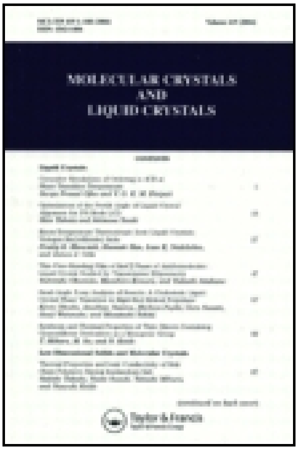

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New Glassing Mesogens

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With the purpose to study the influence of bulky symmetrical and asymmetrical substituents on mesomorphic properties and the tendency to exhibit glass state transition, tetrasubstituted phthalocyanine and porphyrazine derivatives, as well as 1,4- and 1,3,5- substituted benzene derivatives were synthesized. The compounds, simultaneously possessing the ability of glass formation from mesophase with the retention of columnar order, absorption in the visible part of the spectrum and electrophysical characteristics suitable for application, contribute to the essentially new approach to the synthesis of materials for optoelectronics.

Keywords: benzene derivatives; glassing mesogens; phthalocyanine; porphyrazine

INTRODUCTION

Liquid crystalline (LC) state occurs in organic molecules of different geometric shape due to the spontaneous molecular self-arrangement with the microsegregation of some areas of such ensembles. Taking into account their unique optical properties liquid crystals are perspective materials for optical photonic and optoelectronic devices [1]. It is important for many devices in photonics to have materials capable of glassing with the retention the LC order in the solid state without crystallization. This unique class of perspective materials is called glassing mesogens [2].

Usually glass formation is typical for the thin layers of LC polymers. Different glassing low-molecular mesogens can find their application in optical information recording, in non-linear optics, as

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tunnel filters for optoelectronics, compensators for the optimization of the screen angle, solar cells, light emitting diodes etc. [1]. However, up to the present moment there are no fundamental ideas about the reasons for glassing of low molecular weight compounds. At the same time, the possibility of functional materials molecular design is the key question in the development of progressive optical technologies [3].

The analysis of the subject related literature allowed outlining some synthesis methods of glassing compounds with the high glass temperature convenient for industrial application [4–8], among which synthesis of "chemical mixtures" [9] and synthesis of compounds with bulky substituents [10].

EXPERIMENTAL

To establish the interrelation between the molecular structure and glassing in mesophase we synthesized and analyzed mesomorphism and tendency to glassing at the introduction of bulky substituents into molecules of derivatives of phthalocyanine (Fig. 1), porphyrazines (Tables 1, 2) and benzene (Fig. 2).

The synthesis of these compounds and their identification were described earlier [11–13]. Mesomorphic properties were determined using an optical polarizing microscope Leitz Laborlux 12 Pol in conjunction with a hot stage Mettler FP 82. Temperatires and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Netzsch DSC 200 PC Phox calorimeter.

RESULTS AND DISCUSSION

Thermotropic Mesomorphism of Tetra-Substituted Phthalocyanines with Bulky Substituents

The most researched glassing low-molecular compounds are triphenylenes. To be applied in organic light emitting diodes these materials must possess not only high glass temperature, but also low potential of ionization (low value of HOMO) in order to minimize the injection barrier of the transparent anode. It has been shown that the lower the charge injection barrier, the more reliable the device is. However, the branching of triphenylenes leads to the disordering of molecules [14]. To increase the device efficiency the layer of the copper complex of phthalocyanine (CuPc) was introduced between ITO and HTL [15].

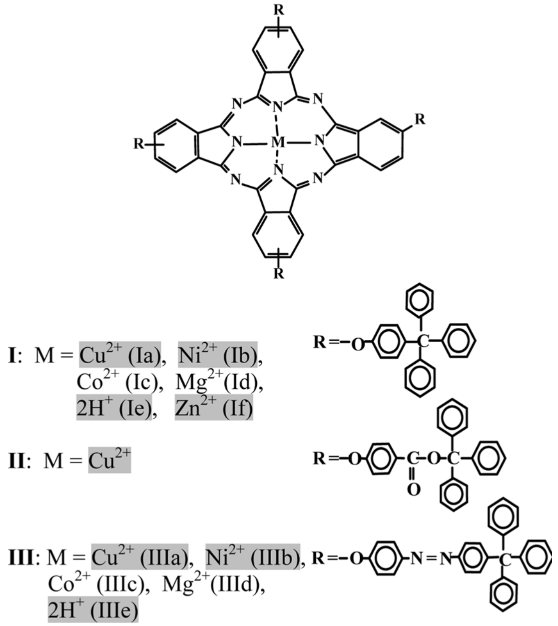


FIGURE 1 Tetrasubstituted phthalocyanines with symmetrical structure, glassing mesogens are marked.

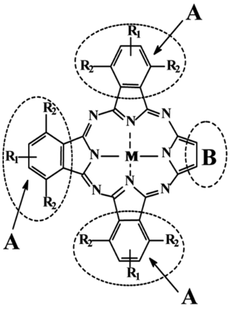
The analysis of the given above data triggered the idea to combine porphine properties as a low barrier for the charge injection (hole conductivity), transparent glassed aligned layer (instead of triphenylenes) and a dye absorbing in the visible part of the spectrum. So the task was set to synthesize new porphine derivatives with high glass temperature [11].

Some phthalocyanine (Pc) derivatives (**Ia**, **b**, **d**, **e**, **f**, **II**, **IIIa**, **b**, **e**) containing terminal bulky triphenylmethyl substituents with various bridge groups, such as *p*-oxybenzoic acid (**I**), oxybenzene (**II**) and *p*-oxyazobenzene (**III**), possess the ability to glass formation keeping columnar mesophase order (Fig. 1) [13,16].

For example, tetrasubstituted phthalocyaninato zinc (**If**) with bulky substituents is highly thermostable. The electrochemical characteristics of **If** were measured by the method of cyclic voltammetry in THF. The redox potentials and energies of HOMO/LUMO are presented in Table 3.

The band gap energies between HOMO/LUMO is high enough and equals 1.58 eV. So, we can suggest this compound as a perspective material for photovoltaic cells.

TABLE 1 Porphyrazine Derivatives of Asymmetrical Structure (Type A_3B)



Type I (A_3B)

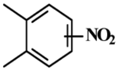
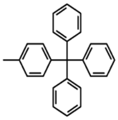
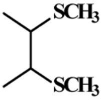
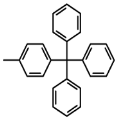
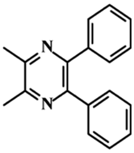
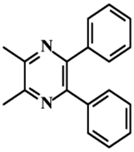
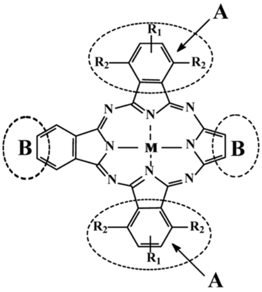
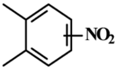
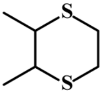
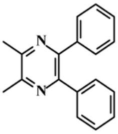
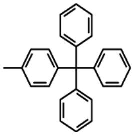
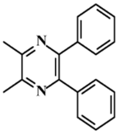
No	M	A: R_1	A: R_2	B
IV	Cu^{2+}	$-H$	$-OC_{10}H_{21}$	
V	$2H^+$		$-H$	
VI	$2H^+$		$-H$	
VII	Ni^{2+}	$-H$	$-OC_{10}H_{21}$	

TABLE 2 Porphyrazine Derivatives of Asymmetrical Structure (Type A_2B_2)



Type II (A_2B_2)

No	M	A: R_1	A: R_2	B
VIII	Cu^{2+}	$-H$	$-OC_{10}H_{21}$	
IX	$2H^+$	$-H$	$-OC_5H_{11}$	
X	Cu^{2+}	$-H$	$-OC_{10}H_{21}$	
XI	$2H^+$		$-H$	

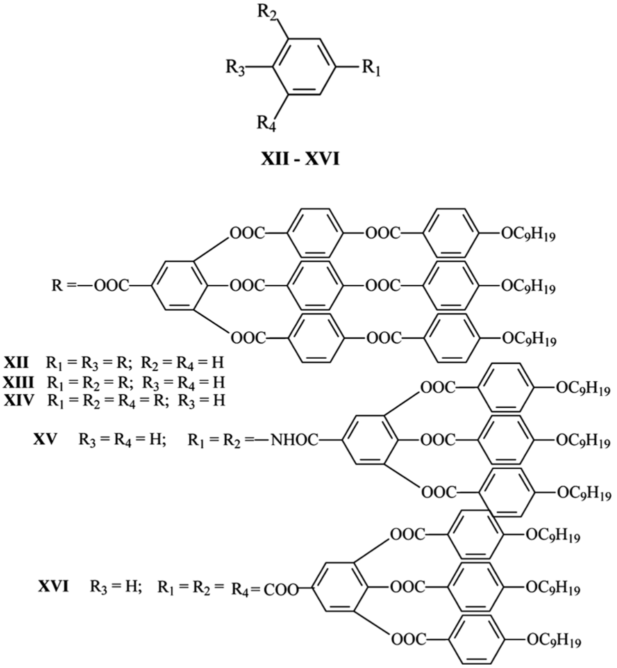


FIGURE 2 Structures of benzene derivatives.

Porphyrazines of Asymmetrical Structure as LC Glassing Materials

Up to the present the main attention was paid to macroheterocyclic compounds of symmetrical structure. Few existing papers on the synthesis and properties of asymmetrical phthalocyanine and porphyrazine derivatives prove that such "chemical mixtures" can reveal mesomorphic properties as well as tendency to glassing [16,17]. In the both cases (porphyrazine derivatives of $\mathbf{A_3B}$ and $\mathbf{A_2B_2}$ structures, Tables 1, 2) mesomorphic compounds with glass formation were obtained.

Compounds **IV**, **VI**, **VIII**, **X** and **XI** are mesogens. In the both groups ($\mathbf{A_3B}$ and $\mathbf{A_2B_2}$) some mesomorphic compounds exhibit glass

TABLE 3 Electrochemical Characteristics of **If**

E_1^{ox}, V	HOMO, eV	E_1^{red}, V	LUMO, eV	ΔE, eV
0.19	4.99	−1.395	−3.405	1.58

transition (compound **VI** and **X**). It is known that a non-peripheral substituted octa-(decyloxy)phthalocyanine Cu does not display thermotropic mesomorphism. In contrast to it, compound **IV** of $\mathbf{A_3B}$ type exhibits a thermotropic monotropic mesophase, and compound **VIII**, containing two nitro-groups of $\mathbf{A_2B_2}$ type, forms enantiotropic mesophase. Compound **VI** with three bulky triphenymethyl groups and one electron acceptor (diphenylpyrazine group) displays mesophase and glass transition at high temperature. In contrast, the similar compound **V**, with donor thiamethyl groups in the **B** position does not display any mesomorphism. It should be noted, that compound **VI**, which possesses a more deformed structure, compared to compound **XI**, glasses on cooling at the high temperature range.

Compound **VII**, containing Ni^{2+} as the central ion, is non-meso-morphic. At high temperatures compound **X**, containing the same substituents, but copper as a complex formation ion, displays mesomorphic state, which is able to transfer to glass state on cooling.

As it is known, mesomorphic state can be induced or stabilized by CT-complex formation between discogens and organic electron acceptors, for example 2,4,7-trinitro-9-fluorenone (TNF) [18]. Therefore, to induce mesomorphic state in non-mesomorphic compounds **V**, **VII** and **IX** the above described method was applied. In contact preparations with TNF mesomorphic state was induced for compound **VII** (enantiotropic mesophase). For this complex the transition from mesomorphic to glass state was observed at 60°C.

Mesomorphic Glassing Benzene Derivatives

The idea of synthesis of *ortho*-, *meta*- and *para*-substituted benzene derivatives belonged to D. Vorländer. About 100 years ago in the early works of Vorländer the important role of benzene in designing molecules of liquid crystal compounds was shown.

In 1977 S. Chandrasekhar has proved existence of a new class of liquid crystal compounds (discotics) by the example of substituted benzene derivatives molecules of which form packings of columnar type in mesophase [19].

It has been established, that substituted hydroxybenzene derivatives on the basis of 3,4,5-trihydroxybenzoic acid (compounds **XII–XVI**, Fig. 2) possess mesomorphic properties.

Compound **XII** containing symmetrically located fragments of 3,4,5-tri-[4-(4′-nonyloxybenzoyloxy)benzoyloxy]benzoic acid in positions 1 and 4 of the benzene ring, possesses thermotropic enantiotropic polymorphism. The textures of mesophases testify to it. Basing on the

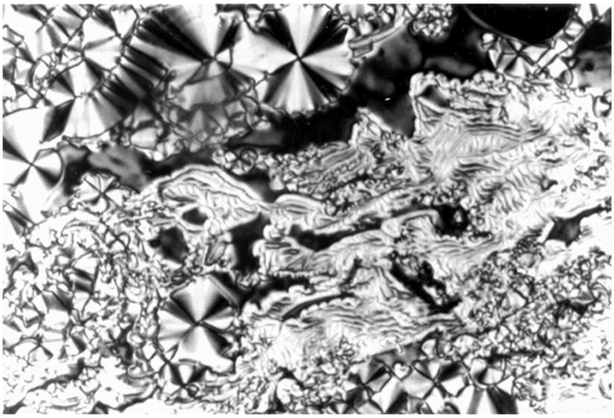


FIGURE 3 Texture of compound **XIII** on heating; T = 98.8°C, x 250.

mesophase textures analysis, one can propose the following sequence of phase transitions:

$\mathrm{Cr} \cdot 96^{\circ}\mathrm{C}\ \mathrm{N_{re}} \cdot 157^{\circ}\mathrm{C}\ \mathrm{Sm_1} \cdot 160.5^{\circ}\mathrm{C}\ \mathrm{Sm_2} \cdot 163.8^{\circ}\mathrm{C}\ \mathrm{N} \cdot 215^{\circ}\mathrm{C}\ \mathrm{I}.$

The types of smectic phases and model of reentrant nematic phase are at the stage of specification. As follows from the obtained data, compound **XII** has a wide range of mesophase existence −119°C. The width of the first nematic range is 61°C, the width of the second one is 51.2°C. Overcooling of mesophase creates glass formation ($T_g = 32^{\circ}C$) instead of phase transition to a crystal.

Compound **XIII**, containing bulky substituents in positions 1 and 3 of the benzene ring, keeps thermotropic mesomorphism. However, periodic streaks, reminding of the "finger-prints" texture, have been found among mesophase textures on heating (Fig. 3).

The fact, that the molecule of compound **XIII** has a broken linearity, suggests the presence of chirality in supramolecular packing. The temperature sequence of phase transitions is as follows:

$\mathrm{Cr} \cdot 45.0^{\circ}\mathrm{C}\ \mathrm{Mes_1} \cdot 78.0^{\circ}\mathrm{C}\ \mathrm{Mes_2} \cdot 95.7^{\circ}\mathrm{C}\ \mathrm{Sm} \cdot 95.9^{\circ}\mathrm{C}\ \mathrm{N} \cdot 163.0^{\circ}\mathrm{C}\ \mathrm{I}.$

In comparison with compound **XII** thermostability of mesophase is much lower. The range of mesophase existence is 118.0°C, the width of nematic range is 67.1°C. The models of mesophases and type of smectic phase are specified. Compound **XIII** also exhibits glass transition on cooling ($T_g = 36.6^{\circ}C$).

Compound **XIV**, containing bulky substituents in positions 1, 3 and 5 of the benzene ring, also possesses mesomorphic properties: $\mathrm{Cr} \cdot 36.0^{\circ}\mathrm{C}\ \mathrm{Mes_x} \cdot 200.0^{\circ}\mathrm{C}\ \mathrm{I}$. This compound exhibits only one type of mesophase with non-geometrical texture. The temperature of phase transition.

Cr–Mes goes down in comparison with disubstituted derivatives of benzene (**XII** and **XIII**) and the temperature range of mesophase existence is widening (164.0°C for compound **XIV**). Compound **XIV** also forms glass state on cooling ($T_g = 40°C$).

Compound **XV** with the broken linearity also possesses polymorphism. The temperature sequence of phase transitions for compound **XV** on cooling is as follows:

$$\mathrm{I} \cdot 283.5°\mathrm{C\ SmCP\ (B_2)} \cdot 279.4°\mathrm{C\ CrII}\alpha \cdot 166.2°\mathrm{C\ CrII}\beta \cdot 70.7\ \mathrm{CrII}\gamma.$$

At room temperature compound **XVI** is viscous with pseudoisotropic texture. It glasses on cooling.

Spatial models of molecules of synthesized compounds **XII–XVI** have been constructed and optimized by the method of molecular mechanics, using the program HyperChem 5.00 (power field MM+) to define possible supramolecular packing in mesophase.

Analyzing the spatial model of the substituted 1,4-dihydroxybenzene (compound **XII**) associate, it should be noticed, that one molecule is practically put on another one, determining a layer motive (Fig. 4).

The variant of twinning is possible at stacking of the molecules of compound **XIII**. Thus, two molecules form a dimer, having the shape of a disk with dense filling of the vacant area on periphery (Fig. 5).

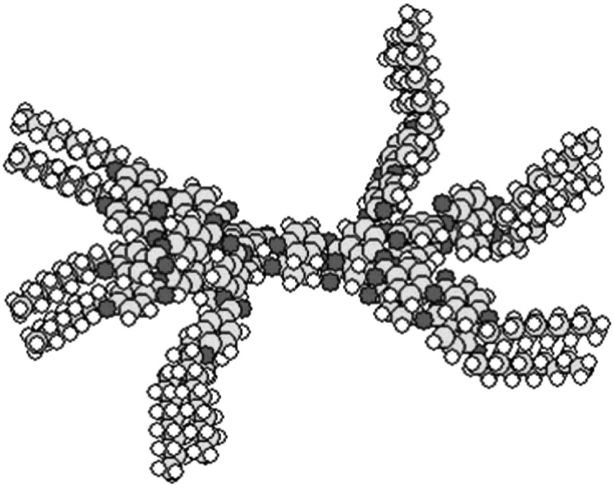


FIGURE 4 Possible spatial structural model of the of substituted 1,4-dihydroxybenzene **(XII)** dimmer.

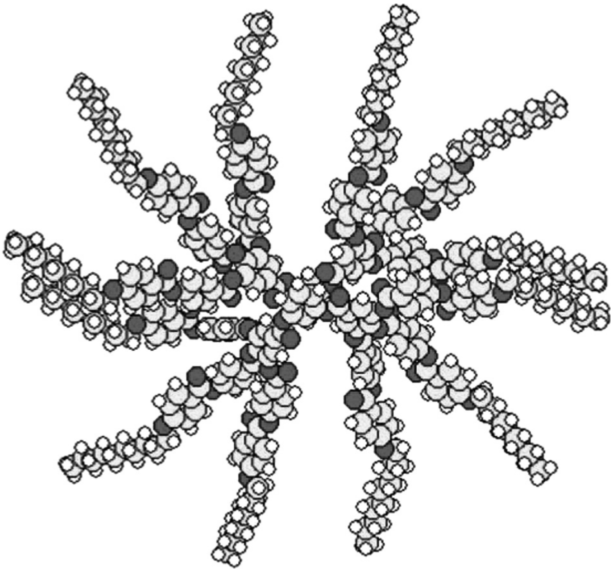


FIGURE 5 Spatial structural model of the of substituted 1,3-dihydroxybenzene (**XIII**) dimmer.

So, the opportunity of columnar type packing existence is not excluded along with layer ordering.

CONCLUSION

An essentially new approach to the synthesis of materials for optoelectronics is offered and carried out: creation of compounds, simultaneously possessing the ability for glass formation from mesophase with the retention of columnar ordering, absorption in the visible part of the spectrum and electrophysical characteristics suitable for application. It has been shown for the first time that tetrasubstituted phthalocyanine metal complexes with bulky terminal groups can also serve as potential materials for optoelectronic devices.

Out of 20 synthesized new phthalocyanines and porphyrazines of symmetric or asymmetric structure with bulky peripheral substituents, 11 compounds are mesomorphic and tend to glass formation. Besides, the induction of such properties was achieved for non-mesogenic porphyrazine derivative **(VII)** by creating CT-complex with TNF.

Five new compounds–substituted hydroxybenzene derivatives on the basis of 3,4,5-trihydroxybenzoic acid are obtained. Introduction of bulky substituents in positions 1,4- and 1,3- or in positions 1,3,5- of the benzene ring leads to the occurrence of thermotropic mesomorphism of these compounds and promotes the occurrence of glass state transition with the preservation of mesophase structure of some researched compounds.

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