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Discotic liquid crystals of transition metal complexes:† 22. synthesis and mesomorphism of octa-alkoxy-substituted tetraphenylporphyrin derivatives and their copper(II) complexes

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Ten novel long-chain-substituted porphyrin derivatives, tetrakis (3,4-dialkoxyphenyl)porphyrins [abbreviated as $(C_nO)_8TPPM$: $M = H_2$, $n = 4, 6, 8, 10, 12, 16, 18$; $M = Cu$, $n = 8, 12$ and $(2EtC_6O)_8TPPH_2$], were synthesized and their mesomorphism was investigated. Among them four derivatives, $(C_nO)_8TPPH_2$ ($n = 12, 16, 18$) and $(C_{12}O)_8TPPCu$, exhibited a monotropic discotic lamellar (D_L) mesophase.

1. Introduction

In general, a discotic liquid crystal has a disk-like core in the molecular centre. The intermolecular force between the disk-like cores may be a driving force to form columnar structures. If large groups in the surroundings of the disk-like core weaken the intermolecular force by steric hindrance, the compounds may show interesting non-columnar mesophases. Hence, we have chosen a tetraphenylporphyrin ($TPPH_2$) macrocycle as a disk-like core with low planarity, because it is well known that the phenyl groups of $TPPH_2$ are perpendicular to the porphyrin core plane in the crystalline state [2]. Shimizu *et al.* reported mesogenic $TPPH_2$ derivatives, $(C_n)_4TPPH_2$ (**1a** in figure 1). Each of the phenyl groups was substituted with a long-*alkyl* chain at the *para* position [3, 4]. These derivatives show discotic lamellar (D_L) mesophases [4]. Kugimiya *et al.* reported that long-*alkoxy*-substituted derivatives $(C_nO)_4TPPH_2$, **1b**, show liquid crystalline properties [5]. However, Shimizu *et al.* revealed from miscibility tests that these derivatives, **1b**, have no liquid crystalline properties [4, 6]. Thus, the mesomorphism of the four-long-chain-substituted $TPPH_2$ derivatives **1** disappears on replacing alkyl groups by alkoxy groups. This may be attributable to stronger intermolecular force between the cores of **1b** than of **1a**, because the more strongly electron donating alkoxy groups may increase the electron density of the $TPPH_2$ core. It is also well

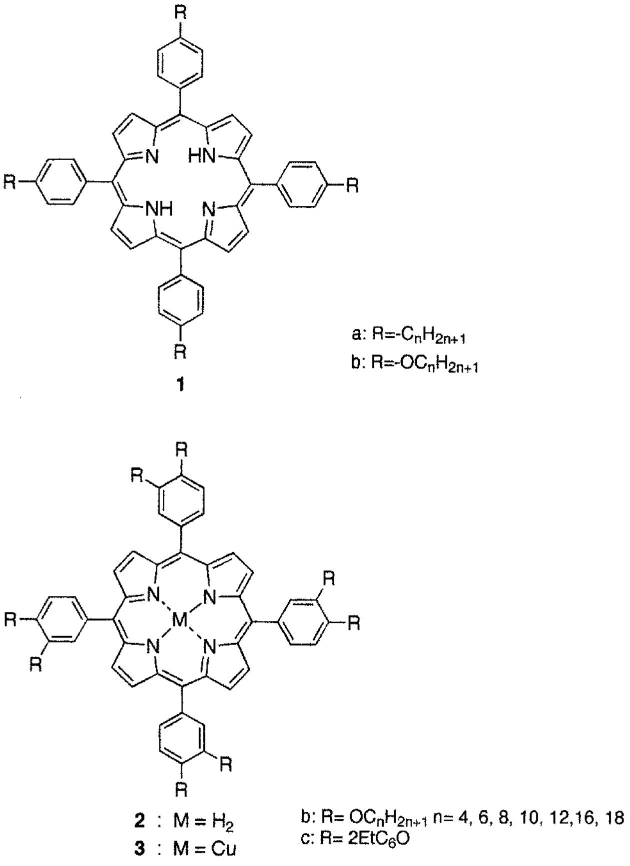

Figure 1. Formulae of the long-chain-substituted tetraphenylporphyrin derivatives. Abbreviations: **1a** $(C_n)_4TPPH_2$, **1b** $(C_nO)_4TPPH_2$, **2b** $(C_nO)_8TPPH_2$, **2c** $(2EtC_6O)_8TPPH_2$, and **3b** $(C_nO)_8TPPCu$.

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known that alkoxy substituents can adopt a planar chain extended conformation more readily than alkyl substituents. As a result, the latter tend to reduce the ability of aromatic rings to pack on top of each other. However, we have now synthesized two new kinds of TPP derivatives, $(C_nO)_8TPPH_2$, **2b**, and $(C_nO)_8TPPCu$, **3b**, which have one more alkoxy group at the *meta*-position for each of the phenyl rings. These additional alkoxy groups may weaken the strong intermolecular force with greater steric hindrance, leading to mesomorphism. These new compounds do indeed show mesomorphism. The metal-free $(C_nO)_8TPPH_2$ ($n = 12, 16, 18$) derivatives, **2b**, and the $(C_{12}O)_8TPPCu$ complex, **3b**, have a monotropic discotic lamellar mesophase D_L.

In this paper, we describe the synthesis and mesomorphism of these octa-alkoxy-substituted TPP derivatives, **2b** and **3b**.

2. Experimental

2.1. *Synthesis*

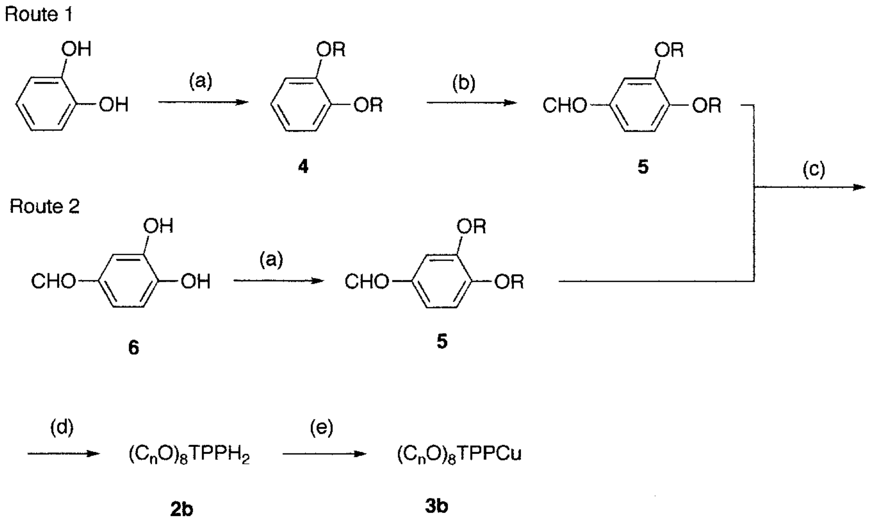
All the synthetic routes are shown in the scheme. The precursor **5** was synthesized by two different routes. Alkylations were carried out by the method of Strzelecka *et al.* [7]. Formylation (**4** → **5**) in route 1 was performed by the method of Rieche *et al.* [8]. Syntheses of **2b** were carried out by the method of Adler *et al.* [9]. The copper(II) complexes **3b** were prepared by modification of the literature method [10]. The detailed procedures for a representative compound, $(C_{12}O)_8TPPCu$, are described below.

2.1.1. *1,2-Didodecyloxybenzene,* **4**; *n = 12*

Under a nitrogen atmosphere, dodecyl bromide (24.9 g, 99.9 mmol), 85% pure potassium hydroxide (5.67 g, 85.9 mmol) and a few drops of Aliquat 336 (tricaprylylmethylammonium chloride, Aldrich) as a phase transfer agent were added to catechol (5.00 g, 45.4 mmol). The mixture was heated under reflux with stirring for 2 h at *c.* 200°C. The reaction mixture was cooled, then extracted with ether and the extract washed with water. The crude product was purified by column chromatography (silica gel, chloroform, $R_f = 0.68$) and recrystallization from isopropyl alcohol. Yield 13.4 g (66.1%) of white crystals, m.p. 45.6°C (lit. 46°C [11]). IR (KBr, cm^{-1}) 2850 (CH_2) 1450, 1500, 1580 (Ph) 1220 (*R*OPh). ^1H NMR (CCl_4: TMS) δ 0.86 (t, 6H) 1.27 (m, 40H) 3.83 (t, 4H) 6.60 (m, 4H).

2.1.2. *3,4-Didodecyloxybenzaldehyde,* **5** *by route 1*

Under a nitrogen atmosphere, 1,2-didodecyloxybenzene **4** (7.00 g, 15.7 mmol) was added to 70 ml of dry dichloromethane. The solution was cooled in an ice bath, and titanium tetrachloride (5.10 g, 26.9 mmol) added with stirring. While the solution was stirred and cooled, dichloromethyl methyl ether (1.50 g, 13.1 mmol) was added dropwise. The mixture was stirred in the ice bath for 30 min and then at r.t. for 60 min. The reaction mixture was poured into a separatory funnel containing crushed ice and shaken thoroughly. The organic layer was extracted with dichloromethane and the extract washed with water. After removal of solvent the crude product was purified by column chromatography (silica gel, benzene, $R_f = 0.17$). Yield 4.80 g (77.4%) of white crystals, m.p. 70°C. IR (KBr, cm^{-1}) 2850 (CH_2) 1440, 1510, 1580 (Ph) 1230 (*R*OPh) 1670 (CHO). ^1H NMR (CCl_4: TMS) δ 0.88 (t, 6H) 1.26 (m, 40H) 3.97 (t, 4H) 7.13 (m, 3H) 9.65 (s, 1H).



Scheme. Synthetic routes for $(C_nO)_8TPPH_2$, **2b** and $(C_nO)_8TPPCu$, **3b**: (a) $C_nH_{2n+1}Br$, KOH, Aliquat 336; (b) $TiCl_4/CH_3OCHCl_2$, (c) pyrrole/C_2H_5COOH, (d) DDQ, (e) $CuCl_2$/DMF.

2.1.3. *3,4-Didodecyloxybenzaldehyde,* ***5*** *by route 2*

A mixture of 3,4-dihydroxybenzaldehyde (71.9 g, 52.1 mmol), dodecyl bromide (28.6 g, 115 mmol), 85% pure potassium hydroxide (6.47 g, 97.8 mmol), and a few drops of Aliquat 336 was heated at 120°C for 3 h with vigorous stirring under nitrogen. The reaction mixture was extracted with ether. After removal of solvent the crude product was recrystallized twice from isopropyl alcohol and ethanol. Yield 15.3 g (61.9%), m.p. 71°C.

2.1.4. *5,10,15,20-Tetrakis(3,4,-didodecyloxyphenyl)-porphyrin, $(C_{12}O)_8TPPH_2$* ***2b***

To propionic acid (18 ml) were added 3,4-dihydroxy-benzaldehyde (2.78 g, 5.86 mmol) and pyrrole (0.46 g, 6.9 mmol). The solution was heated under reflux for 45 min, and cooled to r.t. The reaction mixture was extracted with ether, and the extract washed with water. After removal of solvent the crude product was purified by column chromatography (alumina, chloroform, $R_f = 1.0$). Yield 2.34 g (19.1%).

It is known that this product includes the chlorin derivative; the product was therefore oxidized with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). DDQ (0.75 g) dissolved in a little benzene was added to a chloroform solution of the product (0.92 g), and the mixture was heated under reflux for 3 h. The solution was purified by column chromatography, five times in the following sequence: (alumina, chloroform, $R_f = 1.0$); (alumina, hexane : dichloromethane = 2 : 1, $R_f = 0.40$), (alumina, chloroform, $R_f = 1.0$: 3 times). Yield 0.62 g (67%), of a purple solid mass. IR (KBr, cm^{-1}) 3330 (NH) 2920, 2870 (CH_2) 1460 (CH_3) 1350 (Ph) 1230, 1130 (ROPh). ^1H NMR ($CDCl_3$: TMS) $\delta - 2.76$ (s, 2H) 0.83 (t, 12H) 0.90 (t, 12H) 1.2–1.6 (m, 144H) 1.88 (m, 8H) 2.03 (m, 8H) 4.12 (t, 8H) 4.29 (t, 8H) 7.2–7.8 (m, 14H) 8.90 (s, 8H). UV-Vis spectrum in $CHCl_3$: λ_{max}/nm(log ε) 425.4 (5.72) 518.9 (4.26) 557.0 (4.06) 592.5 (3.75) 649.3 93.75).

2.1.5. *$(C_{12}O)_8TPPCu$,* ***3b****; n = 12*

Under a nitrogen atmosphere, $(C_{12}O)_8TPPH_2$ (0.68 g, 0.33 mmol) and copper(II) chloride anhydrous (0.60 g, 4.5 mmol) were added to *N*,*N*-dimethylformamide (DMF). The mixture was heated under reflux for 5 h. The crude product was separated by filtration and then purified by column chromatography (alumina, carbon tetrachloride : *n*-hexane = 2 : 1, $R_f = 0.90$) and reprecipitation (methanol : acetone = 1 : 1 + dichloromethane). Soxhlet extraction with methanol was then carried out to remove impurities. The final residue was purified again by column chromatography (alumina, chloroform, $R_f = 1.0$). Yield 0.60 g (86%) of a red-purple solid mass. IR (KBr, cm^{-1}) 2925, 2850 (CH_2), 1240 (ROPh). UV-Vis spectrum in $CHCl_3$: λ_{max}/nm(log ε) 421.0 (5.54) 540.7 (4.28) 577.3 (3.55).

The elemental analysis data for compounds **2b** and **3b** are summarized in table 1.

2.2. *Measurements*

The phase transition behaviour of these compounds was observed with a differential scanning calorimeter, Rigaku TG-DSC, and a polarizing microscope equipped with a hot stage controlled by a thermoregulator, Mettler FP80. Temperature-dependent X-ray powder diffraction measurements were performed with Cu-K_α radiation, using a Rigaku Geigerflex and a Shimadzu XD-610 equipped with a hand-made hot stage controlled by a thermoregulator [12], CHINO model KP1250BR00.

3. Results and discussion

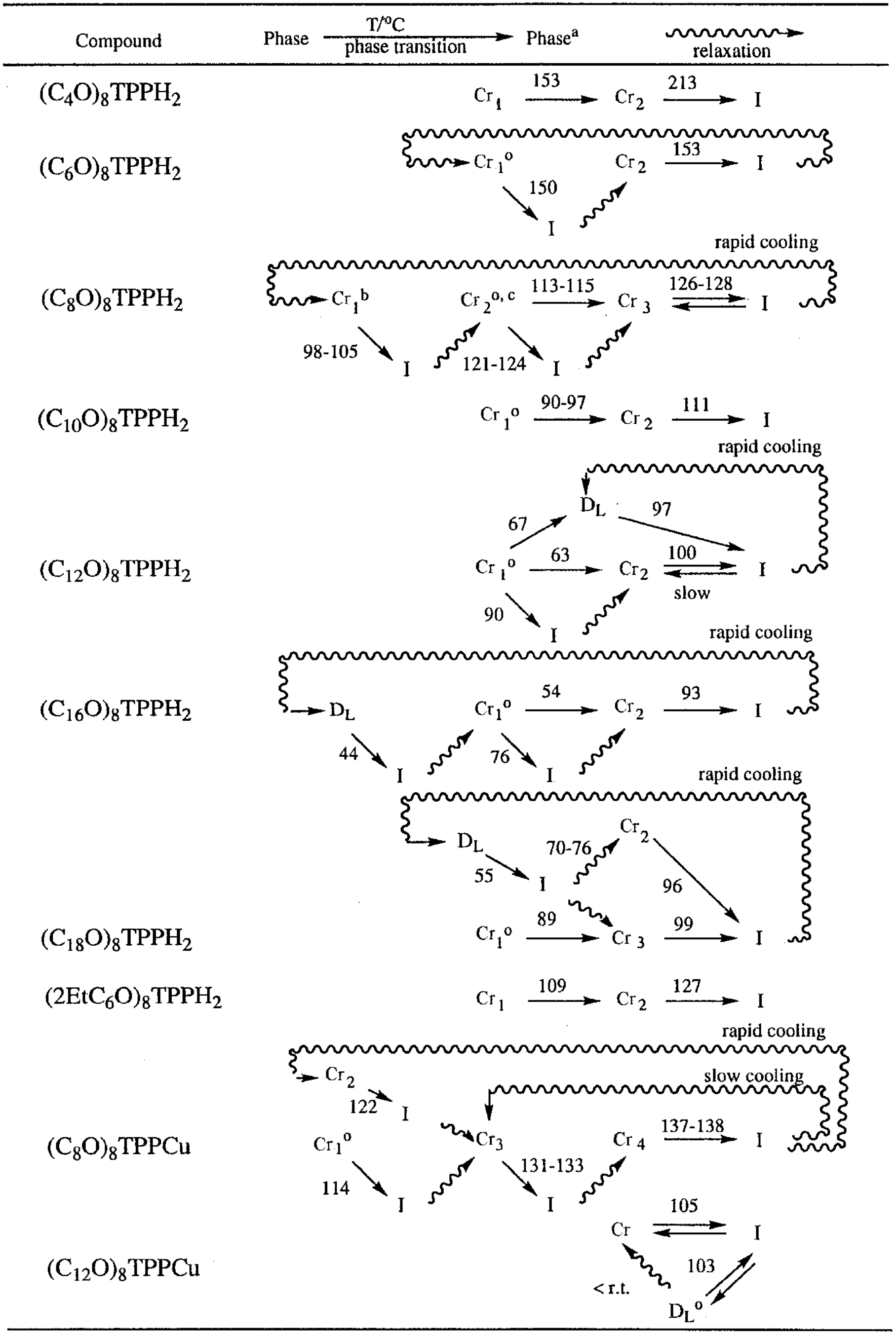
As can be seen from table 2, most of the derivatives synthesized in this work exhibit very complex phase transition sequences.

For example, the $(C_{16}O)_8TPPH_2$ derivative gave the Cr_1 crystalline phase in the virgin state after fresh preparation. When the Cr_1 crystals were heated up from r.t. under a polarizing microscope, they started to transform into another crystalline phase Cr_2 at 54°C but unchanged Cr_1 crystals (without the transformation) melted into the isotropic liquid (I) at the m.p. of Cr_1, 76°C. This I phase relaxed to resolidify into the Cr_2 phase by using the seed-crystals of Cr_2 that had previously formed by solid–solid phase transition. On further heating, the Cr_2 crystals melted into the I phase at the m.p. of Cr_2, 93°C. When this I phase was rapidly cooled to r.t., a liquid crystalline phase (D_L) could be obtained. When it was heated again, it cleared into the I phase at 44°C. This I phase relaxed to resolidify into the Cr_1 phase.

Table 1. Elemental analysis data for $(C_nO)_8TPPH_2$ ($n = 4$, 6, 8, 10, 12, 16, 18), $(2EtC_6O)_8TPPH_2$, and $(C_nO)_8TPPCu$ ($n = 8$, 12).

	Found (calcd)/%		
Compound	N	C	H
$(C_4O)_8TPPH_2$	4.58 (4.70)	76.82 (76.61)	7.79 (7.95)
$(C_6O)_8TPPH_2$	3.75 (3.96)	77.60 (78.04)	8.92 (8.97)
$(C_8O)_8TPPH_2$	3.20 (3.42)	79.39 (79.04)	10.06 (9.71)
$(C_{10}O)_8TPPH_2$	2.86 (3.00)	79.42 (79.86)	10.18 (10.27)
$(C_{12}O)_8TPPH_2$	2.45 (2.68)	80.21 (80.48)	10.73 (10.71)
$(C_{16}O)_8TPPH_2$	2.09 (2.21)	81.25 (81.39)	11.26 (11.36)
$(C_{18}O)_8TPPH_2$	1.85 (2.03)	81.55 (81.74)	11.53 (11.60)
$(2EtC_6O)_8TPPH_2$	3.24 (3.42)	78.72 (79.07)	9.70 (9.71)
$(C_8O)_8TPPCu$	3.28 (3.29)	76.60 (76.22)	9.26 (9.24)
$(C_{12}O)_8TPPCu$	2.52 (2.61)	78.05 (78.18)	10.28 (10.31)

Table 2 Phase transtion temperatures of $(C_nO)_8TPPH_2$ (n= 4, 6, 8, 10, 12, 16, 18) and $(2EtC_6O)_8TPPH_2$, and $(C_nO)_8TPPCu$ (n= 8, 12).



a: Phase nomenclature; Cr= crystal, D_L = discotic lamellar mesophase, and I.L.= isotropic liquid. b: microcrystals. c: needle-like crystals. o = virgin state.

Figure 2 shows two typical X-ray diffraction patterns of the mesophases of $(C_{12}O)_8TPPH_2$ and $(C_{16}O)_8TPPH_2$. Both patterns exhibit two sharp reflections in the low angle region, whose spacings are in a ratio 1 : 1/2 (table 3). This indicates that each of the mesophases has a lamellar structure. Hence, this mesophase could be identified as a discotic lamellar (D_L) phase [13]. In the high angle region $(C_{12}O)_8TPPH_2$ exhibits a broad halo, which corresponds to complete melting of eight long dodecyl chains. On the other hand, $(C_{16}O)_8TPPH_2$ exhibits a fairly sharp reflection around $2\Theta = 21°$. This reflection indicates that these long hexadecyl chains still pack two-dimensional-hexagonally, although they tend to melt. The difference between $(C_{12}O)_8TPPH_2$ and

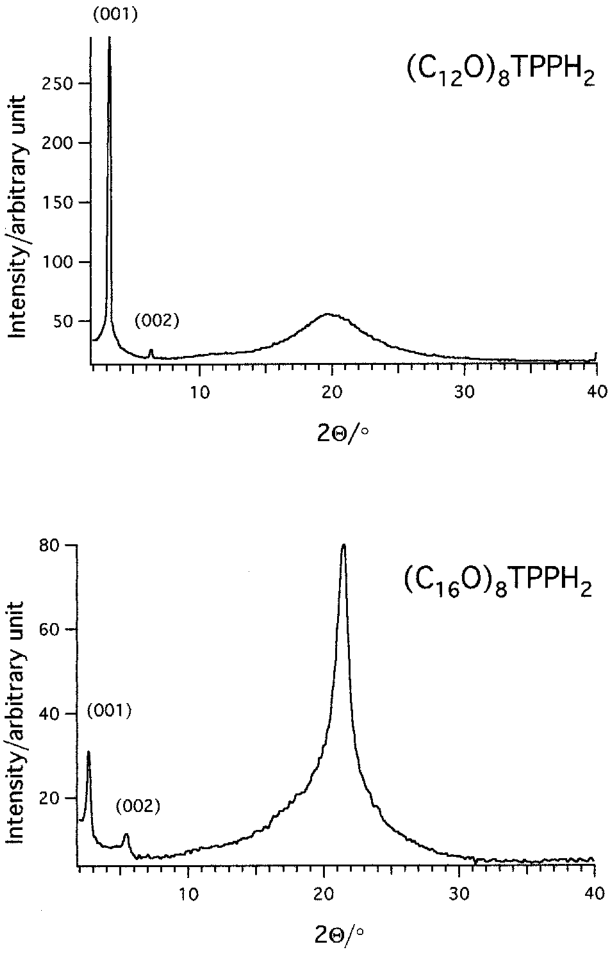


Figure 2. Comparison X-ray diffraction patterns of the D_L mesophases.

$(C_{16}O)_8TPPH_2$ may be due to easier packing of the longer chains $C_{16}H_{33}$ than $C_{12}H_{25}$, in the mesophase.

Table 3 lists all the X-ray diffraction data of the discotic lamellar mesophases of the $(C_nO)_8TPPM$ derivatives. The mesophases of $(C_{12}O)_8TPPH_2$ and $(C_{12}O)_8TPPCu$ undergo complete melting of chains. On the other hand, those of $(C_{16}O)_8TPPH_2$ and $(C_{18}O)_8TPPH_2$ have two-dimensional-hexagonal packing of chains. Comparing the X-ray data of $(C_{12}O)_8TPPH_2$ and $(C_{12}O)_8TPPCu$, the copper complex gives a little longer layer distance and exhibits the (0 0 4) reflection for the layered structure. Nevertheless, each of the mesophases has the same type of lamellar structure with complete melting of chains. Interestingly, complexation of a phthalocyanine metal-free derivative with a metal tends to change the mesophase structure [14]. However, the present porphyrin derivatives do not show such a metal effect.

It is noteworthy that the present porphyrin derivatives, which have a disk-like central core with eight long surrounding alkoxy chains, exhibit a lamellar mesophase rather than a columnar phase.

Table 3. X-ray diffraction data for the discotic lamellar (D_L) mesophases of the $(C_nO)_8TPPM$ derivatives.

Compound	Peak no.	d_{obs}/Å	d_{calcd}/Å	(h k l)
$(C_{12}O)_8TPPH_2$ at r.t.	1	27.1	27.6	(001)
	2	13.8	13.8	(002)
	3	*c.* 4.5	—	[a]
$(C_{16}O)_8TPPH_2$ at r.t.	1	31.9	32.1	(001)
	2	16.1	16.1	(002)
	3	4.12	—	[b]
$(C_{18}O)_8TPPH_2$ at 40°C	1	33.2	33.6	(001)
	2	16.8	16.8	(002)
	3	11.0	11.2	(003)
	4	4.13	—	[b]
$(C_{12}O)_8TPPCu$ at 90°C	1	31.5	30.1	(001)
	2	15.0	15.0	(002)
	3	9.78	10.0	(003)
	4	7.30	7.52	(004)
	5	*c.* 4.4	—	[a]

[a] Broad peak corresponding to melting of the long chains.
[b] Fairly sharp peak corresponding to loose hexagonal packing of the long chains.

4. Conclusion

Ten novel long-chain-substituted porphyrin derivatives, tetrakis(3,4-dialkoxyphenyl)porphyrins [abbreviated as $(C_nO)_8TPPM$: $M = H_2$, $n = 4, 6, 8, 10, 12, 16, 18$; $M = Cu$, $n = 8, 12$ and $(2EtC_6O)_8TPPH_2$], were synthesized and their mesomorphism was investigated. Among them four derivatives, $(C_nO)_8TPPH_2$ ($n = 12, 16, 18$) and $(C_{12}O)_8TPPCu$, exhibited a monotropic discotic lamellar (D_L) mesophase. The D_L mesophases of $(C_{12}O)_8TPPH_2$ and $(C_{12}O)_8TPPCu$ undergo complete melting of chains. On the other hand, those of $(C_{16}O)_8TPPH_2$ and $(C_{18}O)_8TPPH_2$ have two-dimensional-hexagonal packing of chains.

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