 times leads to quite different spectral picture and different compression isotherms as well. Figure 3 shows compression isotherms of monolayers formed from solutions with various degree of dilution. We believe that dilution of the solution past some critical concentration facilitates formation of some kind of coordination interactions between $H_2R_4Pc$ crown-phthalocyanine ligand and chloroform in the process of monolayer formation that leads to the state where chloroform molecules are integrated into monolayer structure, probably, in a similar way as was reported for the case of chloroform embedded in the X-ray structure of ruthenium monophthalocyanines monocrystals upon its formation.[31,32] Thus, monolayers formed from solutions with concentration of $2.5\cdot10^{-6}$ and $10^{-7}$ M have drastically different monolayer areas corresponding to rise of surface pressure ($A_0$ = 1400 and 5000 Å$^2$/molecule, respectively), whereas compression isotherms for monolayers formed from less diluted solutions ($10^{-4}$ and $10^{-5}$ M) exhibit about the same $A_0$ monolayer areas.

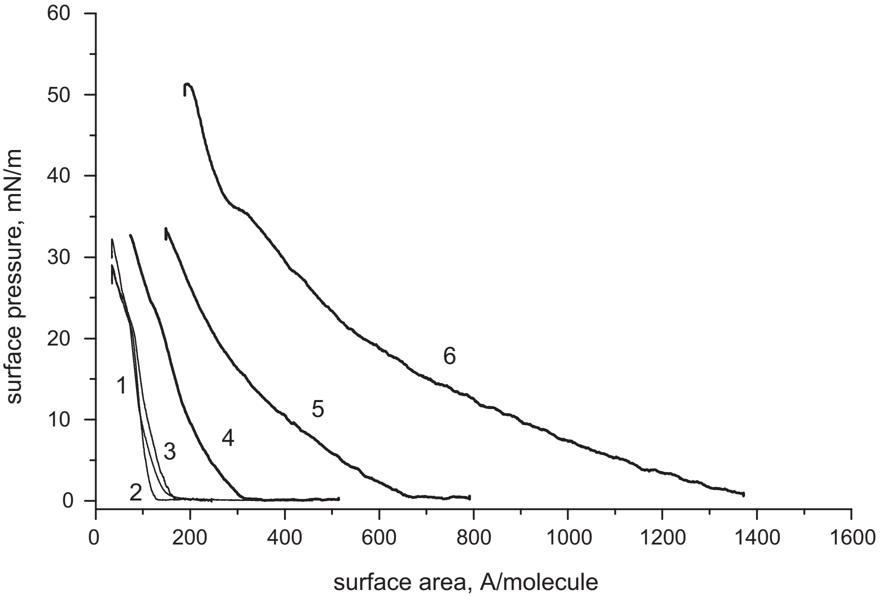

**Figure 3.** Compression isotherms of $H_2R_4Pc$ monolayers formed from solutions of various concentrations: (1) $1.34 \cdot 10^{-4}$ M, (2) $1.1 \cdot 10^{-4}$ M, (3) $6.7 \cdot 10^{-5}$ M, (4) $1.6 \cdot 10^{-5}$ M, (5) $8 \cdot 10^{-6}$ M, (6) $2.5 \cdot 10^{-6}$ M.

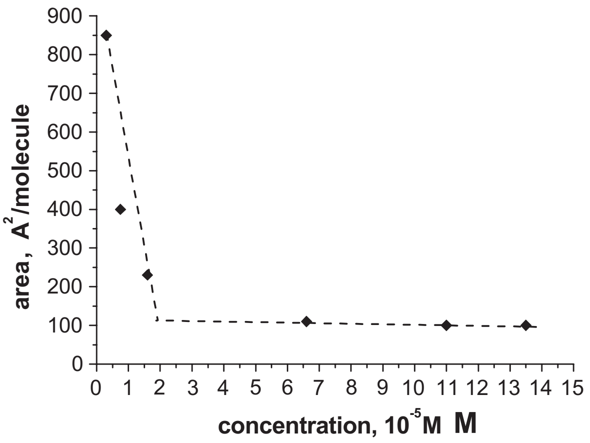

**Figure 4.** Dependence of monolayer area on concentration of monolayer forming solution.

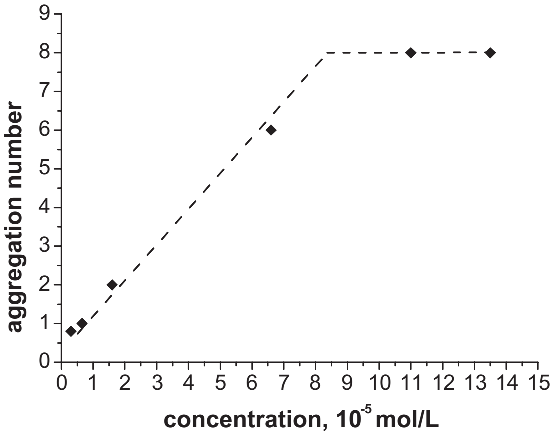

**Figure 5.** Dependence of aggregation number on concentration of monolayer forming solution.

By extrapolation of isotherm linear parts corresponding to liquid-condensed state of ligand monolayer towards X axis, we can determine area per molecule. Dependence of this area on forming solution concentration is shown in Figure 4. This dependence shows a presence of a threshold point that divides whole curve into two concentration areas: in first, $A_0$ of the monolayer significantly depends on concentration of the forming solution, and in second, this dependence is insignificant. Area of about 600 Å²/molecule is equivalent to planar orientation of the ligand molecule (according to theoretical calculation). At concentration of $2.5 \cdot 10^{-6}$ M, $A_0$ equals 850 Å²/molecule, such large area indicates that ligand molecules are parallel to the subphase surface.

From thermodynamic point of view, monolayer of chaotically moving ligand molecules, on large area has significantly higher entropy in comparison to the system of same number of aggregated molecules. However, in this case, entropic advantage can be compensated by contribution of enthalpy to free energy of the system, which is commensurable for two considered states of the system (molecules in stacking-aggregation, and molecules with plane arranged parallel to the subphase surface that interact and contact with water by all four crown-ether-groups).

For quantitative analisis of ligand molecule aggregation we used Volmer equation [33] modified in similar ways by us and other researchers:[34-39]

$$\pi(A - A_0) = k\mathrm{T},$$

where $\pi$ is surface pressure, N/m; $A$ is area per molecule in monolayer, m²/molecule; $A_0$ is limiting value of area per molecule, m²/molecule.

But, as we do not know exact molecular weight of a single particle in monolayer, *i.e.* we do not know aggregation state of the ligand molecules, so for the system, structural elements of which are not single molecules, but aggregates of them that consist of $n$ molecules with surface area $A_n$, we can use this expression in the following form:

$$\pi(S - N_n \cdot A_n) = N_n k\mathrm{T}$$

or, if we divide both parts of the equation by number of molecules in the monolayer:

$$\pi(A - A_n/n) = k\mathrm{T}/\mathrm{n}, \text{ and finally:}$$
$$\pi A = \pi A_n/n + k\mathrm{T}/n,$$

where π is surface pressure, N/m; $A_n$ is surface area of one aggregate; $N_n$ is number of agregates (kinetic units) in monolayer; $A$ is surface area per molecule in the monolayer; $n$ is the number of molecules in one aggregate; $k$ is Boltzmann constant, $k = 1.38 \cdot 10^{-23}$ J/K; T is temperature, that was 293 K for all experiments; $S$ is macroscopic area of monolayer, m$^2$ and $N_n \cdot A_n = S_0$ is excluded macroscopic area, m$^2$ (Langmuir trough area that corresponds to the state with most dense packing of the monolayer).

In the absence of significant attractive forces between separate particles, experimental data graph has linear form in $\pi A$ - $\pi$ coordinate system. By extrapolation of this line to y-axis we are able to obtain value $k\mathrm{T}/n$ and using it one can calculate $n$ - number of molecules in one aggregate. Obtained in such a way dependence of aggregation degree on concentration of forming solution is shown in Figure 5.

As can be seen from the Figure 5, number of molecules in aggregate is 8 at concentrations higher than $8 \cdot 10^{-5}$ M, and with decrease of concentration, this number also decreases. At concentrations of $6.5 \cdot 10^{-6}$ M and lower, molecules do not aggregate. Thus, increase of concentration leads to increased aggregation, number of particles on the surface decreases, and to register interaction between them, they should be located more closely, this is why $\pi$-$A$ isotherms are shifted to the higher areas in the case of low concentrations. Decrease of aggregation degree obtained from experimental data below 1 is, apparently, associated with involvement of chloroform into the monolayer structure.

As aggregation begins even at small concentrations of forming solution, and aggregation number increases quite non-monotonically upon increase of this solution concentration, we can assume that bend on dependence shown in Figure 4 is associated with change of aggregate orientation in relation to subphase surface. Apparently, at low concentrations axis of phthalocyanine molecule aggregates are perpendicular to the subphase surface (or otherwise stacks are vertical), and at high concentrations – aggregate axis are parallel to the surface. Such change of aggregates orientation with increase of their size is associated with the fact that, in the first case (axis is perpendicular to the subphase surface) increase of aggregate number leads to energetically disadvantageous location of all four crown-ether groups of upper molecules in the air phase. In the second case, number of such groups is two times lower.

These results allowed us to suggest the planar orientation of phthalocyanine rings of ligand molecules on the water subphase. In order to check this assumption, to determine more precisely the state of molecules in the monolayer at different surface pressure values, and to study processes, which occur in monolayer upon compression, we employed fiber optic spectroscopy. This technique allows one to record spectra of non-aggregated, thinly and evenly distributed monolayers formed from extremely diluted solutions.

Spectral measurements of the monolayers showed some differences between monolayers formed from solutions with concentrations of $10^{-4}$ and $10^{-5}$ M. Whereas, the monolayer formed from $10^{-4}$ M solution was prone to total aggregation of ligand molecules as it is shown in Figure 2, there are two bands characteristic to the unassociated form of the ligand in the spectra of monolayer formed from solution with concentration of $10^{-5}$ M as can be seen from Figure 6a (curve 1). And spectrum typical for $\mathrm{H_2R_4Pc}$ aggregates arises here only at surface pressures about 7 mN/m (curve 3). Further dilution of the monolayer forming solution leads to further prominence of two peaks at 666 and 705 nm in spectra of the expanded monolayer as shown in Figure 6b-c, curves 1 for monolayers formed from solutions with concentration of phthalocyanine ligand of $10^{-6}$ and $10^{-7}$ M, respectively. Spectral changes associated with aggregation for these

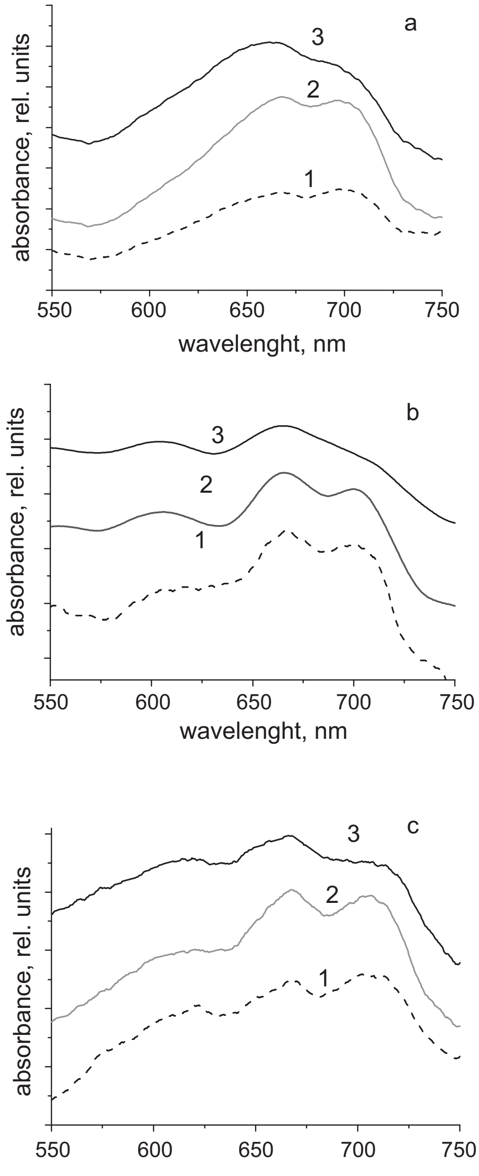

**Figure 6.** Differential reflection-absorption spectra of monolayers formed from solutions with concentrations of (a) $10^{-5}$ M, (b) $10^{-6}$ M, and (c) $10^{-7}$ M at surface pressures of (1) 0, (2) 2, and (a, 3) 7, (b, 3) 9, (c, 3) 11 mN/m.

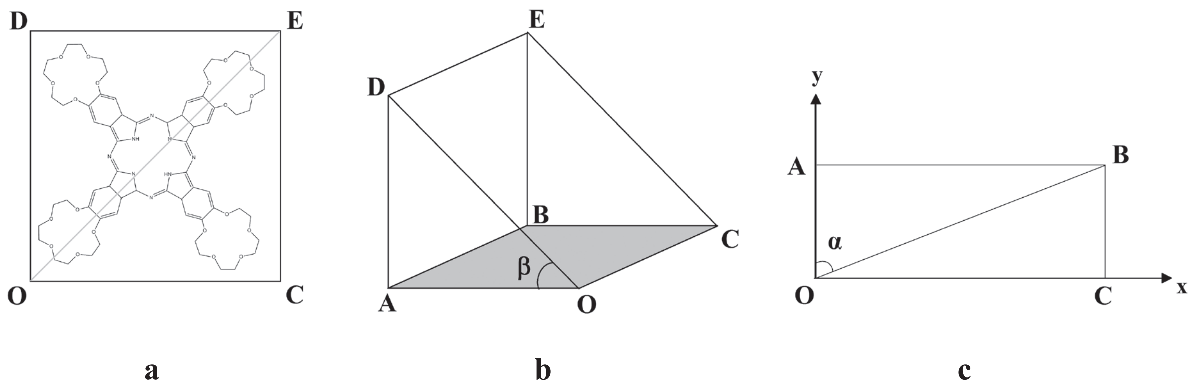

**Figure 7.** Model used for geometric constructions. Phthalocyanine molecule is inscribed into square ODEC (a) angle β is angle of inclination of ligand molecule plane to the sapphire surface (b) angle α is an angle between diagonal of the planar projection of square and direction of monolayer transfer.

solution concentrations begin at surface pressure of 9 mN/m and 11 mN/m, respectively (Figure 6b-c, curves 3). The fact that such changes are observed for various solutions at various values of surface pressures can be explained by coordination of chloroform in the monolayer structure mentioned above, as it impedes occurrence of π-π interactions between separate crown-phthalocyanine ligand molecules and thereby hinders stacking upon the monolayer compression.

Now, knowing what orientation of single $H_2R_4Pc$ molecules and aggregates corresponds to various values of surface pressure and areas of isotherms, it is interesting to know if this orientation persists upon transfer of the monolayer onto solid substrate. And IR spectroscopy techniques can be used for determination of orientation of the molecules on solid/air interface.[27-29]

For estimation of orientation of molecules in single-layer Langmuir-Blodgett films of $H_2R_4Pc$ ligand formed from diluted chloroform solution ($5·10^{-6}$ M) and transferred onto sapphire plates at surface pressures of 20 and 40 mN/m we used two IR-spectra registration techniques: reflection spectra with variable light incidence angle and transmission spectra at various positions of rotating polarizer with subsequent geometrical results processing. Chosen values of transfer surface pressures correspond to planar (20 mN/m) and perpendicular (40 mN/m) arrangements of molecule planes with respect to the subphase surface. Orientation of phthalocyanine ligand molecule in regard of sapphire surface was determined by value of light incidence angle (first method) or angle of polarization plane (second method), at which the most intensive bands corresponding to planar oscillations of indolic, pyrrolic, and benzene cycles (1330, 1430, 1490, and 1563 $cm^{-1}$) were observed. Other observed bands in recorded spectra correspond to crown-ether groups and substrate.

As it is well known, maximum intensity of reflection spectrum bands is achieved upon perpendicular incidence of light beams to plane of the studied discotic molecule. Measurements showed that oscillation absorption bands of phthalocyanine ligand in the spectrum of the film transferred at 20 mN/m were observed at light beam incidence angles of $75-80^{o}$ (incidence angle varies from 80 to $30^{o}$). Obtained result indicates that planes of discotic ligand molecules are arranged almost horizontally, at the angle no more than $10-15^{o}$ to the surface.

In analysis of the spectra recorded at various polarization angles of normal incident light, we carried out the geometrical constructions based on two reasonable assumptions (Figure 7). First, molecule was assumed to be a square, in which maximum absorption of bands of planar oscillations mentioned above had to be observed upon coincidence of incident light polarization direction with diagonal of this square. Second, we assumed that edge of this square, which relied on substrate surface, is parallel to either *x*-axis (perpendicular to direction of film transfer) or *y*-axis (parallel to direction of film transfer). Second assumption is based on the fact that upon variation of polarization direction we always observed two maxima of intensity of spectrum bands located symmetrically in regard of film transfer direction. If molecules were arranged with some angle to either *x*- or *y*-axis, then several asymmetrical maxima would be observed.

If molecule is a square (ODEC), then its projection onto the plane (sapphire surface) is a rectangle ABCO. Let us consider this rectangle. Angle α is angle between the side of the rectangular projection of the molecule and its diagonal, and it corresponds to the light polarization angle, at which most intensity of bands of indolic, pyrrolic, and benzene cycles planar oscillation would be observed. Angle β is an angle between plane of the molecule and substrate surface. Then OD = OC = AB, and cosβ = AO/OD = AO/AB, but AO/AB = ctg α, *i.e.* cosβ = ctgα.

Therefore, knowing angle α on the plane, we can express the desired tilt angle of discotic molecules relative to the substrate surface - angle β.

In the case when α < 45°, ctg α > 1, and cos β does not exist. This means that side of the square DO (and not OC) lies on the substrate surface, i.e. molecules stay parallel to the y-axis and cos β = ctg(90° - α).

Angle α for a film transferred at surface pressure of 20 mN/m was 45°-46° (Figure 8a), which corresponds to cosβ =0.9-1 and β = 0°-15°, *i.e.* orientation of molecules in the Langmuir-Blodgett film is close to the planar. And for samples obtained at 40 mN/m, angle α was 5° (Figure 8b), and in recalculation for spatial angle gave value of β = 85°-

90°, *i.e.* inclination angle of planes of discotic molecules in relation to substrate surface was close to 90°.

Coincidence of estimations of molecule orientation obtained using two different methods for the film transferred at 20 mN/m confirms validity of the proposed geometric approach for measurements with usage of rotating polarizer.

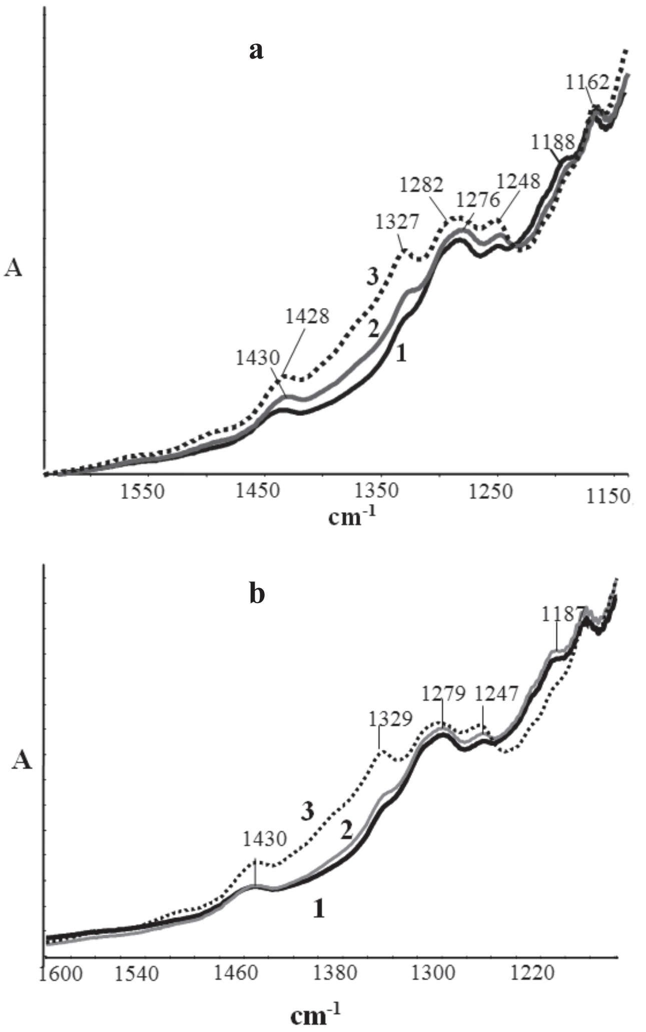

**Figure 8.** IR-spectra of Langmuir-Blodgett film of $H_2R_4Pc$ on sapphire surface formed from monolayer with surface pressure of (a) 20 mN/m and (b) 40 mN/m. Polarization angle α for (a): (1) 40°, (2) 46°, (3) 56°; for (b) (1) 25°, (2) 15°, (3) 5°.

Obtained results are in a good agreement with concepts of aggregational behavior of molecules in the monolayer presented previously in this work. Thus, performed studies confirmed that orientation of ligand molecules remains the same upon transition of monolayer fron water surface onto solid substrate.

## Conclusions

Using Langmuir-Blodgett technique and fiber optic spectroscopy we were able to observe 2-dimensional aggregation of the crown-phthalocyanine ligand molecules in the monolayer formed from solutions that did not exhibit any aggregation behavior. It was found that $H_2R_4Pc$ molecules can form columnar aggregates on air/water interface upon formation of the monolayer, and concentration of the compound in the forming solution plays a major role in this process. So, even solutions with concentrations of $10^{-4}$ M, when no aggregation is observed, can result in formation of aggregation in 2-dimensional environment of Langmuir monolayer.

It was shown that monolayers formed from solutions with concentrations of $10^{-6}$ M and less are true monolayers with planes of phthalocyanine macrocycle parallel to the subphase surface at low surface pressure. Spectra of monolayers of unassociated and stacked forms of the $H_2R_4Pc$ molecules were registered, and it was shown that studied substance forms columnar aggregates upon compression even in monolayer formed from very diluted solution.

Using special methods of IR-spectroscopy, namely, reflection spectra with variable light incidence angle and transmission spectra at various positions of rotating polarizer with subsequent geometrical results processing techniques, we were able to confirm, that orientation of molecules in ultrathin film corresponds to one that was observed in the monolayer from which it was transferred, *i.e.* planes of the ligand molecules are parallel to the substrate surface in the case of transfer at low surface pressure, and are perpendicular at high surface pressures, which correspond to formation of extensive stacking-aggregates.

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