

Supramolecular organization of porphyrin derivatives in the Langmuir films

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Influence of molecular structure of new *meso*-substituted tetraphenylporphyrins with substituents ($-\text{OC}_4\text{H}_9$ or $-\text{OC}_{16}\text{H}_{33}$) in *para*- or *ortho*-positions on their supramolecular organization in the bulk samples and floating layers has been investigated. It is established that only tetraphenylporphyrin substituted in *ortho*-position possess mesomorphic properties among all studied compounds with short terminal substituents ($-\text{OC}_4\text{H}_9$). In contrast, both investigated compounds are *meso*-morphic in the case of long substituents ($-\text{OC}_{16}\text{H}_{33}$).

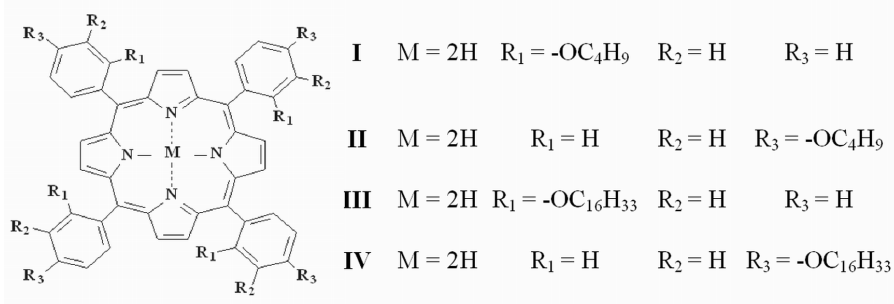
Исследовано влияние молекулярной структуры новых *мезо*-замещенных тетрафенилпорфирина с замещением ($-\text{OC}_4\text{H}_9$ или $-\text{OC}_{16}\text{H}_{33}$) в *пара*- или *орто*-позициях на надмолекулярную организацию в объеме и плавающих слоях. Установлено, что среди соединений с короткими концевыми заместителями ($-\text{OC}_4\text{H}_9$) мезоморфные свойства проявляет только тетрафенилпорфирин с заместителем в *орто*-положении. Напротив, в случае длинных заместителей ($-\text{OC}_{16}\text{H}_{33}$) мезоморфны оба исследуемых соединения.

1. Introduction

When developing a new generation of molecular devices, a topical issue is to obtain structures with a regular molecular resolution [1, 2], which is called "molecular architecture". The Langmuir-Blodgett (LB) technique seems to be the most suitable way to such structures [1]. It makes it possible not only to obtain regular single-component layers with the molecular control of their thickness, but also to create complex structures including the desired combinations of different materials. However, the structure of Langmuir-Blodgett films depends heavily on molecular self-organization in floating layers forming the basis for these films. That is why in the present work, we aimed at the consideration of influence of discotic compound molecular structure features on their mesomorphic properties and supramolecular organization in floating layers.

The structure of realized supramolecular systems depends heavily on the chemical

structure features of compounds forming the systems. While the organization features of phthalocyanine derivatives have been studied in detail [3–7], for porphyrin derivatives, data on the dependence of their supramolecular organization in the bulk and in thin films on the structure of specific ligands and their metal complexes are rather scarce. The urgency of study of porphyrin derivatives supramolecular organization is due to the following points: their supramolecular organization investigation makes a great contribution to the understanding of formation of supramolecular assemblies depending on the structure of these compounds widespread in wildlife, which is very important for understanding the functioning of living systems [8]. Along with the fundamental importance, these studies contribute greatly to the practical use of porphyrin derivatives in engineering, medicine, industry, etc. [9, 10].

Fig. 1. Chemical structure of *meso*-substituted tetraphenylporphyrin.

2. Experimental procedure

Four new compounds with *meso*-substituted were studied. Their synthesis was carried out by the method described before [11]. The phase state of compounds was investigated by polarizing optical microscopy (Leitz Laborlux 12 Pol with a Mettler FP 82 hot stage). Modeling of compounds **I** (R₁ = -OC₄H₉), **II** (R₃ = -OC₄H₉), **III** (R₁ = -OC₁₆H₃₃) and **IV** (R₃ = -OC₁₆H₃₃) as well as calculation of their geometric characteristics (Table 1) were made in the HyperChem program version 7.5 (MM+ method). Geometrical properties of modeling monomolecular packages of studied compounds are represented in Fig. 2 and Table 1.

The Langmuir layers were formed using a FSUE Langmuir trough ("SRC "NIOPIK", Moscow, Russia). The solutions of compound **I** (C = 0.0245 %), **II** (C = 0.0445 %), **III** (C = 0.0249 %) and **IV** (C = 0.0296 %) in chloroform were spread on deionized water at 20 ± 1 °C. The compression rate was 55 cm²/min. Initial extents of surface coating were $c = 19, 24, 30, 37, 45, 50, 63$ %, $c = 45, 49, 59, 74, 83$ %, $c = 101, 114, 154, 183$ % and $c = 63, 77, 96, 116, 130, 164, 178, 193, 212$ %, respectively.

The compression isotherms were analyzed quantitatively using $\pi A - \pi$ graphs. Every linear section corresponds to a stable condition of the layer. The space per molecule (A_{mol}) is equal to slope angle tangent of this linear section. The layer structure is characterized by the molecule slope angle in the stack relative to the air-water interface (ψ).

3. Results and discussion

When studying the bulk samples, we have revealed that alkoxy-substituted ligand of tetraphenylporphyrin **I** (with substitution in *ortho*-position of phenyl rings, Fig. 1) possess mesomorphic properties (Table 2).

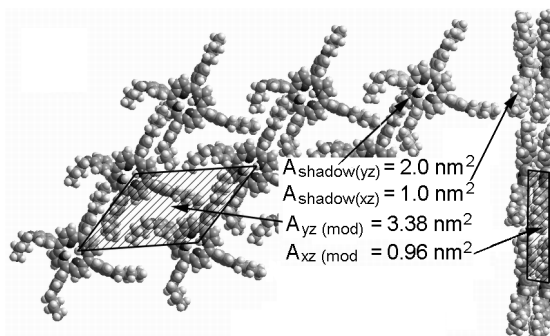
Fig. 2. Types of mounting and geometry characteristics of the molecules **II**.

Table 1. Types of molecular arrangements and geometric characteristics of the molecules.

Compound	Molecular arrangement layer (projection)	Area of shadow, nm ²	Area in descent package, nm ²
I	<i>yz</i>	1.52	1.88
	<i>xz</i>	1.09	1.06
II	<i>yz</i>	2.00	3.38
	<i>xz</i>	1.00	0.96
III	<i>yz</i>	3.39	3.64
	<i>xz</i>	2.76	3.36
IV	<i>yz</i>	3.93	5.29
	<i>xz</i>	1.38	1.54

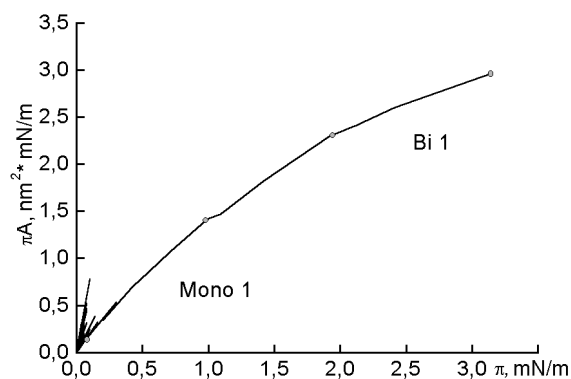
Probably, the short peripheral substituent fits optimally in the free space between phenyl fragments, providing the prerequisites for good microsegregation of supramolecular ensemble at the same time. Such behavior is not typical of related analogues of phthalocyanine where mesophases are formed by molecules with longer lateral substituents.

The substitution in the *para*-position (compound **II**) leads to the mesophase disappearance (Table 2). It has been also found that porphyrin derivatives with -OC₁₆H₃₃

Table 2. Phase transitions of the porphyrin derivatives

No. of compound	Thermotropic mesomorphism	Lyotropic mesomorphism
I	Cr•237.7°C Iso (Iso•176.8°C Mes•60.2°C G) Forms the glass state with the mesophase texture conservation	–
II	Cr•283.8°C Iso	–
III	Cr•79.9°C Iso (Iso•53.3°C Mes•25.0°C Cr)	–
IV	Cr•112.3°C Iso (Iso•93.1°C Mes•59.0°C G) Forms the glass state with the mesophase texture conservation	+ (toluene, benzene, chloroform)

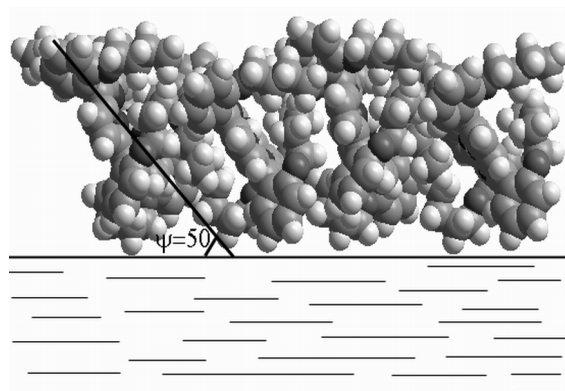
(Phase transitions during the cooling process) Iso — isotropic; Cr — crystalline phase; Mes — liquid crystal phase; + — presence or absence of lyotropic mesomorphism.

Fig. 3. πA - π plot for compound I ($c = 19\%$).

substituents both in *para*- and *ortho*-positions (compounds III, IV) possess mesomorphic properties. Compound IV also forms lyomesophases (in binary systems with solvents like toluene, benzene, chloroform) [12, 13].

The supramolecular organization in thin films of compounds I–IV was investigated by Langmuir method. Analysis of Langmuir layer compression isotherms for the investigated porphyrin derivatives allows to point out several linear sections on the related πA - π graphs corresponding to the stable state of the layers (Fig. 3). The area per one molecule (A_{mol}) and pressure zone where the current stable state is realized are marked by dots on the graphs. For *meso*-alkyloxy substituted tetraphenylporphyrin I with substituent in *ortho*-position, A_{mol} in all the stable states is less than that in the densest package corresponding to the *yz* projection molecular arrangement (even in the zone of low pressure at $c = 19\%$). So, the structure with *yz* projection arrangement in the studied range of coverage is not realized.

Comparison of A_{mol} and A_{xz} in the densest package for the specific compound (Table 1) shows that the stable monolayer is

Fig. 4. Structure of monolayers for compound I ($c = 19\%$).

formed only at $c = 19\%$ for the studied coverage range in the mentioned pressure zone. Pressure increase (at $c = 19\%$) is accompanied by the monolayer transfer with tilt angle $\psi = 50^\circ$ (Fig. 4) (according to our calculations) into bilayer ($\psi = 79^\circ$), and for the larger coverage, by transfer of bilayer into polylayer.

Meso-alkyloxy substituted tetraphenylporphyrin II shows 3D-aggregation in Langmuir layers. Homogeneous layers start to form only at $c = 45\%$. In all the stable states, A_{mol} is less than that in the densest package corresponding to the *xz* projection molecular arrangement (even in the zone of low pressure at $c = 45\%$). So, the studied compound does not form monolayer structures. Compound II is able only to form bilayers for all the studied c . The coverage increase is accompanied by increasing of the molecule tilt angle relative to the water-air interface from $\psi = 48^\circ$ ($c = 45\%$) to $\psi = 90^\circ$ ($c = 83\%$). The decreasing area A_{mol} per one molecule of compound I with the coverage increase can be approximated as $A_{mol} = 0.62 + 513 \cdot \exp(-c/2.63) + 1.36 \cdot \exp(-c/15.3)$ (Fig. 5a). The minimal possible area per one

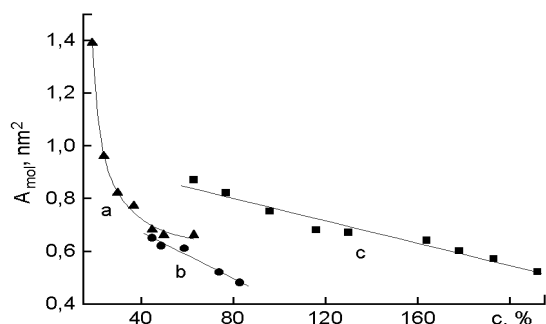


Fig. 5. A_{mol} dependence on the initial coverage (a, for compound I; b, for II; c, for IV).

molecule under the specified experiment conditions is 0.62 nm^2 . For compound II, the corresponding dependence (in the range of the investigation) is expressed by the straight line (Fig. 5b) $A_{mol} = 0.85 - 0.004 \cdot c$. As to compound IV, A_{mol} in all stable states is less or equal to the area per one molecule in the densest package corresponding to the yz projection molecular arrangement. Therefore, the structure with yz projection molecular arrangement is not realized in the studied coverage range. Stable bilayers are formed only for $c = 63$ and 77% . In other cases, polylayer structures are generated. It is established (Fig. 5c) that the area A_{mol} per one molecule of compound IV decreases linearly as the c rises (in the range of the experiment) according to the expression $A_{mol} = 0.97 - 0.002 \cdot c$. *Meso*-alkoxy substituted tetraphenylporphyrin III tends to 3D aggregation in Langmuir layers. Homogeneous polylayer structures start to form only for the coverage of 101% .

4. Conclusion

Influence of molecular structure characteristics on supramolecular organization in the bulk samples and thin layers has been investigated taking four new *meso*-substituted ligands tetraphenylporphyrines with substitution in the alkoxy groups ($-\text{OC}_4\text{H}_9$, $-\text{OC}_{16}\text{H}_{33}$) in *para*- or *ortho*-positions of phenyl rings as examples. It has been found that among compounds with short substituents ($-\text{OC}_4\text{H}_9$), only compound with substituents in the *ortho*-positions of phenyl rings shows mesomorphic properties. At the same time, among compounds with substituents ($-\text{OC}_{16}\text{H}_{33}$), both studied compounds exhibit mesomorphic properties. Compound IV also forms lyomesophases. The mesogenic *meso*-alkoxy substituted tetraphenylporphyrin with substituent in *ortho*-

position (compound I) forms homogeneous stable layers already at the initial coverage of 19% . In this case, the tilt angle to the water-air interface in the first stable state is $\psi = 50^\circ$. The non-mesogenic *meso*-alkoxy substituted tetraphenylporphyrin with substituent in *para*-position (compound II) forms stable layers only starting from $c = 45\%$ and is more inclined to 3D aggregation than mesogenic compound I. In the range of large initial coverages, both compounds form stacks where molecules take up positions of close tilt angles to the surface: at $c = 45\%$ $\psi = 51^\circ$ and $\psi = 48^\circ$ for compounds I and II, respectively.

However, terminal substituent enlargement from $-\text{OC}_4\text{H}_9$ to $-\text{OC}_{16}\text{H}_{33}$ changes cardinally the influence of their position on supramolecular organization in Langmuir layers. For example, compound II with substituents in *para*-position (Fig. 1) shows inclination to the 3D-aggregation for compounds with short substituents $-\text{OC}_4\text{H}_9$, however, for compounds with long substituents $-\text{OC}_{16}\text{H}_{33}$, compound III with substituent ($-\text{OC}_{16}\text{H}_{33}$) in *ortho*-position exhibits the same inclination.

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Надмолекулярна організація похідних порфірину в ленгмюровських шарах

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Досліджено вплив молекулярної структури нових *мезо*-заміщених тетрафенілпорфірину із заміщенням ($-\text{OC}_4\text{H}_9$ або $-\text{OC}_{16}\text{H}_{33}$) у *пара*- або *орто*-положеннях на надмолекулярну організацію в об'ємі та плаваючих шарах. Встановлено, що серед сполук з короткими кінцевими замісниками ($-\text{OC}_4\text{H}_9$) мезоморфні властивості проявляє тільки тетрафенілпорфірин із замісником в *орто*-положенні. Навпаки, у випадку довгих замісників ($-\text{OC}_{16}\text{H}_{33}$) мезоморфні обидві сполуки, що досліджувалися.