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Synthesis and mesomorphism of tetraphenylporphyrin derivatives

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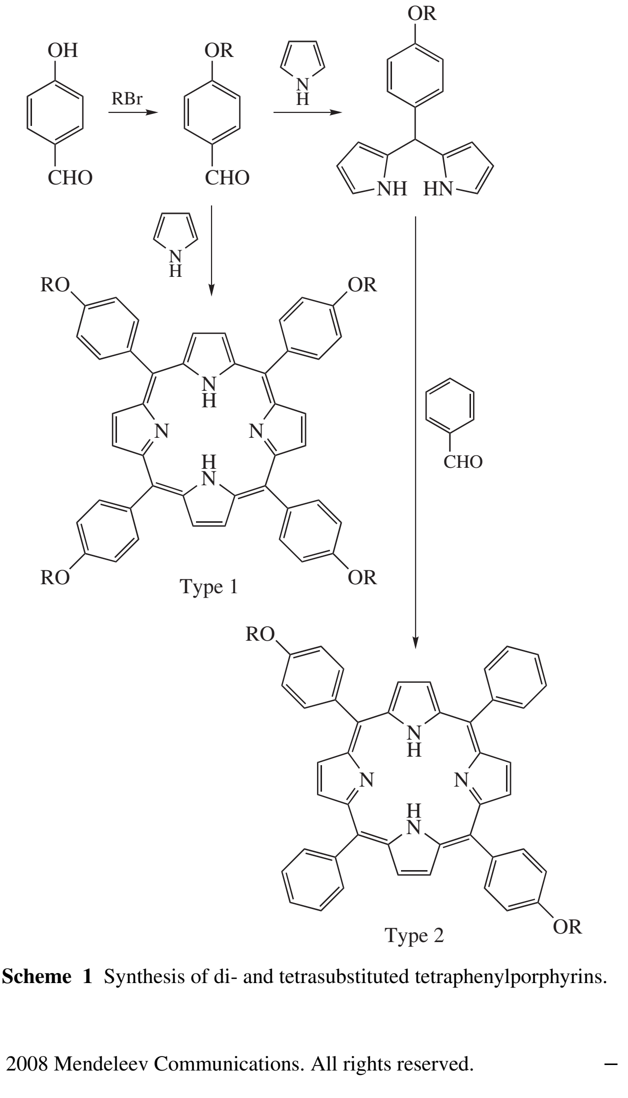
Tetra-*meso*-phenylporphyrins with higher alkoxy substituents at 4-positions of 5,15- or 5,10,15,20-phenyl groups have been synthesised; their liquid-crystal properties have been studied, and compounds that can undergo vitrification with retention of the mesophase structure have been revealed.

Studies on the molecular design of mesogens have been developed intensely since they can be used in the Langmuir–Blodgett technology (sensors) and microelectronics (as structures with one-dimensional conductivity), as well as in optical, photonic and optoelectronic devices.[1–3] For example, the field-induced molecular reorientation in currently developed liquid-crystal displays takes several milliseconds.[4]

Liquid crystals based on porphyrins belong to discotic mesogens and are of considerable interest for optoelectronics and display and data storage devices.[5–8] Combination of a rigid macrocycle with flexible aliphatic substituents facilitates self-assembling of discotic molecules into a supramolecular ensemble owing to plane–plane interactions.[9] The size of aliphatic substituents plays a considerable role in the mesomorphic properties of such compounds and in the formation of certain mesophases.[7]



Scheme 1 Synthesis of di- and tetrasubstituted tetraphenylporphyrins.

Bulky aliphatic substituents at the porphyrin molecule can be located either at outer β-carbon atoms or at the *meso* positions of the macrocycle; in the latter case, they can be attached both directly to carbon atoms 5, 10, 15 and 20, and to the phenyl radicals located there. The latter variant allows porphyrins to be synthesised from more accessible compounds (pyrrole and substituted benzaldehydes) using efficient condensation techniques. In this work, we synthesised similar porphyrins with various long-chain substituents in order to study how the size and number of these substituents affect the liquid-crystal properties of porphyrins.

Currently, the main method for the synthesis of *meso*-alkoxy-substituted porphyrins involves the reaction of hydroxy-substituted tetraphenylporphyrin with alkyl bromides.[11,12] We developed another approach to synthesise lipoporphyrins, according to which the residues of higher fatty alcohols are incorporated into benzaldehyde derivatives at the first stage of the synthesis, which is followed by condensation with pyrrole.[13] Incorporation of aliphatic substituents into a benzaldehyde molecule increases its solubility in organic solvents, which results in more successful condensations of benzaldehydes with pyrrole, shortens and simplifies considerably the synthetic procedure, facilitates the purification of the target products, and after all, provides higher yields of lipoporphyrins. Porphyrins of two structural types were synthesised by monopyrrole condensation (Type 1) and using dipyrrolylmethanes (Type 2) in 36–44% yields (Scheme 1).[†] Zinc and cobalt complexes **4**, **5**, **9**–**11** were obtained in 90–95% yields[‡] from ligands **1**, **6** and **7**[§] using conventional techniques.[14]

The liquid crystal properties of porhyrins **1**–**11** were studied by optical polarisation microscopy. Figure 1 shows the phase transition temperatures of these porphyrins in the course of heating. It was shown that five compounds could form a mesophase.

The thermotropic mesomorphism in the series of 5,15-di-substituted tetraphenylporphyrin derivatives was observed for 5,15-di-(4-tetradecyloxyphenyl)-10,20-diphenylporphyrin **2** and 5,15-di-(4-hexadecyloxyphenyl)-10,20-diphenylporphyrin **3**. An increase in the substituent length in the series of compounds **1**–**3** decreases the melting point from 242.7° to 61.8 °C; 5,15-di-

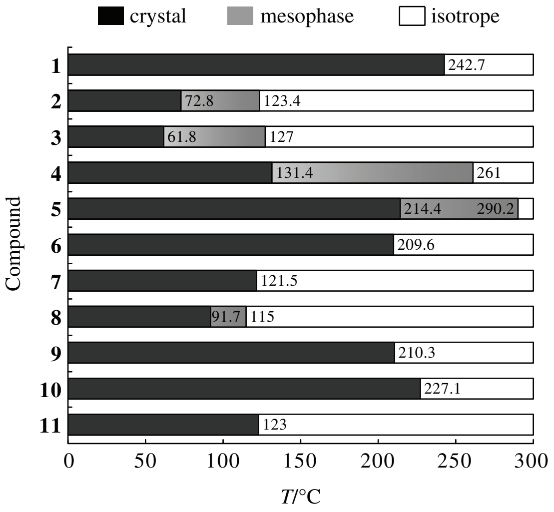


Figure 1 Optical polarization microscopy data (the temperatures of phase transitions in the course of heating).

(4-octyloxyphenyl)-10,20-diphenylporphyrin **1** is non-mesomorphic. For non-mesomorphic compounds, an increase in the substituent length decreases the temperature of the crystal–isotrope phase transition. In the homologous series of 5,10,15,20-tetra(alkoxyphenyl)porphyrins, a narrow mesophase temperature range of 91.7–115 °C is observed only for compound **8**, in which the length of the peripheral substituent is 16 carbon atoms.

Incorporation of coordinatively unsaturated metals (Zn^{2+} and Co^{2+}) modifies considerably the properties of nonmesomorphic ligand **1**: zinc complex **4** shows the broadest range of mesophase existence (129.6 °C), while the cobalt complex forms a mesophase in a high-temperature range (214.4–290.2 °C). Porphyrins **6**, **7** belonging to the first type do not show liquid-crystal properties if a metal is incorporated. Thus, given equal lengths of aliphatic substituents at the *meso*-position, liquid-

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[†] NMR spectra were recorded on a Bruker MSL-300 instrument with a working frequency of 300 MHz; measurements were performed on a δ scale using TMS as an internal reference and $CDCl_3$ as the solvent. Electronic spectra were recorded in dichloromethane using a Jasco UV-7800 spectrophotometer. Elemental analyses were carried out with a FLASH EA 112 Termo Finnigan C, H, N, S analyser.

Mesomorphic properties were studied by optical polarisation microscopy. Thermotropic mesomorphism was studied with a Leitz Laborlux 12 Pol optical thermopolarization microscope equipped with a Mettler FP 82 heating device.

General procedure for the synthesis of 5,15-disubstituted porphyrins **1**–**3**. Boron trifluoride etherate (0.15 equiv.) was added to a solution of dipyrrolylmethane (1 equiv.)[10] and benzaldehyde (1.4 equiv.) in chloroform at room temperature under argon. The reaction mixture was stirred for 1 h; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.9 equiv.) was added and the mixture was stirred for another 1 h at room temperature. The condensation products were separated by flash chromatography and the target product was separated by column chromatography using chloroform–hexane (4:1) for elution.

5,15-Bis(4-octyloxyphenyl)-10,20-diphenylporphyrin **1**. Obtained from *meso*-(4-octyloxyphenyl)dipyrrolylmethane (0.400 g, 1.1 mmol) and benzaldehyde (0.150 g, 1.4 mmol). Yield, 0.170 g (36%), R_f 0.72 ($CHCl_3$); mp 242.7 °C. UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 418.0 (674), 515.2 (35), 550.8 (18.8), 590 (11.1), 646.2 (8.75). ^1H NMR, δ: –2.73 (s, 2H, NH), 0.9 (t, 6H, Me), 1.3 [m, 20H, $(CH_2)_5$], 2.02 (m, 4H, OCH_2CH_2), 4.28 (t, 4H, OCH_2, *J* 7 Hz), 7.75 [m, 10H, 10.20-(ArH)], 8.22 [m, 8H, 5.15-(ArH)], 8.87 (m, 8H, pyrrole). MS, *m/z*: 871.61 [M^+ + 1]. Found (%): C, 82.94; H, 7.21; N, 6.42. Calc. for $C_{60}H_{62}N_4O_2$ (%): C, 82.72; H, 7.17; N, 6.43.

5,15-Bis(4-tetradecyloxyphenyl)-10,20-diphenylporphyrin **2**. Obtained from *meso*-(4-tetradecyloxyphenyl)dipyrrolylmethane (0.330 g, 0.76 mmol) and benzaldehyde (0.120 g, 1.14 mmol). Yield, 0.161 g (44%), R_f 0.68 ($CHCl_3$). UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 418.0 (616), 515.2 (28.3), 550.6 (15.8), 590.4 (9.1), 646.2 (7.47). ^1H NMR, δ: –2.72 (s, 2H, NH), 0.91 (t, 6H, Me), 1.31 [m, 44H, $(CH_2)_{11}$], 2.01 (m, 4H, OCH_2CH_2), 4.27 (t, 4H, OCH_2, *J* 7 Hz), 7.78 [m, 10H, 10.20-(ArH)], 8.23 [m, 8H, 5.15-(ArH)], 8.85 (m, 8H, pyrrole). MS, *m/z*: 1038.78 [M^+]. Found (%): C, 83.22; H, 8.41; N, 5.41. Calc. for $C_{72}H_{86}N_4O_2$ (%): C, 83.19; H, 8.34; N, 5.39.

5,15-Bis(4-hexadecyloxyphenyl)-10,20-diphenylporphyrin **3**. Obtained from *meso*-(4-hexadecyloxyphenyl)dipyrrolylmethane (0.430 g, 0.9 mmol) and benzaldehyde (0.130 g, 1.22 mmol). Yield, 0.189 g (38%), R_f 0.68 ($CHCl_3$). UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 418.0 (610), 515.2 (27.2), 550.3 (14.6), 590.6 (8.3), 646.2 (7.45). ^1H NMR, δ: –2.72 (s, 2H, NH), 0.93 (t, 6H, Me), 1.33 [m, 48H, $(CH_2)_{12}$], 1.61 [m, 4H, $O(CH_2)_2CH_2$], 2.03 (m, 4H, OCH_2CH_2), 4.25 (t, 4H, OCH_2, *J* 7 Hz), 7.75 [m, 10H, 10.20-(ArH)], 8.22 [m, 8H, 5.15-(ArH)], 8.85 (m, 8H, pyrrole). Found (%): C, 83.42; H, 8.71; N, 5.12. Calc. for $C_{76}H_{94}N_4O_2$ (%): C, 83.32; H, 8.65; N, 5.11.

[‡] *General procedure for the synthesis of porphyrin metal complexes* **4**, **5**, **9**–**11**. A metal acetate (6 equiv.) in methanol was added to a porphyrin (1 equiv.) in chloroform and the reaction mixture was stirred for 1 h. The reaction mixture was concentrated, the residue was dissolved in chloroform, inorganic salts were filtered off, and the product was crystallised from heptane.

5,15-Bis(4-octyloxyphenyl)-10,20-diphenylporphyrin zinc complex **4**. Obtained from porphyrin **1** (20 mg, 0.023 mmol) and zinc acetate (25 mg, 0.138 mmol). Yield, 19 mg (90%). UV [λ_{max}/nm (relative intensity)]: 423, 550.2, 590.4 (1:0.064:0.024).

5,15-Bis(4-octyloxyphenyl)-10,20-diphenylporphyrin cobalt complex **5**. Obtained from porphyrin **1** (11 mg, 0.0127 mmol) and cobalt acetate (20 mg, 0.0762 mmol). Yield, 10 mg (89%). UV [λ_{max}/nm (relative intensity)]: 414.4, 530 (1:0.078).

5,10,15,20-Tetra(4-octyloxyphenyl)porphyrin zinc complex **9**. Obtained from porphyrin **6** (25 mg, 0.133 mmol) and zinc acetate (30 mg). Yield, 21 mg (90%). UV [λ_{max}/nm (relative intensity)]: 423, 550, 590 (1:0.064:0.028).

5,10,15,20-Tetra(4-octyloxyphenyl)porphyrin cobalt complex **10**. Obtained from porphyrin **6** (20 mg, 0.13 mmol) and cobalt acetate (25 mg). Yield, 18 mg (90%). UV [λ_{max}/nm (relative intensity)]: 415, 530 (1:0.08).

5,10,15,20-Tetra(4-tetradecyloxyphenyl)porphyrin zinc complex **11**. Obtained from porphyrin **7** (20 mg, 0.125 mmol) and cobalt acetate (30 mg). Yield, 18 mg (92%). UV [λ_{max}/nm (relative intensity)]: 423, 549, 591 (1:0.061:0.02).

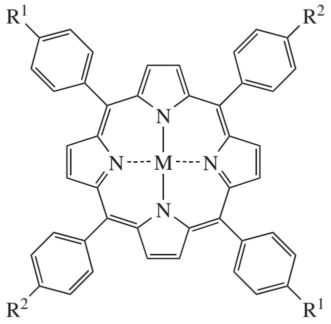
[§] *General procedure for the synthesis of tetrasubstituted porphyrins* **6**–**8**. Boron trifluoride etherate (0.1 equiv.) and a catalytic amount of anhydrous ethanol were added to a solution of benzaldehyde (1 equiv.) and pyrrole (1 equiv.) in dichloromethane at room temperature under argon. The reaction mixture was stirred for 1 h in an inert gas stream at room temperature; 2,3-dichloro-5,6-dicyano-1.4-benzoquinone (0.9 equiv.) was added and the mixture was stirred for another 1 h. The reaction products were separated by flash chromatography and eluted with chloroform. The target product was purified by column chromatography and eluted with chloroform. After that, it was crystallised from methanol.

5,10,15,20-Tetra(4-octyloxyphenyl)porphyrin **6**. Obtained from 4-octyloxybenzaldehyde (0.240 g, 1 mmol) and pyrrole (0.067 g, 1 mmol). Yield, 0.120 g (33%), R_f 0.9 ($CHCl_3$). UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 418 (390), 519 (22.4), 556.2 (14.7), 591 (7.0), 646.6 (5.7). ^1H NMR, δ: –3.36 (s, 2H, NH), 0.29 (t, 12H, Me), 1.02 [m, 40H, $(CH_2)_5$], 1.38 (m, 8H, OCH_2CH_2), 3.65 (t, 8H, OCH_2CH_2, *J* 7 Hz), 6.65–7.15 [m, 16H, *meso*-(ArH)], 8.25 (s, 8H, pyrrole). Found (%): C, 80.95; H, 8.40; N, 4.97. Calc. for $C_{76}H_{94}N_4O_4$ (%): C, 80.81; H, 8.24; N, 4.86.

5,10,15,20-Tetra(4-tetradecyloxyphenyl)porphyrin **7**. Obtained from 4-tetradecyloxybenzaldehyde (0.320 g, 1 mmol) and pyrrole (0.067 g, 1 mmol). Yield, 0.151 g (40%), R_f 0.9 ($CHCl_3$). UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 418.2 (524), 515.4 (24.9), 550.4 (16.3), 590.6 (9.12), 646 (5.18). ^1H NMR, δ: –3.36 (s, 2H, NH), 0.29 (t, 12H, Me), 1.04 [m, 88H, $(CH_2)_{11}$], 1.4 [m, 8H, $OCH_2CH_2(CH_2)_{11}Me$], 3.65 (t, 8H, OCH_2, *J* 7 Hz), 6.65–7.15 [m, 16H, *meso*-(ArH)], 8.25 (s, 8H, pyrrole). Found (%): C, 83.03; H, 9.67; N, 3.83. Calc. for $C_{100}H_{142}N_4O_4$ (%): C, 83.12; H, 9.64; N, 3.86.

5,10,15,20-Tetra(4-hexadecyloxyphenyl)porphyrin **8**. Obtained from 4-hexadecyloxybenzaldehyde (0.350 g, 1 mmol) and pyrrole (0.067 g, 1 mmol). Yield, 0.102 g (39%), R_f 0.9 ($CHCl_3$). UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 418.2 (623), 515.4 (21.9), 550.4 (15.3), 590.6 (9.1), 646 (7.8). ^1H NMR, δ: –3.2 (s, 2H, NH), 0.31 (t, 12H, Me), 1.12 [br. m, 104H, $(CH_2)_{13}$], 1.4 (m, 8H, $OCH_2CH_2CH_2$), 3.65 [t, 8H, $OCH_2(CH_2)_2$, *J* 7 Hz], 7.53 [d, 8H, 2.6-(ArH)], 8.22 [d, 8H, 2.4-(ArH)], 8.9 (s, 8H, pyrrole). Found (%): C, 82.28; H, 10.10; N, 3.55. Calc. for $C_{108}H_{158}N_4O_4$ (%): C, 82.12; H, 10.14; N, 3.66.

Table 1 Structures of the *meso*-alkoxyphenylporphyrins synthesised.



Compound	$\mathrm{R^1}$	$\mathrm{R^2}$	M
1	$\mathrm{O(CH_2)_7Me}$	H	2H
2	$\mathrm{O(CH_2)_{13}Me}$	H	2H
3	$\mathrm{O(CH_2)_{15}Me}$	H	2H
4	$\mathrm{O(CH_2)_7Me}$	H	Zn
5	$\mathrm{O(CH_2)_7Me}$	H	Co
6	$\mathrm{O(CH_2)_7Me}$	$\mathrm{O(CH_2)_7Me}$	2H
7	$\mathrm{O(CH_2)_{13}Me}$	$\mathrm{O(CH_2)_{13}Me}$	2H
8	$\mathrm{O(CH_2)_{15}Me}$	$\mathrm{O(CH_2)_{15}Me}$	2H
9	$\mathrm{O(CH_2)_7Me}$	$\mathrm{O(CH_2)_7Me}$	Zn
10	$\mathrm{O(CH_2)_7Me}$	$\mathrm{O(CH_2)_7Me}$	Co
11	$\mathrm{O(CH_2)_{13}Me}$	$\mathrm{O(CH_2)_{13}Me}$	Zn

crystal properties are more likely in the case of 5,15-disubstituted porphyrins and the corresponding metal complexes.

The mesophase in all of the compounds is characterised by a non-geometric grain structure presumably associated with a column-type packing [Figure 2(*a*)].

Many photonics applications demand materials capable of vitrification with preservation of the liquid-crystal order in a solid phase without crystallisation.[15] Thermotropic mesogens **2–5**, **8** form a vitrified state on cooling with preservation of the preceding mesophase packing [Figure 2(*b*)]. Various vitrifying mesogens may find use in optical information recording, nonlinear optics, tunneling filters for optical communication, compensators for optimizing the viewing angle of displays, solar batteries and light-emitting diodes.

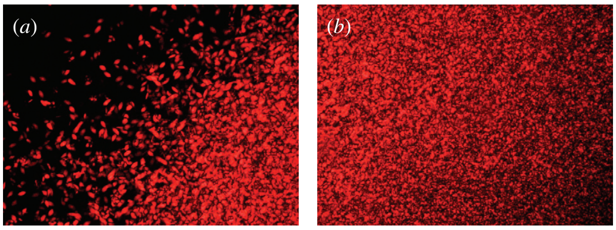


Figure 2 Micrographs of (*a*) the texture of the thermotropic mesophase of compound **3** in the course of heating, at 61.8 °C (crystal + isotrope); (*b*) the vitrified state of the texture of the thermotropic mesophase of compound **3** on cooling, at 27.1 °C. The Nicols were crossed, ×250.

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