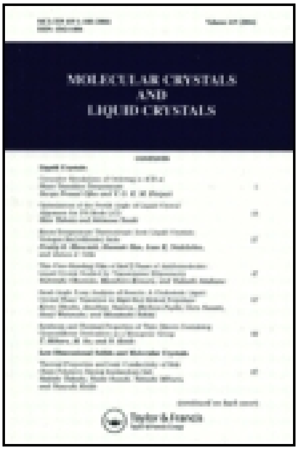

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Induction of Mesomorphic Properties in Non-Mesogenic Octa(decyloxy) phthalocyanines

Nadejda Usoltseva [a], Venera Bykova [a], Evgeny Kudrik [b], Gennady Shaposhnikov [b], Antonina Smirnova [a], Galina Ananjeva [a] & Ivan Nikolaev [b]

[a] Laboratory of Liquid Crystals, Ivanovo State University, 153025, Ivanovo, Russia

[b] Ivanovo State University of Chemistry and Technology, 153460, Ivanovo, Russia

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Induction of Mesomorphic Properties in Non-Mesogenic Octa(decyloxy)phthalocyanines

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GENNADY SHAPOSHNIKOV[b], ANTONINA SMIRNOVA[a],
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[a]*Laboratory of Liquid Crystals, Ivanovo State University, 153025 Ivanovo, Russia and* [b]*Ivanovo State University of Chemistry and Technology, 153460 Ivanovo, Russia*

As it is well known [1, 2], non-peripheral substituted octa(alkoxy)-phthalocyanines (Pc) do not exhibit neither thermotropic nor lyotropic mesomorphism (in binary mixtures with organic solvents). In this work we induced an *enantiotropic* mesophase due to charge-transfer (CT) interactions in mixtures of Pc derivatives **I-III** (viscous or oil-like liquids) with a strong electron acceptor 2,4,7-trinitro-9-fluorenone (TNF). Decreasing of number and length of substituents and modification of chemical structure of phthalocyanine macrocycle by introduction of four sulfur atoms (compound **IV**) resulted in crystallinity of this compound. In contact preparation of **IV** with TNF a wide area of CT-complex showing the *monotropic* mesomorphic phase is found out. All above mentioned CT-complexes do not form any lyomesophases in binary mixtures with number of organic solvents.

Keywords: CT-complexes; columnar mesophases; phthalocyanines

INTRODUCTION

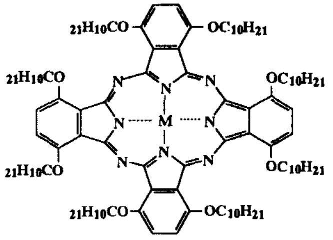
Interaction between π-systems is the leading factor of supramolecular aggregate formation at packing of aromatic molecules in crystals and at association processes of porphyrin and phthalocyanine derivatives. The last is the basis of columnar mesophase formation [3]. The position of substitution and the length of aliphatic substituent can exert an essential influence on an opportunity of realization of mesomorphic properties. It is known that the substitution of phthalocyanine (Pc) in non-peripheral positions by alkoxy-groups does not result in appearance of mesophase [1]. At the same time, there are researches showing an opportunity of strengthening of interaction between organic molecules along an axis of their supramolecular ensembles due to the formation of charge-transfer complexes (CT-complexes) between the electron donor and the strong electron acceptor [4]. The Ringsdorf's investigation [5] was the pioneer work in this direction. Earlier we induced the mesomorphic properties using electron acceptors in binary systems: hexasubstituted dinuclear palladium organyls with 2,4,7-trinitrofluorenone (TNF) [6]. As far as we know there were no earlier attempts to induce liquid crystal properties for non-mesomorphic phthalocyanine derivatives at the expense of CT-complex formation.

MATERIALS AND METHODS

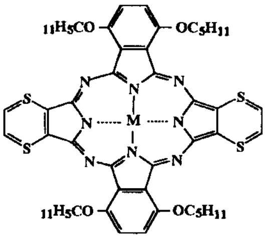
1, 4, 8, 11, 15, 18, 22, 25-octa(decyloxy)phthalocyanine Pc (**I**) and its copper (**II**) and nickel (**III**) complexes were synthesized as described elsewhere [7].

The new 1,4,15,18(thiocyclohexene)-8,11,22,25(pentoxyphenyl)-porphyrazine **IV** (deep violet crystals, m.p. 86,2 ^{0}C) was synthesized by the mixed condensation of 2,3-dicyano-1,4-dithiocyclohexane with 3,6-dipentoxyphthalodinitrile in pentanol-1 media at presence of 1-magnium pentylate. Received magnium complexes were demethylated by CF_3COOH at room temperature. The compound **IV** was yielded by a columnar chromatography method. The residue was chromatographed on a column (Al_2O_3; chloroform/acetone 10:1) to yield compound **IV**.

The structure and the purity of compounds were checked up by the data of the elemental analysis, thin layer chromatography and IR-spectroscopy. The spectral characteristics of **I-III** in the various organic solvents (chloroform, benzene, pyridine etc.) were investigated using UV-VIS-spectrophotometer. X-ray analysis of compound **II** and its CT-complex with TNF (31 mol% of TNF) was carried out on the DRON device (CuKα-radiation, Ni-filter) at temperature 20 °C.



I: M= 2H^{+}
II: M=Cu^{2+}
III: M=Ni^{2+}



IV: M= 2H^{+}

RESULTS AND DISCUSSION

As it was shown earlier [1, 2, 9], the synthesized non-peripheral substituted octa(alkyloxy)phthalocyanine derivatives **I-III** do not show any mesomorphic properties in the pure state. At room temperature the compounds **I** or **II** are viscous liquids; the compound **III** possesses oil-like consistency.

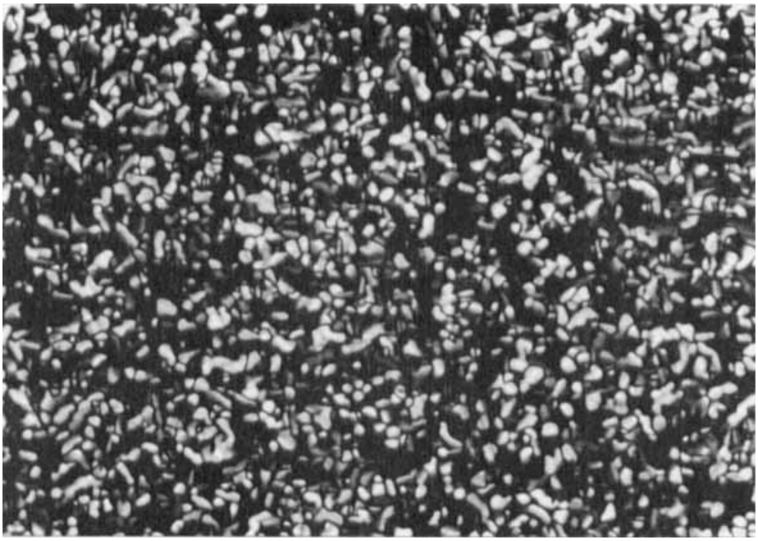
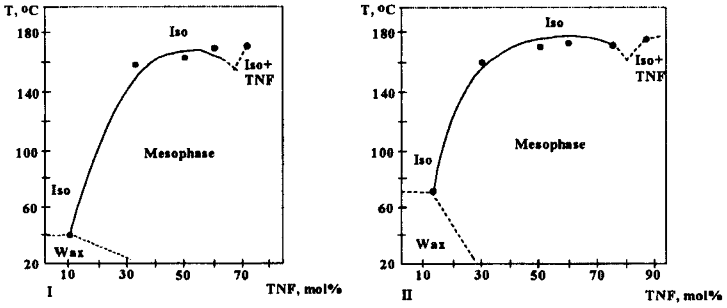


FIGURE 1. Microphotograph of **II**/TNF mixture (31 mol% of TNF in charge-transfer complex), T=25 ^{0}C, after heating from isotropic state, crossed polarizers, x 250.
See Color Plate VI at the back of this issue.

In contact preparations of compounds **I** - **III** with TNF the distinct area of CT-complex was observed. This area possesses a significantly deeper color than neat components as an indication of strong π-π interactions. The CT-complex shows mesophase with mosaic or non-geometrical texture already at room temperature (see Fig. 1). Similar textures are characteristic for the two-dimensional ordered columnar phases. The thermostability and area of the mesophase existence on the phase diagram (Fig. 2) depend mainly on TNF concentration in a CT-complex and practically do not depend on metal in complex. The clearing temperature raised with increase of TNF concentration in a CT-complex with the maximum of stabilization for 50-70 mol% of TNF (it corresponds to the 1:1 or 3:7 donor – acceptor ratio, correspondingly). It is interesting, those mesomorphic properties were observed even at TNF concentration about 11-12 mol%.



(a) (b)

FIGURE 2. Schematic phase diagrams of binary mixtures of phthalocyanine derivatives with TNF:
a) I/TNF; b) II/TNF.
Wax – waxy state, Iso – isotropic region.

On X-ray diffraction pattern of the II/TNF CT-complex (31 mol% of TNF) an indistinct reflex is observed in wide-angle area at 3,44 Å. This peak is absent in pure compound **II**. It is characteristic of Van der Waals distance between planes of aromatic compounds and testifies the existence of columnar ensembles in mesophase, most probably of *disordered* type. Bragg's peak ratio of 1:0,5 - for **II**/TNF CT-complex could be connected with lamello-columnar structure of its mesophase [10]. Besides, on X-ray diffraction patterns of phthalocyanine derivative and its CT-complex there is a diffuse reflex with a maximum at 4,5 Å, which is characteristic for distances between disordered alkyl chains.

The decreasing of number of alkyloxy non-peripheral substituents and the modification of chemical structure of phthalocyanine macrocycle by introduction of four sulfur atoms (compound **IV**) resulted in crystallinity of this compound (Cr → Iso phase transition at 86,2 ^{0}C), but it did not lead to the formation of mesomorphic properties. In contact preparation of **IV** with TNF a wide CT-complex area showing a *monotropic* mesomorphic properties is found out. Non-geometrical texture is typical for this mesophase.

The study of lyotropic mesomorphism using contact preparations of the CT-complexes of compounds **I** - **IV** with a number of the organic solvents (benzene, chloroform, decane etc.) has shown that their previous mesomorphic phase is dissolved and no lyomesophase is formed.

Comparison of absorption spectra of pure compounds **I-IV** and their 1:1 CT-complexes with TNF in chloroform or benzene (a good dissolution of CT-complex) has not revealed essential distinctions in a location of first and second maximum of absorption bands. Besides, on the border with UV-area an additional peak has been observed which is characteristic for neat TNF (Fig. 3).

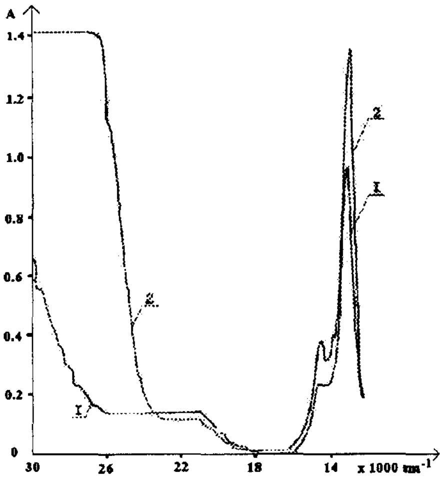


FIGURE 3. Electronic spectra of: 1 – binary system of neat compound **III** with chloroform, c=1,098·10^{-4} mol/l; 2 – **III**/TNF (1:1) CT-complex with chloroform, c=9,15·10^{-5} mol/l.

It testified that in a solution there is no any strengthening of associative processes characteristic for CT-complexes formation. On this basis we assume that these complexes are not stable enough and they break up under the action of the solvent. This is why the columnar structure of previous mesophase is destroyed at the presence of the solvents.

Acknowledgments

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References

[1] J. Barbera, In: *Metallomesogens: synthesis, properties and applications*, Ed. by J.L. Serrano., VHC Weinheim, New York, Basel, Cambridge, Tokio, 160 (1996).
[2] N. Usol'tseva, A. Smirnova, A. Rasumov, E. Kudrik, *6th Inter. Symposium on Metallomesogens*, June 10–13, 1999, Rotenburg a.d. Fulda, Germany, P. 88 (1999).
[3] A.N. Cammidge, J.R. Bushby, In: *Handbook of Liquid Crystals*, D. Demus ... – Weinheim; New-Yoork; ... Toronto: Wiley-VCH. **2B**. Chapt XVI., 739 (1998).

[4] K. Praefcke, D. Singer and B. Kohne, *Liq. Cryst.*, **13**, No3, 445 (1993).
[5] H. Ringsdorf, R. Wuestefeld, E. Zerta, M. Ebert, J.H. Wendorff, *Angew. Chem.*, **101**, 934 (1989); *Angew. Chem., Int. Ed. Engl.*, **28**, 914 (1989).
[6] N. Usol'tseva, K. Praefcke, D. Singer and B. Gündogan, *Mol. Mat.*, **4**, 253 (1994).
[7] M.J. Cook, M.F. Daniel, K.J. Harrison, N.B. McKeown, A.J. Thomson, *J. Chem. Soc. Chem. Commun.*, 1086 (1987).
[8] K. Praefcke, D. Singer, *Liq. Cryst.*, **13**(3), 445 (1993).
[9] N.V. Usol'tseva, In: *Advances* in *porphyrin chemistry*, **2** SPb.: The Scientific Research Institute of Chemistry, St-Petersburg University, 142 (1999).
[10] K. Praefcke, D. Singer, In: *Handbook of Liquid Crystals* / D. Demus ... – Weinheim; New-Yoork; ... Toronto: Wiley-VCH. **2B**. Chapt XVI, 946 (1998).