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Thermodynamics and *in-situ* absorption of Langmuir monolayers of selected copper phthalocyanine substituted with different peripheral groups

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ABSTRACT

The paper deals with thermodynamic and spectroscopic characterization of Langmuir layers of phthalocyanines substituted with different peripheral groups: copper(II) 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine, copper(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine, copper(II) tetrakis(4-cumylphenoxy)phthalocyanine. The isotherms, compressibility and stability of the Langmuir layers are investigated. Molecular arrangement of the molecular skeleton on water substrate is also evaluated. The essential influence of the substituents attached to the phthalocyanine macroring on dye thermodynamic properties is shown. The *in-situ* absorption of the phthalocyanine monolayers and electronic absorption spectra of dye solution in chloroform support existence of aggregates which architecture depends on the dye molecular structure.

1. Introduction

Phthalocyanines (Pcs) are dyes of unique spectroscopic, photoelectric and magnetic properties [1]. Some of them are characterized by the high absorption coefficients and are known as thermally stable molecular materials. Phthalocyanines are able to create coordination bonding, aggregates, organic polymers and low-dimensional semiconductors [1,2]. Therefore, since decades they are still a subject of many studies also because of their very practical applications like for example: modeling of photosynthesis, photoconversion of light energy to electric energy, photodynamic therapy, photocatalysis and sensors [1–4].

In electronic devices organic materials are usually in close contact with a metal electrode and thus interfacial phenomena of the system are essential. Therefore, it seems to be interesting to characterize ultra-thin films with densely packed dye molecules. In the thin films their thickness can be controllable on the order of nanometers and they can give information on organic material/interface and organic molecules/organic molecules interaction. Moreover, functionality of the films and their molecular arrangement can be also controlled before using them for operation in electronic devices. Since a number of phthalocyanine dyes are rather insoluble in organic solvents, substitution of the dyes with peripheral group provides enhancing their solubility. Tetra-tert-butyl, octakis(octyloxy) and cumylphenoxy derivatives of copper(II) phthalocyanine fulfill the solubility requirement and thus their solutions in chloroform are used in our experiments. Moreover, some phthalocyanines have tendency to create aggregated structures when the molecules are densely packed in highly concentrated solutions or thin films [2]. The thin films can be characterized by the use of different techniques like for example UV–Vis, FTIR, reflectance-absorption IR, resonance Raman spectroscopies, transmission-electron and atomic force microscopy's [5–10]. However, many spectroscopic methods are rather unsuitable for characterization of molecular multilayers because testing depths are often much larger than the thickness of monolayers. Another limitation in examination of thin molecular layers and their applications in optoelectronic devices is that charge photogeneration takes place only in a thin layer near heterojunction. Thus, we have decided to take an advantage from a Langmuir technique supported by the *in-situ* absorption method in study of the substituted phthalocyanine monolayers to get information on interaction of molecules with their vicinity (subphase and neighbor molecules). The results could be useful in further investigation of molecular interaction near heterojunctions.

Abbreviations: CuPc, copper phthalocyanine.

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The dye mono- and multi-layers have been studied previously in [2,4] with the use of various techniques [5–10] but it is still little known about their thermodynamic behavior. Thus, in our investigations we have characterized Langmuir monolayers of the dyes and followed their thermodynamics (pressure–area isotherms (π–A), compressibility, stability). However, because of some difficulties in spectroscopic characterization of thin layers due to disadvantageous relation of the monolayer thickness with regard to the instrumental sampling depth we have also decided to study our Langmuir monolayers with the use of the *in-situ* absorption technique, which can give deep insight into interaction of the dyes when spread in the densely packed Langmuir layers. As far as we know the *in-situ* absorption spectroscopy of these phthalocyanine dyes has been used for the first time. Electronic absorption examinations of our samples in solution can also give us support about aggregates structures.

This paper deals with thermodynamics and *in-situ* UV–Vis absorption of Langmuir monolayers composed of selected phthalocyanines substituted with different peripheral groups. Electronic absorption of these dyes in chloroform at the wide range of dye concentrations (10^{-3}–10^{-6} M) are also presented. The molecular arrangement of the dyes in the Langmuir monolayers is also evaluated.

2. Experimental

The studies have been performed for three CuPc dyes (Table 1). All samples were obtained from Aldrich Chemical Company and were used as received. Sample **1** is copper(II) 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine, sample **2** is copper(II) 2,3,9,10,16,17,23,24-octakis (octyloxy)-29H,31H-phthalocyanine and sample **3** is copper(II) tetrakis(4-cumylphenoxy)phthalocyanine. They are symmetrical CuPcs bearing various lateral groups. For our purpose the samples are formed as Langmuir monolayers and dissolved in chloroform because of their solubility in this solvent, which is required for making a good Langmuir layer. Concentrations of the dyes in solution range from 10^{-3} to 10^{-6} M.

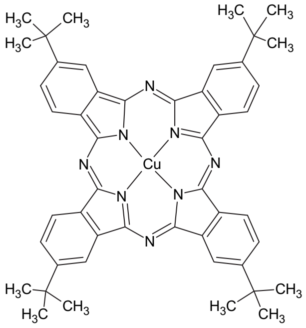
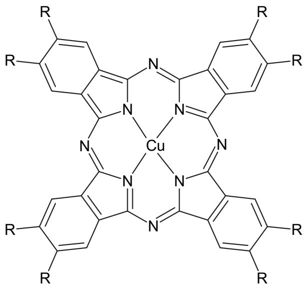
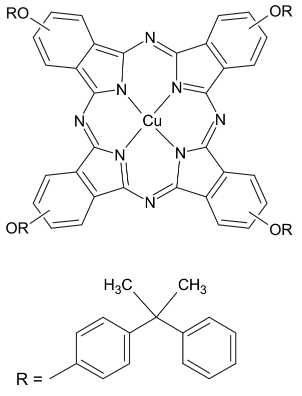
Langmuir monolayers of CuPcs were produced with a KSV 2000 minitrough (KSV Instruments Ltd.) equipped with a temperature control system. The Langmuir trough area was 380 × 75 mm^2. Temperature of subphase is achieved and kept constant (20 °C) with a cooling circulator. As the subphase deionized water (electrical resistivity 18.2 MΩ) was used and the monolayer of the dyes was obtained with a Mili-Q water purification system (Milipore Corp.). The samples were dissolved in chloroform and 10^{-4} M solution was spread carefully onto the subphase and let chloroform to be evaporated (15 min). The floating film of the Langmuir layer was compressed symmetrically from both sides with motion barrier speed of 3 mm/min.

The *in-situ* electronic absorption spectra of the Langmuir layers were recorded in the range of 200–850 nm with an Ocean Optics spectrometer QE65000, which was localized in proximity to a quartz window of the KSV instrument. Electronic absorption spectra of the dyes in chloroform were performed with the use of a spectrophotometer Cary 4000 (Varian) in the range 250–850 nm.

3. Results and discussion

3.1. Thermodynamics of Langmuir layers

Table 1
Molecular structure of phthalocyanine under study.

Molecular structure	Chemical name	Short name
	Copper(II) 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine	**1**
 R = —$OCH_2(CH_2)_6CH_3$	Copper(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine	**2**
	Copper(II) tetrakis (4-cumylphenoxy) phthalocyanine	**3**

In the first stage of the papers we have focused our attention on the thermodynamic properties of the dyes thin films created in a form of the Langmuir monolayers to get deeper insight into interaction between the dyes when spread on a hydrous subphase. Fig. 1 presents the π–A isotherms (pressure–area isotherms) on water surface measured at 20 ± 1 °C (the isotherms were reproducible in the error range of ±2 Å^2 per molecule). As shown these dyes are able to form Langmuir monolayers. However, each dye is characterized by the isotherm having a shape dependent on the molecular dye structures. The main molecular core of the dyes under study are porphyrazine macroring and the dyes differ from each other with the substitutes; **1** has four butyl groups, in **2** there are eight octakis(octyloxy) chains and the cumylphenoxy groups are attached to the main core in **3**. As seen the presence of the different groups in the dyes influences strongly thermodynamic properties of **1**, **2** and **3**. The evaluated values of collapse points (π_c), areas at the collapse point (A_c) and average area per molecule (A_{avr}) are collected in Table 2; the average area per molecule (A_{avr}) was evaluated through extrapolation of the π–A isotherm. These parameters depend on the type of dye and differ insignificantly from those found for tetra-tert-butyl CuPc and some other

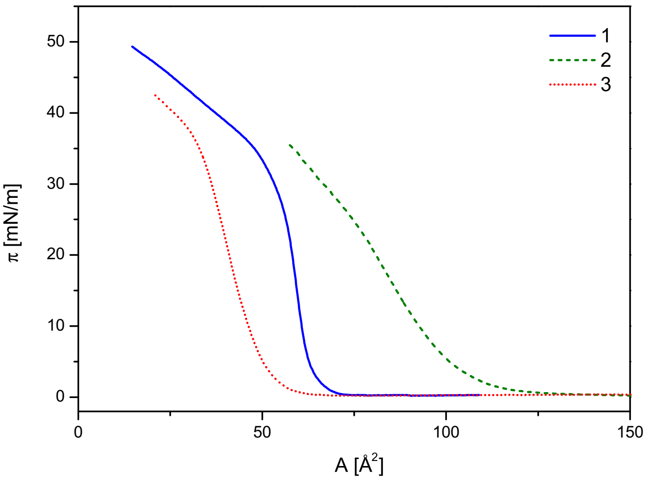


Fig. 1. The π–A isotherms of phthalocyanine monolayers at 20 °C.

phthalocyanines [4,6,11–14]. According to the literature data the geometrical area of phthalocyanine dyes (120–190 Å^2) depends on dyes and attached groups [15–17]. Without substituents the geometrical size of phthalocyanine skeleton was found as about 100 Å^2 [18]. From the geometrical size of phthalocyanine molecular skeleton [15–19] and our experimental A_{avr} we are able to estimate a tilt angle between the molecular plane and water surface; the molecular planes of **1** and **3** do not lie directly on the water surface – the tilt angle (taken as an angle between the molecular plane and water surface) is nearly 70°, indicating almost out-of plane arrangement of these molecules with respect to water surface. Molecular arrangement of **2** is markedly different when compare to those of their counterparts **1** and **3** (Table 2); the tilt angle of **2** is about 45° and implies quite different orientation of this dye skeleton on the subphase from those of **1** and **3**. Thus we can claim that the dye arrangement depends on the molecular phthalocyanine dye structures (it means on the kind of substituent groups). The similar tilt values were obtained for some porphyrins, magnesium and lead phthalocyanines [19]. The differences in molecular plane arrangements of **2** with respect to water surface result probably from the strong hydrophobic character of the oxyalkyl chains and creation of different dimers than those of **1** and **3**. In **1** and **3** the methyl groups are present; they are attached directly to the indole rings in **1** and indirectly through the phenoxy rings to the indole units of **3**. The differences in molecular orientation of the studied dyes could be explained by at least some effects: (i) differences in the dye molecular structures and peripheral groups (steric barrier), (ii) dyes ability to aggregate creation and the different types of aggregates, (iii) different dye monolayer compressibility and stability, and (iv) different hydrophobic-hydrophilic characters of the dyes.

We have done also examination of the Langmuir monolayer compressibility and stability [4]. The compressibility modulus was evaluated as $C_S^{-1} = -A(d\pi/dA)$ [20,21] on the basis of the results presented in Fig. 2 (in this experiment temperature, external pressure and amount of the molecular materials are constant). The maximal compressibility parameters C_S^{-1} of the dye layers change and they are collected in Table 2. In accordance with the literature data [21] the C_S^{-1} values higher than 200 m N/m indicate formation of the 2D solid. As seen in Fig. 2 the compressibility parameter of **1** suggests formation of the 2D solid resulting from large molecular packing and it does not increase at pressure higher than 14 m N/m. The C_S^{-1} values of **2** and **3** indicate creation of liquid phase and condensed liquid phase, respectively [21]. The results confirm the different thermodynamic properties of the dye monolayers when the different external groups are attached to the main phthalocyanine molecular corn. Comparison of the dyes compressibility curves evidently confirms different interaction of the dyes with water surface because of the presence of different external groups. The different properties of dye compressibility together with the different shapes of the isotherm curves as well as the different values of A_{avr} confirm univocally differentiation in the interaction of dyes with water surface. These results can also confirm the various type of aggregates formed by the dyes under study.

The study of monolayer stability in the time range 0–60 min is also done. Stability parameter is defined as a ratio of the molecular area values A/A_0 (Fig. 3). The changes in the A/A_0 values can indicate monolayer relaxation. The values of the relative changes of the molecular area are determined as $(A_{60} - A_0)/A_0$ (A_0 and A_{60} are the areas measured in time $t = 0$ and 60 min, respectively). The data are gathered in Table 2. The relative change is the smallest one for **1** whereas **2** and **3** show similar changes. It means that **1** is the most stable dye with respect to the remaining dyes under investigations. The phthalocyanines under study have hydrophobic character. Therefore they might interact stronger with the dye molecules in the neighbourhood than with the water molecules. The changes in the molecular area can be also assigned to creation of molecular aggregates during compression of layers. The difference in ability to aggregate formation could be caused by the presence of various

Table 2
Thermodynamic parameters of Langmuir layer of phthalocyanine on water surface.

Dye	Average area per molecule A_{avr} [Å^2]	Area at the collapse point A_c [Å^2]	Collapse point π_c [m N/m]	Tilt angle δ [deg]	C_S^{-1} [m N/m][a]	Area change $(A_{60} - A_0)/A_0$ [%]
1	63	52	31	67	236	2.8 (7) 2.9 (14) 3.3 (21)
2	103	77	23	45	77	5.0 (7) 5.5 (14) 7.8 (21) 11.4 (28)
3	49	32	36	72	90	6.7 (14) 8.0 (21) 10.9 (28)

ΔA_{avr}, $\Delta A_c = \pm 1$ Å^2, $\Delta\pi_c = \pm 1$ m N/m, $\Delta\delta = \pm 2°$, $\Delta A(t)/A(0) = \pm 0.1\%$.
A_{60} – area in $t = 60$ min, A_0 – area in $t = 0$ min; in brackets ( ) the values of pressure.
[a] **1** – at pressure $\pi = 14$ m N/m, **2** – at pressure $\pi = 16$ m N/m, **3** – at pressure $\pi = 21$ m N/m.

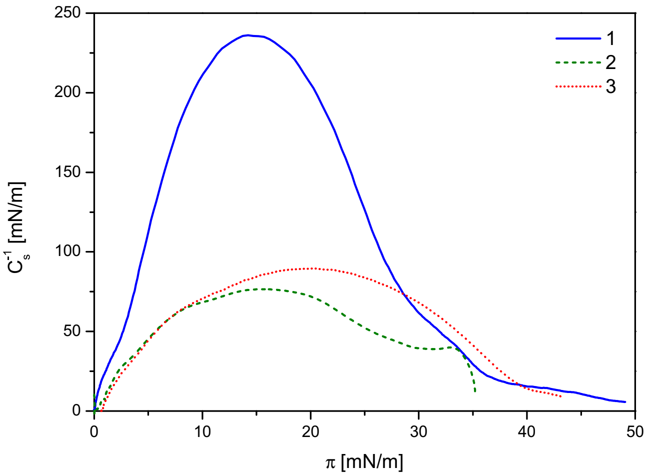


Fig. 2. Compressibility of the phthalocyanine monolayers at 20 °C.

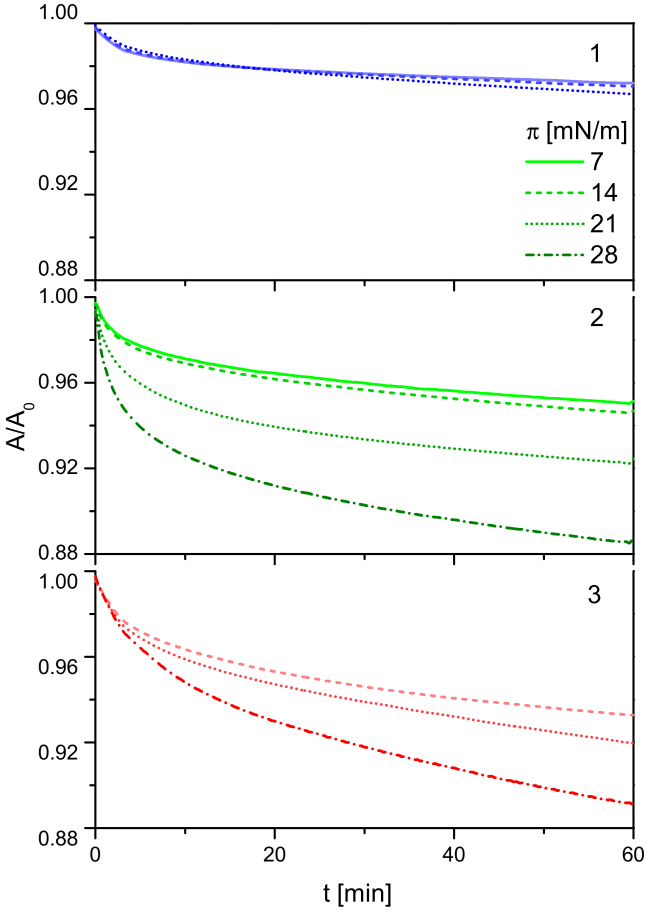


Fig. 3. Relaxation of isotherms of phthalocyanines at different surface pressure.

external groups and their hydrophobic/hydrophilic properties. The details concerning the type of aggregates will be discussed in the following chapters.

3.2. *In-situ absorption of Langmuir layers*

The *in-situ* absorption study could give us a proof for creation of aggregates upon compression of the Langmuir layers. The aggregate structures differ from one another by geometrical arrangement of their dipole moments: in the ideal H aggregates, the molecular frames are oriented face-to-face with parallel transition dipole moments of interacting monomer units oriented perpendicularly to the line joining the molecular centres. Otherwise, in the ideal J aggregates the polarization axis for the in-line transition dipoles is directed along the line joining the molecular centres. In double molecules with the coplanar transition dipoles inclined to the axis connecting the molecules' centres, the angle between the dipole moment's directions varies from 54.7° to 90° and 0 to 54.7° in H and J, respectively [22–25]. The blue and red absorption shifts (1000–2500 cm^{-1}) are expected to appear in the absorption spectra of the H and J aggregates, and they correspond to increasing and lowering energy, respectively [2,26]. According to the Kasha vector model [27] the existence of oblique aggregated species is also possible. In the oblique transition configuration, the dipole transitions are polarised mutually perpendicularly and the configuration of the dipole arrangement (as a composition of in-phase transition dipole arrangement and out-of-phase one) leads to the decreased energy and increased energy of the excited states of dimerized molecules.

The results of the *in-situ* absorption confirm the presence of aggregates. The type of aggregates depends on the peripheral groups attached to the dye core. Exemplary results of the *in-situ* absorption of the samples at the different surface pressure (in the range from 5 m N/m to 35 m N/m) are shown in Fig. 4A, C, E. Shapes, locations and spectral widths (500–1200 cm^{-1}) of the bands in the spectra of the Langmuir layer are different from those observed in the spectra of the dyes in chloroform. Selected absorption parameters are collected in Table 3. The shapes of the absorption bands depend substantially on the dye used in the experiments. The results indicate the large influence of the butyl groups, cumylphenoxy groups and the long octyloxy chains, on the spectral properties of CuPc. In each spectrum two sets of bands are well seen: three bands in the range of Soret region (200 nm–450 nm) and two bands (or a band with hump) in the longwavelength range. The background observed between 200 nm and 450 nm can be caused probably by the effect of light scattering fluctuation. Considerable modification in the absorption region 600–800 nm is observed in all samples. The blue-shifts in the spectra of **1** and **3** is observed resulting from H aggregates creation whereas two separated bands (654 and 694 nm) are observed in the spectra of **2** resulting from formation of oblige coplanar aggregates. Moreover, the shortwavelength region (200–460 nm) of **2** *versus* that of **1** and **3** shows substantial modification. On the basis of our results of isotherms for **2** we can suppose the angle of about 45° (Table 2). Thus, the evaluated angle between the molecular planes in **2** is about 90°. Creation of aggregates of copper phthalocyanines is also shown in [28–30]. Moreover, the atomic force microscopy confirmed also the presence of CuPc aggregates [4]. Of course, the reason of the various type of aggregates of **2** with regard to **1** and **3** lies in different configuration of the dipole transitions in **2** *versus* **1** and **3**. However, the type of monolayer can also influence aggregate formation. The conclusion as to the different configuration in the aggregated structure of **2** *versus* that of its counterparts **1** and **3** can be confirmed by our results of compressibility. Different configuration of the dipole transitions in **2** *versus* **1** and **3** could also result from the different type of monolayers; non-condensed monolayer (**2**) and 2D solid and compressed layer (**1** and **3**). The scheme of the model of the molecular arrangement of **1**, **2** and **3** on the water subphase is presented in Fig. 5.

3.3. *Electronic absorption of dyes in solution*

To support our conclusions about the aggregate presence in the samples we have also done absorption experiments for dyes in chloroform at various concentrations ($c = 10^{-6}$, 10^{-5} and 10^{-4} M). Exemplary results of absorption study are shown in Fig. 4B, D, F. The 10^{-6} M sample is used to minimize the presence of aggregates and serves as a standard sample. Some absorption parameters are collected in Table 3. There is no particular difference between the shapes of spectra monitored in the range of 680 nm for the samples at different concentrations; this band can be assigned to the monomeric species. However, some differences in the spectra (400–450 nm) are observed; in **2** and **3** the extra broad bands are well recognized. Moreover, the 623 nm bands show the 10 nm-blue-shift (10^{-4} M *versus* 10^{-6} M) clearly seen for **3**. The changes in relations of the band intensity are also clear. Moreover, the presence of the 623 nm band and its increasing in the spectra of concentrated samples can be assigned to the presence of aggregates [2,29,30]. The shifts in the absorption spectra can be related to other several effects like for example: point charges, charge transfer complexes, redox potential and others; these effects were discussed widely in [29,30] and they do not affect our observation. The intermolecular interaction between dye molecules in aggregates

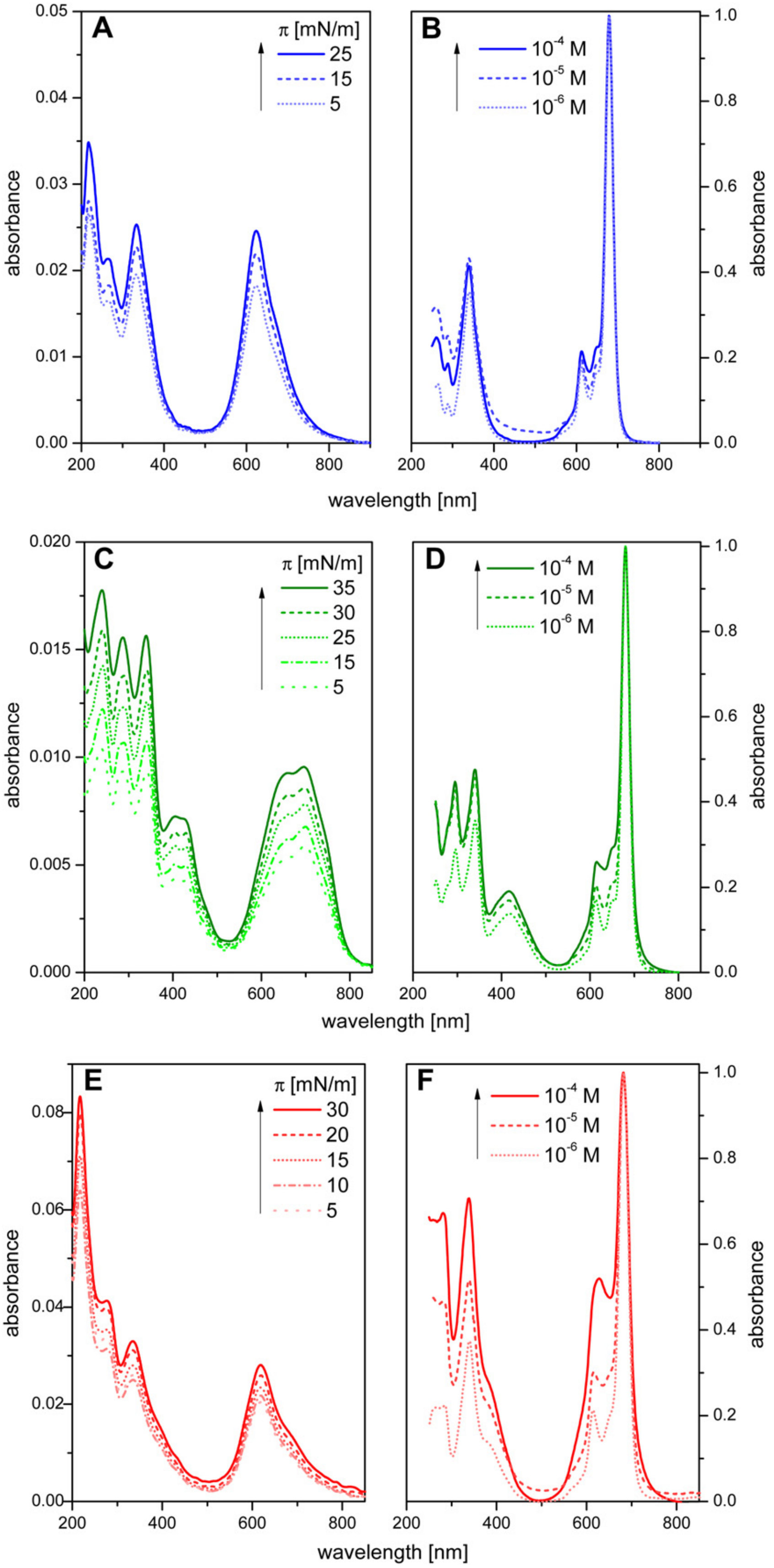


Fig. 4. *In-situ* absorption spectra at different surface pressure and absorption spectra in chloroform (normalized at the maximal Q band) of **1** – A, B, **2** – C, D and **3** – E, F; in solution; $c = 10^{-6}, 10^{-5}, 10^{-4}$ M.

Table 3
Absorption parameters of phthalocyanine Langmuir layer and dye in solution.

Dye	Absorption Langmuir layer		Absorption in chloroform	
	Absorption band λ [nm]	Absorption ratio	Absorption band λ [nm]	Absorption ratio
1	218		263	
	265		289	
	334		339	
	623		612	
			647	
	680 (hump)	0.49 (1)	679	5.6 (2)
2	240		253	
	287		296	
	340		340	
	402		419	
	429			
			612	
	656–660		651	
	696–700	1.09 (3)	680	5.8 (4)
3	217		285	
	227		340	
	334		379	
			577	
	618		614–628	
	682 (hump)	0.47 (5)	682	4.6 (6)

$\Delta\lambda = \pm 1$ nm.
Absorption ratio at the maximal intensities of bands: (1) – 680/623, (2) – 679/612, (3) – 700/660, (4) – 680/612, (5) – 682/618, (6) – 682/614; concentration in solution $c = 10^{-6}$ M.

resulting either in the band splitting or the band shift; for our samples these values are of about 600–700 cm^{-1}.

The results of the *in-situ* absorption and in chloroform can help us to discuss the type of aggregates created in the Langmuir monolayers. Of course, we realize that the geometrical distances between the dye molecules in Langmuir layer are much shorter than those between molecules in 10^{-4} M solution. Thus, the package of molecules in the Langmuir layers is larger than that in 10^{-4} M solution. Just for that reason, it is obvious that amount of aggregated dyes in layers exceeds quantity of those in chloroform. It is clearly seen when one compares the results of the *in-situ* absorption with those in chloroform. Nevertheless, our absorption results confirm the presence of aggregates. The intensive band in the range of 623 nm of **3** in chloroform supports domination of the aggregates over monomers (in layers as well as in chloroform) and confirm the present of the H type aggregate. Coexistence of aggregates and monomers are proofed in **1** and **2**.

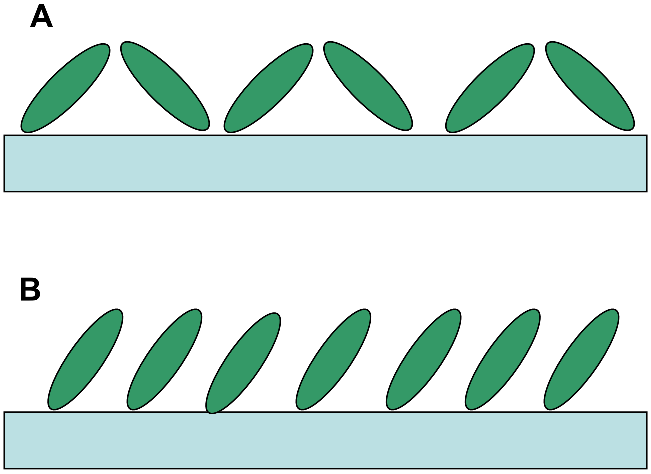


Fig. 5. Scheme of the model of molecular aggregates of 1, 3 (B) and 2 (A) and their arrangements on the water subphase.

4. Conclusions

On the basis of our results of thermodynamic investigation (monolayer isotherms, compressibility and stability) as well as of the *in-situ* and in chloroform absorption studies of copper phthalocyanines: copper(II) 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine (**1**), copper(II) 2,3,9,10,16,17,23,24-octakis (octyloxy)-29H,31H-phthalocyanine (**2**), copper(II) tetrakis(4-cumylphenoxy) phthalocyanine (**3**) following conclusions can be drawn:

1. **1** and **3** form the 2D solid and compressed layer, respectively, whereas the Langmuir monolayer of **2** is a non-compressed one,
2. **1** and **3** aggregate as the H dimers and **3** has the structure of the oblique coplanar dimer,
3. the molecular skeletons of **1** and **3** are oriented almost perpendicularly to water subphase, whereas of **2** creates about 45° with regard to the surface.

Summarizing, the considerable changes of the properties of the dye absorption, observed in our *in-situ* experiment, indicate the electron redistribution in the molecular structures upon compression because of the presence of aggregates.

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