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The first asymmetrically β-polysubstituted porphyrin-based hexagonal columnar liquid crystal

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The preparation of a new β-tetrasubstituted porphyrin through a short synthesis with liquid crystalline properties in a wide range of temperatures including room temperature is described.

Since the discovery of discotic liquid crystals,[1] a large number of disc-like molecules have been found to form columnar mesophases. There has been increasing interest in designing and synthesizing discotic liquid crystals due to their potential applications in several fields like charge-transfer processes,[2] photoconductivity,[3] ferroelectric switching,[4] optical information storage and retrieval[5] and organic light-emitting diodes.[6]

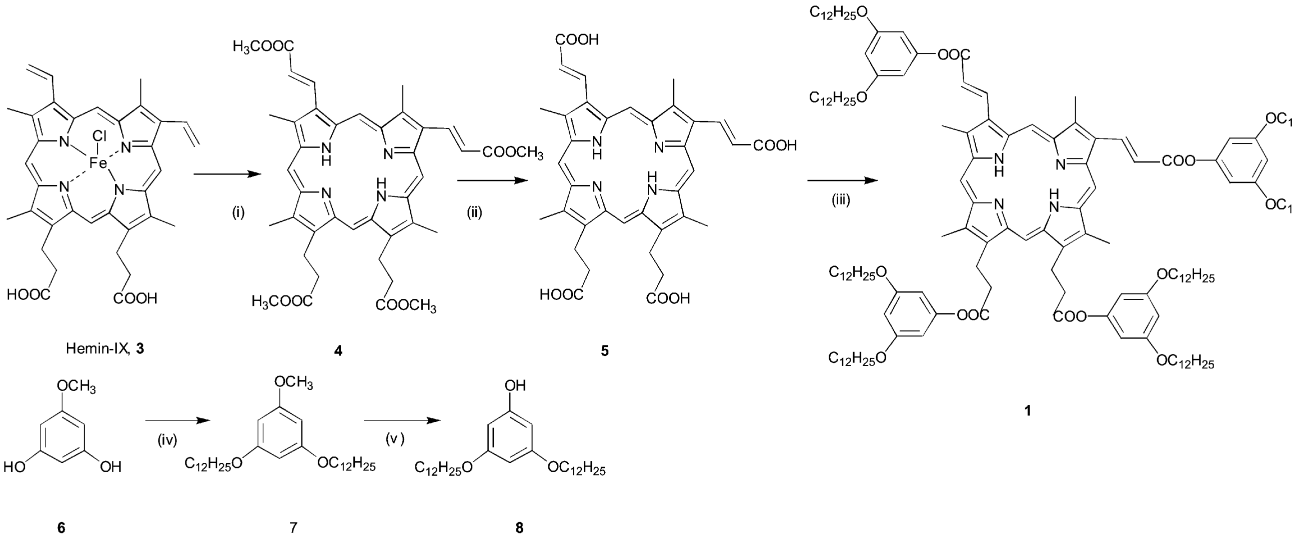
Most discotic liquid crystals have a molecular structure that consists of a flat central core with six or eight alkyl chains placed symmetrically around the outside edge of the core.

Liquid-crystalline porphyrins have received considerable attention as materials for molecular electronics, due to their peculiar properties as uni-dimensional conductors[7] and semiconductors.[8] Uroporphyrin-I octa-n-dodecyl ester, which shows a monotropic mesophase within a temperature range of 0.1 °C, was the first mesogenic porphyrin to be reported.[9] Since then, several mesogenic porphyrin derivatives have been reported.[10–12] They can be divided into two broad categories depending on the location of the substitution in the macrocyclic ring and the number of side chains. On the one hand, porphyrins octa-substituted at the β-positions of the pyrrole rings have been reported to present one or two columnar mesophases,[10] which usually do not exist at room temperature. The temperature range of the mesophases (5–160 °C) depends on whether porphyrins are metallated and on the length of the surrounding alkyl chains. On the other hand, porphyrins di- and tetra-substituted at the *meso* positions show nematic/smectic phases[11] or lamellar discotic phases,[12] respectively, in a narrow range (30–40 °C). These porphyrins and metalloporphyrins have been prepared *via* routes that generate the macrocycles from monopyrroles. This normally entails low yields and very tedious purification.

Our goal was to prepare a polysubstituted porphyrin through a short synthesis from the commercially available hemin-IX **3**, providing the structure **1** with stable enantiotropic hexagonal columnar mesophases over a wide range of temperatures including room temperature, making this compound suitable for a wide variety of applications.†

The synthetic route to porphyrin **1** is shown in Scheme 1. The direct precursor 2,7-bis[2-(methoxycarbonyl)ethenyl]-12,16-bis[2-(methoxycarbonyl)ethyl]-1,6,11,17-tetramethylporphyrin **4** was obtained in 70% yield from hemin-IX **3** as described elsewhere.[13] Porphyrin **4** was saponified quantitatively to the tetra-acid compound **5**, which was then esterified with 3,5-didodecyloxyphenol **8**, prepared as shown in Scheme 1, from the commercial product 5-methoxyresorcinol **6**. This esterification was performed in two steps due to the low solubility of **5** in any organic solvent. The preparation of the corresponding tetra-acid chloride followed by reaction with 3,5-didodecyloxyphenol **8** in CH_2Cl_2 yielded a complex mixture of the tri-, di- and mono-ester compounds, together with the unreacted porphyrin **5**. The total conversion was completed by a second esterification with DCCI/DMAP, giving porphyrin **1** in 40% yield.

Polarized optical microscopy of **1** at room temperature showed birefringence. The material can be sheared leaving a pasty birefringent trace expected for a highly viscous phase.



Scheme 1 Synthetic path for the preparation of the target molecule **1**. *Reagents and conditions*: (i) Prepared in 70% yield from hemin-XI **3** as described.[13] (ii) DME/KOH (0.7 N), rt, 5 days, η = 100%. (iii) a) 1. $SOCl_2$, 2. **8** (1.3 eq.), Et_3N, CH_2Cl_2, reflux, 24 h; b) DCCI/DMAP, CH_2Cl_2, **8** (0.7 eq.), rt, 24 h, η = 40%. (iv) $C_{12}H_{25}Br$ (2.5 eq.), K_2CO_3, DMF, 140 °C, 19 h, η = 60%. (v) NaSEt, DMF, 120 °C, 19 h, η = 80%.

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During the first heating ($v = 2$ °C min^{-1}), the sample transformed at 50–52 °C to a more birefringent shearable texture which cleared at 128–130 °C. Subsequent slow cooling ($v = 2$ °C min^{-1}) from the isotropic melt led, after a considerable supercooling (*ca.* 10 °C), to the growth of a typical texture (broken focal-conic) for a columnar mesophase. Further cooling to room temperature produced, after an annealing of 24 h at 25 °C, a new one columnar texture.

The thermal behavior of **1** was examined by DSC (Mettler Toledo S). First, the sample was homogenized by heating to the isotropic. An exothermic peak at 139 °C ($\Delta H = -1.7$ J g^{-1}) followed by a second transition at −33 °C, constituting of a small peak ($\Delta H = -2.7$ J g^{-1}) and a slope change in the heat-flow curve, was obtained on cooling from the liquid state. Both transitions reappeared in the second heating experiment. However a new endothermic peak, which had not been detected on the previous cooling, was registered at 51 °C ($\Delta H = 0.4$ J g^{-1}). These results agree with the microscope observation and suggest the presence of two mesophases: the first from −33 to 51 °C and the second from 51 °C to the clearing point at 139 °C. The two phases were stable during consecutive heating and cooling processes. The small broad transition located around 20 °C in the second heating run does not seem to correspond to any process observed, neither by polarized optical microscopy nor by X-rays. To ensure that no polymerization nor degradation of the acrylic system had taken place, the sample was analyzed by ^{1}H NMR spectroscopy before and after the heating cycle. The same spectra were obtained in both cases. In addition, the sample was heated at 150 °C for half an hour and it remained unchanged from spectroscopic data. No evidence for polymerization or degradation of the sample was detected.

The nature of these two liquid crystalline phases was examined from their X-rays at different temperatures. The sample was first led to its liquid state in order to homogenize it. Then, several X-rays were registered cooling the porphyrin from the liquid state, showing at any temperature from 120 to 25 °C, the same diffraction pattern, which corresponds to an hexagonal columnar mesophase. The inter-columnar distance was 36.6 Å (calculated from the (100) diffraction ring). In addition, the broad halo located at 4.5 Å can be attributed to the disordered alkoxy chains and the sharp ring that appeared at 3.6 Å can be attributed to the intermolecular periodicity along the axis of the column. We conclude that the compound shows an ordered hexagonal columnar mesophase Col$_{ho}$.

However, when the sample was annealed at 25 °C for 24 h, a new diffraction pattern appeared, whose peaks are consistent with a second two-dimensional hexagonal lattice Col$_h$ (Table 1) in which the inter-columnar distance is now 38.9 Å (calculated from the (100) diffraction ring). At this point, the sample was again heated, so that the Col$_h$ remained invariable until 51 °C, but at higher temperatures the above mentioned Col$_{ho}$ reappeared until its isotropization. These results agree with those obtained by DSC and polarized optical microscopy.

The dimension of the molecular structure of compound **1** was calculated by the CS Chem3D 5.0 program, placing all the alkyl chains in their total elongated conformation and it was found to be 48.1 Å. Taking into account that the inter-columnar distance, estimated by X-rays, is 38.9 Å and 36.6 Å, respectively, for the two observed liquid crystal phases, we assumed that the interdigitation between the aliphatic chains within adjacent columns as well as their conformational disorder causes a decrease of 20–25% in the chain length in both mesophases.

The asymmetrically substituted porphyrin **1** showed interesting mesomorphic behavior, with two hexagonal columnar mesophases from −33°C to its clearing point at 139 °C. It is unusual to find the most ordered mesophase at higher temperatures. However, this is clearly shown by the appearance of an intra-columnar periodicity of 3.6 Å, as a result of the π–π stacking, in the X-ray analyses when the sample was heated to 51 °C. Similar findings have been reported elsewhere.[14,15] Thus the re-entrancy phenomena is well known, even for a discotic molecule,[14] in which a less ordered phase appears both at low temperatures and before the liquid state. However, the observed behavior for molecule **1** seems to be different from the re-entrant one, since the more disordered phase is observed only at low temperatures, and at high temperatures does not appear anymore. A similar phenomena to ours, has been described for some truxene derivatives,[15] in which an ordered hexagonal columnar phase appeared at higher temperatures than disordered rectangular and nematic mesophases. This unusual behavior could be a result of the competition between intermolecular forces. As the temperature is raised it causes some of the weaker bonds to be broken first and the supramolecular organization resulting from the new balance of intermolecular interactions may result in more ordered packing.[15]

Table 1 X-Ray data for molecule **1** at different temperatures

T/°C	[a]Lattice const./Å	Observed spacing/Å	Miller ind. (hkl)	Phase
25	$a = 38.9$	33.7	(100)	Col$_h$
		19.7	(110)	
		17.5	(200)	
		12.6	(210)	
		4.5	[b]	
100	$a = 36.6$	31.7	(100)	Col$_{ho}$
		4.5	[b]	
		3.6	[c]	

[a] Calculated from (100) diffraction ring. [b] Alkoxy chains. [c] Intracolumnar periodicity.

The study of the mesomorphic properties of porphyrin analogues of **1** with side chains of different length, together with their corresponding metalloporphyrins, is now in progress.

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Notes and references

† All compounds had spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR) consistent with the assigned structure.

1 S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 1977, **9**, 471.
2 A. M. can de Craats and J. M. Warman, *Adv. Mater.*, 2001, **13**, 130.
3 Y. Yuan, A. B. Gregg and M. F. Lawrence, *J. Mater. Res.*, 2000, **15**, 2494.
4 G. Heppke, D. Kruerke, C. Lohnung, D. Lotzsch, D. Moro, M. Muller and H. Sawade, *J. Mater. Chem.*, 2000, **10**, 2657.
5 S. Forget and H.-S. Kitzrow, *Liq. Cryst.*, 1997, **23**, 919.
6 S. A. Benning, T. Habheider, A. Keuker-Baumann, H. Bock, F. della Sala, T. Frauenheim and H.-S. Kitzerow, *Liq. Cryst.*, 2001, **28**, 1105.
7 H. Eichhorn, *J. Porphyrins Phthalocyanines*, 2000, **4**.
8 J. Simon and J.-J. André, *Molecular Semiconductors*, Springer-Verlag, Berlin, 1985.
9 J. W. Goodby, P. S. Robinson, B.-K. Teo and P. E. Cladis, *Mol. Cryst. Liq. Cryst.*, 1980, **56**, 303.
10 V. Paganuzzi, P. Guatteri, P. Riccardi, T. Sacchelli, J. Barberá, M. Costa and E. Dalcanale, *Eur. J. Org. Chem.*, 1999, 1527; M. A. Fox, J. V. Grant, D. Melamed, T. Torimoto, C.-Y. Liu and A. J. Bard, *Chem. Mater.*, 1998, **10**, 1771; B. A. Gregg, M. A. Fox and A. J. Bard, *J. Chem. Soc., Chem. Commun.*, 1987, 1134; B. A. Gregg, M. A. Fox and A. J. Bard, *J. Am. Chem. Soc.*, 1989, **111**, 3024.
11 Q. M. Wang and D. W. Bruce, *Tetrahedron Lett.*, 1996, **37**, 7641.
12 Y. Maeda and Y. Shimizu, *Liq. Cryst.*, 1999, **26**, 787; K. Ohta, N. Ando and I. Yamamoto, *Liq. Cryst.*, 1999, **26**, 663.
13 S. B. Kahl, J. J. Schaeck and M.-S. Koo, *J. Org. Chem.*, 1997, **62**, 1875 and references therein.
14 W. K. Lee, B. A. Wintner, E. Fontes, P. A. Heiney, M. Ohba, J. N. Haseltine and A. B. Smith, *Liq. Cryst.*, 1989, 87.
15 N. H. Tihn, J. Malthete and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 1981, **64**, 291.