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# Structure of Monolayers of Copper Tetra-(3-nitro-5-*tert*-butyl)-phthalocyanine at the Air–Water Interface

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The structure of floating layers of soluble copper tetra-(3-nitro-5-*tert*-butyl)-phthalocyanine (CuPc\*) is studied through surface pressure–area ( $\pi$ – $A$ ) isotherms measured at various initial surface concentrations ( $N_0$ ) of CuPc\*. In the gaseous layers, the CuPc\* molecules are surrounded by a hydration sphere. Condensation of the layers under compression results in an increase in the tilt angle of the CuPc\* molecules relative to the air–water interface. Though it is accompanied by a loss of weakly bound water, an inner part of the hydration sphere sustains compression and enters the condensed layers. Depending on the  $N_0$  and  $\pi$  values, the molecular tilt angle ranges from 30 to 90° indicating the phase states of the  $\beta$ -,  $\alpha$ -, and  $\chi$ -types. The different nature of the bilayers formed through compression of the rare monolayers and through spreading of large amounts of CuPc\* is stated.

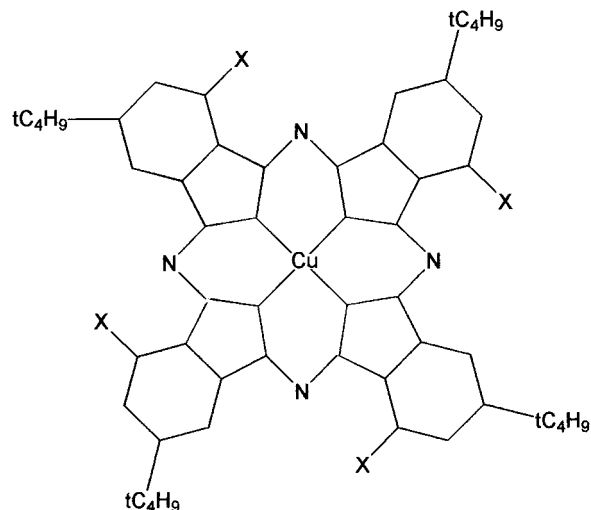
## Introduction

Langmuir–Blodgett (LB) films of phthalocyanines are of importance in many fields of applied research.<sup>1</sup> Because of high solubility in organic media and facilities to modify the molecular structure, *tert*-butyl substituted derivatives (Pc', structure I) are convenient objects to study relationships between the supramolecular structure and physical properties of phthalocyanine LB films. However, LB films of CuPc\* (structure II) seem to be a more prospective material than ones of CuPc' because of enhanced chemical stability of the nitro-substituted phthalocyanine macrocycle.<sup>2,3</sup> Because crystalline phthalocyanines are prone to polymorphic transformations, the LB film structure depends on compression extent.<sup>4</sup> Therefore, the present paper seeks to analyze the  $\pi$ – $A$  isotherms characterizing compression of the CuPc\* layers and, thus, to determine the structure of the CuPc\* layers depending on conditions of layer formation.

## Experimental Section

CuPc\* was synthesized from 3-nitro-5-*tert*-butylphthalonitrile<sup>2</sup> and characterized with its NMR, IR, and UV–vis spectra. Crude CuPc\* consists of four spectroscopically identical structural isomers that were separated on an alumina column using benzene and benzene–pyridine mixtures as an eluting agent. The most symmetrical  $C_{4v}$  isomer (37% of the crude sample) eluted with benzene–pyridine (5:1) was used in the work.

The layers were prepared on an MDT (Zelenograd, Russia) Langmuir trough. Solution in benzene ( $6.25 \times 10^{-4}$  M) was spread



I – CuPc' (X=H); II - CuPc\* (X=NO<sub>2</sub>)

on tridistilled water. The solvent was allowed to evaporate over 10 min, and the layers were compressed during a period of 30 min. The experiments were carried out at a temperature of  $20 \pm 1$  °C and a relative humidity of  $50 \pm 1\%$ .

Geometric characteristics of a CuPc\* molecule (Table 1) were calculated from data on van der Waals atomic radii. Analysis of the  $\pi$ – $A$  isotherms was performed by means of the linear least-squares method. The correlation coefficient used as the criterion of linearity was not less than 0.9990.

**Table 1. Geometric Characteristics of the CuPc\* Molecule**

overall dimensions, nm	area per molecule, nm <sup>2</sup>			
	$A_{\text{face}}$		$A_{\text{edge}}$	
	rectangle describing molecular contour	projection	rectangle describing molecular contour	projection
	$1.8 \times 1.8 \times 0.65$	3.2	2.4	1.2

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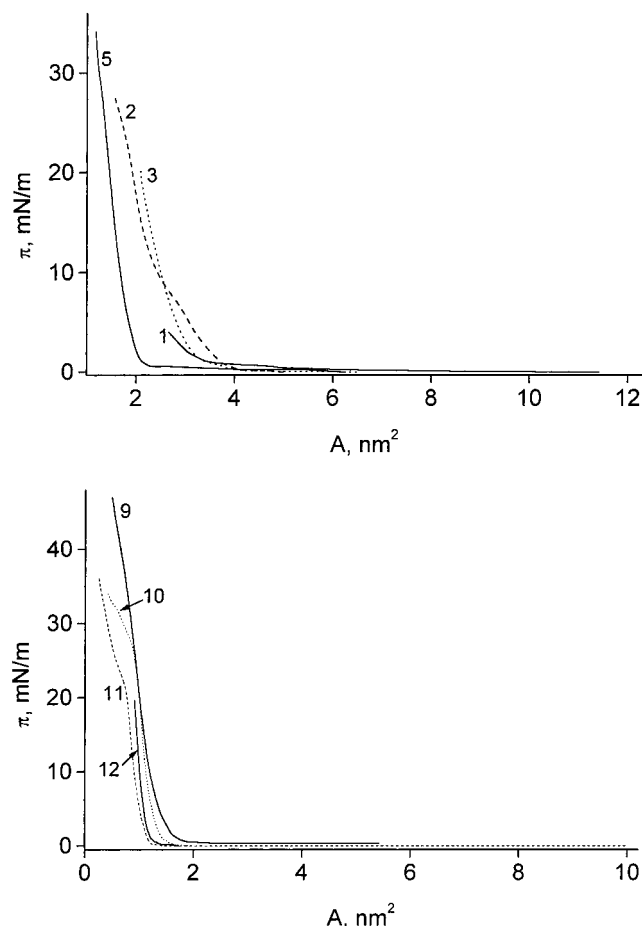
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**Figure 1.** The  $\pi$ - $A$  isotherms for the CuPc\* layers. The numbers correspond to those in Table 2.

## Results and Discussion

**1. Phase States of CuPc\* in Floating Layers.** The  $\pi$ - $A$  isotherms of CuPc\* at the air-water interface are shown in Figure 1. In general, the isotherms are lines without pronounced linear segments. Area per molecule depends not only on the  $\pi$  but on the  $N_0$  value as well: the more  $N_0$ , the less  $A$  values measured at equal  $\pi$ . Such dependence observed earlier for CuPc' <sup>5</sup> is caused by assembling of the molecules accompanied by increase in the molecular tilt angle relative to the air-water interface. Therefore, in this work, we formed the layers within a broad range of the  $N_0$  values, limiting coverage values at "face-on" molecular orientation ranging from 0.12 to 1.43 (Table 2).

To study the supramolecular structure of the layers, the following considerations were taken into account. The equation of state for the ideal two-dimensional gas is known to be <sup>6</sup>

$$\pi A = kT$$

In 1925, Volmer <sup>7</sup> showed that the area of spread molecules should not be neglected and proposed the equation of state for the real two-dimensional gas as follows:

$$\pi(A - A_{\text{mol}}) = C$$

where  $A_{\text{mol}}$  is the limiting molecular area in a fully compressed layer and  $C$  is a constant at fixed temperature.

Thus, characteristics of gaseous layers may be determined from experimental data through construction of the linear  $\pi$ - $A^{-1}$  and  $\pi A$ - $\pi$  plots in accordance with eqs 1 and 2:<sup>8</sup>

$$\pi = a + CA^{-1} \quad (1)$$

$$\pi A = C + \pi A_{\text{mol}} \quad (2)$$

where  $C$  is characteristic of layer compressibility. Lately, Abramson et al. <sup>9</sup> analyzed  $\pi$ - $A$  isotherms of fatty acids and found that the  $\pi$ - $A^{-1}$  plots are nonlinear for the gaseous layers but linear for the liquid ones. This fact indicating that the linearity is due to homogeneity of the layers rather than the gaseous state inspired us to analyze the phase state of CuPc\* at the air-water interface using eqs 1 and 2 simultaneously.

The  $\pi$ - $A^{-1}$  plots characterizing compression of the CuPc\* layers consist of linear and nonlinear portions (Figure 2). From the coordinates of the intersection points of straight lines approximating the linear portions, the limits of the one-phase regions ( $\Delta\pi_1$ ) and effective molecular areas ( $A_{\text{eff}}$ ) at the phase onset may be determined. The  $\pi A$ - $\pi$  plots (Figures 3 and 4) for layers constructed in accordance with eq 2 also consist of several linear portions, the first portion corresponding to the gaseous state and the rest corresponding to the condensed ones. Thus, the limits of the one-phase regions ( $\Delta\pi_2$ ) as well as the  $A_{\text{mol}}$  values may be determined.

The layers of CuPc\* formed at  $N_0$  up to ca.  $10 \times 10^{-7}$  mol m<sup>-2</sup> exhibit the gaseous region. In the gaseous state, the  $A_{\text{eff}}$  value equal to 10.3 nm<sup>2</sup> is the largest at the minimum  $N_0$  value. At moderate concentrations ( $1.0 \times 10^{-7} < N_0 < 2.1 \times 10^{-7}$  mol m<sup>-2</sup>),  $A_{\text{eff}}$  is ca. 5–6 nm<sup>2</sup> being 1.5 times higher than an area of the main projection of the CuPc\* molecule (Table 1). These facts indicate that the CuPc\* molecules are surrounded by a hydration sphere. Because such a phenomenon is not observed in the CuPc' layers, <sup>6</sup> nitro groups should be considered as centers of hydration. Isotherms 2 and 3 measured at equal  $N_0$  (Figure 1) demonstrate that stability of the gaseous state to compression is susceptible to minute variations of initial conditions of layer formation. This fact can be interpreted in the following way. Obviously, stability of the gaseous state depends on the size of the hydration sphere surrounding the CuPc\* molecules. The size is determined by local surface concentrations of CuPc\*. Because of unevenness of benzene spreading at the subphase surface, these concentrations deviate from an average  $N_0$  value acting as a factor controlling homogeneity of the uncompressed layers and, thus, limiting reproducibility of the isotherms.

Compression of the gaseous layers entails condensation manifesting in, first, a sharp decrease in layer compressibility (an increase in the  $C'$  values by 20–50 times) and, second, a decrease in the molecular area (especially, a decrease in the  $A_{\text{eff}}$  value). The latter indicates that condensation is accompanied not only by the change in the molecular tilt angle but also by a partial loss of the hydration sphere. The  $\Delta\pi_1$  and  $\Delta\pi_2$  values (Table 2) are close for the condensed monomolecular layers but differ substantially for the gaseous ones. Taking into account isotherm 1, one can understand a cause of this difference. According to eq 1, a part of the gaseous region where an area per molecule decreases because of a loss of the hydration sphere without the change in the tilt angle is supposed erroneously as a two-phase region. The inequal-

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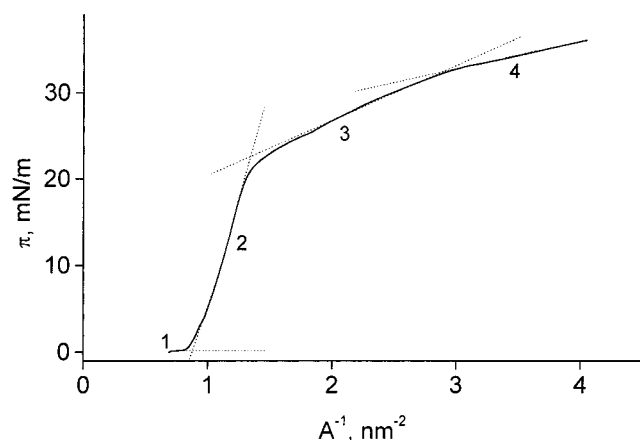
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**Table 2.** Characteristics of the CuPc\* Layers at the Air–Water Interface Determined from the Langmuir Isotherms at Various Initial Surface Concentrations<sup>a</sup>

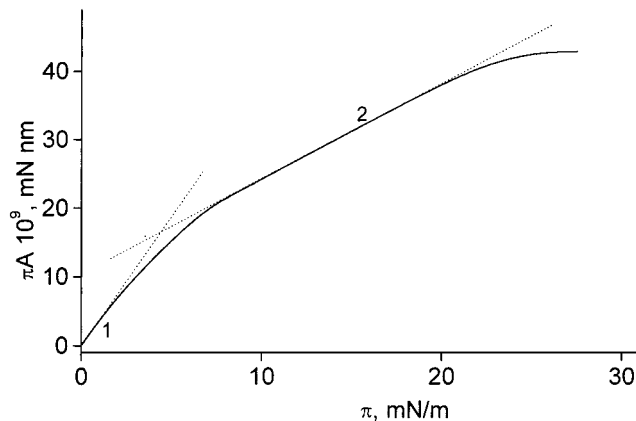
no.	$N_0 \times 10^7$ , mol m <sup>-2</sup>	coverage		phase state	eq 1			eq 2		$\psi$ , deg
		face-on	edge-on		$\Delta\pi_1$ , mN m <sup>-1</sup>	$A_{\text{eff}}$ , nm <sup>2</sup>	$C' \times 10^{21}$ , J	$\Delta\pi_2$ , mN m <sup>-1</sup>	$A_{\text{mol}}$ , nm <sup>2</sup>	
1	0.9	0.12	0.04	MG	<2	10.3	5.1	<4	2.6	0
2	1.1	0.16	0.05	MG	<2	5.0	6.3	<2.5	3.4	0
3	1.1	0.16	0.05	MC	>7	3.6	77	7–22	1.4	60
				MG	<0.8	6.6	2.1	<0.8	3.5	0
4	1.2	0.17	0.05	MC	>7	3.2	119	7–20	1.7	45
				MG	<0.7	5.0	4.8	<4	2.2	35
5	1.7	0.24	0.08	MC	>10	2.2	187	>16	1.2	90
				MG	<2	6.4	2.9	<10	1.7	45
6	2.0	0.28	0.09	MC	>5	2.0	103	>10	1.0	90
				MG	<1	6.2	1.1	<3	1.9	40
7	2.1	0.30	0.10	MC	>9	1.8	65	>7	0.90	90
				MG	<1	5.5	2.0	<2	2.1	35
8	2.2	0.31	0.12	MC	>10	2.0	75	12–30	0.85	90
				MG	<0.6	3.4	1.9	<2	1.6	50
9	3.0	0.44	0.15	MC	>5	1.6	115	>3	1.2	90
				MG	<1	2.3	2.1	<0.8	1.6	50
10	4.0	0.59	0.20	MC	1–6	1.7	32	2–6	1.2	90
				MC	8–28	1.3	65	9–17	0.85	90
11	6.1	0.87	0.29	B	>40	0.80	13	>37		
				MG	<0.4	1.9	1.0	<4	1.3	70
12	8.8	1.20	0.41	MC	10–21	1.3	91	5–15	0.95	90
				B	>32	0.85		28–31		
13	10.2	1.43	0.47	MG	<0.6	1.5	2.1	<3	1.1	90
				MC	6–20	1.1	51	3–9	0.85	90
14	10.2	1.43	0.47	B	22–31	0.75	7.1	26–33		
				P	>32	0.35	3.1			
15	10.2	1.43	0.47	MG	<0.2	1.7	4.4	<2.5	1.1	90
				MC	>8.5	1.1	90	3–13	0.90	90
16	10.2	1.43	0.47	B				>13	0.80	
				B	2–12	0.95	69	2–14	0.70	

<sup>a</sup>  $N_0$ , initial surface concentration.  $\psi$ , molecular tilt angle in a phase. MG, monolayer gaseous; MC, monolayer condensed; B, bilayer; P, polylayer.  $\Delta\pi_1$  and  $\Delta\pi_2$ , pressure intervals of the one-phase state.  $A_{\text{eff}}$  and  $A_{\text{mol}}$ , effective and actual molecular areas at the onset of a phase.  $C'$ , characteristic of layer compressibility (per molecule).

**Figure 2.**  $\pi$ – $A^{-1}$  plot for isotherm 11: 1, monolayer gaseous; 2, monolayer condensed; 3, bilayer; 4, polylayer.

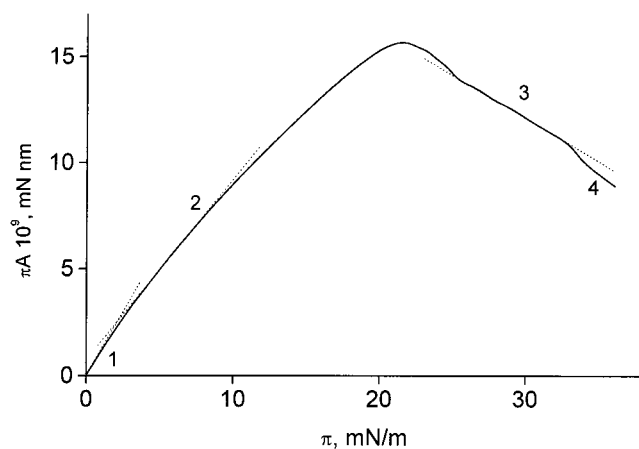
ity  $A_{\text{eff}} > A_{\text{mol}}$  holding in all phase states indicates that under compression the CuPc\* molecules lose only an external part of the sphere whereas an inner one subsists and enters the condensed monolayers. Because the  $C'$  values for the condensed layers fall in a broad interval  $(32\text{--}187) \times 10^{-21}$  J, the inner hydration sphere may be hardly considered as rigidly structured.

Comparing  $A_{\text{eff}}$  and  $A_{\text{mol}}$  in the condensed layers with  $A_{\text{edge}}$  (Table 1) shows that at high  $\pi$  and  $N_0$  values the bi- and polymolecular layers are formed (isotherms 9–13 in Table 2). Monolayer–bilayer transition under compression is accompanied by an increase in compressibility which is particularly explicit on the  $\pi$ – $A^{-1}$  plots at  $\pi > 20$  mN m<sup>-1</sup> (Figure 2). Corresponding  $\pi A$ – $\pi$  plots have an inflection point (Figure 4) where the slope becomes

**Figure 3.**  $\pi A$ – $\pi$  plot for isotherm 2: 1, monolayer gaseous; 2, monolayer condensed.

negative and the equation of state does not hold. Further compression generates polyphase and polymolecular states as, on one hand, nonlinearity of the  $\pi A$ – $\pi$  plot at  $\pi > 30$  mN m<sup>-1</sup> (Figure 4) and, on the other hand, the  $A_{\text{eff}}$  values less than  $0.35$  nm<sup>2</sup> (isotherm 11 in Table 2) indicate.

When the bilayer is formed at the high  $N_0$  values (isotherm 13), the polymolecular phase state arises even in the uncompressed layers. Such a layer exhibits the following specific features. First, the  $A_{\text{mol}}$  value ( $0.70$  nm<sup>2</sup>) in these layers is intermediate between the  $A_{\text{edge}}$  ones in the mono- ( $0.85$  nm<sup>2</sup>) and bimolecular ( $0.40\text{--}0.45$  nm<sup>2</sup>) layers. Second, its compressibility is as low as that of one of the condensed monolayers formed at moderate  $N_0$ . Third, compression of this layer entails neither phase transitions nor collapse. These features make us consider the phase state of the layer as unique distinguished by,



**Figure 4.**  $\pi A$ – $\pi$  plot for isotherm 11: 1, monolayer gaseous; 2, monolayer condensed; 3, bilayer; 4, polylayer.

first, constructive Pc–Pc interactions directed perpendicularly to the subphase surface and, second, hydration of the polymolecular layer throughout the whole depth. For the layer characterized by isotherm 12, the analogous phase state is preceded by the ordinary ones at  $\pi < 13$  mN m<sup>−1</sup>.

**2. Structure of CuPc\* Layers.** In the rare layers with face-on coverage of 0.16, the  $A_{\text{mol}}$  values are equal to 2.6 and 3.4–3.5 nm<sup>2</sup> being close to areas of the main projection of the CuPc\* molecule and the square describing this projection, respectively. The former layer is characterized by the extremely high  $A_{\text{eff}}$  value and cannot be condensed within the experimentally reachable pressure interval. Thus, the gaseous state of the CuPc\* monolayers may be of two types differing in their stability to condensation under compression. As the  $A_{\text{mol}}$  values indicate, different stability is caused by structural factors. The  $A_{\text{mol}}$  value close to  $A_{\text{face}} = 3.2$  nm<sup>2</sup> (Table 1) indicates existence of “edge-to-edge” interactions of the CuPc\* molecules leading to parquet organization in the face-on layers. It is this organization, which may be a prerequisite of the molecular reorientation from face-on to “edge-on” under compression. In the face-on layer with  $A_{\text{mol}}$  close to  $A_{\text{face}} = 2.4$  nm<sup>2</sup> (isotherm 1), the CuPc\* molecules are oriented chaotically because of the powerful hydration sphere.

To estimate the molecular tilt angles ( $\psi$ ) and, thus, determine the phase state of CuPc\* in the condensed monolayers, the following physical model of the phthalocyanine layers appears to be useful. In the condensed monolayers, the  $A_{\text{mol}}$  value should be equal to 1.2 nm<sup>2</sup> at  $\psi = 90^\circ$  (Table 1) and dependent on  $\Psi$  in accordance with the equation

$$A_{\text{mol}} = 1.2(\sin \psi)^{-1} \quad (3)$$

In the ultimately compressed monolayers where the overlapping of adjacent molecules is the largest, perpendicular molecular orientation may be adopted, the  $A_{\text{mol}}$  value being estimated as 0.85 nm<sup>2</sup>. Table 2 presents the data on  $\Psi$  calculated through eq 3. Comparing the  $\psi$  values with ones in the copper phthalocyanine stacks of different

types,<sup>10</sup> identification of the phase states in the floating layers is possible; in the layers of the  $\beta$ -,  $\alpha$ -, and x-types, the  $\psi$  values are expected to be close to 45, 67, and 90°, respectively.

In the gaseous layers of CuPc\*,  $\psi$  is equal to 35–50° at  $N_0 \leq 3.0 \times 10^{-7}$  mol m<sup>−2</sup> and 70° at  $N_0 = 4.0 \times 10^{-7}$  mol m<sup>−2</sup>. At  $N_0 > 4.0 \times 10^{-7}$  mol m<sup>−2</sup>,  $\psi$  is close to 90° (Table 1) indicating the tightly packed monolayer with perpendicular molecular orientation. Thus, the  $\beta$ -form of the layers seems to be the most stable in the gaseous phase. The  $\alpha$ -form occurs only within a narrow range of the  $N_0$  values. At high  $N_0$  values, the phase of the x-type with no or small molecular overlapping takes place. In the same way, the phase states of condensed monolayers may be identified as ones of the  $\beta$ - and  $\alpha$ -forms at  $N_0 = 1.1 \times 10^{-7}$  mol m<sup>−2</sup> and  $\pi < 20$  mN m<sup>−1</sup>. Thus, the x-form of the CuPc\* layers is the most stable.

The data above indicate that the bilayers formed through compression of the rare monolayers (formed at  $N_0 \leq 4.0 \times 10^{-7}$  mol m<sup>−2</sup>) and through spreading of large amounts of CuPc\* (affording face-on coverage more than 1.2) are structurally different. The low  $C'$  values of the former layers prove existence of vacancies free of water molecules which arise in the course of migration of the CuPc\* molecules into the upper level of the bilayer. However, the major point seems to be the different nature of the edge-to-edge interactions between molecules belonging to the upper and lower levels (as is the case for the face-on monolayers discussed above). This supposition is generally supported by data<sup>11</sup> on aggregation of cumylphenoxy-substituted phthalocyanines on the water surface which manifests itself in measured  $A$  values lower than the  $A_{\text{mol}}$  one and results in strongly inhomogeneous LB films. Specific features of intermolecular interactions in the CuPc\* assembly will be clarified by structural investigation of the LB films of CuPc\* formed from the monolayers studied in this work.

Taking into account structural differences between the bilayers formed under different initial conditions, the mechanism of formation of the incollapsible CuPc\* polylayers may be proposed as follows. When a large amount of solution is spread onto the subphase, it covers not only the water surface but also the primary monolayer consisting of the hydrated CuPc\* molecules. CuPc\* redissolves in a form of the hydrated molecules which aggregate in the benzene medium producing hydrated clusters. Because the CuPc\* molecules in the clusters are bound by the strong Pc–Pc interactions, the clusters do not collapse under compression but slip out into the upper levels without a loss of coordinated water.

## Conclusions

The phase state of CuPc\* in the floating layers is controlled by two parameters, namely, two-dimensional pressure and initial surface concentration. At low values of these parameters, the layers are gaseous and may be condensed by compression. Physically, condensation is an increase in the tilt angle of CuPc\* molecules relative to the air–water interface entailing partial elimination of the molecular hydration sphere. In the monolayers with edge-on molecular orientation, the CuPc\* assembly may be of the  $\beta$ -,  $\alpha$ -, or x-type. At high surface pressures and concentrations, bi- and polymolecular layers are formed, their structure being dependent on the layer prehistory.

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