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N. Usol'tseva [a], V. Bykova [a], G. Ananjeva [a], N. Zharnikova [a] & E. Kudrik [b]

[a] Liquid Crystal Laboratory, State University, Ivanovo, Russia

[b] Ivanovo State University of Chemistry and Technology, Russia

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MESOMORPHISM AND GLASS FORMATION OF PHTHALOCYANINE METAL COMPLEXES WITH BULKY SUBSTITUENTS

N. Usol'tseva, V. Bykova, G. Ananjeva, and N. Zharnikova
Liquid Crystal Laboratory, State University, Ivanovo, Russia

E. Kudrik
Ivanovo State University of Chemistry and Technology, Russia

This paper deals with the synthesis of phthalocyanine complexes, containing four oligo(oxyethylene)-, oxybenzene-, esther of p-oxybenzoic acid or p-oxyazobenzene side chains terminated by a bulky trityl substituent. Their purity was established by column chromatography and by satisfactory elemental analysis. The structures of resultant phthalocyanines were characterized by nuclear magnetic resonance (NMR), fast atom bombardment mass spectroscopy (FAB-MS), ultraviolet-visible (UV-VIS) and infrared (IR) spectroscopy and their phase transitions were studied by polarizing optical microscopy. Some of these complexes exhibit enantiotropic mesomorphic properties and transition into glass state on cooling. The glass appearance is influenced not only by side chains' structure, but also by the nature of metal.

Keywords: bulky substituents; glass formation; phthalocyanine derivatives; thermotropic and lyotropic mesomorphism

INTRODUCTION

Materials with hole conductivity, with distinctive properties of film formation as well as with high temperature transition into glass state are ideal for developing a number of devices in the field of optoelectronic [1]. These substances are the disc-like aromatic compounds such as triphenylene or phthalocyanine (Pc) derivatives, which form columnar mesophases [2]. To the present moment, the information about the influence of their molecular structure on the glass-forming ability is very scarce. It is

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Address Correspondence to N. Usol'tseva, Liquid Crystal Laboratory, State University, Ivanovo, Russia

considered that substances with such properties are an exception rather than a rule [3]. Therefore, the synthesis of new discotic mesomorphic compounds possessing the phase transition into glass state should be considered an important branch of research.

A well-characterized isotropic glass was recently described for Pc derivatives containing four bulky groups attached directly to the macrocycle [4,5]. Having chosen this way, we have synthesized Pc derivatives containing a bulky trityl substituent with various bridge-groups.

MATERIALS AND METHODS

Pc derivatives (Fig. 1), containing four oligo(oxyethylene)-(**I**–**III**), oxybenzene- (**IV**), esther of *p*-oxybenzoic acid (**V**) and *p*-oxyazobenzene-(**VI**) side chains terminated by a bulky trityl substituent were synthesized. Their purity was established by column chromatography and by satisfactory elemental analysis. The structures of resultant Pcs were characterized by nuclear magnetic resonance (NMR), fast atom bombardment mass

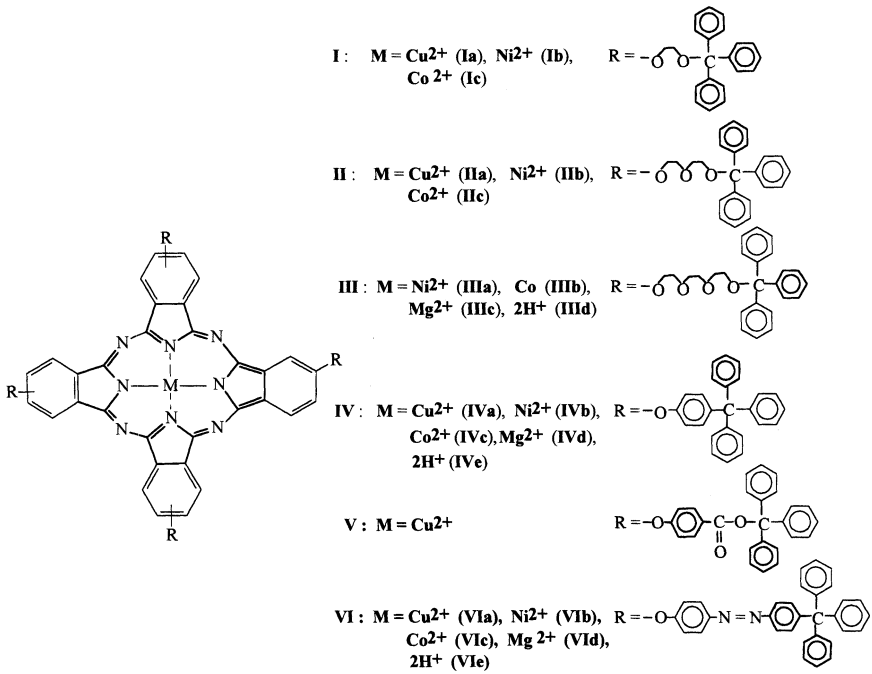


FIGURE 1 The structure of tetrasubstituted phthalocyanine derivatives **I–VI** with bulky substituents.

spectroscopy (FAB-MS), ultraviolet-visible (UV-VIS) and infrared (IR) spectroscopy.

The thermal behaviour of Pc derivatives was performed using polarizing optical microscopy (Leitz Laborlux 12 Pol microscope in conjunction with a Mettler FP 82 hog stage). The texture photographs were taken with a 24×36 mm microscope camera and a Photoautomat Wild MPS51.

The study on lyotropic mesomorphism of the given compounds was carried out by means of contact preparations with benzene, toluene or chloroform as a solvent. These solvents were obtained from E. Merh Ltd. Darmstadt, Germany.

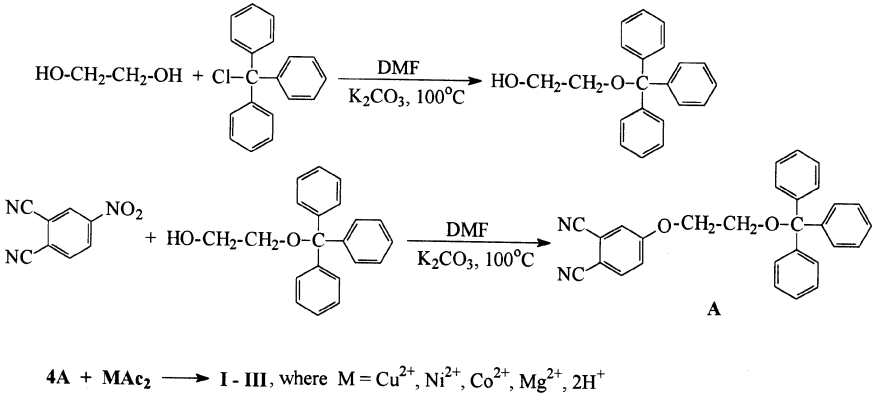
SYNTHESIS

Synthesis and Characterization of Pc Derivatives I–VI (Fig. 1)

1. Synthesis of Pc Complexes I–IIIa,b,c,d

The synthetic route to the Pcs **I–III** is shown in the Scheme 1.

The tetrasubstituted Pc complexes **I–III** were obtained by alloying of correspondent substituted phthalodinitriles with copper, nickel, cobalt or magnesium acetates. The starting phthalodinitriles were obtained by interaction of 4-nitrophthalodinitrile and the suitable monotriphenylmethylated ethylene glycol. The latter were obtained by interaction of ethylene glycol with triphenylchlormethane. The purification of Pcs **I–III** was carried out by column chromatography (Al_2O_3). The impurities were washed away by benzene, and the main products were washed by the mixture of benzene – chloroform (5:2). The structure and purity of all obtained compounds was



SCHEME 1 Synthesis of the phthalodinitrile precursors and of the tetrasubstituted Pc complexes **I–III**.

controlled by elemental analysis, thin-layer chromatography, IR-, NMR-, UV-VIS spectroscopy.

2. Synthesis of Pc Complexes IV

The synthetic route to the Pcs **IV** is shown in the Scheme 2.

The compounds **IVa–c** were obtained by alloying of 4-(2-trityl-phenoxy)-1,2-dicyanobenzene with copper, nickel or cobalt acetates at the presence of urea at 220°C. The method of synthesis of the precursors is similar to a method of synthesis **I–III**. The purification of obtained Pcs was carried out by column chromatography (Al_2O_3). The impurities were extracted by acetonitrile, and the main products were washed by benzene.

The compound **IVd** was synthesized by boiling 4-(2-trityl-phenoxy)-1, 2-dicyanobenzene in butanol at the presence of butylate Mg. The resultant Pc was purified by column chromatography (Al_2O_3). The impurities were washed away by benzene, and the main product was washed by chloroform.

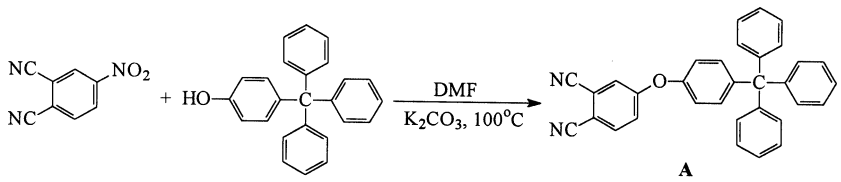
The complex **IVe** was prepared by boiling 4-(2-tritylphenoxy)-1,2-dicyanobenzene in N,N-dimethyl-3-amino-1-propanol. The synthesized Pc **IVe** was purified in a Soxhlet apparatus. The impurities were washed away by acetonitrile, and main product was extracted by benzene. The final purification was carried out by column chromatography (Al_2O_3, benzene as eluent).

The structure and purity of all synthesized compounds **IVa–e** was controlled by elemental analysis, thin-layer chromatography, IR-, NMR-, UV-VIS spectroscopy and FAB-MS.

3. Synthesis of Pc Complex V

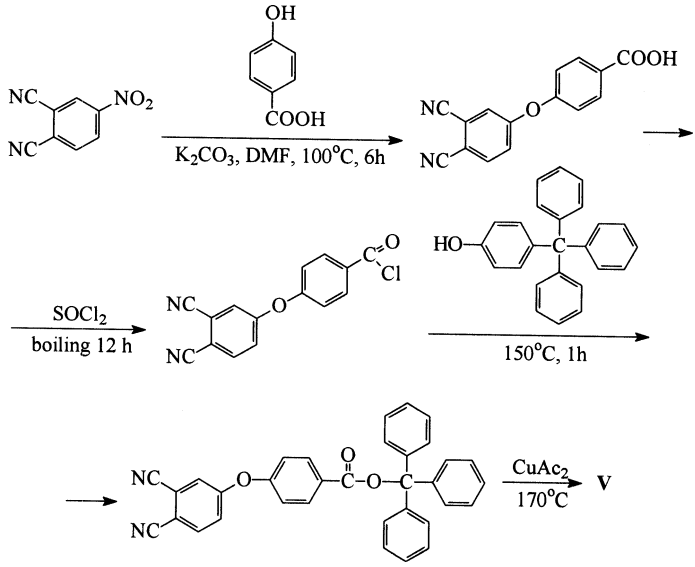
The synthetic route to the Pc **V** is shown in the Scheme 3.

The compound **V** was obtained by alloying of trityl ester of 4-phenoxy-4′-carboxyphthalodinitrile with copper acetate at 179°C. The impurities were removed by acetonitrile in a Soxhlet apparatus. The obtained product



4A + MAc_2 ⟶ **IV**, where M = Cu^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, $2H^+$

SCHEME 2 Synthesis of the phthalodinitrile precursors and of the tetrasubstituted Pc complexes **IV**.



SCHEME 3 Synthesis of the phthalodinitrile precursors and of the tetrasubstituted Pc complexes **V**.

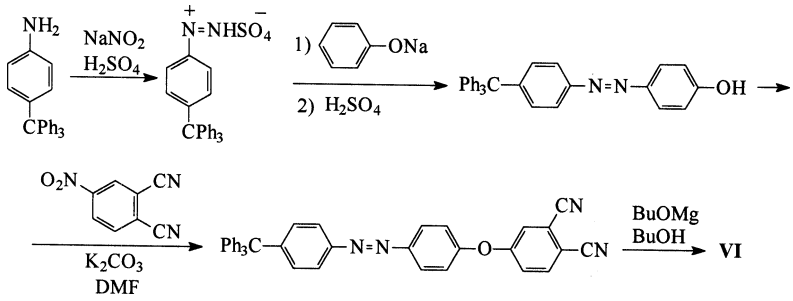
was carefully purified by column chromatography (Al_2O_3, benzene – chloroform (1:1) as eluent). The trityl ester of 4-phenoxy-4′-carboxyphthalodinitrile was obtained by interaction of excess triphenylmethanol with chloroanhydride of 4-phenoxy-4′-carboxyphthalodinitrile. The latter was prepared by nucleophilic substitution of *p*-oxybenzoic acid for 4-nitrogroup of 4-nitrophthalodinitrile at the presence K_2CO_3 in medium DMF. The purification of synthesized Pc **V** was carried out by column chromatography (Al_2O_3).

The structure and purity of the compound **V** was controlled by elemental analysis, thin-layer chromatography, IR-, NMR-, UV-VIS spectroscopy.

4. Synthesis of Pc Complexes **VI**

The synthetic route to the Pcs **VI** is shown in the Scheme 4.

The starting 4-hydroxy-4′-tritylazobenzene was obtained by diazotization reaction of 4-tritylaniline and $NaNO_2$ in acetone at the presence of H_2SO_4. Further the 4-hydroxy-4′-tritylazobenzene was combined with phenol in alkalescent medium. After completing of the reaction the suspension was diluted by water. Then the precipitate was filtered, washed with 0.5% solution of sulfuric acid, and the water up to neutral reaction. The crude product was purified by column chromatography (Al_2O_3, benzene as eluent). Further, the 4-[p-(p′-tritylphenylazo)phenoxy]-1,2-dicyanobenzene



SCHEME 4 Synthesis of the phthalodinitrile precursors and of the tetrasubstituted Pc complexes **VI**.

was obtained by interaction of 4-hydroxy-4′-tritylazobenzene and 4-nitrophthalodinitrile in medium DMF at the presence of K_2CO_3. The reaction mixture was diluted by water and after a filtration and drying was purified by column chromatography (Al_2O_3).

The synthesis of Pc derivatives **VIa–c** was carried out by alloying of obtained phthalodinitrile with copper, nickel or cobalt acetates. The Pc complexes **VIa–c** were purified by column chromatography (Al_2O_3). The impurities were washed away by benzene, and so were MPc, by the mixture of benzene – chloroform (5:1).

The compound **VId** was prepared by boiling 4-[p-(p′-tritylphenylazo)-phenoxy]-1,2-dicyanobenzene in butanol at the presence of butylate Mg.

The **VIe** was obtained by heating of the mixture of phthalodinitrile and CF_3COOH. The crude product was purified by column chromatography (Al_2O_3): the impurities were washed away by benzene, and H_2Pc was washed by the mixture benzene – chloroform (6:1).

The structure and purity of all synthesized compounds **VIa–e** was controlled by elemental analysis, thin-layer chromatography, IR-, UV-VIS spectroscopy and MALDI-TOF MS.

MESOMORPHIC PROPERTIES

The polarizing optical microscopy study of mesomorphism of the given compounds revealed that the **Ib**, **IIa**, **IV(a,c)**, **V** and **VI(c,e)** display thermotropic mesomorphism of columnar type (Fig. 2).

Table 1 shows temperatures of phase transitions of the phthalocyanine derivatives on heating.

It is worth pointing out that the following compounds **Ib**, **IIa**, **IV(a,c)**, **V** and **VI(c,e)** form high-temperature phase transition into glass state on cooling (Fig. 3).

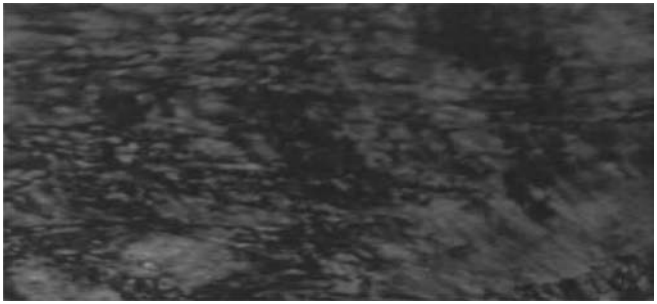


FIGURE 2 Optical texture of the mesophase of Pc **VIe** on heating, (250°C, 250 × magnification, crossed polarizes).

The study of binary systems composed of the above-listed compounds (**I**–**VI**) with benzene, toluene or chloroform showed that the lyotropic mesomorphism is typical for **IIa**, **V** and **VI(a, b, e)**.

In the series of oxyethylene phthalocyaninato nickel complexes (**Ib**, **IIb**, **IIIa**) the mesomorphic properties of these compounds are changed. The

TABLE 1 Phase Transition for **I**–**VI** Compounds: Cr = crystalline, Col = columnar, I = isotropic

No	Thermotropic mesomorphism, °C	Lyotropic mesomorphism
Ia	**Cr**—175 **I**	–
Ib*	**Cr** — 92 **Col** — 219 **I**	–
Ic	**Cr** — 56 **I**	–
IIa*	**Cr** — 50 **Col** 180 **I**	+
IIb	**Cr** — 130 **I**	–
IIc	**Cr** — 115 **I**	–
IIIb	**Cr** — 200 **I**	–
IIIc	**Cr** — 150 **I** + **Cr**	–
IVa*	**Cr** — 175 **Col** — 290 **Col** + **I**	–
IVc*	**Cr** — 145 **Col** — 185 **Col** + **I**	–
IVd	**Cr** — 250 **I**	–
IVe	**Cr** — 200 **I**	–
V*	**Cr** — 245 **Col** > 300 **Col**	+
VIa	**Cr** > 300 **I**	+
VIb	**Cr** — 212 **I**	+
VIc*	**Cr** — 180 **Col** — 190 **I**	–
VId	**Cr** — 150 **I**	–
VIe*	**Cr** — 230 **Col** > 300 **Col** + **I**	+

*Mesophase – glass phase transition on cooling;
" + " – Compound is mesomorphic;
" – " – Compound is not mesomorphic.

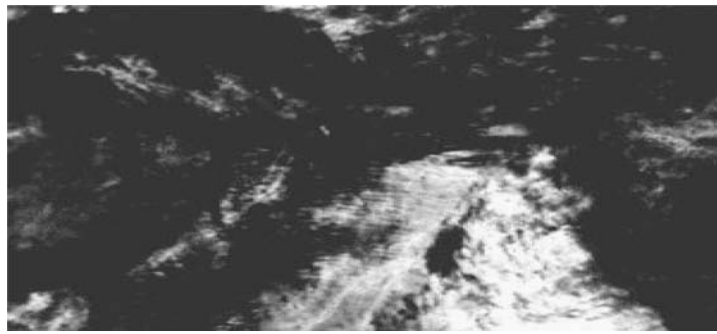


FIGURE 3 Optical texture of the mesophase of Pc **VIe** frozen into the solid glass state (18°C, 250 × magnification, crossed polarizes).

Ib, having one oxyethylene-group is mesomorphic, but the derivatives with two or three oxyethylene-groups **IIb** and **IIIa** are not mesomorphic. At transition from **Ib** to **IIIa**, i.e. with increase of length oxyethylene-spacer, the mesomorphic properties disappear, and therefore glass state is not formed.

At change of bridge-group in range of **IV** compounds, only **IV(a,c)** metal complexes exhibited mesomorphic properties. In range of **VI** compounds, the **VI(a,b,c,e)** derivatives are mesomorphic.

CONCLUSION

As a result, the Pc derivatives containing four oligo(oxyethylene)-, oxybenzene-, esther of *p*-oxybenzoic acid or *p*-oxyazobenzene- side chains terminated by a bulky trityl substituent were synthesized and characterized. Was shown, that in the presence of bulky trityl side groups the discotic mesomorphic Pc derivatives with such bridge-groups as oligo(oxyethylene)-, oxybenzene- or *p*-oxyazobenzene- fragments exhibit the mesomorphic properties and can form glass state on cooling. Not only side substituent structure, but also the nature of metal influences on the mesomorphic properties and glass appearance.

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