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Synthesis and liquid-crystal properties of new amphiphilic long-chain derivatives of *meso*-arylporphyrins with terminal polar groups

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New amphiphilic alkoxyarylporphyrins with long-chain substituents bearing carboxy, methoxycarbonyl and hydroxy groups, and their metal complexes, were synthesized. Those of them having mesogenic properties were identified by optical polarisation microscopy, and their liquid-crystal properties were studied.

Synthesis of analogues of natural tetrapyrrole compounds and design of new functional structures based on these compounds by means of self-assembly and self-organization of molecules are currently a field of intense studies.[1,2] The amphiphilic structure of molecules is the determining factor in the self-assembly of supramolecular ensembles driven by noncovalent interactions.[1,3] Of particular interest in this respect are *meso*-arylporphyrins containing both hydrophobic substituents that favour surface immobilisation of molecules and give them mesogenic properties,[4] and polar groups that can be subjected to various chemical transformations and used as sites for binding with various ligands, including nanoparticles.[5] Polar hydroxy and carboxy groups in which hydrogen bonds act as the driving force are used most commonly for this purpose.[1,3,6] The liquid-crystal state is also considered as a method for the structural self-organisation of molecules,[1] and porphyrin liquid-crystal ensembles are promising compounds for optoelectronics and for creating data display and storage devices.[7–9]

Previously, we have synthesized amphiphilic cationic 5,10,15,20-tetra-*meso*-aryl-substituted porphyrins bearing long-chain substituents with terminal pyridinium groups.[10] These compounds and their metal complexes possessed thermotropic mesomorphism, whereas the length of the aliphatic spacer and the metal nature affected considerably their liquid-crystal properties.

Herein, we studied new structural analogues, namely, amphiphilic *meso*-aryl-substituted porphyrins with terminal carboxy, methoxycarbonyl and hydroxy groups, as well as their metal complexes (Scheme 1).

Porphyrins **2a**,**b** were synthesized from substituted benzaldehydes **1a**,**b** in 35–40% yields using reported techniques.[†,11,12] Alkaline hydrolysis in a two-phase aqueous–organic system quantitatively gave amphiphilic porphyrins **3a**,**b** with terminal carboxy groups. Reduction of terminal methoxycarbonyl groups in intermediates **2a**,**b** with lithium aluminium hydride afforded alcohol porphyrins **4a**,**b**.[‡] Complexes with zinc, cobalt and copper

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[†] For synthesis of compounds **1a**,**b**, see Online Supplementary Materials.

General procedure for the preparation of porphyrins **2a**,**b**. Pyrrole (100 mg, 1.42 mmol) and 4-(5-methoxycarbonylpentyloxy)benzaldehyde **1a** (0.38 g, 1.5 mmol) were dissolved in dichloromethane (50 ml). The mixture was bubbled with argon for 5 min under continuous stirring at room temperature, then boron trifluoride etherate (20 μl, 0.15 mmol) and anhydrous ethanol (20 μl) were added, and the mixture was stirred for 30 min at room temperature in a stream of argon. DDQ (300 mg, 1.35 mmol) was then added, and stirring was continued for another 1 h at room temperature. The reaction mixture was concentrated *in vacuo*. The oligomeric products were separated by flash chromatography on G60 silica gel on eluting with dichloromethane. The target product was finally purified by column chromatography on G60 silica gel on eluting with dichloromethane–hexane (6:1).

5,10,15,20-Tetrakis[4-(5-methoxycarbonylpentyloxy)phenyl]porphyrin **2a**: yield 0.14 g (31%). R_f 0.9 (CH_2Cl_2). UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 419.5 (365), 515.8 (14.3), 554.8 (6.3), 589.6 (4.89), 649.2 (3). ^{1}H NMR, δ: –2.81 (s, 2H, NH), 1.63 [m, 8H, $O(CH_2)_3$], 1.78 [m, 8H, $O(CH_2)_4COOMe$], 1.95 (m, 8H, OCH_2CH_2), 2.37 (t, 8H, CH_2COOMe, *J* 7 Hz), 2.47 (t, 8H, OCH_2, *J* 7 Hz), 3.67 (s, 12H, COOMe), 7.21 (d, 4H, H_{Ar}, *J* 7 Hz), 8.18 (d, 4H, H_{Ar}, *J* 7 Hz), 8.82 (s, 8H, pyrrole). MS, *m/z*: 1193 [$M^+ + 1$].

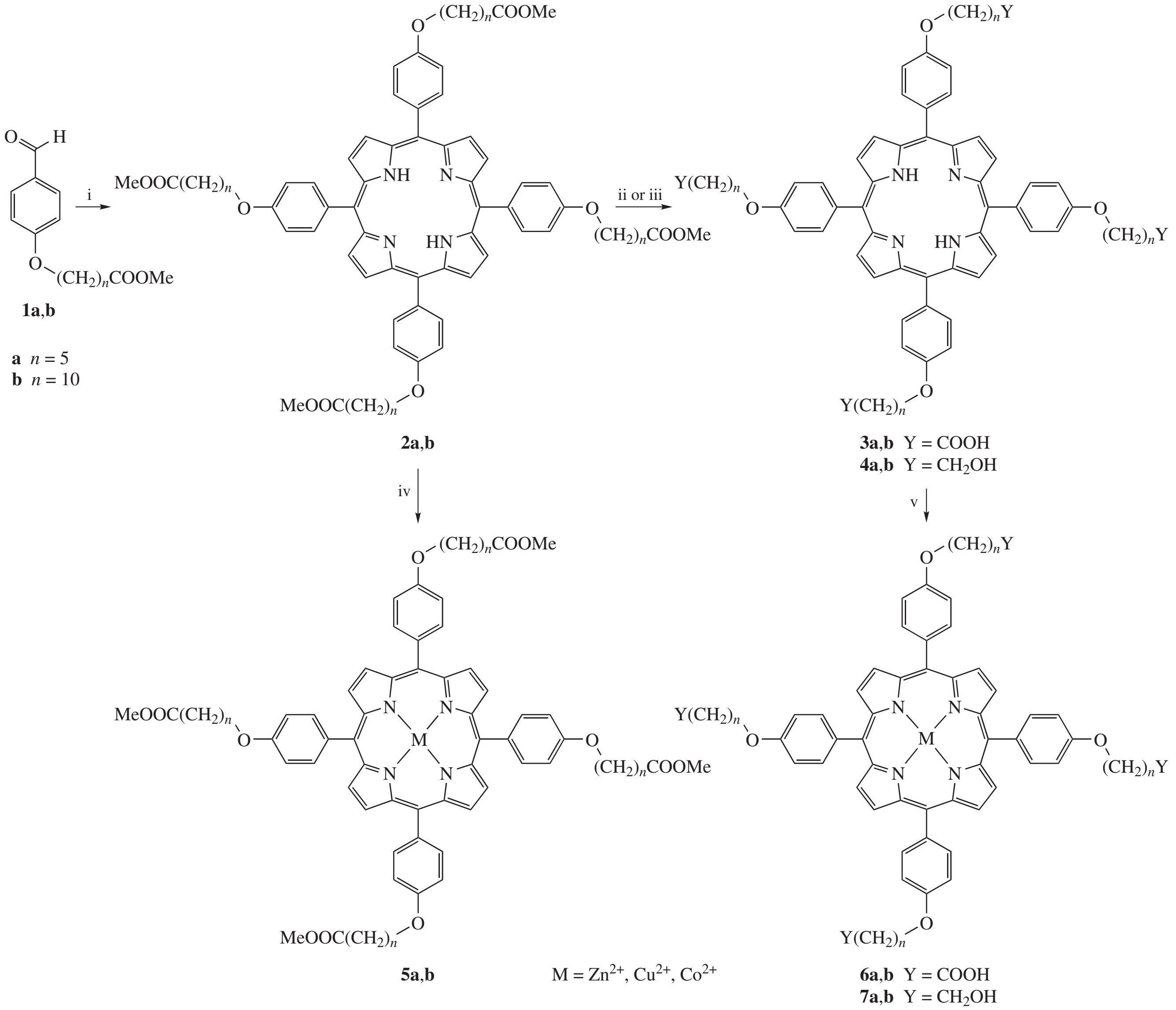
5,10,15,20-Tetrakis[4-(10-methoxycarbonyldecyloxy)phenyl]porphyrin **2b**: yield 0.19 g (34%). R_f 0.9 (CH_2Cl_2). UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 421.5 (360), 518.6 (15), 556.2 (6.2), 592 (4.49), 650.4 (3.1). ^{1}H NMR, δ: –2.72 (s, 2H, NH), 1.31 [br. m, 40H, $(CH_2)_5$], 1.60 [m, 8H, $O(CH_2)_8$], 1.93 [m, 8H, $(CH_2)_7COOMe$], 2.01 [m, 8H, $O(CH_2)_8$], 2.75 (t, 8H, CH_2COOMe, *J* 7 Hz), 3.91 (s, 12H, COOMe), 4.27 [t, 8H, $O(CH_2)_8$, *J* 7 Hz], 7.46 (d, 8H, H_{Ar}, *J* 2.6 Hz), 8.22 (d, 8H, H_{Ar}, *J* 3.5 Hz), 8.9 (s, 8H, pyrrole). MS, *m/z*: 1473 [$M^+ + 1$].

[‡] *General procedure for the preparation of porphyrins* **3a**,**b**. Aqueous sodium hydroxide (50%, 7 ml) was added to a solution of ester porphyrin **2a**,**b** (90 mg) in THF (10 ml). The reaction mixture was stirred for 16 h at 60 °C, acidified with conc. HCl until the product was completely transferred to the organic phase, and washed with water. The organic phase was dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was recrystallised from diethyl ether. R_f 0.2 (CH_2Cl_2–MeOH, 9:1).

5,10,15,20-Tetrakis[4-(5-carboxypentyloxy)phenyl]porphyrin **3a**: yield 75 mg (87%). ^{1}H NMR, δ: –2.81 (s, 2H, NH), 1.61 [m, 8H, $O(CH_2)_3$], 1.76 [m, 8H, $O(CH_2)_4COOH$, *J* 7 Hz], 1.95 (m, 8H, OCH_2CH_2, *J* 7 Hz), 2.39 [t, 8H, $O(CH_2)_4COOMe$], 4.16 (t, 8H, OCH_2, *J* 7 Hz), 7.18 (d, 8H, H_{Ar}, *J* 7 Hz), 8.04 (d, 8H, H_{Ar}, *J* 7 Hz), 8.8 (s, 8H, pyrrole). UV [λ_{max}/nm, ($\varepsilon\times10^{-3}$)]: 420 (345), 517 (10.2), 552 (4.80), 592 (3.96), 649 (2.3). MS, *m/z*: 987 [$M^+ + 1$].

5,10,15,20-Tetrakis[4-(6-hydroxyhexyloxy)phenyl]porphyrin **4a** was obtained by reduction of compound **2a** (65 mg, 0.31 mmol) with $LiAlH_4$ (25 mg, 0.66 mmol) in THF. The mixture was stirred for 20 min, then water (10 ml) was added. The mixture was extracted with CH_2Cl_2, filtered, concentrated and crystallised from diethyl ether. Yield, 60 mg (96%). R_f 0.14 (CH_2Cl_2–MeOH, 9:1). UV [λ_{max}/nm ($\varepsilon\times10^{-3}$)]: 418.2 (455.8), 519 (14.4), 556 (7.30), 591 (4.52), 646 (3.79). ^{1}H NMR, δ: –2.81 (s, 2H, NH), 8.68–8.51 (s, 8H, pyrrole), 7.86–7.69 (d, 8H, H_{Ar}), 6.98–6.86 (d, 8H, H_{Ar}), 3.88 (t, 8H, CH_2OH, *J* 6.4 Hz), 3.41 (t, 8H, OCH_2, *J* 6.6 Hz), 1.69 (m, 8H, $C\mathit{H}_2CH_2OH$, *J* 6.2 Hz), 1.53–1.18 [m, 24H, $HOCH_2CH_2(C\mathit{H}_2)_3$]. MS, *m/z*: 1078.6 [$M^+$].

For characteristics of compounds **3b** (yield, 88%) and **4b** (yield, 83%), see Online Supplementary Materials.



Scheme 1 Synthesis of porphyrins **2**–**7**. *Reagents and conditions*: i, pyrrole, $Et_2O \cdot BF_3$, CH_2Cl_2, DDQ; ii, 50% NaOH, heating; iii, $LiAlH_4$, THF; iv, $M(OAc)_2$, CH_2Cl_2, MeOH; v, $M(OAc)_2$, DMF, heating.

were obtained from free ligands **2**–**4** in 75–90% yields routinely.[§,13] The structures of the compounds were confirmed by TLC, UV, ^1H NMR spectroscopy and liquid chromatography–mass spectrometry (LCMS). The obtained products are crystalline compounds soluble in organic solvents; porphyrins containing carboxy groups colourize aqueous alkaline solutions.

The liquid-crystal properties of compounds **2**–**7** were studied by optical polarization microscopy in two modes: heating to 300 °C (Figure 1) and cooling to room temperature. In comparison with the previously studied cationic analogues,[10] only a limited number of compounds that we obtained had mesomorphic properties, namely five compounds: Co-**5a**, Zn-**5a** and Co-**7b** were enantiotropic, whereas **3b** and Zn-**5b** were monotropic (Figure 1).

Note that on cooling, all the compounds formed a glassy state with preservation of the mesophase texture. A study by the method of contact agents with organic solvents showed that mesogenic

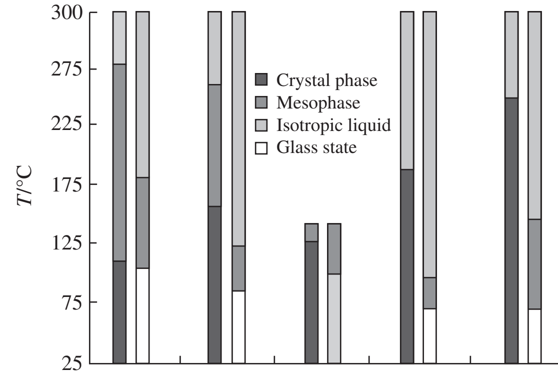


Figure 1 Optical polarisation microscopy results: phase transition temperatures of mesogenic compounds in the course of heating (left columns) and cooling (right columns). Observation limit for Co-**7b** is 139 °C.

[§] *General procedure for the synthesis of porphyrin metal complexes* **5a**,**b**. Zinc, cobalt or copper acetate (10 equiv.) in methanol was added to porphyrin **2a** or **2b** (1 equiv.) in methanol and the mixture was stirred for 3 h. The reaction course was monitored by UV spectroscopy. The reaction mixture was concentrated *in vacuo*; the residue was dissolved in CH_2Cl_2, filtered and crystallised from diethyl ether.

General procedure for the preparation of porphyrin metal complexes **6** *and* **7**. A metal acetate (10 equiv.) was added to porphyrin **3** or **4** (1 equiv.) in DMF and the mixture was refluxed for 6 h with stirring. The reaction completion was monitored by UV spectroscopy. The reaction mixture was concentrated; the residue was dissolved in CH_2Cl_2, filtered and crystallised from diethyl ether. The yields were 60–95%.

compounds Co-**5a** and Co-**7b** manifest liotropic mesomorphism; furthermore, non-mesogenic compounds **2b**, Co-**5b** and Zn-**7b** manifested liotropic mesomorphism in binary systems with chloroform, DMF and DMSO. Along with induction of mesomorphism due to solvents, mesomorphism was also induced in charge transfer complexes of compounds **2a**,**b** with an electron acceptor, 2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid [(–)-TAPA], as well as in the complex of compound Cu-**5b** with an electron acceptor, trinitrofluorenone (TNF).

Similarly to lipophilic porphyrin derivatives,[14] incorporation of coordination-unsaturated metals (Zn or Co) changed considerably the properties of non-mesomorphic free ligands **2a**,**b**, **4b**. Metal complexes of porphyrins with terminal methoxycarbonyl groups (Zn-**5a**, Co-**5a**, Zn-**5b**) were found to be most liable to manifest liquid-crystal properties. Of free bases, mesomorphism was observed for 5,10,15,20-tetrakis[4-(10-carboxydecyloxyphenyl)]porphyrin **3b**, whereas its lipophilic analogues manifest liquid-crystal properties at a greater length of polymethylene chains.[13] Its structural analogue, porphyrin **3a** with C_5 spacer, does not possess liquid-crystal properties; in this case, apparently, hydrogen bonding prevails over hydrophobic 'stacking' interaction in the formation of ordered structures. Metal complexes of porphyrin **3b** do not possess mesogenic properties, perhaps due to the chelating properties of carboxy groups.[15] Free ligands **4a**,**b** that have terminal hydroxy groups did not show mesomorphism, either, but the metal complex with the cobalt(II) ion Co-**7b** with C_{10} chains manifested enantiotropic liquid-crystal properties on heating. Due to its decomposition on heating to 160 °C (isotrope region), heating and observation of the mesophase were limited to 139 °C.

In summary, 24 new amphiphilic porphyrins with terminal polar groups have been obtained in this work. Five of them manifest thermotropic mesomorphism, like their cationic analogues.[10] The porphyrins containing 10 carbon atoms in the aliphatic chain, both free ligands and their metal complexes, can spontaneously form liquid-crystal phases, whereas their structural analogues with shorter spacers manifest mesomorphic properties only in metal complexes. All mesogenic compounds of this series can undergo glass transition while maintaining the texture of the parent mesophase. Manifestation of liquid-crystal properties is affected by the length of the aliphatic moiety, the nature of terminal polar groups, and the presence of a complex-forming metal. We succeeded in inducing mesomorphism in five non-mesogenic compounds (**2a**, **2b**, Cu-**5b**, Co-**5b** and Zn-**7b**) by means of creating charge transfer complexes, as well as in systems with organic solvents.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.09.018.

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