

## Synthesis and Properties of Sulfo and Alkylsulfamoyl Substituted Cu<sup>II</sup> and Ni<sup>II</sup> Phthalocyanines Bearing 1–Benzotriazolyl and 4–(1–Methyl–1–phenylethyl)phenoxy Groups

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Dedicated to the Corresponding member of Russian Academy of Sciences Prof. Oscar I. Koifman on the occasion of his Anniversary

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*Synthesis of heterosubstituted sulfo and alkylsulfamoyl derivatives of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines of copper and nickel was carried out. Their spectral and liquid-crystalline properties were studied.*

**Key words:** Phthalocyanines, metal complexes, synthesis, mesomorphism.

## Синтез и свойства сульфо– и алкилсульфамойлпроизводных Cu<sup>II</sup> и Ni<sup>II</sup> фталоцианинов с 1–бензотриазолильными и 4–(1–метил–1–фенилэтил)фенокси группами

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Посвящается Член-корреспонденту РАН Оскару Иосифовичу Койфману по случаю его 70-летнего юбилея

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*Синтезированы смешанно-замещенные сульфо- и алкилсульфамойлпроизводные 2,9,16,23-тетра(1-бензотриазолил)-3,10,17,24-тетра[4-(1-метил-1-фенилэтил)фенокси]-фталоцианинов меди и никеля. Изучены их спектральные и мезоморфные свойства.*

**Ключевые слова:** Фталоцианины, металлокомплексы, синтез, мезоморфизм.

## Introduction

Design of novel liquid-crystalline (LC) materials is an actual area of study in organic chemistry.<sup>[1-6]</sup> Phthalocyanine derivatives are quite interesting objects for such studies and widely used on many fields of science and technology.<sup>[7-9]</sup> Particularly phthalocyanines with volumetric substituents are very prospective materials for optoelectronic devices due to the ability of glass-like state formation<sup>[10]</sup> and light absorption in strongly fixed spectrum region.<sup>[7]</sup> Herewith it is desirable for them to be mesogen at a temperature which is as low as possible. It is achieved by introducing aliphatic chains on phthalocyanine molecule periphery.<sup>[5,9]</sup> Moreover, possibility to form lyomesophases in binary systems with different solvents is a very important property of this phthalocyanine derivatives.<sup>[9,11]</sup> Solubility of this compounds in water is valuable property for their investigation and application. The simplest way for designing water-soluble phthalocyanines is sulfonation. As it was previously shown,<sup>[12]</sup> sulfoderivatives of phthalocyanine have lyotropic mesophase in aqueous media.<sup>[7]</sup>

It is known<sup>[13,14]</sup> that benzotriazolyl substituted phthalocyanines readily form sulfochlorides at room temperature. This makes possible to obtain readily, on the one hand, sulfo derivatives by hydrolysis of sulfochlorides and, on the other hand, alkylsulfamoyl derivatives (sulfonamides) with extended aliphatic chains by reaction of sulfochlorides with alkylamines.

Previously it was found<sup>[15]</sup> that 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines of copper and nickel without extended aliphatic chains exhibit enantiotropic mesomorphism and ability of glass-like state preserving texture of mesophase' formation.

Thus, further modification of metal complexes of mesogenic 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine by forming sulfo and alkylsulfamoyl derivatives is of interest for investigation of effect of their structure on liquid-crystalline behavior.

But the synthesis of these phthalocyanine derivatives is complicated. Therefore it is important to assess how

these compounds are promising from the point of view of the appearance of liquid-crystalline properties. Therefore, anticipating the synthesis, design and prognosis of these compounds' mesomorphism was carried out.

Thereby synthesis of water-soluble sulfoderivatives and high organic-soluble sulfonamides of copper and nickel complexes of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines which can form a low-temperature mesophase is relevant.

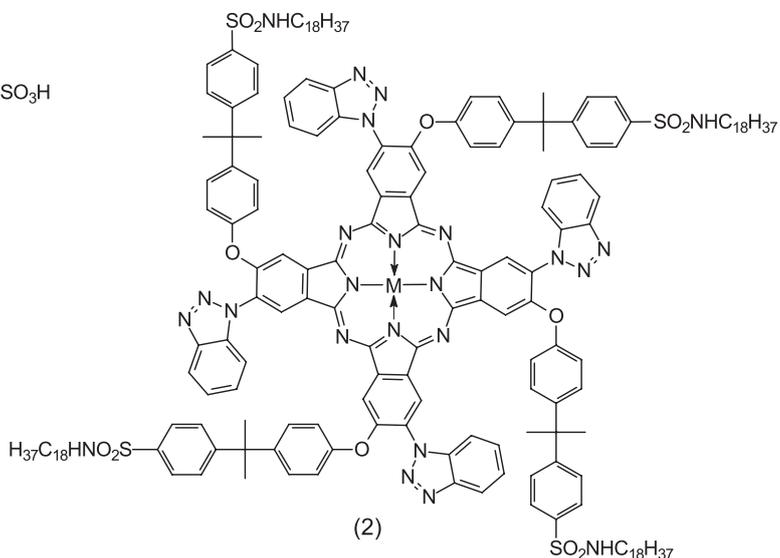
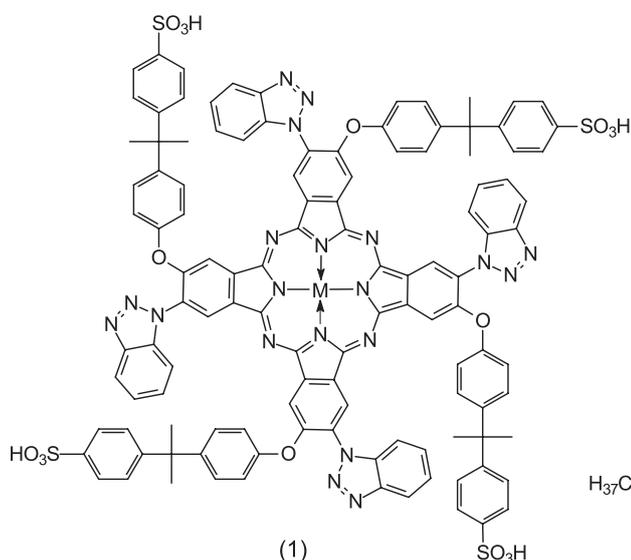
Therefore, the aim of this work is the prognosis of mesomorphism, synthesis of modified copper and nickel complexes of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines (compounds with structures **1**, **2**) and study of their liquid-crystalline properties.

## Experimental

UV-Vis spectra of solutions of synthesized phthalocyanines in DMF and chloroform were fixed on HITACHI U-2001 spectrophotometer at a room temperature on the spectral range 325-900 nm. IR spectra were recorded on Avatar 360 FT-IR ESP spectrophotometer at room temperature. NMR <sup>1</sup>H spectra of [D<sub>6</sub>] DMSO and CDCl<sub>3</sub> test solutions of **1b**, **2b** of TMS internal standard were carried out on «Bruker DRX-500». Elemental analysis was performed on Flash EA<sup>TM</sup> 1112 instrument. Spectral studies and elemental analysis were carried out on the equipment of the Center for Collective Use (Ivanovo, ISUCT).

Phase state of sulfo **1a,b**, and octadecylsulfamoyl derivatives **2a,b** of phthalocyanine was studied on optical thermal polarization microscope «Leitz Laborlux 12 Pol» with «Mettler FP 82» heating stage. Forming thermotropic and lyotropic mesophases of binary systems of studied compounds with organic solvents (DMF, DMSO, toluene, CHCl<sub>3</sub>) and water was investigated on the equipment of the Research Institute of Nanomaterials (Ivanovo, IvSU).

*Synthesis of sulfoderivatives of copper and nickel complexes of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines (1a,b).* Compounds **4a,b** (188 mg, 0.1 mmol) were dissolved in mixture of 2 ml (18 mmol) of chlorosulfonic acid and 2 ml (18 mmol) of thionyl chloride and stirred at a room temperature for 2 h. Further reaction mixture was poured in mixture of ice and NaCl. Obtained precipi-



M = Cu (a), Ni (b)

tate was collected on the Shott filter and dried on desiccator over concentrated  $\text{H}_2\text{SO}_4$  at 36 h. Sulfochlorides were extracted by acetone. Finally, the solvent was removed. Then compounds **5a,b** were boiled with water until complete dissolution and water was removed. Finally, compounds **1a,b** were purified by chromatography (sorbent – silica gel M 60, eluent - DMF). Sulfo derivatives are water-soluble dark-green crowd products, which soluble in water, aqueous solutions of alkalis and ammonia.

**Copper complex of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)-phenoxy]phthalocyanine (1a)** was synthesized by general method from compound **5a** (175 mg, 0.08 mmol, 78% on phthalocyanine **4a**). Found, %: C 62.90, N 12.02, H 4.10, S 5.64;  $\text{C}_{116}\text{H}_{84}\text{CuN}_{20}\text{O}_{16}\text{S}_4$ ; Calculated, %: C 63.16, N 12.70, H 3.84, S 5.81. IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 2930, 2860 ( $\text{CH}_3$ ), 1349 ( $\text{S}=\text{O}_{\text{unsym}}$ ), 1240 (Ar-O-Ar), 1173 ( $\text{S}=\text{O}_{\text{symm}}$ ), 1100 (C-S), 1040 (N=N), 747 (C-N).

**Nickel complex of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)-phenoxy]phthalocyanine (1b)** was synthesized by general method from compound **5b** (187 mg, 0.09 mmol, 82% on phthalocyanine **4b**). Found, %: C 62.71, N 12.56, H 4.01, S 5.58;  $\text{C}_{116}\text{H}_{84}\text{NiN}_{20}\text{O}_{16}\text{S}_4$ . Calculated, %: C 63.30, N 12.73, H 3.85, S 5.83. IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 2920, 2854 ( $\text{CH}_3$ ), 1346 (unsymm. S=O), 1237 (Ar-O-Ar), 1170 (symm. S=O), 1107 (C-S), 1042 (N=N), 744 (C-N).  $^1\text{H NMR}$  ( $[\text{D}_6]$  DMSO, 393 K)  $\delta_{\text{H}}$  ppm (numbering of protons is shown in Scheme 3): 9.49 (s, 4H,  $\text{SO}_3\text{H}$ ); 8.59 (t, 4H,  $\text{H}^1$ ); 8.23 (t, 4H,  $\text{H}^3$ ); 8.13 (s, 4H,  $\text{H}^2$ ); 8.03 (s, 4H,  $\text{H}^6$ ); 7.91 (s, 4H,  $\text{H}^4$ ); 7.73-7.77 (m, 8H,  $\text{H}^{10,11}$ ); 7.55-7.57 (m, 4H,  $\text{H}^5$ ); 6.88 (m, 8H,  $\text{H}^{7,8}$ ); 1.43 (s, 24H,  $\text{H}^9$ ,  $\text{CH}_3$ ).

**Synthesis of sulfonamides of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines of copper and nickel (2a,b)**. Compounds **4a,b** (188 mg, 0.1 mmol) were dissolved in mixture of 2 ml (18 mmol) of chlorosulfonic acid and 2 ml (18 mmol) of thionyl chloride and stirred at the room temperature for 2 h. Further reaction mixture was poured in mixture of ice and NaCl. Precipitate obtained was collected on the Shott filter and dried on desiccator over concentrated  $\text{H}_2\text{SO}_4$  at 36 h. Sulfochlorides **5a,b** were extracted by acetone. Excess (0.22 g, 0.8 mmol) of octadecylamine was added to solution of **5a** or **5b** in acetone. Reaction mixture was boiled at 60 °C for 1-1.5 h. Control of process was conducted by the completeness of dissolution in chloroform of the sample of the reaction mixture. Finally, acetone was removed. Compounds **2a** or **2b** were extracted by chloroform. Purification of targeting derivatives of phthalocyanine was carried out by columnar chromatography (sorbent – silica gel M 60, eluent - chloroform). Products **2a, b** are dark-green solids with good soluble on benzene, acetone and chloroform, and poorly soluble on DMF.

**Copper complex of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,23-tetrakis[4-(1-methyl-1-(4-octadecylsulfamoylphenyl)ethyl]phenoxy]phthalocyanine (2a)** was synthesized from compound **5a** (180 mg, 0.08 mmol) by general method. (256 mg, 0.08 mmol, 80% on phthalocyanine **4a**). Found, %: C 71.70, N 10.66, H 7.22, S 4.01;  $\text{C}_{188}\text{H}_{232}\text{CuN}_{24}\text{O}_{12}\text{S}_{14}$ ; Calculated, %: C 70.30, N 10.47, H 7.28, S 3.99. ( $\text{C}_{188}\text{H}_{232}\text{CuN}_{24}\text{O}_{12}\text{S}_{14}$ ). IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 2921, 2852 ( $\text{CH}_2$ ,  $\text{CH}_3$ ), 3075 (NH), 1615 (def.  $\text{NH}_{\text{sec}}$ ), 1346 ( $\text{S}=\text{O}$  асимм), 1302 (valent,  $\text{NH}_{\text{sec}}$ ), 1246 (Ar-O-Ar), 1171 (symm. S=O), 1090 (C-S), 1048 (N=N), 743 (C-N).

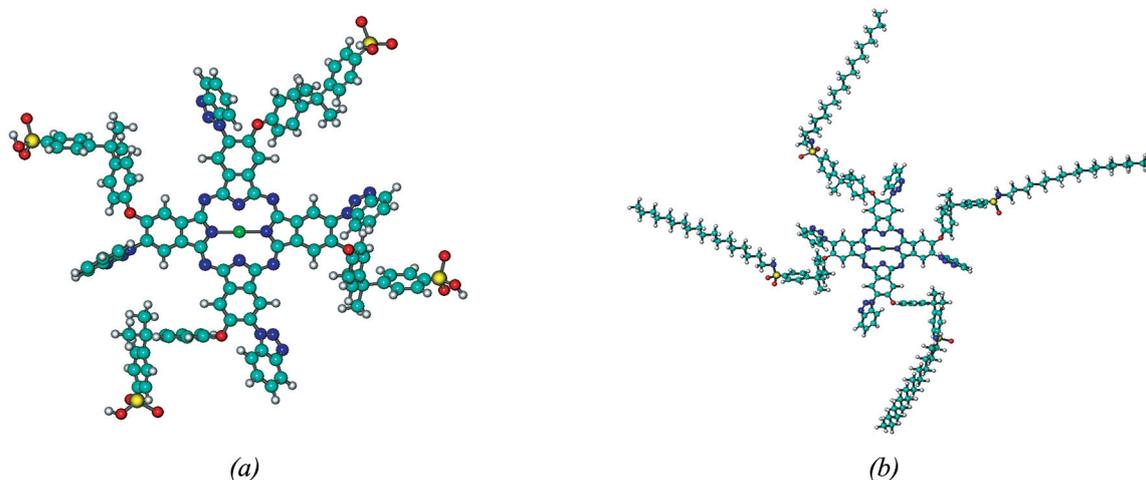
**Nickel complex of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,23-tetrakis[4-(1-methyl-1-(4-octadecylsulfamoylphenyl)ethyl]phenoxy]phthalocyanine (2b)** was synthesized from **5b** (180 mg, 0.08 mmol) by general method. (263 mg, 0.08 mmol, 82% on phthalocyanine **4b**). Found, %: C 71.98, N 10.07, H 7.35, S 3.92;  $\text{C}_{188}\text{H}_{232}\text{NiN}_{24}\text{O}_{12}\text{S}_{14}$ ; Calculated, %: C 70.41, N 10.48, H 7.29, S 4.00. IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 2921, 2853 ( $-\text{CH}_2$ ,  $-\text{CH}_3$ ), 1626 (deform.,  $\text{NH}_{\text{sec}}$ ), 1304 (valent  $\text{NH}_{\text{sec}}$ ), 1174 (symm. S=O), 1200 (Ar-O-Ar), 1148 (C-S), 1040 (N=N), 752 (C-N).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 393 K)  $\delta_{\text{H}}$  ppm (numbering of protons is shown in Scheme 3): 8.57 (s, 4H,  $\text{H}^1$ ); 8.20 (s, 4H,  $\text{H}^3$ ); 8.10 (t, 4H,  $\text{H}^2$ ); 8.01 (s, 4H,  $\text{H}^6$ ); 7.90 (s, 4H,  $\text{H}^4$ ); 7.57 (m, 12H,  $\text{H}^{5,10,11}$ ); 6.99 (m, 8H,  $\text{H}^{7,8}$ ); 4.87 (s, 4H, NH); 1.40 (s, 24H,  $\text{H}^9$ ,  $\text{CH}_3$ ); 2.98, 1.82, 1.65, 1.25 ( $\text{CH}_2$  in  $\text{NHC}_{18}\text{H}_{37}$ ); 0.9 (s, 12H,  $\text{CH}_3$  in  $\text{NHC}_{18}\text{H}_{37}$ ).

## Results and Discussion

This work consists of several logical steps. The possibility for compounds **1a,b** and **2a,b** to form mesophases was evaluated on the first stage of the investigation. Synthesis of the objects studied was carried out on the second stage. Finally, liquid-crystalline properties of the target compounds **1a,b** and **2a,b** were experimentally studied and compared with the results of prognosis.

### Prognosis of Mesomorphism on Compounds **1a,b** and **2a,b**

On the first stage design of discotic molecules and prognosis of columnar mesomorphism for compounds **1a,b** and **2a,b** was performed by method which was previously used for other phthalocyanine derivatives.<sup>[16,17]</sup> This methodology is based on the construction of molecular models of the compounds and analysis of molecular parameters (MP).<sup>[18,19]</sup> MP



**Figure 1.** Models of molecule of compounds **1a** (a) and **2a** (b).

are dimensionless quantities which are calculated on the basis of structure of individual molecule of compound investigated. Preliminary construction and optimization of models of molecules **1a,b** and **2a,b** were carried out by Molecular Mechanics (MM<sup>+</sup>) method from the HyperChem software package.

Then calculation and analysis of *MP* was performed by using geometrical characteristics of the compounds, as well as a number of other indicators. Obtained values were compared with classification number (1).

$$K = 2-8.5; K_c = 1-2.6; K_p = 0.2-0.7; K_s = 0.25-1.00; \\ M_m = 0.2-0.8; M_r = 0.15-0.80; K_{ar} = 0.08-0.30 \quad (1)$$

*K* characterizes anisometry of molecule as a whole. *K<sub>c</sub>* and *K<sub>p</sub>* parameters characterize anisometry of central core and periphery of molecule, respectively. *K<sub>s</sub>* indicates the degree of substitution of the central fragment by the peripheral substituents. *M<sub>m</sub>* parameter takes account the mass ratio of the central core and peripheral fragments. *M<sub>r</sub>* parameter takes account the degree of the environment of the central core of the molecule by peripheral substituents. Parameter *K<sub>ar</sub>* is proposed to account for the packing density of peripheral substituents. Detailed description of the parameters and their application for predicting of mesomorphism in different compounds are given in works.<sup>[16-20]</sup> Deviation of each value of the calculated *MP* from the limiting values of the classification number (1) illustrated the failure of investigated compounds exhibit mesomorphism characteristic for DM. Results of prognosis for **1a,b** - **2a,b** are shown in Table 1.

Prognosis was positive for sulfoderivatives of phthalocyanine **1a,b**, equally probable for alkylsulfamoyl derivative of copper phthalocyanine **2a** and negative for nickel complex **2b**.

### Synthesis

Synthesis of sulfo and alkylsulfamoyl derivatives of 2,9,16,23-tetrakis(1-benzotriazolyl)-3,10,17,24-tetrakis[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines of copper and nickel (**1a,b**, **2a,b**) was performed by methods visualized in Schemes 1-3 for verification of results of the prognosis.

Initial metallophthalocyanines **4a,b** were synthesized by heating of 4-(1-benzotriazolyl)-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitrile (**3**) with copper or nickel acetate at 190-220 °C (Scheme 1).<sup>[21]</sup> All physicochemical characteristics of the synthesized compounds **4a,b** coincide with previously published data.<sup>[21]</sup>

Next step was the synthesis of sulfochlorides **5a,b** by interaction of metallophthalocyanines **4a,b** with mixture of equimolar quantities of thionyl chloride and chlorosulfonic acid at room temperature for 2 h (Scheme 2). Reaction mixture was poured into mixture of ice and NaCl. Precipitate was collected on a Shott filter and thoroughly dried in a desiccator over concentrated sulfuric acid for 3 days.

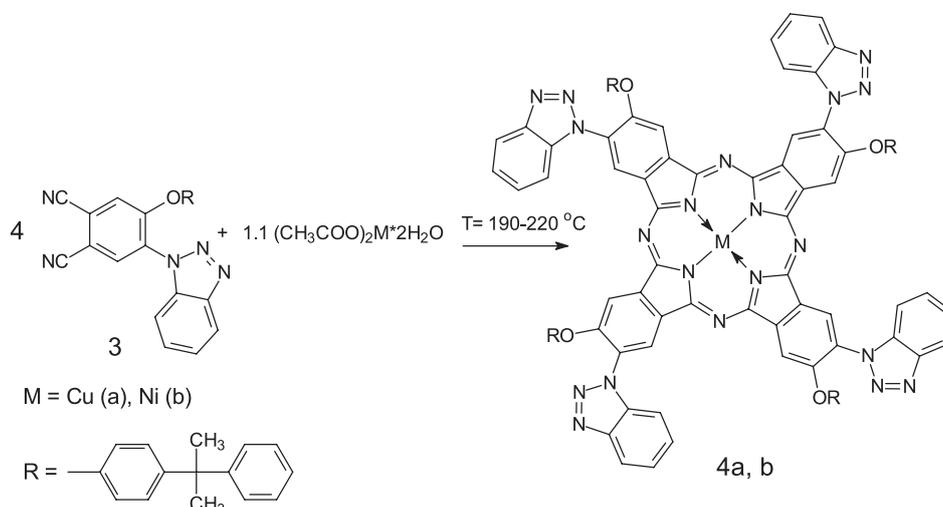
Subsequently, compounds **5a,b** obtained at this stage were extracted with acetone. The solution was filtered for removal of inorganic impurities and then acetone was removed.

Sulfoderivatives **1a,b** were obtained by hydrolysis of sulfochlorides **5a,b** with 78-82 % (Scheme 3). Compounds

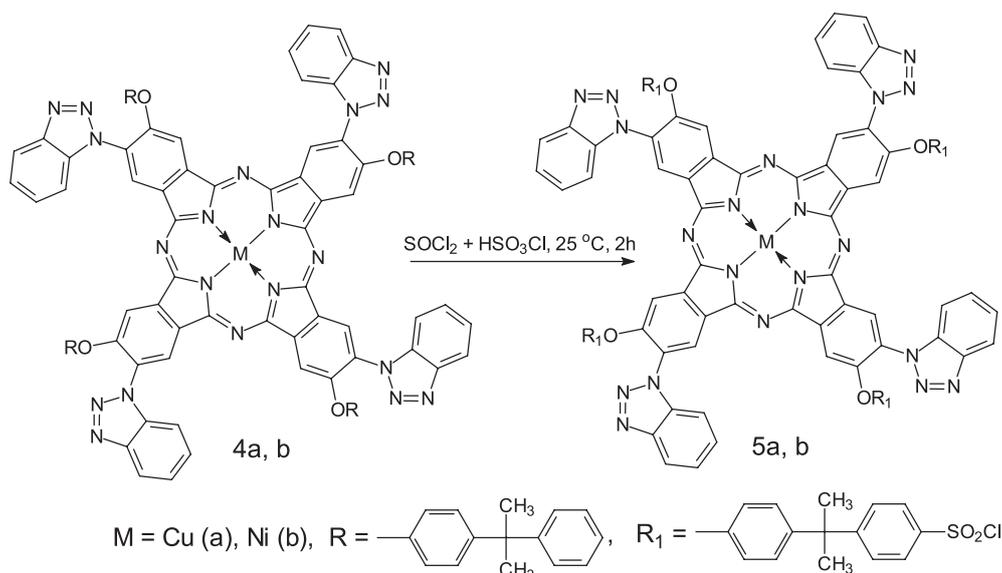
**Table 1.** Calculated *MP* and the data of prognosis for substituted phthalocyanines **1a,b** and **2a,b**.

№	<i>E<sub>opt</sub></i> , kcal/mol	Molecular parameter						<i>P</i>	<i>E</i>
		<i>M<sub>m</sub></i>	<i>M<sub>r</sub></i>	<i>K<sub>p</sub></i>	<i>K</i>	<i>K<sub>c</sub></i>	<i>K<sub>ar</sub></i>		
<b>1a</b>	263.44	0.45	0.23	0.52	2.49	1.29	0.24	+	+
<b>1b</b>	262.99	0.45	0.23	0.52	2.49	1.33	0.24	+	-
<b>2a</b>	336.23	0.27	0.14*	0.17*	2.57	1.29	0.08	±	+
<b>2b</b>	328.15	0.27	0.14*	0.17*	1.56'	1.34	0.08	-	-

Note: *E<sub>opt</sub>* – optimization energy, *K<sub>s</sub>* = 0.50 for all compounds, *P* – prognosis of mesomorphism typical for DM; *E* – result of experiment. *MP*\* value closed to the boundary of classified number (1). *MP*' value deviated significantly from number (1).



**Scheme 1.**



Scheme 2.

**5a,b** were refluxed in water for complete dissolution and then water was removed.

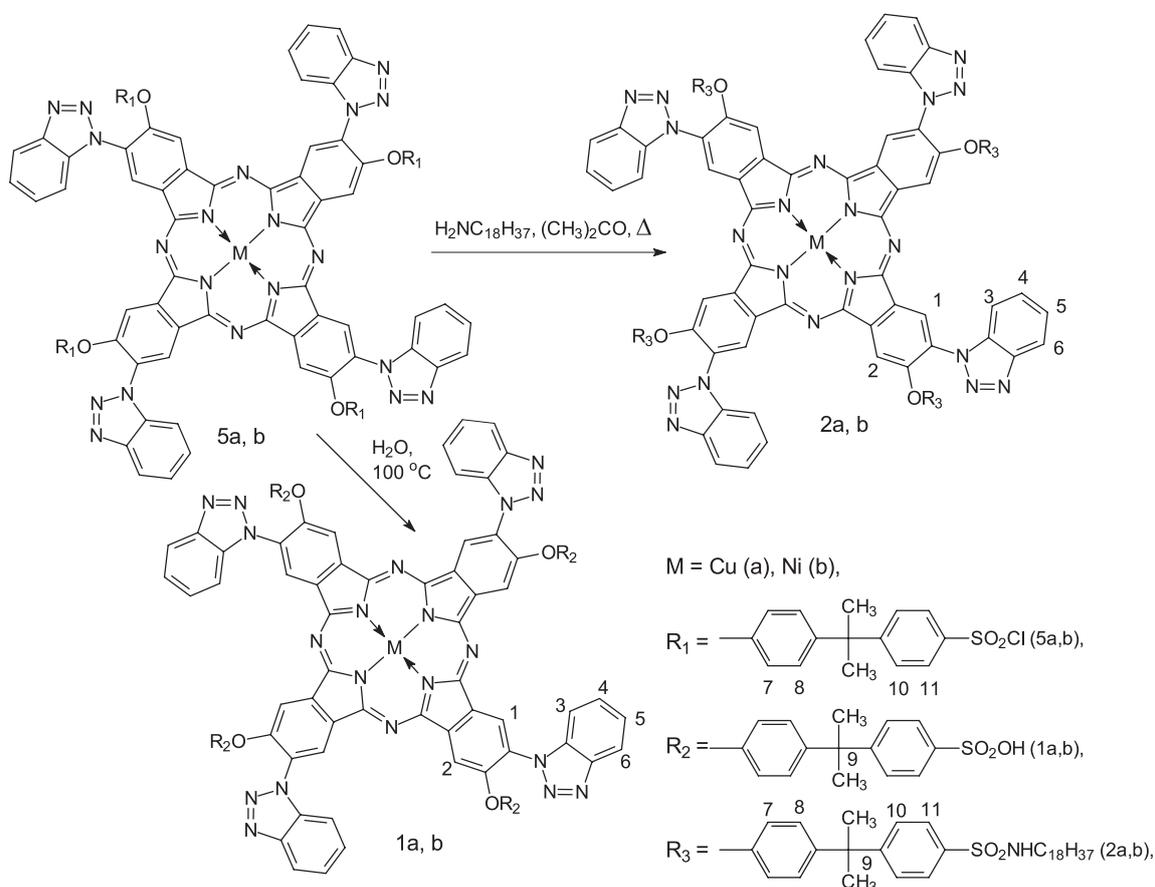
Sulfonamides **2a,b** were synthesized by refluxing of acetone solution of compounds **5a,b** and octadecylamine with 80-83 % yield (Scheme 3).

Purification of sulfo (**1a,b**) and alkylsulfamoyl (**2a,b**) derivatives of copper and nickel phthalocyanines was carried out by column chromatography.

Synthesized phthalocyanines **1a,b**, **2a,b** were identified by the data of elemental analysis, NMR  $^1\text{H}$ , IR and UV-Vis spectroscopy.

According to elemental analysis 4 sulfo or alkylsulfamoyl groups were entered on the periphery of molecule of compounds **4a,b**.

The IR spectra of compounds **1a,b** and **2a,b** maintain the bands of stretching vibrations of hydroxyaryl (1200-1240



Scheme 3.

cm<sup>-1</sup>) and benzotriazolyl (at 1040-1050 cm<sup>-1</sup> and 740-750 cm<sup>-1</sup>) substituents previously noted<sup>[21]</sup> in the spectra of their synthetic precursors **4a,b**.

Bands of stretching and deformation vibrations of C-S (1090-1110 cm<sup>-1</sup>) and S=O (1150-1170 cm<sup>-1</sup>) bonds of sulfonic groups<sup>[22]</sup> appear in the IR spectra of sulfoderivatives **1a,b**. Bands of stretching (1310-1350 cm<sup>-1</sup>) and deformation (1550-1650 and 1510 cm<sup>-1</sup>) vibrations of secondary aminogroups and band at 3050-3150 cm<sup>-1</sup> of N-H appear in IR spectra of sulfonamides **2a,b**. Bands of symmetric (1160-1180 cm<sup>-1</sup>) and unsymmetric (1330-1360 cm<sup>-1</sup>) vibrations of S=O, as well as the band of valence vibrations of the C-S are also observed.

<sup>1</sup>H NMR spectra of phthalocyanines **1b,2b** contained signals of protons of aryloxy (6.90-7.90 ppm), benzotriazolyl (8.20, 7.88, 7.55, 8.00 ppm) fragments and benzene rings (8.57 and 8.10 ppm). The position of these signals did not affect on the introduction of sulfo or alkylsulfamoyl groups into aryloxy substituents of compound **4b**. This fact confirms the modification of compounds **4a,b** in *para*-position of phenyl ring of 4-(1-methyl-1-phenylethyl)phenoxy groups because signal of proton in the *ortho*-position of the aryloxy fragment (key 2 in Scheme 3) is observed practically in the same range (8.13 ppm in spectrum of **1b**, 8.10 ppm in spectrum of **2b**) as in the spectrum of the starting compound **4b** (8.10 ppm).<sup>[21]</sup> Introduction of sulfogroups into *ortho*-position relatively the oxygen bridge would result in a noticeable shift of these signal in the 8.30-8.36 ppm region. Shift of signal 2 is not observed in this case.

The signal of sulfo protons of sulfo substituted phthalocyanine **1b** appears in low field (9.49 ppm) of <sup>1</sup>H NMR spectrum. Intensive signals of protons of methylene groups of octadecyl chains of sulfonamide **2b** are observed in the upfield region (3.2-1.2 ppm). Signal of four protons of terminal methyl groups are fixed at 0.92 ppm. Singlet signal of protons of secondary aminogroups of octadecylsulfamoyl substituents presents at 4.87 ppm.

Synthesized sulfoderivatives **1a,b** are soluble in DMF, water and aqueous-alkaline media, unlike the initial compounds **4a,b**. Sulfonamides **2a,b** are soluble in organic solvents such as benzene, chloroform and acetone. Results of studies of the electronic absorption spectra of the synthesized phthalocyanine derivatives (**1a,b** and **2a,b**) are summarized in Table 2 and shown in Figures 2-5.

Hypsochromic shift of long-wavelength absorption Q bands in concentrated sulfuric acid is observed at substitution

of aryloxyfragments of **4a, b** by sulfogroups (Table 2). This shift is slightly increased at transition from sulfo substituted phthalocyanines **1a,b** to sulfonamides **2a,b** (Table 2). It should be noted that the nature of Q bands in sulfuric acid under such modification remains unchanged (broad un the case of nickel complexes and cleaved into two parts in the case of copper complexes).

Sulfosubstituted phthalocyanines **1a,b** are not associated in DMF media. The position of Q bands of these compounds is identical to that in UV-Vis spectra of their synthetic precursors **4a,b**.<sup>[21]</sup> Additional absorption band (Figure 3) is observed in spectrum of compound **1b** in DMF solution and is not observed in water and aqueous-alkaline media. This band was previously fixed<sup>[21]</sup> in the spectra of other nickel complexes of benzotriazolyl substituted phthalocyanines. It should be noted that compounds **1a,b** are in associated form in water and aqueous-alkaline media according to its UV-Vis spectra (Figures 2, 3).

Compounds **2a,b** are not associated form in organic solvents (Figures 4, 5). In the spectrum of **2b** in DMF an additional absorption band is fixed at 760 nm (Figure 5, Table 2) as in the case of sulfosubstituted phthalocyanine **1b**.

### Investigation of Mesomorphic Properties of Compounds **1a,b** and **2a,b**

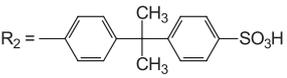
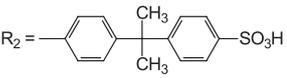
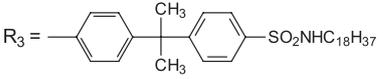
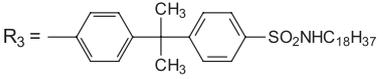
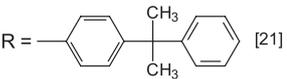
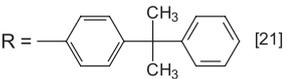
Liquid crystalline properties of the synthesized compounds **1a,b** and **2a,b** were studied by method of thermal polarization microscopy. Results of investigation (Table 3, Figures 6-10) were compared with results of prognosis obtained in the analysis of molecular parameters (Table 1).

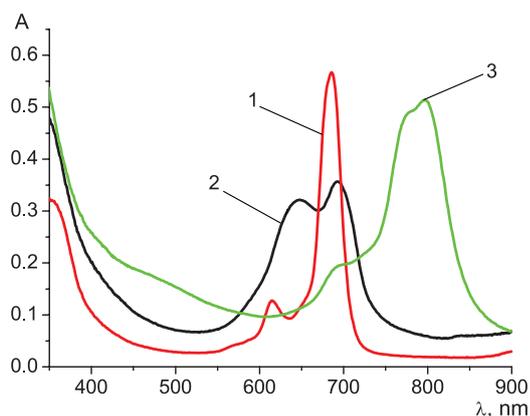
Sulfosubstituted phthalocyanine **1a** is able to form lyotropic mesophase in binary system with dimethylsulfoxide (Figure 7) at heating and to form thermotropic mesophase at 183-227 °C in heating cycle and at 209-184 °C in cooling cycle.

Thus, substitution of aryloxy groups of compound **4a** by sulfo group does not lead to the disappearance of mesogenic properties and leads to a shift of existence interval of the mesophase of compound **1a** in the region of higher temperatures (Table 3). Furthermore, we have found that sulfosubstituted phthalocyanine **1a** forms mesophase at heating in binary systems with dimethylsulfoxide (Figure 7).

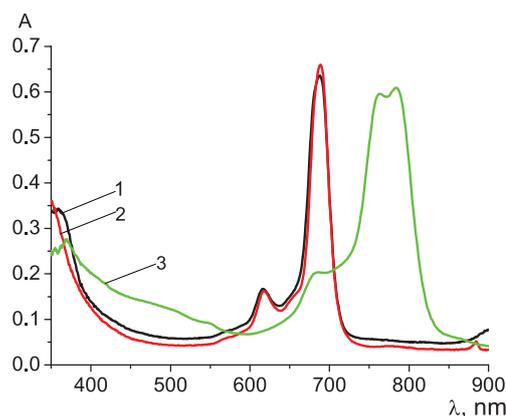
Nickel complex of this structure **1b** does not exhibit mesomorphic properties (Table 3). Thus, the introduction of

**Table 2.** The data of UV-Vis spectra of **1a,b** and **2a,b**.

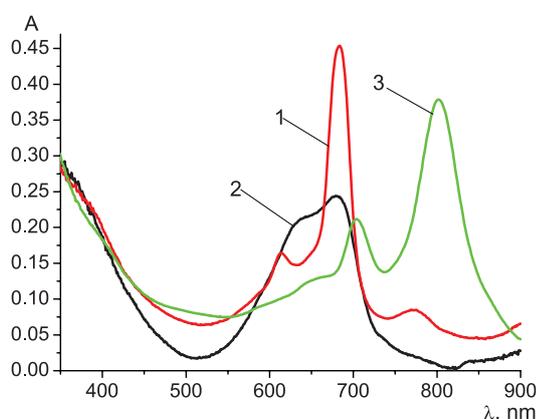
№	Substituent	M	UV-Vis spectra, λ <sub>max</sub> , nm			
			H <sub>2</sub> O	NH <sub>4</sub> OH <sub>aqueous</sub>	DMF	H <sub>2</sub> SO <sub>4</sub>
<b>1a</b>		<b>Cu</b>	698	648, 693	615, 686	796
<b>1b</b>		<b>Ni</b>	684	679	684, 668 <sub>broad</sub>	803
			DMF	CHCl <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	
<b>2a</b>		<b>Cu</b>	616, 687	618, 689	784	
<b>2b</b>		<b>Ni</b>	613, 682, 767	611, 679, 773	800	
<b>4a</b>		<b>Cu</b>	615, 684	616, 688	805	
<b>4b</b>		<b>Ni</b>	611, 679, 767	612, 676, 774	806	



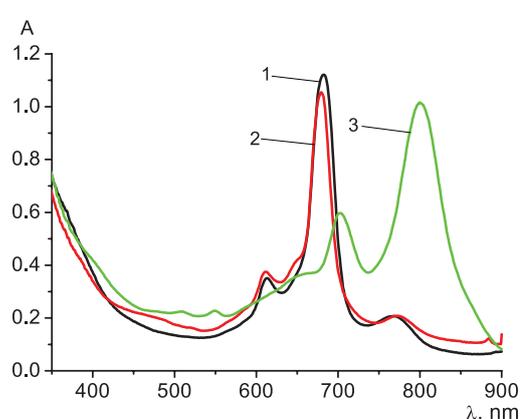
**Figure 2.** UV-Vis spectra (**1a**) in different solvents ( $C = 0.8 \cdot 10^{-5}$  mol/l): 1 – DMF, 2 – aqueous  $\text{NH}_4\text{OH}$  (5%), 3 –  $\text{H}_2\text{SO}_4$ .



**Figure 4.** UV-Vis spectra (**2a**) in different solvents ( $C = 0.9 \cdot 10^{-5}$  mol/l): 1 – DMF, 2 –  $\text{CHCl}_3$ , 3 –  $\text{H}_2\text{SO}_4$ .



**Figure 3.** UV-Vis spectra (**1b**) in different solvents ( $C = 0.7 \cdot 10^{-5}$  mol/l): 1 – DMF, 2 – aqueous  $\text{NH}_4\text{OH}$  (5%), 3 –  $\text{H}_2\text{SO}_4$ .



**Figure 5.** UV-Vis spectra (**2b**) in different solvents ( $C = 1.1 \cdot 10^{-5}$  mol/l): 1 – DMF, 2 –  $\text{CHCl}_3$ , 3 –  $\text{H}_2\text{SO}_4$ .

**Table 3.** Liquid-crystalline properties of compounds **1a,b** and **2a,b**.

№	Substituent	M	Mesomorphism	
			Thermotropic	Lyotropic
<b>1a</b>		Cu	Heating: Cr • 183,3 °C Mes • 227,1 °C Iso Cooling: Iso • 209,1 °C Mes • 164,5 °C Cr	DMSO
<b>1b</b>		Ni	Heating: Cr • 299,0 °C Iso	–
<b>2a</b>		Cu	Heating: Cr • 108 °C Mes • 197 °C Iso Cooling: Iso • 170 °C Mes • 70 °C G	–
<b>2b</b>		Ni	Heating: 170-175 °C – decomposition of amorphous compound	–
<b>4a</b> <sup>[15]</sup>		Cu	Heating: Cr • 131 °C Mes • 174 °C Iso Cooling: Iso • 112 °C Mes • 75 °C G	DMF
<b>4b</b> <sup>[15]</sup>		Ni	Heating: Cr • 151 °C Mes • 184 °C Iso Cooling: Iso • 175 °C Mes • 114 °C G	–

sulfo groups into mesogenic molecule of compound **4b** is negatively affected on the ability of sulfo derivative **1b** to form mesophase.

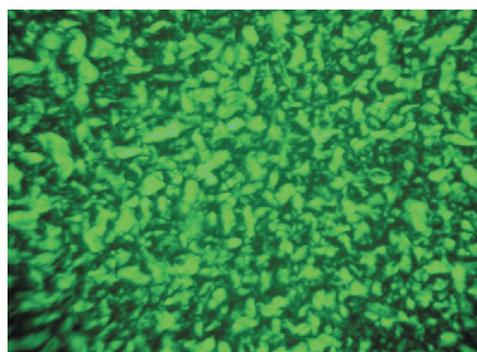
Observation of sulfonamide samples' texture of **2a** in cycles of heating and cooling shows that the mesophase is detected only after several cycles of heating and cooling. This compound shows enantiotropic mesomorphism.

Apparently, multiple heating and cooling cycles are necessary to achieve the thermodynamically stable state. This is probably related with the high viscosity of the sample **2a**. Orientational ordering is manifested at shear deformation (Figure 8a-c).

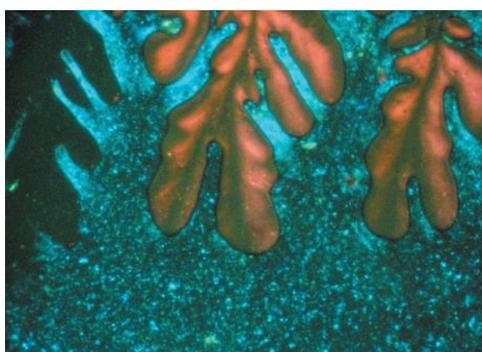
Mobility of the sample increases during heating. Big domain texture<sup>[23]</sup> with characteristic spherulites<sup>[24]</sup> in some



**Figure 6.** Microscopic image of texture of thermotropic mesophase of compound **1a** (heating cycle, crossed polarizers, 218.1 °C).



**Figure 10.** Glassed mesophase texture of compound **2a**, crossed polarizers, 45 °C.



**Figure 7.** Microscopic image of texture of lyotropic mesophase of compound **1a** (contact preparation with DMSO).

areas was shown. This testifies the possible formation of SmA phase (Figure 9a,b).

Sample of compound **2a** was glassed upon cooling preserving mesophase texture (Figure 10).

Compound **2a** forms mesophase in a wider temperature range than its synthetic precursor **4a**. The phase transition Cr → Mes of **2a** is observed at a significantly lower temperature than that of compound **4a**. Apparently this fact is due to increasing of the length of 4-[1-methyl-1-phenylethyl] phenoxy group at introduction of octadecylsulfamoyl chain.<sup>[25]</sup>

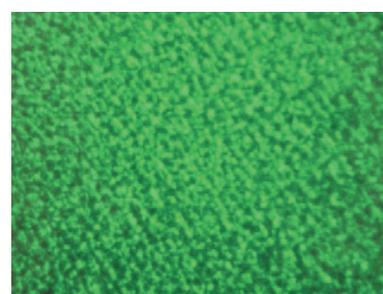
Influence of the nature of the central metal on mesomorphism of the synthesized compounds is also observed in this case. It was found that nickel phthalocyanine **2b**, unlike its synthetic precursor **4b**, is non-mesomorphic.



a) Parallel polarizers, 147 °C

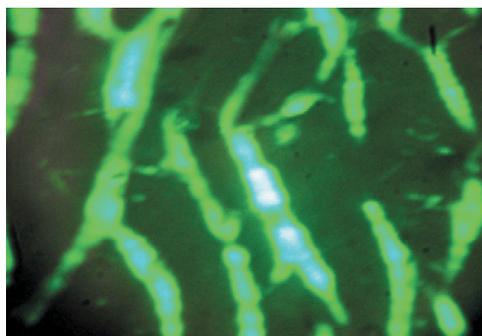


b) Crossed polarizers (45°), 150 °C

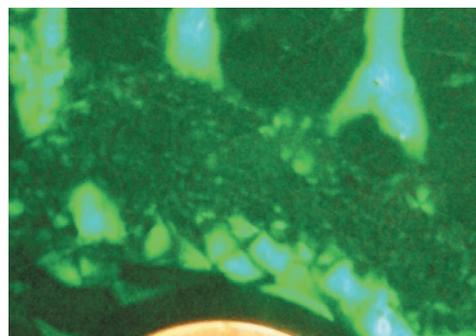


c) Crossed polarizers (90°), 153 °C

**Figure 8.** Textures of compound **2a** during heating cycle.



a)



b)

**Figure 9.** Textures of compound **2a** during heating cycle: a) Heating cycle, crossed polarizers, 192 °C, near transition to the isotropic phase; b) Heating cycle, crossed polarizers, 176 °C.

## Conclusions

Thus, the sulfo or alkylsulfamoyl derivatives of 2,9,16,23-tetrakis-(1-benzotriazolyl)-3,10,17,24-tetrakis-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines of copper and nickel were synthesized at first time.

Design and prognosis of column mesomorphism characteristic of discotic mesogens for these compounds were held. The results of prognosis were positive for sulfoderivatives **1a,b**, equally likely to alkylsulfamoyl substituted copper phthalocyanine **2a**, and negative for nickel complex **2b**.

Study of UV-Vis spectra of compounds **1a,b** and **2a,b** shows influence of substitution in 4-(1-methyl-1-phenylethyl)phenoxy fragments on the position of Q bands in spectra in concentrated sulfuric acid. Introduction of sulfo groups causes hypsochromic shift of the Q bands. Replacing of sulfo groups instead of alkylsulfamoyl increases this shift. Position of absorption bands in the organic solvents does not change.

In the study of liquid-crystalline properties of the sulfoderivatives **1a,b** a shift of interval of **1a** mesophase existence towards higher temperatures was found.

Alkylsulfamoyl derivative **2a** shows enantiotropic mesomorphism. Presence of octadecyl chains in the periphery of **2a** causes the decrease in the mesophase transition temperature and significant expansion of the range of existence of liquid-crystalline state in comparison to the parent compound **4a**. In addition, the temperature interval of existence of the mesophase alkylsulfamoyl substituted phthalocyanines **2a** was much wider than that of the corresponding sulfo substituted phthalocyanine **1a**. This is probably due to the significant increase of the length of 4-[1-methyl-1-phenylethyl]phenoxy fragments by introduction of octadecylsulfamoyl chains.

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