Copper 2,9(10),16(17),23(24)- and 1,8(11),15(18),22(25)-tetra-(4-carboxyphenoxy)phthalocyanines and their esters: the synthesis and liquid-crystalline properties

**E. V. Kudrik,[a]* A. I. Smirnova,[b] V. E. Maizlish,[a] T. V. Tararykina,[a]
G. P. Shaposhnikov,[a] and N. V. Usol´tseva[b]***

[a]Ivanovo State University of Chemistry and Technology,
7 prosp. F. Engel´sa, 153000 Ivanovo, Russian Federation.
Fax: +7 (093 2) 32 9502. E-mail: ttoc@isuct.ru
[b]Ivanovo State University,
39 ul. Ermaka, 153025 Ivanovo, Russian Federation.
Fax: +7 (093 2) 32 6600. E-mail: usol@ivanovo.ac.ru

Copper 2,9(10),16(17),23(24)- and 1,8(11),15(18),22(25)-tetra(4-carboxyphenoxy)phthalocyanines and their carboxylic esters were synthesized and their spectral characteristics and liquid-crystalline properties were studied. 2,9(10),16(17),23(24)-Tetrasubstituted complexes exhibit both thermotropic and lyotropic mesomorphism in mixtures with a number of organic solvents.

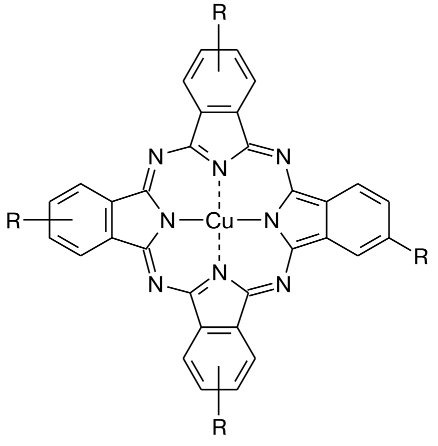
Key words: phthalocyanines, mesogen, mesophase, lyotropic mesomorphism, amphotropy, liquid crystals.

Until recently, hydrophobic octasubstituted phthalocyanines were considered as compounds whose liquid-crystalline properties were best studied. They were mentioned in all communications concerned with discotic mesogens.[1] Tetrasubstituted phthalocyanines possessing amphotropic properties (*i.e.*, both thermotropic and lyotropic mesomorphism) have been much less studied.[2—5]

Recently, we found that the presence of numerous lateral substituents in the phthalocyanine molecules is not a necessary pre-requisite for the formation of mesophases. For instance, it was shown that tetra-4-(n-alkoxycarbonyl)phthalocyaninatocopper **1** can possess both thermotropic and lyotropic mesomorphism in binary systems with organic solvents.[6]

By varying the length of the aliphatic chain in the lateral substituent we obtained different types of two-dimensionally ordered textures in the thermotropic state. By preparing binary systems involving organic solvents we succeeded to induce a mesomorphic state of non-mesomorphic homologs.

Recent studies[7] on the liquid-crystalline properties of various tetrasubstituted phthalocyanine complexes having bulky substituents revealed that the compounds can not only possess the mesomorphic properties, but also form glasses. This makes them promising materials for practical applications in, *e.g.*, optoelectronics for solar cell production.



1

R = $COOC_nH_{2n+1}$ (n = 3, 4, 6, 7, 9—11, 16)

Hexaesters of *scillo*-inositole are the classical discotic materials having a small central fragment (in contrast to phthalocyanine derivatives). Taking them as examples, we showed that introduction of a cyclic fragment[8] into the lateral substituent significantly stabilizes the mesomorphic properties compared to similar alkoxycarbonyl-substituted compounds.[6]

It is noteworthy that the liquid-crystalline properties of octasubstituted copper phthalocyanine complexes hav-

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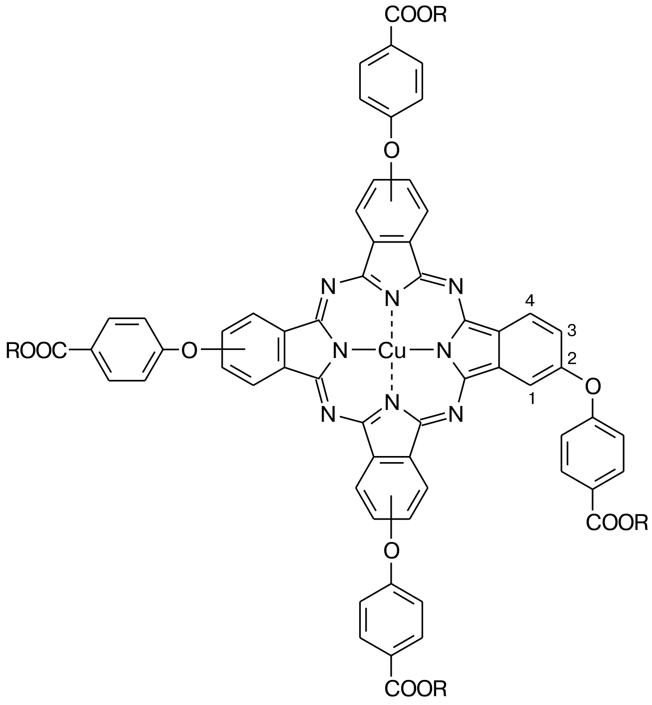
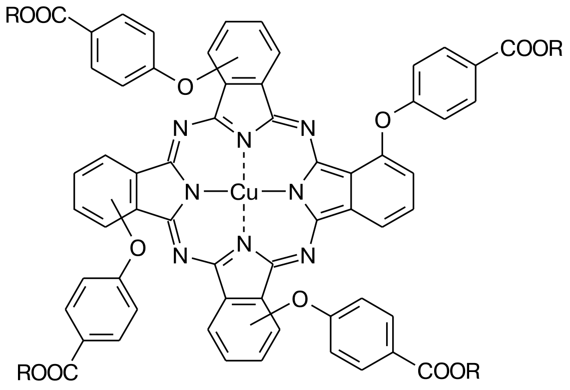


2a—i



3a,b

2: R = H (**a**), Pr (**b**), Bu (**c**), C_5H_{11} (**d**), *i*-C_5H_{11} (**e**), C_6H_{13} (**f**), C_7H_{15} (**g**), C_8H_{17} (**h**), C_9H_{19} (**i**); **3:** R = H (**a**), C_5H_{11} (**b**)

ing cyclic fragments in lateral substituents have already been reported.[9] The cyclic fragment was introduced into the lateral substituent of the phthalocyanine molecule in a target manner in order to obtain single-domain samples. Of particular importance was to separate the phenyl fragment and the aliphatic residue by a bridging oxygen atom,[10] because adjacency of these fragments caused a significant increase in viscosity and thus precluded the obtaining of single-domain samples. All these factors were taken into account in the design and studies of novel tetrasubstituted phthalocyanine derivatives.

The aim of this work was to synthesize and study the liquid-crystalline properties and spectroscopic characteristics of novel tetrasubstituted phthalocyanine derivatives **2a—i** and **3a,b** containing cyclic fragments in the lateral substituents, namely, two acids (compounds **2a** and **3a** (R = H)) and their esters (compounds **2b—i** and **3b** (R = C_nH_{2n+1})).

Results and Discussion

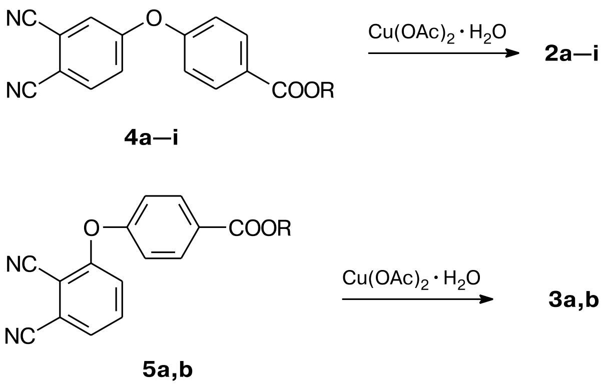
Synthesis. Extensive recent literature[11—19] on the synthesis and investigation of the properties of various tetra-4-hydroxyphthalocyanine derivatives including alkoxy-, aryloxy-, and pyridyloxy-substituted ones is available. Such complexes are usually obtained by the interaction of 4-R-oxyphthalodinitriles with a corresponding metal salt. The starting phthalodinitriles can be obtained by nucleophilic substitution of alcohols or phenols for the nitro group in the 4-nitrophthalodinitrile molecule.[15,20,21] This type of phthalocyanines has found applications as pH-sensitive dyes,[12] photosensitizers for photodynamic therapy of cancer,[13,14] catalysts for fuel cells and solar cells,[14] and in other fields of science and technology.[11,15—19]

Carboxy-substituted phthalocyanines were used as the starting compounds in the synthesis of corresponding esters that are characterized by high solubility in organic solvents[6,7,22,23] and possess both thermotropic and lyotropic mesomorphism.[6,7]

Based on the aforesaid, interest in the compounds combining the properties of aryloxy- and carboxy-substituted metal phthalocyanines is quite understandable. We synthesized a number of tetra-4- and tetra-3-hydroxyphthalocyaninatocopper derivatives starting from 4- or 3-(4-carboxyphenoxy)phthalodinitriles and their derivatives and studied their properties. Copper(II) cation was chosen to be the complex-forming agent because phthalocyaninatocopper(II) derivatives have square-planar geometries and most of them possess the mesomorphic properties.

Complexes **2** and **3** were synthesized by the interaction of corresponding aryloxy-substituted phthalodinitriles with copper acetate at 200 °C (Scheme 1). The starting 4- or 3-(4-carboxyphenoxy)phthalodinitriles **4a** and **5a** were obtained by the reaction of 4- or 3-nitrophthalodinitrile with 4-hydroxybenzoic acid in DMF in the presence of potassium carbonate.[24] Chloroanhydrides necessary for esterification were synthesized by boiling of 4- or 3-(4-carboxyphenoxy)phthalodinitriles with an excess of thionyl chloride.

Scheme 1



4: R = H (**a**), Pr (**b**), Bu (**c**), C_5H_{11} (**d**), *i*-C_5H_{11} (**e**), C_6H_{13} (**f**), C_7H_{15} (**g**), C_8H_{17} (**h**), C_9H_{19} (**i**); **5:** R = H (**a**), C_5H_{11} (**b**)

Unlike the starting phthalodinitrile **4a**, the chloroanhydride synthesized in this work is insoluble in dilute aqueous alkali solutions at room temperature. Dissolution of the compound occurs only on heating for a few minutes, which is due to hydrolysis of the compound and transfer of the corresponding carboxylate thus obtained in solution. On heating above 190 °C the chloroanhydride decomposes with liberation of hydrogen chloride. The 3-isomer **5a** behaves analogously.

The need of transforming carboxy dinitriles **4a** and **5a** to chloroanhydrides is due to the fact that esterification of carboxylic acids is always a complicated task owing to the ability of phthalodinitriles to react with alcohols to give isoindole derivatives under conditions for both acid and base catalysis. Chloroanhydrides are readily transformed to esters **4b—i** and **5b** on heating with an excess of corresponding alcohol. Compounds **4b,c,f** are low-melting white substances; other substituted phthalodinitriles are wax-like at room temperature. All of them are readily soluble in organic solvents ($CHCl_3$, CCl_4, acetone), being insoluble in water and aqueous ammonium hydroxide.

Individual character of the substituted phthalodinitriles was confirmed by elemental analysis and IR spectroscopy data.

The IR spectra of aryloxyphthalodinitriles exhibit the absorption bands characteristic of CN groups (2224—2240 cm^{-1}) and aryloxy groups (1244—1292 cm^{-1}).[25] The carboxyl C=O stretching bands lie in the range 1695—1705 cm^{-1} for the carboxy phthalodinitriles **4a** and **5a** and in the range 1715—1727 cm^{-1} for the esters **4b—i**.

Compounds **2a** and **3a** can be dissolved in alkali solutions. Phthalocyanine **2a** is only soluble in aqueous ammonium hydroxide solutions. The 3-isomer **3a** can also be dissolved in aqueous sodium hydroxide solutions. All the complexes synthesized are soluble in DMF, DMSO,

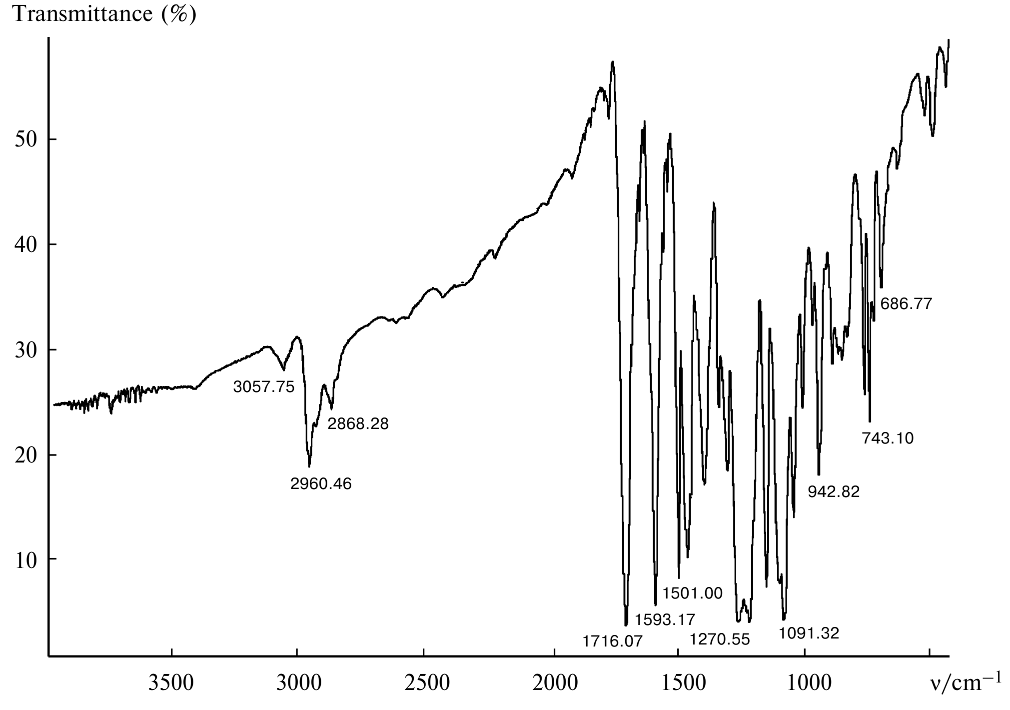


Fig. 1. IR spectrum of complex **2b**.

and conc. H_2SO_4; compounds **2b—i** and **3b** can also be dissolved in chloroform or benzene.

The IR spectra of the complexes (Fig. 1) exhibit the absorption bands characteristic of phthalocyanines;[26] the absorption bands corresponding to the functional groups in the lateral substituents are also observed. The spectra of tetra-4-(*n*-alkoxycarbonyl)phthalocyaninatocopper **1** (see Ref. 6) and complexes **2b—i**, **3b** are almost identical except for the absorption bands at 1234—1236 cm^{-1} in the spectra of the last-named compounds.

High solubility of the newly synthesized compounds allowed them to be studied by ^{1}H NMR spectroscopy. The low-field region of the ^{1}H NMR spectra of complexes **2b—i** and **3b** exhibits four groups of signals corresponding to absorption of the protons bonded to the phenyl ring carbon atoms, the signal positions being almost independent of the nature of the hydrocarbon radical. As an example, we will analyze the ^{1}H NMR spectrum of compound **2g** (R = C_7H_{15}) (Fig. 2).

The doublet δ 8.15 corresponds to eight phenylene protons in *ortho*-positions relative to the $COOC_7H_{15}$ group while other eight phenylene protons appear as a doublet at δ 7.30. The signals at δ 7.77, 7.26, and 7.40 can be attributed to protons in positions 4, 1, and 3 of the isoindole fragments, respectively. In the high-field region, the spectra of all the esters synthesized exhibit the signals of aliphatic radicals. In particular, in the region δ 0.70—4.30 the spectrum of compound **2g** shows the signals of twenty-four methylene and four methyl protons. Namely, a triplet in the region δ 4.30—4.40 corresponds to four α-methylene groups; proton signals of the β-methylene groups appear as a multiplet in the region δ 1.70—1.90; the signals of other four methylene groups and terminal methyl groups appear as multiplets in the regions δ 1.30—1.60 and 0.75—1.00, respectively. Thus, as the distance from the electron-withdrawing carbonyl group increases, the signals of aliphatic protons are shifted to the low-field region; this is a characteristic feature of all alkoxy- and alkoxycarbonyl-substituted compounds. The NMR spectra of the newly synthesized compounds **2b—i** and **3b** are more pronounced than those of the known[6] tetra-4-(*n*-alkoxycarbonyl)phthalocyaninatocopper **1** and exhibit signals of the aromatic protons in the region δ 7—10 (see Fig. 2). We believe this indicates a much less pronounced tendency of these complexes to association. This was confirmed in the analysis of their electronic absorption spectra.

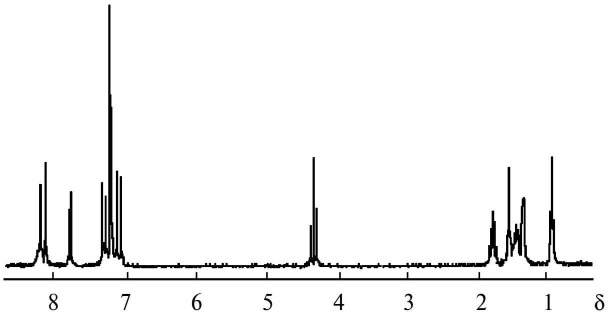


Fig. 2. ^{1}H NMR spectrum of complex **2g**.

Table 1. Positions of long-wavelength absorption bands in electronic absorption spectra of aryloxy-substituted copper phthalocyanines **2a—i** and **3a,b**

Compound	R	λ_{max}/nm		
		DMF	$CHCl_3$	Benzene
2a	H	621, 667	—	—
2b	Pr	—	612, 679	612, 648, 678
2c	Bu	—	613, 679	—
2d	C_5H_{11}	—	612, 679	—
2e	*i*-C_5H_{11}	—	612, 679	—
2f	C_6H_{13}	—	614, 677	—
2g	C_7H_{15}	—	613, 678	613, 647, 677
2h	C_8H_{17}	—	612, 678	613, 647, 677
2i	C_9H_{19}	—	611, 676	609, 646, 675
3a	H	669, 706	—	—
3b	C_5H_{11}	—	627, 694	628, 696

The electronic absorption spectra of the complexes in chloroform are typical of metal phthalocyanines. They exhibit an intense Q-band in the region 676—694 nm and a less intense band at 611—627 nm (vibrational satellite, Table 1). The character of the spectral curves shows that the complexes mainly exist in solutions in the monomeric form.

Analysis of the electronic absorption spectra of esters **2b—i** and **3b** suggests that the length and structure of the alkyl chain have almost no effect on the spectral pattern and positions of the most important absorption bands (Fig. 3 and Table 1).

It should be noted that 2,9(10),16(17),23(24)-tetra[(4-alkoxycarbonyl)phenoxy]phthalocyaninatocopper compounds **2b—i** are less prone to association than tetra-4-(*n*-alkoxycarbonyl)phthalocyaninatocopper **1**,[6] although the electronic absorption spectra of carboxylic acids **2a** and **3a** in DMF indicate the presence of associates in solutions similarly to the case of tetra-4-phenoxyphthalocyaninatocopper having unsubstituted phenoxy groups.[27] The substituent at position 3 of the benzene residues of the phthalocyanine molecule causes a large bathochromic shift of the Q-band (up to 40 nm) compared to the corresponding 4-isomers (see Fig. 3 and Table 1).

Thermotropic mesomorphism. Compounds **2a** and **3a** are brittle dark-violet crystals with good adhesion to the cover glass (probably, they can be electrized with ease). No melting and thermal decomposition of the samples occurs on heating of these acids to ~300 °C (upper limit of observation), *i.e.*, the substances are high-melting and do not exhibit the liquid-crystalline properties below 300 °C.

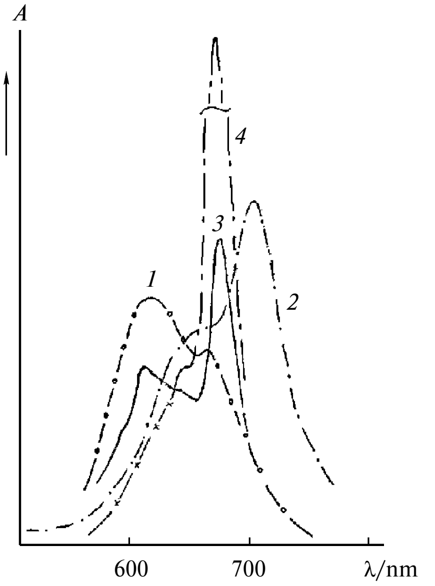


Fig. 3. Electronic absorption spectra of complexes **2a** (*1*), **3a** (*2*), and **2g** (*3*) in DMF and **2i** (*4*) in CCl_4.

Ester **3b** substituted at non-peripheral position 3 also does not exhibit mesomorphism.

A study of 2(4),9(10),16(17),23(24)-tetra[(4-alkoxycarbonyl)phenoxy]phthalocyaninatocopper compounds **2b—i** substituted at peripheral position 4 of the benzene rings showed that all of them possess liquid-crystalline properties in the temperature range from ~40 to 280 °C. The alkyl chain length affects the temperature interval in which the mesophase exists. At temperatures about 20 °C, the compounds are in the glassy state, which was confirmed by DSC (DSC curves obtained both on heating and on cooling show no peaks and a kink indicating the glass transition).

When heated, compounds **2b—i** undergo a transition from the glassy state to the liquid-crystalline state, which is retained up to a temperature of ~280 °C corresponding to the onset of thermal decomposition without transition to the isotropic phase. The absence of crystallization can probably be explained by the fact that the compounds under study represent mixtures of four isomers that are difficult to separate.

The viscous mesophase shown by the homologs **2b—i** is characterized by a non-geometric texture (Fig. 4, *a*), which develops to a herring-bone texture (Fig. 4, *b*) typical of columnar hexagonal mesophases at high temperatures.

Now we will consider two homologs, **2c** (R = Bu) and **2i** (R = C_9H_{19}) with a short and long aliphatic fragments in the substituents, respectively, in more detail. Our choice is due to the fact that earlier we observed a change in the type of translational ordering of columns in the mesophase formed by tetra-4-(*n*-alkoxycarbonyl)phthalocyaninatocopper **1** depending on the length of the aliphatic substituent.[6] Namely, the homologs with the alkyls C_4, C_6, and C_7 showed a tetragonally packed columnar mesophase while the homologs with the alkyls C_{11} and C_{16} showed a hexagonally packed one.

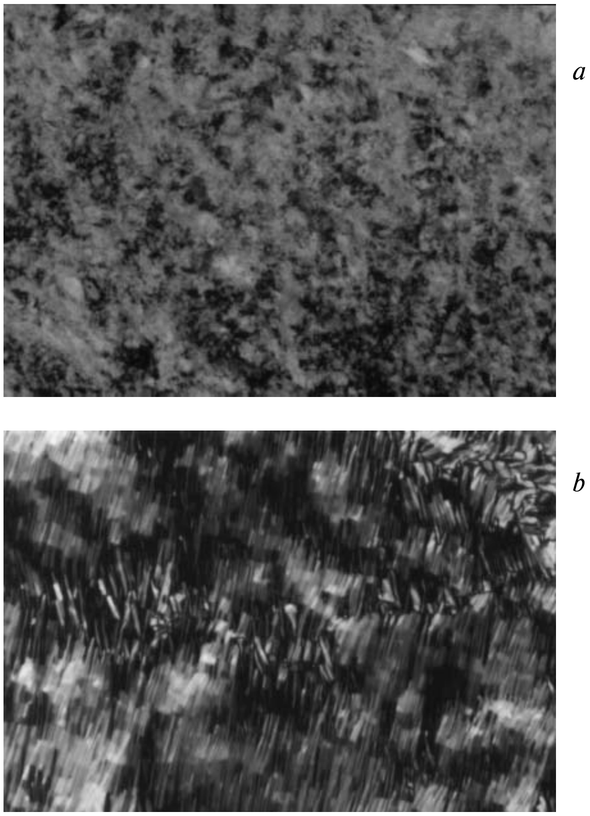


Fig. 4. Textures of columnar hexagonal mesophase observed for compound **2d** in crossed Nicol prisms at 78 (*a*) and 260 °C (*b*).

*Thermotropic mesomorphism of compound **2c***. A polarization microscopy study revealed an anisotropic glassy state of homolog **2c** at room temperature. When heated, the sample undergoes a gradual transition to the liquid-crystalline highly viscous phase. At ~60 °C, it is possible to prepare thin-layer samples and observe a non-geometric texture typical of columnar hexagonal mesophase. Further heating causes even greater gradual reduction of viscosity, but the texture remains unchanged up to a temperature of ~280 °C corresponding to the onset of thermal decomposition of the compound (according to TGA data). On cooling the mesophase undergoes a glass transition with retention of its texture.

The DSC curves obtained both on heating and on cooling exhibit a kink and one relaxation peak, which is most pronounced on heating (Fig. 5). This pattern of the DSC curves indicates that the substance undergoes a glass transition. The glass transition temperature (T_g) is ~33 °C on heating and ~29 °C on cooling.

The X-ray study of compound **2c** was carried out at two temperatures, 30 and 80 °C, which lie in the tempera-

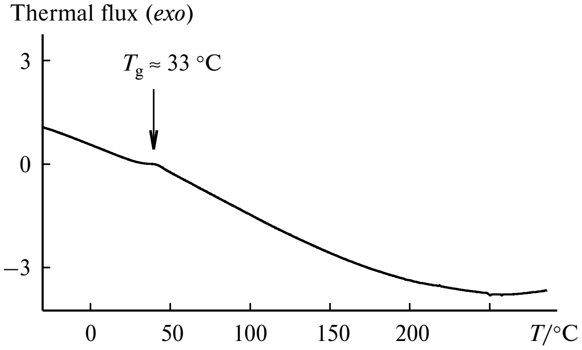


Fig. 5. DSC curve (third heating cycle) for ester **2c** (heating rate 10 deg min^{-1}).

ture ranges of existence of the glassy state and the mesophase, respectively. Experimental X-ray diffraction patterns obtained at both temperatures are identical, which also confirms the presence of a glass transition from the mesophase and the absence of crystallization. The X-ray diffraction patterns (Fig. 6) show clearly seen 100, 110 and 200 reflections characterized by a Bragg distance ratio of 1 : $1/3^{0.5}$: 1/2, which is typical of columnar hexagonal mesophase. The calculated hexagonal lattice constant a equals 24.75 and 24.87 Å at 30 and 80 °C, respectively. Additionally, both X-ray diffraction patterns show a clearly seen reflection in the large-angle region (d = 3.3 Å), which indicates an ordered arrangement of the molecules in columns.

Usually, X-ray diffraction patterns of discotic compounds with aliphatic lateral substituents exhibit a broad halo characteristic of "molten" disordered arrangement of hydrocarbon chains. In the X-ray diffraction pattern of compound **2c** the halo is weak and has a maximum in the range $10 < \theta < 11°$ (*i.e.*, d = 4—4.5 Å). Probably, low intensity of this maximum is due to the presence of short-chain lateral substituents (the aliphatic chain in the substituent includes only four carbon atoms).

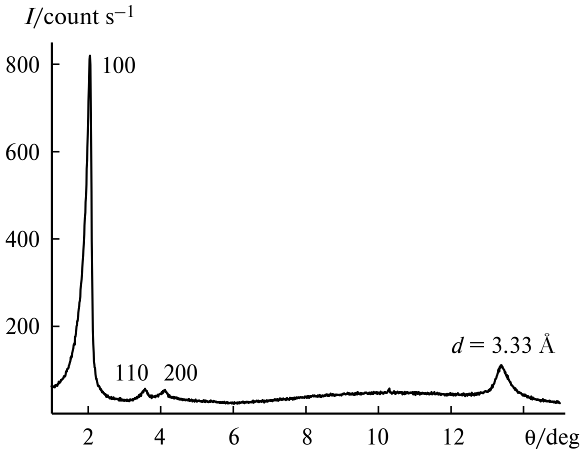


Fig. 6. X-Ray diffraction pattern of non-oriented sample of compound **2c** at 80 °C.

Thus, the results obtained by polarization microscopy, DSC, and X-ray analysis suggest that compound **2c** forms an ordered thermotropic columnar hexagonal mesophase of the $\mathrm{Col_{ho}}$ type, which exists in the temperature range from 33 to ~280 °C. At higher temperatures, thermal decomposition of the substance occurs without transition to the isotropic state. On cooling below 29 °C the mesophase undergoes a glass transition.

*Thermotropic mesomorphism of compound **2i**.* Based on the polarization microscopy data, it is difficult to determine whether compound **2i** is in the mesomorphic or in the glassy state at room temperature. The substance is highly viscous and therefore preparation of a uniform thin layer is a complicated task. However, we can say with certainty that this is not a crystalline substance. The viscosity decreases on heating and at ~65 °C it is possible to prepare a thin-layer sample, which has a non-geometric texture in polarized light.

The DSC curves obtained both on heating and on cooling in the temperature range from –40 to 280 °C exhibit only a kink, which proves the existence of the glassy state at low temperatures and the absence of crystallization. The temperature interval corresponding to glass transition is rather broad. The glass transition temperature T_g is ~88 °C on heating and ~58 °C on cooling. No measurements were carried out above 280 °C because the TGA data revealed thermal decomposition of the substance.

An X-ray study was carried out at room temperature and at 65 and 110 °C. Raising the temperature causes an increase in the intensities of the small-angle reflections and peaks become more pronounced (Fig. 7). For instance, only one signal (100) is observed at room temperature, whereas at 65 °C we also observed the 110 and 200 reflections. This is particularly pronounced at 110 °C, namely, a fourth reflection (210) is added to the three reflections (100, 110, and 200) . It should be noted that the positions of the reflections are almost independent of temperature. According to calculations, the ratio of the Bragg distances for the signals observed is 1 : $1/3^{0.5}$: 1/2 : $1/7^{0.5}$, being typical of the columnar hexagonal mesophase. The hexagonal lattice constant a is 30.35 Å. As for compound **2c** (R = Bu), at all temperatures the X-ray diffraction patterns of homolog **2i** (R = C_9H_{19}) show a signal in large-angle region ($d \approx 3.4$ Å), which indicates an ordered type of the columnar hexagonal mesophase. A broad halo ($d \approx 4.7$ Å) is more pronounced compared to that observed for homolog **2c**. This is probably due to longer aliphatic fragments in lateral substituents.

Thus, our X-ray study of complexes **2c** (R = Bu) and **2i** (R = C_9H_{19}) showed that they form highly ordered columnar hexagonal mesophases with intermolecular distance in columns 3.3—3.4 Å.

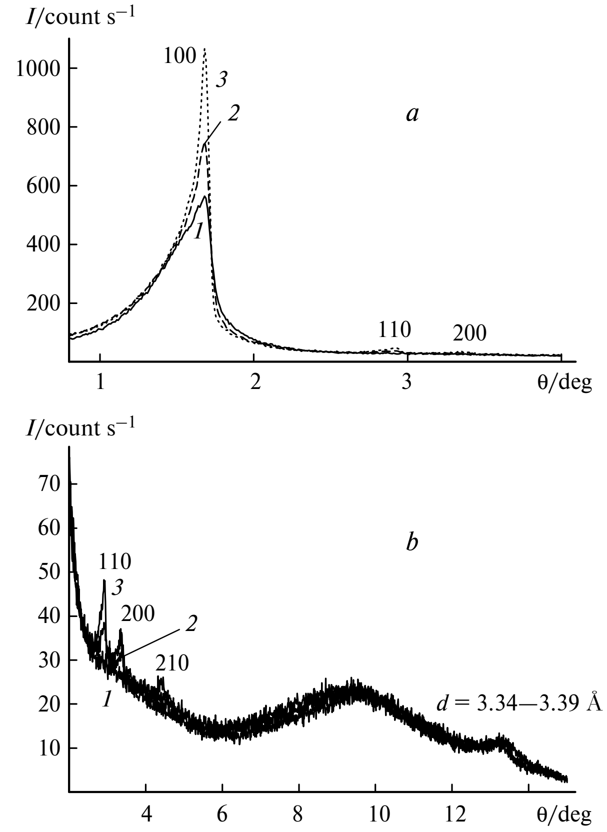


Fig. 7. X-Ray diffraction pattern of non-oriented sample of compound **2i** in the region of the first reflection 100 (small-angle region) (*a*) and in the region of other reflections and in the large-angle region (*b*): $T = 25$ (*1*), 65 (*2*), and 110 °C (*3*).

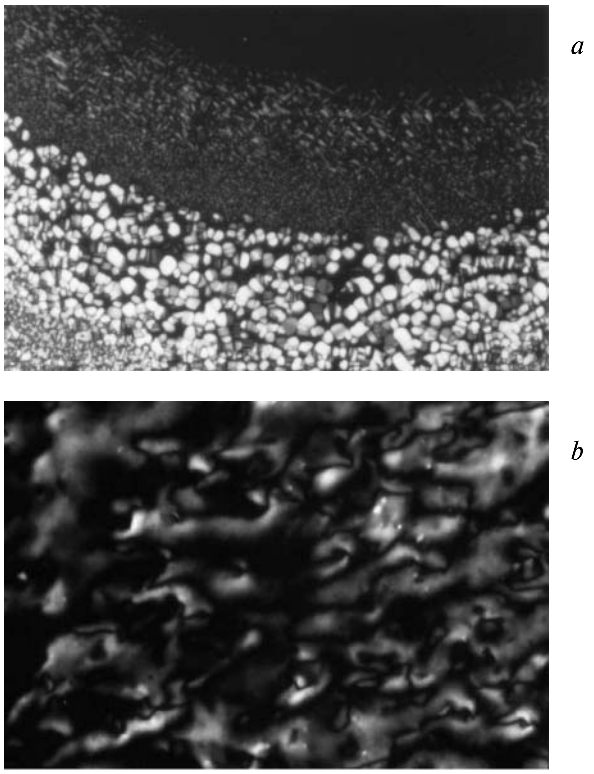


Fig. 8. Textures observed in contact preparation of binary system **2a**—DMSO at room temperature (after cooling): mosaic texture, nuclei of Schlieren textures, isotrope (upward) (*a*) and the Schlieren texture (*b*). Crossed Nicol prisms, ×250.

Lyotropic mesomorphism. A study of binary compositions formed by non-mesomorphic compounds **3a,b** substituted at non-peripheral position 3 with such solvents as cyclohexane, chloroform, benzene, cyclohexanone, DMSO, DMF, water, and aqueous NaOH (pH 12) and NH_4OH (pH 11) solutions showed that none of these systems possesses lyotropic mesomorphism.

At the same time non-mesomorphic acid **2a** substituted at peripheral position 4 in binary systems with DMSO, DMF, and aqueous ammonia solution at room temperature forms two types of lyomesophases: 1) mesophase with non-geometric or soap-like texture, which transforms to a mosaic texture on cooling (Fig. 8, *a*) and 2) mesophase with spherolites and Schlieren texture (Fig. 8, *b*), which is more viscous than conventional nematic mesophase. Based on the textures observed and on the viscosities of the lyomesophases formed, we can suggest that the former phase can have a columnar two-dimensionally ordered structure and the latter can have a nematic or lamellar columnar structure.

It should be noted that unlike tetra-4-carboxyphthalocyaninatocopper,[6b,28] complex **2a** is prone to lyomesomorphism not only in aqueous ammonium hydroxide solutions, but also in polar organic solvents, such as DMSO and DMF. Thus, hydrophobic "bridges" (oxyphenylene groups) in complex **2a** undoubtedly make a large contribution to intermolecular interactions, which manifests itself as a tendency to association and affects the microsegregation of this complex.

Among esters **2b—i**, lyotropic mesomorphism studies were carried out for compounds **2c—e**. We found that they possess lyotropic polymesomorphism with various organic solvents. The temperature range of existence of the lyomesophase depends on the degree of saturation of chemical bonds in the cyclic solvents. For instance, compounds **2c—e** are readily soluble in mixtures with unsaturated cyclic hydrocarbons (benzene or cyclohexene) and chloroform and show three types of lyomesophases in the contact preparations at room temperature. One lyomesophase has a texture similar to that observed in the thermotropic state (Fig. 9, *a*). The other two lyomesophases are probably nematic ones, being characterized by the Schlieren and cloud textures (Fig. 9, *b*). These two types of textures were observed in our previous studies of lyotropic compositions of macrocyclic tetranuclear metal complexes[29] and octasubstituted phthalocyanines.[30]

Mixtures of homologs **2c—e** with cyclic saturated hydrocarbons (cyclohexane, cyclooctane, or cyclodecane)

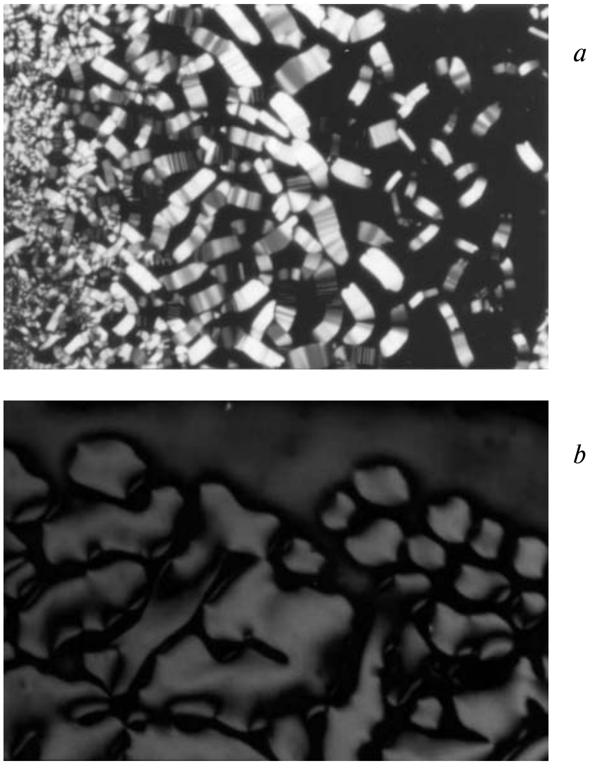


Fig. 9. Photomicrographs of lyotropic systems **2d**—organic solvent (crossed Nicol prisms, magnification ×250): nucleation of two-dimensionally ordered columnar mesophase on cooling from the isotrope to **2d**—$CHCl_3$ contact preparation, T = 23 °C (*a*) and two types of nematic phases (Schlieren texture is shown below and a cloud texture is shown above) in the contact preparation **2d**—cyclohexene at room temperature (*b*).

form the same lyomesophases, but this occurs at higher temperatures.

It is important that a study of the contact preparations of compounds **2c—e** with linear alkanes (from pentane to pentadecane) revealed no formation of new mesophases, except for the two-dimensionally ordered columnar phase, which existed in the thermotropic state. Therefore, mixing of phthalocyanines **2c—e** with linear saturated hydrocarbons is only accompanied by the swelling due to penetration of the solvent into peripheral regions of supramolecular columnar ensembles. In other words, in this case linear alkanes do not induce lyotropic mesomorphism in contrast to the previously studied series of tetra-4-(*n*-alkoxycarbonyl)phthalocyanines **1** whose mixtures with linear hydrocarbons form a nematic lyomesophase.[6]

Based on the aforesaid, we can conclude that simultaneous presence of a bridging oxyphenylene fragment and the ester or carboxyl groups in the phthalocyanine molecule makes a tendency of these compounds to form highly ordered lyomesophases more pronounced and the spectrum of the lyomesophases becomes much broader.

Although the tendency to association of compounds in solutions is a prerequisite for the formation of lyotropic mesophases in these systems, it is not a key factor. Indeed, some compounds possessing this property do not show lyomesomorphism, while complexes **2a—i** present in solutions mainly as monomers showed a mesophase.

Our study of mesomorphism in the homologous series **2b—i** revealed that they can form both thermotropic and lyotropic mesophases (amphotropy). The amphotropic properties of these compounds depend on the length of the lateral substituents.

Thus, we synthesized and characterized novel representatives of tetrasubstituted copper phthalocyanines, namely, compounds **2** and **3** containing phenyl fragments in the substituents. We showed the effects of the substitution site (peripheral/non-peripheral) in the benzene fragments of the phthalocyanine molecules and of the structure of the lateral substituent on the liquid-crystalline properties. Phthalocyanines containing OC_6H_4COOH fragments at peripheral positions of the benzene rings (*e.g.*, compound **2a**) do not form thermotropic mesophases (as in the case of simple replacement of four carboxyl groups[6b]); however, two types of lyotropic mesophases can be formed in the binary systems including **2a** and DMSO, DMF, or aqueous ammonia solution. Further modification of the lateral substituents by esterification of carboxy groups causes compounds **2b—i** not only to form an ordered thermotropic columnar hexagonal mesophase Col_{ho}, but also to exhibit lyotropic mesomorphism in mixtures with organic solvents. This type of substituents in non-peripheral positions of the benzene rings in the phthalocyanine molecules causes suppression of the mesomorphic (both thermotropic and lyotropic) properties of tetra-3-(4-carboxyphenoxy)phthalocyaninatocopper **3a** and the corresponding ester **3b**. Unlike tetra-4-(*n*-alkoxycarbonyl)phthalocyaninatocopper **1**,[6] compounds **2b—i** can undergo a glass transition, which creates prerequisites for the use of these compounds in optoelectronics.

Experimental

The phase state of individual compounds and phthalocyanine—solvent binary systems were studied by the classical methods of investigation of liquid crystals including polarization microscopy, DSC, and X-ray analysis.

The phase state of the samples was studied with a Leitz Laborlux 12 Pol polarization microscope equipped with a Mettler FP 82 heating stage and a Wild MPS 51 photograph accessory (24×36 mm^2). Lyotropic mesomorphism was studied by the contact preparations method. The second components of the binary systems studied were linear alkanes from pentane to pentadecane, as well as cyclohexane, cyclooctane, cyclodecane, cyclohexene, and chloroform (Merck and Aldrich). These compounds are traditionally used as solvents in studies of hydrophobic discotic mesogens.

DSC experiments were carried out on a Perkin Elmer DSC 7 instrument at a heating rate of 10 deg min^{-1}.

X-Ray study was carried out on a Huber Guinier-goniometer 600 instrument equipped with a Huber 611 quarz monochromator, a Huber HTC 9000 stepping motor controller, and a Huber 9634 temperature controller, with a standard resolution of 0.01°, acquisition time of 20 s per 1 step. A tube with a Cu cathode (λ = 1.54051 Å) was used for generation of X-ray radiation.

Electronic absorption spectra were recorded on a Perkin Elmer Lambda 200 UV/VIS spectrophotometer. IR spectra were obtained with an IR-Beckmann 9 instrument. ^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer (250 MHz) in $CDCl_3$ solutions with Me_4Si as a reference.

Synthesis of (carboxyphenoxy)phthalodinitriles 4a and 5a (general procedure). To DMSO (60 mL), 4- or 3-nitrophthalodinitrile (1.73 g, 0.01 mol), 4-hydroxybenzoic acid (2.07 g, 0.015 mol), and freshly calcined potassium carbonate (4.14 g, 0.03 mol) were added at 20—25 °C. The mixture was stirred for 6 h at 100 °C, cooled, the solution thus obtained was poured into a fourfold amount of water, filtered, the filtrate was acidified by hydrochloric acid solution, the precipitate was washed with water until neutral pH value and recrystallized from water.

4-(4-Carboxyphenoxy)phthalodinitrile (4a). Yield 1.2 g (45%). IR (KBr), ν/cm^{-1}: 2232 ($C\equiv N$); 1290, 1252 (Ar—O—Ar); 1695 (COOH). Found (%): N, 10.80. $C_{15}H_8N_2O_3$. Calculated (%): N, 10.60.

3-(4-Carboxyphenoxy)phthalodinitrile (5a). Yield 1.1 g (42%). IR (KBr), ν/cm^{-1}: 2232 ($C\equiv N$); 1290, 1252 (Ar—O—Ar); 1705 (COOH). Found (%): N, 10.40. $C_{15}H_8N_2O_3$. Calculated (%): N, 10.60.

4-(Dicyanophenoxy)benzoyl chlorides were synthesized following a known procedure[24] by the interaction of compounds **4a** or **5a** (2.64 g, 0.01 mol) with boiling thionyl chloride (50 mL) with continuous stirring for 20 h. Excess thionyl chloride was removed by evaporation at ~20 °C and the residue was dried *in vacuo* at 50 °C.

4-(3,4-Dicyanophenoxy)benzoyl chloride, yield 2.5 g (84%). Found (%): Cl, 11.75; N, 9.43. $C_{15}H_7ClN_2O_3$. Calculated (%): Cl, 11.87; N, 9.38.

4-(2,3-Dicyanophenoxy)benzoyl chloride, yield 2.42 g (81%). Found (%): Cl, 11.76; N, 9.43. $C_{15}H_7ClN_2O_3$. Calculated (%): Cl, 11.87; N, 9.38.

Synthesis of phthalodinitriles 4b—i and 5b (general procedure). Chloroanhydride of compound **4a** or **5a** (0.3 g, 0.001 mol) and corresponding preliminarily dehydrated alcohol (10 mL) were boiled with continuous stirring until HCl liberation ceased (~1.5—2 h). Then the excess of alcohol was removed *in vacuo* and the reaction products were dried. The yields and elemental analysis data are listed in Table 2.

Synthesis of substituted copper phthalocyanines 2a—i and 3a (general procedure). A thoroughly ground mixture of corresponding substituted phthalodinitrile (0.015 mol) and copper(II) acetate hydrate (0.76 g, 0.004 mol) was heated at 200 °C with stirring for 20—30 min. The melt was thoroughly ground, washed with 10% hydrochloric acid and water until neutral pH value, and dried.

Table 2. Yields and elemental analysis data for phthalodinitriles **4b—i**

Compound	R	Yield (%)	Found/Calculated (%)			Molecular formula
			C	H	N	
4b	Pr	67	70.50 70.58	4.80 4.61	9.09 9.15	$C_{18}H_{14}N_2O_3$
4c	Bu	69	70.99 71.24	5.04 5.03	8.68 8.74	$C_{19}H_{16}N_2O_3$
4d	C_5H_{11}	69	71.80 71.84	5.50 5.43	8.35 8.38	$C_{20}H_{18}N_2O_3$
4e	*i*-C_5H_{11}	57	71.81 71.84	5.51 5.43	8.35 8.38	$C_{20}H_{18}N_2O_3$
4f	C_6H_{13}	63	72.36 72.40	6.00 5.79	8.02 8.04	$C_{21}H_{20}N_2O_3$
4g	C_7H_{15}	66	72.73 72.91	6.14 6.12	7.66 7.73	$C_{22}H_{22}N_2O_3$
4h	C_8H_{17}	64	73.35 73.38	6.50 6.43	7.45 7.44	$C_{23}H_{24}N_2O_3$
4i	C_9H_{19}	64	73.81 73.82	7.00 6.71	7.15 7.17	$C_{24}H_{26}N_2O_3$

Table 3. Yields and elemental analysis data for tetrasubstituted copper phthalocyanines **2a—i** and **3a,b**

Compound	R	Yield (%)	Found/Calculated (%)			Molecular formula
			C	H	N	
2a	H	45	64.60 64.32	3.00 2.88	9.97 10.00	$C_{60}H_{32}CuN_8O_{12}$
2b	Pr	46	67.08 67.10	4.45 4.38	8.66 8.69	$C_{72}H_{56}CuN_8O_{12}$
2c	Bu	66	68.00 67.87	5.00 4.80	8.24 8.33	$C_{76}H_{64}CuN_8O_{12}$
2d	C_5H_{11}	61	68.48 68.58	5.24 5.18	8.01 8.00	$C_{80}H_{72}CuN_8O_{12}$
2e	*i*-C_5H_{11}	56	68.42 68.58	5.24 5.18	7.98 8.00	$C_{80}H_{72}CuN_8O_{12}$
2f	C_6H_{13}	54	69.16 69.24	5.70 5.53	7.58 7.69	$C_{84}H_{80}CuN_8O_{12}$
2g	C_7H_{15}	53	70.02 69.85	6.00 5.86	7.35 7.40	$C_{88}H_{88}CuN_8O_{12}$
2h	C_8H_{17}	57	70.38 70.41	6.24 6.17	7.10 7.14	$C_{92}H_{96}CuN_8O_{12}$
2i	C_9H_{19}	59	70.61 70.94	6.56 6.45	7.00 6.89	$C_{96}H_{104}CuN_8O_{12}$
3a	H	42	64.59 64.32	3.00 2.88	9.80 10.00	$C_{60}H_{32}CuN_8O_{12}$
3b	C_5H_{11}	47	68.49 68.58	5.23 5.18	7.80 8.00	$C_{80}H_{72}CuN_8O_{12}$

Complexes **2a** and **3a** were dissolved in 3% hydroxide ammonium, filtered, the solution was acidified with dilute hydrochloric acid, the precipitate was washed with water until neutral pH value of the rinse water and the absence of chloride ions in the filtrate, and then reprecipitated from concentrated sulfuric acid.

Compounds **2b—i** and **3b** were pre-extracted with chloroform or benzene and purified by chromatography on alumina with a benzene—chloroform (1 : 1) mixture as eluent. The solvent was removed *in vacuo*. All complexes were dried *in vacuo* at 140—170 °C. The yields and elemental analysis data are listed in Table 3.

Unlike other compounds, complex **3b** was obtained without isolation of phthalodinitrile. The interaction of 4-(2,3-dicyanophenoxy)benzoyl chloride with pentan-1-ol was followed by immediate addition of copper acetate to the solution and the reaction mixture was kept at 195—200 °C.

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