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First asymmetrically β-tetrasubstituted porphyrin-based discotic lamellar liquid crystal

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The synthesis and liquid crystalline properties of a new asymetrically tetrasubstituted porphyrin, namely 2,4-bis[2-(*o*-didodecyloxyphenoxycarbonyl)ethenyl]-6,7-bis[2-(*m*-didodecyloxycarbonyl)-ethyl]-1,3,5,8-tetramethylporphyrin, **1** (figure 1), obtained from a commercially available porphyrin, hemin **2**, are reported here. The synthetic route basically consists of two reactions: on the one hand, one esterification of the two propionic acid groups in positions 6 and 7 in the hemin **2** with the phenol **12**, and on the other hand, a Heck-type reaction between the two vinyl groups in positions 2 and 4 of the hemin **2** and the iodo-aryl derivative **9**. This is the first example of a porphyrin-based discotic liquid crystal which is neither symmetrically substituted nor prepared via total synthesis from monopyrrole units. It exhibits a well-defined enantiotropic discotic lamellar mesophase (D_L) in a range of temperature from −2°C to the clearing point at 70°C. This interval includes room temperature, which makes this molecule suitable for a wide variety of applications.

1. Introduction

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

Most discotic mesogens have a molecular structure that consists of a flat central core with eight, six or, more rarely, four alkyl chains symmetrically placed 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 over a temperature range of 0.1°C, was the first mesogenic porphyrin to be reported [9]. Since then, several porphyrin derived mesogens have been reported [10–12]. They can be divided into two broad categories depending on the location of the substitution around 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] in a range of temperatures (5–160°C) depending on whether or not they are metallated and on the length of the alkyl chains introduced. On the other hand, porphyrins di-substituted and tetra-substituted at the *meso*-positions show nematic/smectic phases [11] or lamellar discotic phases [12], respectively, in a narrow range of temperatures (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.

2. Synthesis

The synthetic route is shown in the scheme. **Zn-3** was obtained from hemin **2** under the conditions described in [13, 14], in a global yield of 70%. **Zn-3** was reacted in a Heck-type reaction [15], using the catalyst *syn*-di(μ-acetate)-bis[*o*-(benzylphenylphosphino)benzyl]-dipalladium(II), with the iodo-aryl derivative **9**, obtained

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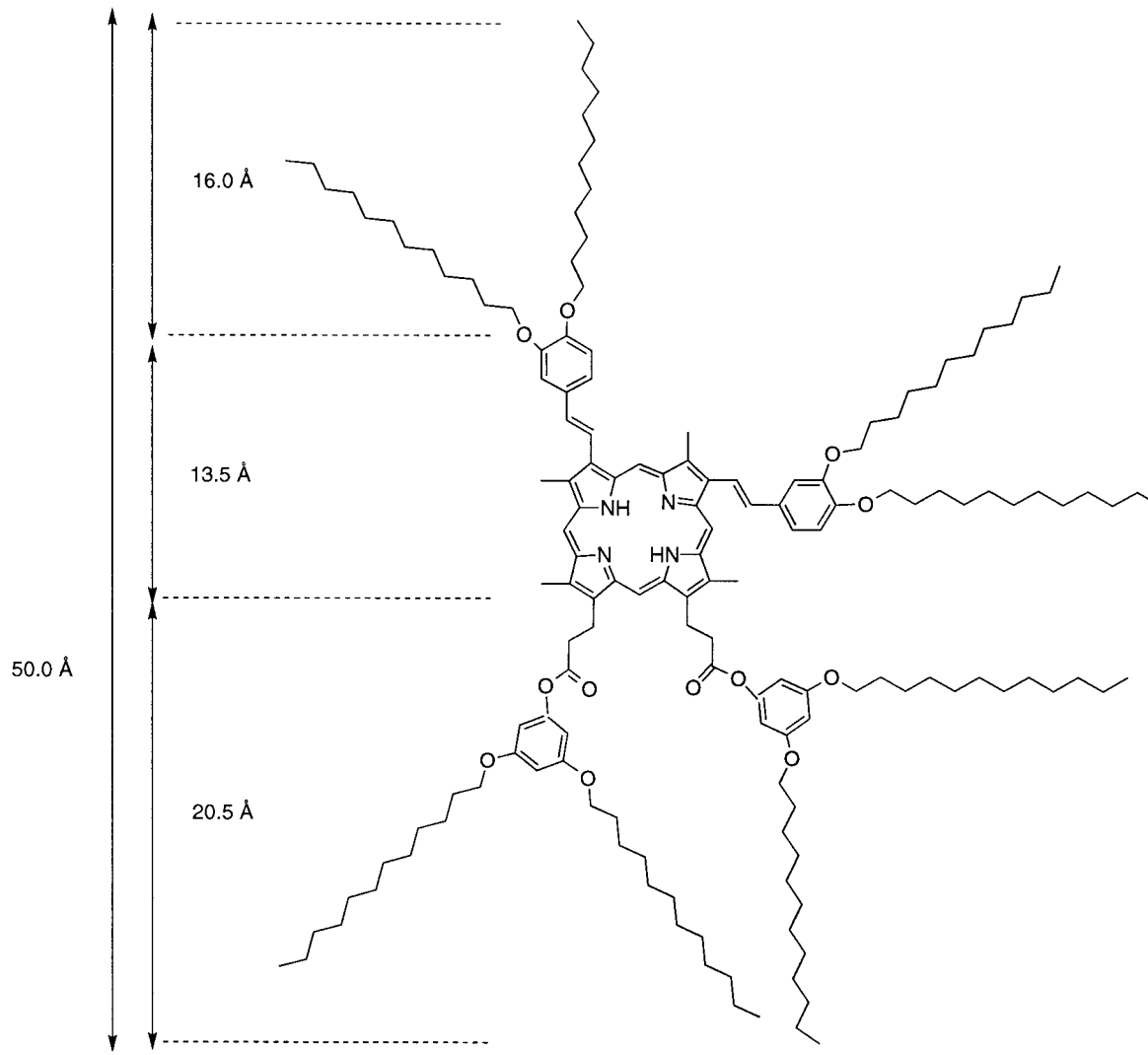
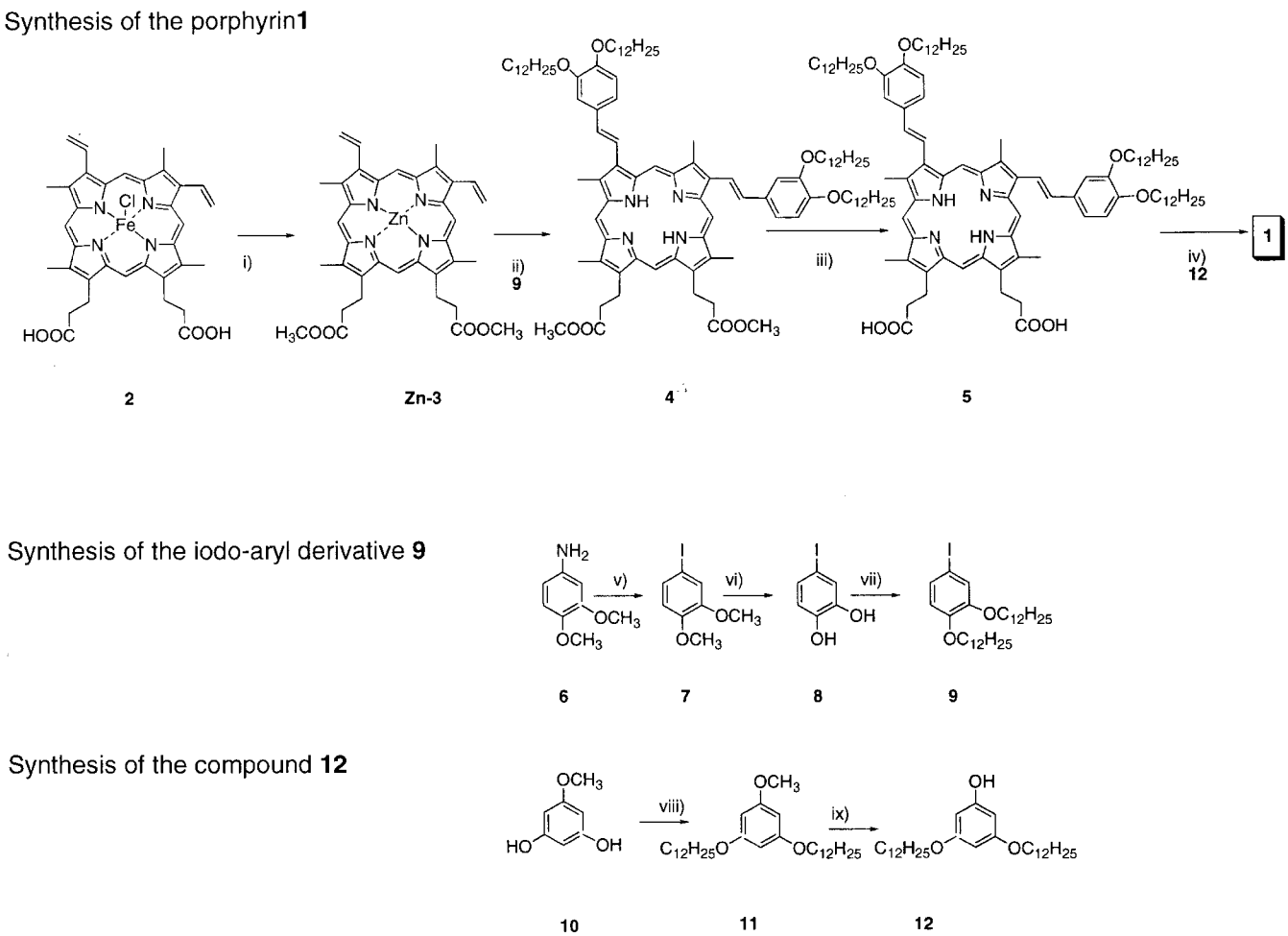


Figure 1. Structure and molecular distances calculated for the liquid crystal porphyrin **1**.

as the scheme describes, giving the compound **4** in 15% yield. The two methyl esters of porphyrin **4** were then saponified quantitatively to give the di-acid **5**, which was esterified with 3,5-didodecyloxyphenol **6** prepared as shown in the scheme from commercial 5-methoxyresorcinol. This esterification was performed in a yield of 18%. The detailed procedures for compound **1** are described below.

2.1. *2,4-Bis[2-(o-didodecyloxyphenoxycarbonyl)ethenyl]-6,7-bis[2-(m-didodecyloxycarbonyl)ethyl]-1,3,5,8-tetramethylporphyrin, **1***

A solution containing 20 mg (0.097 mmol) of DCCI and 39 mg (0.084 mmol) of **12** in 3 ml of anhydrous CH_2Cl_2 was slowly dropped at room temperature into a solution of 35 mg (0.024 mmol) of **5** and a catalytic amount of DMAP in 8 ml of anhydrous CH_2Cl_2. Once the addition was completed, stirring of the mixture was continued under a nitrogen atmosphere for 24 h. The solvent was then removed and the crude product purified by preparative TLC on Al_2O_3, eluting 10 mg of the target porphyrin **1** with CH_2Cl_2: hexane (1:1) in 18% yield; m.p. 70–72°C. TLC (Al_2O_3; CH_2Cl_2: hexane (3:2)) $R_f = 0.49$. IR (KBr, ν, cm^{-1}): 3317 (st NH); 1740 (CO ester). ^1H NMR ($CDCl_3$, δ, ppm): 10.32; 10.27; 10.15; 10.13 (4s, H_{meso}, 4H); 8.53; 8.52 (2d, porphyrin–C$\underline{H}$=CH–, $J_{trans} = 16.5$ Hz, 2H); 7.69; 7.68 (2d, porphyrin–CH=C$\underline{H}$–, $J_{trans} = 16.5$ Hz, 2H); 7.51 (m, $\underline{H}_{ortho}$ aromatic unit attached to $C_{2,4}$ of the porphyrin, 4H); 7.11; 7.10 (2d, $\underline{H}_{meta}$ aromatic unit attached to $C_{2,4}$ of the porphyrin, $J_{ortho} = 8.1$ Hz, 2H); 6.03; 6.02 (2t, $\underline{H}_{para}$ aromatic unit attached to $C_{6,7}$ of the porphyrin, $J_{meta} = 2.4$ Hz, 2H); 5.57; 5.54 (2d, $\underline{H}_{ortho}$ aromatic unit attached to $C_{6,7}$ of the porphyrin $J_{meta} = 2.4$ Hz, 4H); 4.48 (t, –C$\underline{H}_2$–CH_2–COO–,



(i) (a) CH_2Cl_2/MeOH, $FeSO_4.7H_2O$, HCl(g); (b) $Zn(AcO)_2$, pyr. (ii) DMF, pd catalyst [15], NaAcO, **9**. (iii) DME/KOH (0.7 M). (iv) DCCI/DMAP, CH_2Cl_2, **12**. (v) (a) $NaNO_2/H^+$, (b) KI (1.2 eq). (vi) BBr_3, CH_2Cl_2, $-78°C$–$0°C$, 5.5 h. (vii) $C_{12}H_{25}Br$, K_2CO_3, DMF. (viii) $C_{12}H_{25}Br$, K_2CO_3, DMF. (ix) NaSEt, DMF.

Scheme. Synthetic route for **1**.

$J = 7.8$ Hz, 4H); 4.26; 4.25; 4.16; 4.15 (4t, $-OC\underline{H}_2-$ aromatic unit attached to $C_{2,4}$ of the porphyrin, $J =$ 6.6 Hz, 8H); 3.80; 3.79; 3.68; 3.66 (4s, $C\underline{H}_3$–ring, 12H); 3.44 (t, $-CH_2-C\underline{H}_2-COO-$, $J = 7.8$ Hz, 4H); 3.07; 3.04 (2t, $-OC\underline{H}_2-$ aromatic unit attached to $C_{6,7}$ of the porphyrin, $J = 6.6$ Hz, 8H); 1.95 (m, $-OCH_2-C\underline{H}_2-$, 8H); 1.31–1.00 (m, $-C\underline{H}_2-$, 144H); 0.89 (m, $-CH_2-C\underline{H}_3$, 24H); -3.47 (s, N$\underline{H}$, 2H). Elemental Analysis: calc. for $C_{154}H_{242}N_4O_{12}$ C 78.97, H 10.44, N 2.39; found C 78.99, H 10.34, N 2.41%.

2.2. *Zn-protoporphyrin-IX dimethyl ester,* ***Zn-3***

A solution containing hemin **2** (150 mg, 0.230 mmol), $FeSO_4.7H_2O$ (815 mg, 2.933 mmol), MeOH (25 ml) and CH_2Cl_2 (16 ml) was saturated with HCl gas for 50 min. The crude material was washed with water, 10% aqueous ammonia, and again water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed by evaporation. The red solid obtained was chromatographed on silica gel with CH_2Cl_2 containing MeOH (0.7%) as eluant. 115 mg of pure red solid **3** was obtained in 85% yield. M.p. 218–220°C (lit 225–230 [13]). TLC (SiO_2; CH_2Cl_2: MeOH (10:1)) $R_f = 0.73$. IR (KBr, ν, cm^{-1}): 3319 (st NH); 1737 (CO ester). ^1H NMR ($CDCl_3$, δ, ppm): 10.10; 10.08; 9.97; 9.95 (4s, H_{meso}, 4H); 8.27; 8.18 (dd, $-C\underline{H}=CH_2$, $J_{cis} = 11.6$ Hz, $J_{trans} = 17.8$ Hz, 2H); 6.35 (d, $-CH=CH_{cis}\underline{H}_{trans}$, $J_{trans} = 17.8$ Hz, 2H); 6.18 (d, $-CH=C\underline{H}_{cis}H_{trans}$, $J_{cis} = 11.6$ Hz, 2H); 4.36 (t, $-C\underline{H}_2-CH_2-COO-$, $J = 7.6$ Hz, 4H); 3.67; 3.66; 3.65 (4s, CH_3–ring, 12H); 3.58 (s, $-COO-C\underline{H}_3$, 6H); 3.25 (t, $-CH_2-C\underline{H}_2-COO-$, $J = 7.6$ Hz, 4H); -3.89 (s, NH, 2H).

382 mg (0.647 mmol) of **3** and 370 mg of $Zn(OAc)_2$ were dissolved in 10 ml of pyridine. The mixture was stirred and heated at reflux for 15 min. The solution was then poured into 100 ml of CH_2Cl_2 and washed three

times with water. The violet porphyrin **Zn-3** was purified by recrystallization from MeOH (397 mg, 0.608 mmol, 94%); m.p. 223–225°C. TLC (SiO_2; CH_2Cl_2: MeOH (50:1)) $R_f = 0.66$. IR (KBr, ν, cm^{-1}): 1739 (CO ester). ^1H NMR ($CDCl_3$, δ, ppm): 9.79; 9.75; 9.63; 9.55 (4s, H_{meso}, 4H); 8.17 (dd, $-C\underline{H}=CH_2$, $J_{cis} = 11.7$ Hz, $J_{trans} = 17.1$ Hz, 2H); 6.26 (d, $-CH=CH_{cis}\underline{H}_{trans}$, $J_{trans} = 17.1$ Hz, 2H); 6.08 (d, $-CH=C\underline{H}_{cis}H_{trans}$, $J_{cis} = 11.7$ Hz, 2H); 4.26 (t, $-C\underline{H}_2-CH_2-COO-$, $J = 7.6$ Hz, 4H); 3.64 (2s, $-COO-CH_3$, 6H); 3.56; 3.54; 3.50; 3.47 (4s, CH_3–ring, 12H); 3.17 (t, $-CH_2-C\underline{H}_2-COO-$, $J = 7.6$ Hz, 4H)

2.3. *2,4-Bis[2-(o-didodecyloxyphenoxycarbonyl)-ethenyl]-6,70bis[2-methoxycarbonylethyl]-1,3,5,8-tetramethylporphyrin,* ***4***

240 mg (0.367 mmol) of **Zn-3** were dissolved in 20 ml of dried and nitrogen saturated DMF in a Schlenk flask. Then 10 mg (0.011 mmol) of the Pd catalyst [15] and 105 mg of NaOAc were added to the porphyrin solution. The mixture was heated to 120°C, stirred for 24 h under an atmosphere of nitrogen and then poured into 100 ml of CH_2Cl_2 and washed three times with water. The mixture of regioisomers obtained was briefly demetallated with TFA at room temperature in CH_2Cl_2. The solution was again washed with water, dried over anhydrous Na_2SO_4 and filtered. The desired porphyrin **4** was purified by preparative TLC on Al_2O_3 using CH_2Cl_2: MeOH (2:3) as eluant. 81 mg of porphyrin **4** were obtained in 15% yield; m.p. 83–85°C. TLC (Al_2O_3; CH_2Cl_2: hexane (3:2)) $R_f = 0.20$. IR (KBr, ν, cm^{-1}): 3317 (st NH); 1739 (CO ester). ^1H NMR ($CDCl_3$, δ, ppm): 10.30; 10.23; 10.11; 10.05 (4s, H_{meso}, 4H); 8.53; 8.52 (2d, porphyrin$-C\underline{H}=CH-$, $J_{trans} = 16.5$ Hz, 2H); 7.68; 7.67 (2d, porphyrin$-CH=C\underline{H}-$, $J_{trans} = 16.5$ Hz, 2H); 7.50 (m, $\underline{H}_{ortho}$, 4H); 7.09 (d, H_{meta}, $J_{ortho} = 8.4$ Hz, 2H); 4.42 (t, $-C\underline{H}_2-CH_2-COO-$, $J = 7.5$ Hz, 4H); 4.25; 4.15 (2t, $-OC\underline{H}_2-$, $J = 6.6$ Hz, 8H); 3.79; 3.72 (2s, $-COOC\underline{H}_3$, 6H); 3.66; 3.65; 3.63 (3s, CH_3–ring, 12H); 3.29 (t, $-CH_2-C\underline{H}_2-COO-$, $J = 7.5$ Hz, 4H); 1.95 (m, $-OCH_2-C\underline{H}_2-$, 8H); 1.30–1.26 (m, $-C\underline{H}_2-$, 72H); 0.90; 0.86 (m, $-CH_2-C\underline{H}_3$, 6H); −3.89 (s, N$\underline{H}$, 2H).

2.4. *2,4-Bis[2-(o-didodecyloxyphenoxycarbonyl)-ethenyl]-6,7-bis[2-carboxyl]-1,3,5,8-tetramethyl-porphyrin,* ***5***

37 mg (0.025 mmol) of **4** were dissolved in 8 ml of a solution of 1:1 DME:KOH 0.7M. The mixture was stirred at room temperature for 5 days and then AcOH was added dropwise until a pH of around 5 was reached. The dark precipitated solid was centrifuged down and washed twice with water, giving 35 mg of **5** in 97% yield; m.p. >350°C. TLC (Al_2O_3; CH_2Cl_2: MeOH:AcOH (5:1:0.1)) $R_f = 0.60$. IR (KBr, ν, cm^{-1}): 3310 (st NH); 1700 (CO acid).

2.5. *4-Iodo-1,2-dimethoxybenzene,* ***7***

3 g (19.585 mmol) of 3,4-dimethoxyaniline were dissolved in 9.75 ml of concentrated HCl and 98.4 ml of water and cooled in an ice bath. A solution of 1.374 g (19.910 mmol) of $NaNO_2$ in 39 ml of water was slowly dropped into the first solution, keeping the temperature below 5°C. Ten minutes after the addition, a solution of 3.924 g (23.134 mmol) of KI in 60 ml of water was poured in at 0°C. The mixture was stirred first at 110°C for 15 min and then at room temperature for 14 h. The crude product was extracted into $CHCl_3$, dried over anhydrous $MgSO_4$, filtered and evaporated. The desired product **7** was then purified by column chromatography on SiO_2, eluting with $CHCl_3$. 4.135 g (0.016 mmol, 80%) of an orange oil **7** were obtained. TLC (Al_2O_3; $CHCl_3$) $R_f = 0.51$. IR (KBr, ν, cm^{-1}): 3078; 3000 ($C_{ar}-H$); 2956; 2906; 2833 (CH_3); 1584; 1501 ($C_{ar}-C_{ar}$). ^1H NMR ($CDCl_3$, δ, ppm): 7.23 (dd, H_{ar} *ortho* to *iodo* and *para* and *meta* to the methoxy group, $J_{meta} = 1.8$ Hz, $J_{ortho} = 8.4$ Hz, 1H); 7.12 (d, H_{ar} *ortho* to *iodo* and to the methoxy group, $J_{meta} = 1.8$ Hz, 1H); 6.62 (d, H_{ar} *meta* to *iodo* and *ortho* and *meta* to the methoxy group, $J_{ortho} = 8.4$ Hz, 1H); 3.86; 3.85 (2s, $-OC\underline{H}_3$, 6H).

2.6. *4-Iodo-2-hydroxyphenol,* ***8***

A solution of 1.5 g (5.680 mmol) of **7** in 23 ml of anhydrous CH_2Cl_2 was slowly added to a M solution (28.4 ml) of BBr_3 in CH_2Cl_2 at −78°C. The mixture was then stirred at 0°C for 5.5 h, and poured over 200 ml of ice; the product was extracted into ether, and the extract dried over anydrous $MgSO_4$, filtered and evaporated. The purification of **8** was effected by column chromatography on SiO_2, using CH_2Cl_2: MeOH (100:0.9) as eluant. Product **8** was obtained in 95% yield; m.p. 90–92°C. TLC (Al_2O_3; CH_2Cl_2: MeOH (10:0.3)) $R_f = 0.19$. IR (KBr, ν, cm^{-1}): 3489; 3301 (OH); 1590; ($C_{ar}-C_{ar}$). ^1H NMR ($CDCl_3$, δ, ppm): 7.04 (d, H_{ar} *ortho* to *iodo* and to the methoxy group, $J_{meta} = 2.2$ Hz, 1H); 6.94 (dd, H_{ar} *ortho* to *iodo* and *para* and *meta* to the methoxy group, $J_{meta} = 2.2$ Hz, $J_{ortho} = 8.4$ Hz, 1H); 6.49 (d, H_{ar} *meta* to *iodo* and *ortho* and *meta* to the methoxy group, $J_{ortho} = 8.4$ Hz, 1H).

2.7. *4-Iodo-1,2-didodecyloxybenzene,* ***9***

1.279 g (5.381 mmol) of **8**, 4.024 g (16.142 mmol) of 1-bromododecane, 2.974 g (21.518 mmol) of anhydrous K_2CO_3 and a catalytic amount of KI were dissolved in 45 ml of dried DMF. The mixture was stirred at 150°C for 18 h. The solution was then poured over 150 ml of ice and shaken with diethyl ether. The organic layer was washed three times with water and brine, dried over anhydrous $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on SiO_2, eluting with CH_2Cl_2. 2.222 g (3.880 mmol, 72%)

of **9** were obtained; m.p. 50–53°C. TLC (Al_2O_3; CH_2Cl_2) $R_f = 0.74$. IR (KBr, ν, cm^{-1}): 2958; 2921, 2852 (CH_3); 1582; 1502 (C_{ar}–C_{ar}). ^1H NMR ($CDCl_3$, δ, ppm): 7.18 (dd, H_{ar} *ortho* to *iodo* and *para* and *meta* to the methoxy group, $J_{meta} = 2.2$ Hz, $J_{ortho} = 8.4$ Hz, 1H); 7.13 (d, H_{ar} *ortho* to *iodo* and to the methoxy group, $J_{meta} = 2.2$ Hz, 1H); 6.66 (d, H_{ar} *meta* to *iodo* and *ortho* and *meta* to the methoxy group, $J_{ortho} = 8.4$ Hz, 1H); 3.95 (t, $-OC\underline{H}_2-$, $J = 6.6$ Hz, 4H); 1.78 (m, $-OCH_2-C\underline{H}_2-$, 4H); 1.44–1.27 (m, $-C\underline{H}_2-$, 36H); 0.89 (t, $-CH_2-C\underline{H}_3$, $J = 6.6$ Hz, 6H).

2.8. *3,5-Didodecyloxymethoxybenzene,* ***11***

The synthesis was carried out as described for **9** giving a colourless oil **11** in 50% yield. TLC (SiO_2; CH_2Cl_2) $R_f = 0.69$. IR (KBr, ν, cm^{-1}): 2929, 2852 (CH_3); 1600; 1466 (C_{ar}–C_{ar}). ^1H NMR ($CDCl_3$, δ, ppm): 6.08 (3s, H_{ar}, 3H); 4.76 (s, $-OC\underline{H}_3$, 3H); 3.91 (t, $-OC\underline{H}_2-$, $J = 6.6$ Hz, 4H); 1.75 (m, $-OCH_2-C\underline{H}_2-$, 4H); 1.43–1.30 (m, $-C\underline{H}_2-$, 20H); 0.89 (t, $-CH_2-C\underline{H}_3$, $J = 6.6$ Hz, 6H).

2.9. *3,5-Didodecyloxyphenol,* ***12***

EtSH (3.2 ml) was poured into 1.099 g (27.475 mmol) of NaH in 27 ml of dried DMF at 0°C. After the addition the mixture was stirred at room temperature for 15 min. Immediately afterwards, 534 mg (1.464 mmol) of **11** were added and the mixture was stirred at 120°C for 19 h. A few drops of water were then introduced and the solution was neutralized by the addition of HCl 10%. The crude product was extracted into AcOEt; the extract was washed with water, dried over anhydrous $MgSO_4$, filtered and evaporated. Product **12** was purified in 70% yield by column chromatography on SiO_2 using hexane: AcOEt (9:1) as eluant; m.p. 41–43°C. TLC (SiO_2; hexane: AcOEt (8:2)) $R_f = 0.34$. IR (KBr, ν, cm^{-1}): 3413 (OH); 2929, 2852 (CH_3); 1600 (C_{ar}–C_{ar}). ^1H NMR ($CDCl_3$, δ, ppm): 6.07 (t, H_{para}, $J_{meta} = 2$ Hz, 1H); 6.01 (d, H_{ortho}, $J_{meta} = 2$ Hz, 2H); 5.45 (s, $-O\underline{H}$, 1H); 3.88 (t, $-OC\underline{H}_2-$, $J = 6.2$ Hz, 4H); 1.73 (m, $-OCH_2-C\underline{H}_2-$, 4H); 1.41–1.29 (m, $-C\underline{H}_2-$, 20H); 0.89 (t, $-CH_2-C\underline{H}_3$, $J = 6.2$ Hz, 6H).

3. Mesomorphic properties of 1

The thermal behaviour of this compound was analysed by differential scanning calorimetry (Mettler Toledo DSC821) and polarizing optical microscopy (Leitz Orttholux II Pol-BK) in conjunction with a hot stage controlled by a thermoregulator, Mettler FP80. Temperature-dependent X-ray powder diffraction measurements were taken with Cu-K_α radiation, using a Debye-Scherrer Inel CPS-120 with an Inel Cry-950 cryostat.

The DSC analysis of **1** displayed a broad exothermic peak at 70°C with an associated enthalpy of 8 J g^{-1} on the first heating at 10°C min^{-1}. On cooling from the melt at 10°C min^{-1}, a first transition to the liquid crystal phase took place at 48°C with an enthalpy of 2 J g^{-1}, showing a considerable supercooling effect, and a second transition appeared at −2°C with an enthalpy of 6 J g^{-1}. Both transitions at −2°C and 70°C were also observed in the second heating experiment at 10°C min^{-1}. Figure 2 gives the transition temperatures with the associated enthalpy data registered on the second heating cycle.

Polarizing optical microscopy at room temperature of **1** showed a slight birefringence. The material could be

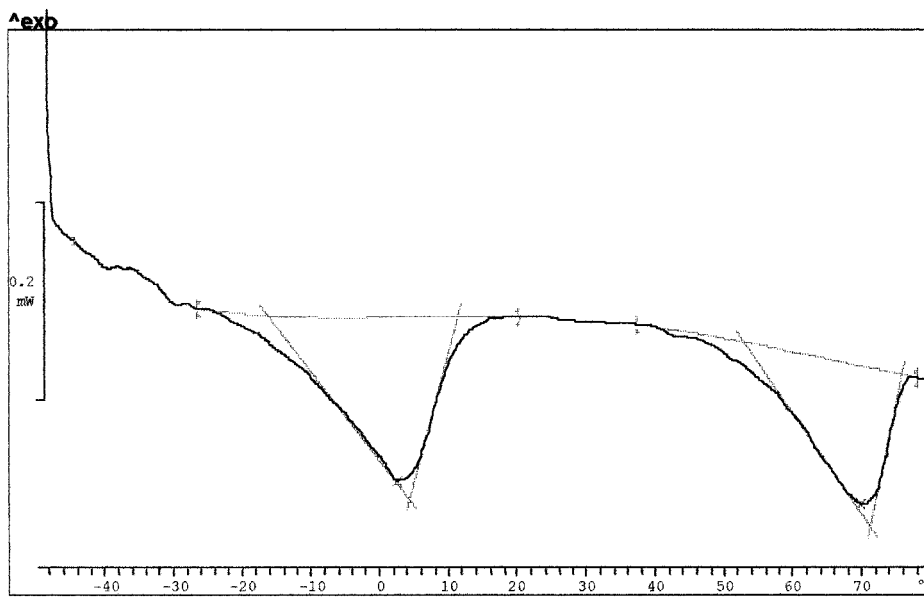


Figure 2. Transition temperatures and associated enthalpy data for porphyrin **1**. Second heating (10°C min^{-1}) of the sample: $T_1 = 2.5$°C (6.5 J g^{-1}); $T_2 = 70$°C (4 J g^{-1}).

easily sheared, causing a strong shear-induced birefringence. This behaviour suggested a homeotropic alignment of the molecules in the liquid crystal phase. No changes in the texture occurred when the sample was heated to its clearing point at 70°C. It proved to be very difficult to obtain a non-homeotropic texture characteristic for the lamellar discotic mesophase (D_L), even if the sample was cooled from the isotropic state.

Powder X-ray diffraction analyses of the porphyrin **1** at room temperature on cooling from the isotropic phase, showed only two diffraction rings in the low angle region, corresponding to a lamellar discotic structure, since their ratio is 1 : 1/2 (see the table). In addition, a broad halo was located at 4.4 Å; this was attributed to the disordered alkoxy chains.

The *d* spacing of the low angle reflection, around 34.6 Å, represents the layer spacing in the lamellar discotic mesophase, consistent with other results which have been reported to date [12, 16] for porphyrins and metalloporphyrins having a lamellar discotic structure.

The molecular distances for compound **1**, calculated by the CS Chem3D 5.0 program, placing all the alkyl chains in their totally elongated conformation, are represented in figure 1. Taking into account the molecular dimensions for **1** and the interlayer distance in the lamellar discotic mesophase determined from the X-ray diffractogram, it is possible to propose the model shown in figure 3.

According to this model, the rigid core would be constituted by the porphyrin nuclei and the phenyl

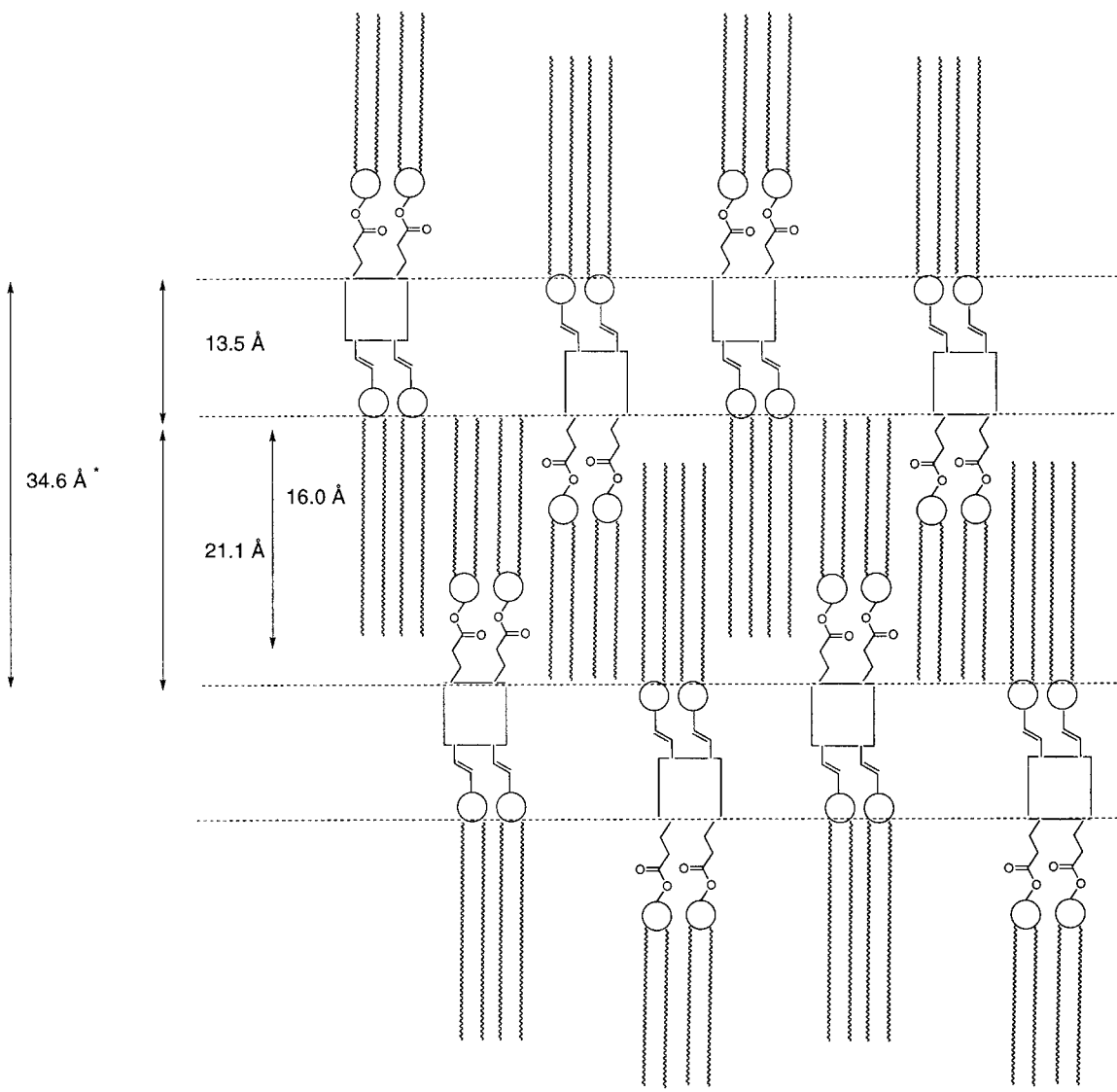


Figure 3. Proposed packing model in the lamellar discotic mesophase.

Table. Powder X-ray diffraction data for porphyrin **1** at room temperature.

Temperature/°C	Observed spacing/A	Miller indices (h k l)
Room[a]	34.6	(0 0 1)
	17.3	(0 0 2)
	4.4	alkoxy chains
−30	34.6	(0 0 1)
	17.3	(0 0 2)
	4.4	alkoxy chains
−70	34.3	(0 0 1)
	17.6	(0 0 2)
	6.8	—
	4.4	alkoxy chains

[a] Coming from the isotropic state.

groups attached to the porphyrin ring by the double bonds in positions 2 and 4. The free rotation about the σ-bonds of the propionate groups in positions 6 and 7 puts the corresponding phenyl groups out of conjugation with the porphyrin, so that they do not belong to the rigid core in the lamellar discotic mesophase.

The difference between the interlayer spacing, 34.6 Å, and the molecular dimension, 50 Å, can be assumed to be the result of the interpenetration of the alkyl chains, as well as of the propionate groups in positions 6 and 7 of the porphyrin core.

At −30°C the registered X-ray data do not suffer any transformation in comparison with those at room temperature, giving the same diffraction pattern (see the table). Thus the transition indicated by DSC at 2.5°C leaves the X-ray pattern unaffected. At −70°C porphyrin **1** shows a similar X-ray diffraction pattern, but with slight differences in the spacings. In addition, a new reflection in the wide angle region appears at 6.8 Å.

In summary, the asymmetrically tetrasubstituted porphyrin **1** shows an enantiotropic lamellar discotic mesophase (D_L) in a range of temperature that includes room temperatures.

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