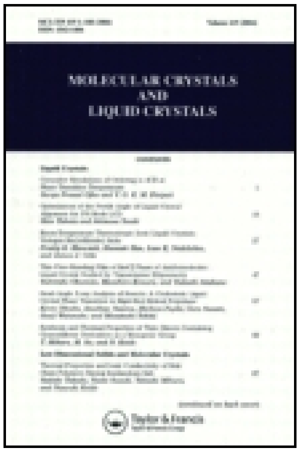

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Lyotropic Phase Behaviour of Phthalocyanine Derivatives in Apolar Organic Solvents

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LYOTROPIC PHASE BEHAVIOUR OF PHTHALOCYANINE DERIVATIVES IN APOLAR ORGANIC SOLVENTS

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Abstract Copper (II) and nickel (II) complexes of 2,3,9,10,16,17,23,24-octa(dodecyloxy)phthalocyanine (**1a**, **1b**) and copper (II) complex of 2,9,16,23-tetra(decylthio)phthalocyanine (**1c**) have been synthesized and their liquid crystalline properties have been studied. It was established, that **1a-c** possess both thermotropic and lyotropic (with apolar organic solvents) mesomorphism. Lyomesomorphism exhibited by compounds can be attributed to chromonic type.

INTRODUCTION

Various phthalocyanine derivatives and their metal complexes are of great interest for practical applications. They are also being used as model systems for the study of a number of biological processes.[1,2] The kind of broad spectrum of applications is mainly connected with the ability of these substances to form liquid crystalline phases of the columnar type. Thermotropic mesomorphism of these compounds is being varied by synthesizing derivatives with the different positions or length of lateral chains,[3] with various metals in complexes[4] and other modifications.[5]

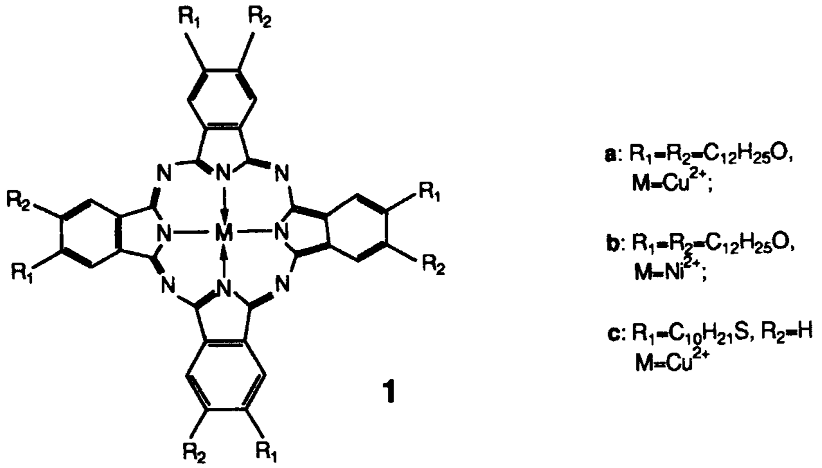
It has been previously established,[6-9] that the formation of lyotropic phases by hydrophobic substances in apolar organic solvents not only allows to stabilize the columnar mesomorphism but also induces new types of supramolecular packing. It was found, that for the sheet-like hydrophobic Pd- and Pt-organyls lyotropic nematic and twisted nematic phases can be found. They exist in bynary or ternary systems with the apolar organic solvents beside the two-dimensionally ordered columnar phases characteristic for thermotropic mesomorphism of pure organyls.[6-8] Lath-like metal mesogens in lyotropic condition can form nematic or twisted nematic phases in broad temperature interval, up to the room temperature.[9]

It was showed[10] that Pt-complex of phthalocyanine derivatives is apt to associations in the diluted solutions of apolar organic compounds. Our research[11,12] clearly proves that the tendency to association in diluted solutions for phthalocyanine *amphiphilic* derivatives is the reason for their lyotropic mesomorphism.

All mentioned above made us synthesize metal complexes of phthalocyanine derivatives with *hydrophobic* substituents (Figure 1) and study their lyomesomorphism in apolar organic solvents.

EXPERIMENTAL

Copper(II) and nickel(II) complexes of 2,3,9,10,16,17,23,24-octa(dodecyloxy)phthalocyanine (Figure 1, **1a,b**) were prepared using the synthetic route described previously.[10-13] 2,9,16,23-Tetra(decylthio)phthalocyaninato copper(II) (Figure 1, **1c**) was synthesized by heating of copper(II) acetate with 4-decylthiophthalonitrile.



a: $R_1=R_2=C_{12}H_{25}O$, $M=Cu^{2+}$;

b: $R_1=R_2=C_{12}H_{25}O$, $M=Ni^{2+}$;

c: $R_1=C_{10}H_{21}S$, $R_2=H$ $M=Cu^{2+}$

FIGURE 1 Molecular structures of the metal-complexes of alkyloxy- and alkylthiophthalocyanine derivatives **1a-c**.

4-Decylthiophthalonitrile (I). Triethylamine (1.12 ml) was dropped to the solution of 4-nitrophthalonitrile (1.14 g) and 1-decanethiole (1.5 ml) in 10 ml dimethylformamide, reaction mixture was stirred 15 min, diluted with 100 ml slightly acidified cold water and extracted with benzene. Evaporation of benzene gave compound **1** with quantitative yield. M.p. 54.5-55.5°C (from hexane). *Anal.* Calcd. for $C_{18}H_{24}N_2S$: C 71.95%, H 8.05%, N 9.32%, S 10.67%. Found: C 71.51%, H 8.13%, N 9.37%, S 10.92%.

2,9,16,23-Tetra(decylthio)phthalocyaninato copper (1c). Mixture of 1.35 g of dinitrile **1**, 0.40 g of copper(II) acetate and 0.04 g of ammonium molibdate was heated 2 hr at 200-210 °C and washed with boiled dimethylformamide. The product was chromatographed on silica column with benzene. Reprecipitation from benzene with dimethylformamide gave 0.45 g (31%) of complex **1c**. *Anal.* Calcd. for $C_{72}H_{96}CuN_8S_4$: C 68.34%, H 7.65%, N 8.86%, S 10.13%. Found: C 68.51%, H 7.55%, N 8.72%, S 10.42%.

Organic solvents, e.g. benzene, cyclohexane or linear alkanes, are commercially available and were used without further purification.

The thermal behaviour of pure compounds **1a-c** and their lyotropic compositions were investigated by the polarizing microscopy, using a MIN-8 or a Leitz Laborlux 12 microscopes, equipped with a Mettler FP hot stage, heating rate 2K min^{-1}.

The lyotropic mesomorphism of binary systems **1a**, **1b**, or **1c**/organic solvent was studied as described earlier.[6–8, 13]

RESULTS AND DISCUSSION

Thermotropic properties of the compounds **1a** and **1b** were known from the data in the literature.[14] Nevertheless, we found it necessary to compare these previously obtained results with our data. The aim was to study the *lyotropic* mesomorphism of various compound, synthesized by us, more precisely.

Using the method of polarizing microscopy it has been established that **1a** appears to be a thermotropic mesogen with the phase transition crystal → mesophase at 95 °C. Thermodestruction of the sample without any transition to isotrop takes place at the temperature above 300 °C. Thermotropic mesomorphism of nickel (**1b**) complex is similar to the one of the compound **1a**. The phase transition crystal → mesophase can be observed at the temperature 90 °C. Metal complex **1c** has definitely lower temperature of phase transition crystal → liquid crystal: 50.8 °C on heating and 11,1 °C on cooling. This substance can exist in mesomorphic state even at room temperature, if not exposed to deep cooling. X-ray investigation of the structure[13a] showed that **1a** and **1b** in mesomorphic state form columnar hexagonal phases (ordered or disordered accordingly). The type of mesomorphic packing of **1c** compound is also supposedly of $Col._{hd}$ character, which has not been determined finally up to now. Research in this direction is being continued.

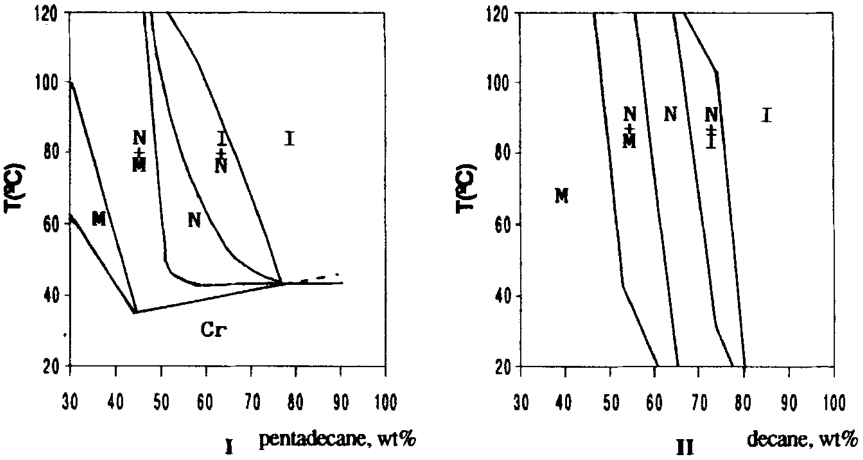


FIGURE 2 Fragments of the simplified phase diagrams of the **1a**/pentadecane (I) and **1c**/decane (II) systems, on cooling from the isotropic phase; Cr - crystalline phase, M - the highly viscous, most probably two-dimensional columnar lyotropic phase, N - colunmar nematic phase, I - isotropic phase.

FIGURE 3 Texture of the nematic-isotropic biphasic region in the system composed of **1a**/pentadecane at 60 °C, on cooling. (See Color Plate VI).

Each of the synthesized compounds **1a-c** with organic solvents (e.g. linear alkanes, cyclohexane, benzene or chloroform) displays lyotropic mesomorphism in contact preparation. The exception is the case of **1b** with the linear alkanes, where lyotropic mesomorphism can be observed only monotropically. Phase diagrams of binary systems **1a**, **1b**/pentadecane or **1c**/decane obtained by us, prove that the system **1c**/decane possesses the most broad field of lyomesophases. In the latter binary system lyomesophases exist at concentration from 20 wt% up to 75 wt% **1c**, moreover, at cooling, up to the room temperature (Figure 2). Schlieren (Figure 3) and herring-bone textures observed using the polarizing microscope are analogous to those described for chromonic mesogenes.[15] The succession of phase disposition on the phase diagram is also similar to the one of the chromonic lyomrsophases. X-ray structural investigations, carried out by us, confirm the columnar character of appearing lyomesophases.[13a] It is very interesting, that at the solvent concentration up to 40 wt% in the system **1a**/pentadecane, parameter *a* of M-phase practically equals to the one, observed in the mesophase of solvent-free compound, on heating. It is possible that the linear alkane condenses the structure of hydrophobic region without any substantial changes in the parameter of the of the packing, when integrating in the region of lateral chains, reflecting only the temperature dependence of parameter *a* existing in **1a**.

CONCLUSION

Synthesized metal complexes of phthalocyanine derivatives **1a-c** possess both thermotropic and lyotropic (in apolar organic solvents) mesomorphism. Phase transition crystal → mesophase of compound **1c** exist at considerably lower temperatures in comparison with the compounds **1a** or **1b**. This characteristic makes the compound **1c** very attractive for practical applications. Lyomesomorphism exhibited by compounds **1a-c** can be categorized as chromonic type. Thermotropic and lyotropic mesophases of **1c** may become an interesting material for the electronic applications, because the similar type of triphenylene derivative[16a] happened to be a liquid crystalline material that can exhibit high mobilities for photoinduced charge carriers.[16b] The existence of phase transition $\mathrm{Col}_N \rightarrow \mathrm{I}$ in the given lyotropic systems forms the basis for their usage for the study of the radiation-induced conductivity dependence on the phase state of discotic mesogens.

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