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LIQUID CRYSTALS, 1995, VOL. 19, NO. 6, 887–889

Preliminary Communications

Stable glass formation by a hexagonal ordered columnar mesophase of a low molar mass phthalocyanine derivative

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The synthesis of a novel phthalocyanine mesogen, containing four flexible side chains terminated with a bulky trityl moiety, is described. This compound forms a well defined anisotropic glass, indefinitely stable at room temperature, in which the hexagonal ordered structure of its columnar mesophase is preserved. Such a glassy state should be useful for anisotropic conductivity studies.

Disc-shaped aromatic compounds such as triphenylene or phthalocyanine (Pc) derivatives, when suitably substituted with flexible side chains, form columnar mesophases [1]. These self-assembling materials are of great interest due to their proven anisotropic electronic [2] and photoconductivity [3] which arise due to the transport of charge along the axis of the column. The study of Pc-based columnar mesophases is of particular relevance due to the extensive use of Pcs as photoconductors in xerography [4] and their well established electronic conductivity when doped with oxidants [5]. It has been assumed that the large cofacial π–π overlap obtained in Pc columnar mesophases, especially the untilted mesophase designated D_{ho} (figure 1) which is characterized by a hexagonal lattice and periodicity along the columns, would benefit conductivity relative to the tilted crystalline phases [6]. However, a recent extensive study has concluded that conductivity is generally greater in the crystalline phase than in the columnar mesophase [7]. This result was attributed to the motional disorder of the side chains, reducing the cofacial ordering, and the negative influence of the molecular axial rotation on the charge carrier hopping frequency.

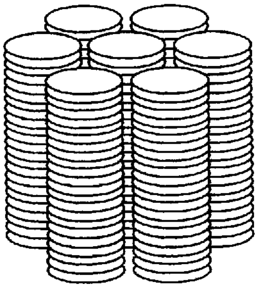

Figure 1. Diagramatic representation of the D_{ho} columnar mesophase.

In this context we have sought a Pc mesogen which forms a glassy solid in which the columnar structure may be maintained, but molecular rotation would be frozen and side chain motion reduced. This material could be aligned in the mesophase (e.g. by a magnetic field) and then cooled into the glass for anisotropic conductivity studies.

Anisotropic glassy solids are a common feature of many liquid crystal polymers based on conventional rod-shaped (calamitic) mesogens and are important in the production of optical data storage devices [8]. Analogously, side chain and main chain polymers which incorporate discotic triphenylene mesogenic units have been shown to exhibit well defined glassy states in which the columnar structure is preserved [9, 10]. Interestingly, Spiess has reported easily aligned low molecular mass (LMM) triphenylene mesogens, substituted by five pentyloxy groups and a single ester-linked side chain, which also form distinct anisotropic columnar glasses on cooling below room temperature (215–232 K) [11–13]. However, well defined glasses formed from Pc-based materials are rare. Side chain polymers derived from mesogenic Pcs have proved not to form a fluid phase or possess a glassy state [14]. A recent report of mesogenic Pc trimers suggested that they form a glassy state in which the structure of the hexagonal mesophase (D_{hd}) was preserved, on cooling to room temperature, but no glass transition was observed by differential scanning calorimety (DSC) [15]. A well characterized isotropic glass was recently described for a LMM Pc derivative containing four bulky groups attached directly to the macrocycle [16]. This communication will demonstrate that a well defined anisotropic glass, of hexagonal ordered structure, can be obtained from a novel LMM Pc mesogen (Pc **1**), containing four flexible

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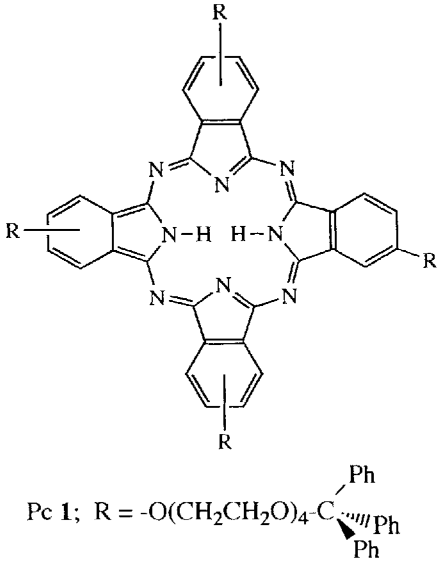
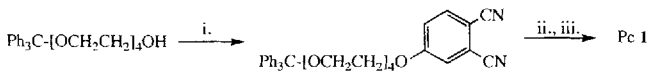
oligo(oxyethylene) side chains terminated by bulky trityl groups.



Pc **1**; $R = \text{-O(CH}_2\text{CH}_2\text{O)}_4\text{-CPh}_3$

The synthetic route to Pc **1** is shown in the Scheme. The direct precursor, 4-(14,14,14-triphenyl-1,4,7,10,13-pentaoxatetradecyl)phthalonitrile, was prepared by the base catalysed aromatic nucleophilic substitution reaction between commercially available 4-nitrophthalonitrile and 13,13,13-triphenyl-3,6,9,12-tetraoxatridecan-1-ol [17].



Scheme *Reagents and conditions*: (i) 4-nitrophthalonitrile, DMF, anhydrous K_2CO_3, 50°C, 48 h; (ii) lithium pentoxide, pentanol, 130°C, 4 h; (iii) acetic acid.

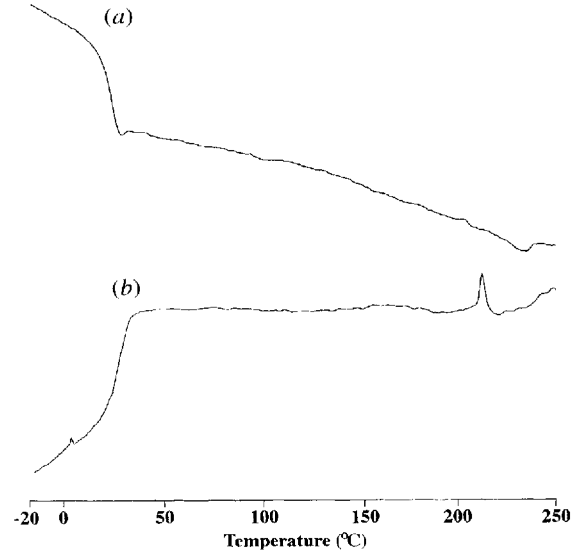


Figure 2. DSC thermograms of Pc **1** on heating (*a*) and cooling (*b*) at a rate of 10°C min^{-1}.

The addition of an excess of lithium metal to a boiling pentanol solution of the phthalonitrile precursor produced Pc **1** which could be purified by column chromatography and was characterized by fast atom bombardment mass spectroscopy (FABMS), elemental analysis and high resolution NMR spectroscopy (500 MHz) [18]. NMR analysis confirmed that the Pc was isolated as a statistical mixture of four regioisomers. For the purpose of this study, the presence of regioisomers may have the beneficial effect of reducing the tendency of the Pc to crystallize and thus promote glass formation.

The thermal behaviour of Pc **1** was examined by DSC (figure 2). This indicates a distinct glass transition both on heating and cooling (at a rate of 10°C min^{-1}) with a T_g of 30°C. In addition a broad, small (0·5 mJ mg^{-1}) endotherm is observed at higher temperature (225°C) on heating. On cooling, a sharper exotherm is observed (218°C, 0·6 mJ mg^{-1}). No other transitions are apparent. Polarized optical microscopy shows that Pc **1** becomes a fluid, birefringent liquid at 30°C and clears to an isotropic liquid at 223°C. The mesophase of Pc **1** has a fan-like texture (figure 3) and forms as digitate stars on cooling from the isotropic liquid (this effect is best observed with uncrossed polarizers—figure 4). These observations strongly indicate a mesophase of hexagonal symmetry [6].

On cooling Pc **1** to room temperature, the optical texture of the mesophase is retained. Powder X-ray diffraction studies of the mesophase show diffraction rings which have Bragg spacings corresponding to a two-dimensional hexagonal lattice (see the table) in which the intercolumnar distance is 32·9 Å. In addition, a broad halo located at 4·4 Å and a sharp ring at 3·47 Å, which can be attributed to the disordered oligo(oxyethylene) chains and the intermolecular periodicity along the axis of the column, respectively, are consistent with a D_{ho} mesophase. An

Figure 3. Optical texture of the D_{ho} mesophase of Pc **1** frozen into the solid glass state (18°C, 200 × magnification, crossed polarizers).

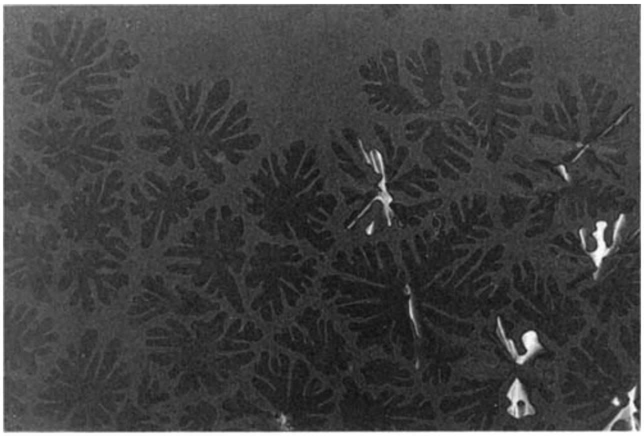


Figure 4. The dendritic formation of the D_{ho} mesophase of Pc **1** (220°C, 200 × magnification, parallel polarizers).

X-ray diffraction study of Pc **1** (see the table) at room temperature (15°C) gave a diffraction pattern of an identical appearance to that obtained for the mesophase, confirming that the D_{ho} structure is preserved on cooling below the glass transition temperature. It is of interest to compare the melting behaviour of Pc **1** with that of Pcs substituted by four methyl-terminated oligo(oxyethylene) side-chains, previously prepared in our laboratory [17], which possess a D_{ho} mesophase, but also had distinct melting points. This contrast in properties illustrates the importance of the bulky trityl terminating groups in the formation of the glassy state.

The hard, mechanically robust glass obtained from Pc **1** possesses no cracks resulting from cooling to room temperature and appears to be stable indefinitely with respect to crystallization. This was confirmed by a DSC study on a four-month old sample of Pc **1**, kept at room temperature, which gave a glass transition rather than a melting endotherm on heating. In addition, the sample used for the X-ray structure determination gave an identical diffraction pattern to that initially obtained for the cooled glass, after being kept in a capillary tube over this extended time period.

Table. Powder X-ray diffraction data for Pc **1**.

Bragg spacing (*d*)	Intensity	Hexagonal lattice assignment (*h*, *k*)
100°C, † Intercolumnar distance (*D*) = 32·9 Å		
28·5	strong	1, 0
16·9	medium	1, 1
14·3	weak	2, 1
4·40	broad	oligo(oxyethylene) chains
3·47	sharp	intracolumnar periodicity
15°C, † Intercolumnar distance (*D*) = 32·9 Å		
28·5	strong	1, 0
16·9	medium	1, 1
14·3	weak	2, 1
4·40	broad	oligo(oxyethylene) chains
3·44	sharp	intracolumnar periodicity

† Intercolumnar spacings calculated from (1, 0) diffraction ring.

In conclusion, we believe that the Pc described in this communication possesses a combination of properties which should allow the fabrication of solid materials with strongly anisotropic conductivity.

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[18] Found: C, 74·33; H, 6·12; N, 5·0. $C_{140}H_{238}N_8O_{20}$ requires: C, 74·64; H, 6·18; N, 4·97. UV/vis (toluene, λ_{max} nm) 702, 666, 641, 606, 394, 340. δ_H (500 MHz, solvent C_6H_6) − 3·0 (2H, br s), 3·45 (8H, t), 3·70 (8H, m), 3·76 (8H, m), 3·81 (8H, m), 3·89 (16H, m), 4·10 (8H, m), 4·40 (8H, m), 7·0–9·0 (72H, m), FABMS: *m/e* Found 2254. $^{13}C_2C_{138}H_{138}N_8O_{20}$ $(M + H)^+$ requires 2253.