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Synthesis and mesomorphism of cationic derivatives of *meso*-aryl-substituted porphyrins and their metal complexes

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The water-soluble derivatives of 5,10,15,20-tetra-*meso*-aryl-substituted porphyrins and their metal complexes have been synthesised, and the liquid crystal properties of mesogenic compounds have been studied.

Amphiphilic porphyrin derivatives capable of forming ordered aggregates are of considerable current interest.^{1–3} The reason is that porphyrins find use in studies on super-fast photoprocesses in supramolecular systems simulating fundamental natural processes, as well as in the creation of photoconductive organic materials. Mesogenic tetrapyrrole compounds as self-organizing supramolecular structures are of particular interest for opto-electronics and for devices intended for displaying and storing information.^{4–7} Liquid crystals based on porphyrins belong to the class of discotic mesogens that can form three main types of thermotropic mesophases: columnar (Col), discotic nematic (N_D) and lamellar (L).⁸

The functionalisation of *meso*-aryl-substituted porphyrins by long chain aliphatic substituents makes it possible to successfully perform goal-oriented searches for mesomorphic lipophilic derivatives.^{5,7,9–12} The incorporation of metals generally changes mesomorphic properties.^{13–16} It has been shown that amphiphilic porphyrin derivatives containing sulfonic groups possess lyotropic mesomorphism in solutions;^{17,18} thermotropic mesomorphism of amphiphilic porphyrins was not reported.

The aim of this work was to synthesise amphiphilic cationic *meso*-aryl-substituted porphyrins and their metal complexes and to study their mesomorphic properties. We synthesised cationic porphyrins **5** and **6** and their complexes with Zn, Cu, Ni and Co metals **15–22** (Scheme 1). Incorporation of hydrophilic functional groups allowed us to obtain amphiphilic compounds soluble in water.

In order to attain thermotropic mesomorphism, we modified the structure of porphyrins by incorporating spacer hydrocarbon bridges $(CH_2)_n$ (n = 5 or 10) that separate cationic pyridinium groups from the porphyrin macrocycle. Obviously, positively charged *meso*-substituents can affect the charge distribution (electron density) in the porphyrin ring *via* induction effects only. Therefore, as such substituents become farther from the macrocycle, the porphyrin basicity increases, which weakens the electrostatic repulsion between porphyrin macrocycles when ordered structures are formed.

Porphyrins **3** and **4** were synthesised by monopyrrole condensation according to Lindsey¹⁹ followed by modification of substituents at the aromatic rings.[†] *meso*-Tetrakis[4-(6-bromohexanoyloxyphenyl)]- and *meso*-tetrakis[4-(11-bromoundecanoyloxyphenyl)]porphyrins obtained from pyrrole and the respective substituted 4-hydroxybenzaldehydes in 35–40% yields according to the procedure developed for synthesising lipophilic porphyrins²⁰ were used as the precursors of target porphyrins. Zinc, cobalt, nickel and copper metal complexes^{7–14} were obtained from ligands **3** and **4** using standard techniques.²¹ Cationic porphyrins **5**, **6** and **15–22** were obtained by the quaternisation of pyridine with bromo-substituted precursors in 93–95% yields. The authenticity and structures of the compounds were confirmed by elemental analyses, TLC, UV, ¹H NMR spectroscopy and mass spectrometry.[‡]

The liquid crystal properties of compounds 5, 6 and 15–22 were studied by optical polarisation microscopy in two modes:



Scheme 1 Reagents and conditions: i, pyrrole, BF₃:Et₂O, CHCl₃, DDQ; ii, pyridine, reflux; iii, acetate of the corresponding metal, CHCl₃, MeOH.

heating to 300 $^{\circ}\text{C}$ (Figure 1) and cooling to room temperature (Figure 2).

Ligands **5** and **6** and their metal complexes **15–22** possess thermotropic mesomorphism. Porphyrins with cationic pyridinium groups, both with 5 carbon atoms in the spacer **5** and with 10 carbon atoms **6**, were found to form liquid-crystal phases. Porphyrin metal complexes with cobalt **21**, **22**, copper **17**, **18** and nickel **19**, **20** form a mesophase either upon heating or cooling (enantiotropic mesomorphism), whereas ligand **5** forms a mesophase only upon cooling (monotropic mesomorphism). A common feature of all of the compounds is that the phase

[†] The NMR spectra were recorded on a Bruker MSL-300 instrument (Germany) at a working frequency of 300 MHz; measurements were carried out in the δ scale using TMS as the internal reference. Electronic spectra were recorded using a Jasko UV-7800 spectro-photometer (Japan) in dichloromethane. Elemental analyses were performed on a FLASH EA 112 C, H, N, S analyser (Termo Finnigan, Italy).

Mesomorphic properties were studied by optical polarisation microscopy using a Leitz Laborlux 12 Pol optical thermopolarisation microscope equipped with a Mettler FP 82 heating device for thermotropic mesomorphism, whereas lyotropic mesomorphism was studied in water, toluene, benzene, chloroform, DMF and other solvents.

General procedure for the preparation of substituted benzaldehydes 1, 2. A solution (20 ml) of 6-bromohexanoyl chloride (2.52 g, 11.8 mmol) or 11-bromoundecanoyl chloride (3.35 g, 11.8 mmol) in dichloromethane (10 ml) was added dropwise for 30 min to a solution (25 ml) of *p*-hydroxybenzaldehyde (1.20 g, 9.83 mmol) and DMAP (0.90 g, 7.37 mmol) in dichloromethane. The components were stirred for 24 h at room temperature. The excess solvent was removed *in vacuo*. To purify the compound, the reaction mixture was treated by column chromatography on G 60 silica gel. Elution was carried out using chloroform–hexane (4:1).

4-(6-Bromohexanoyloxy)benzaldehyde 1: yield 2.35 g (80%), R_f 0.3, (chloroform–hexane, 7:3). ¹H NMR (CDCl₃) δ : 1.59 [m, 2H, OCO(CH₂)₂-CH₂(CH₂)₂Br], 1.81 (m, 2H, OCOCH₂CH₂), 1.92 (m, 2H, CH₂CH₂Br), 2.62 (t, 2H, OCOCH₂), 3.44 (t, 2H, CH₂CH₂Br), 7.26 (d, 2H, 2,6-H_{Ar}), 7.92 (d, 2H, 3,5-H_{Ar}), 10.00 (s, H, CHO). IR (ν/cm^{-1}): 2926, 2848 [(CH₂)₅], 1676 (C=O), 1467 (Ar), 1160, 1138 (C–O), 642, 550 (C–Br).

4-(11-Bromoundecanoyloxy)benzaldehyde **2**: yield 3.41 g (94%), $R_{\rm f}$ 0.4 (chloroform–hexane, 7:3). ¹H NMR (CDCl₃) δ : 1.32 [br. m, 12H, OCO-(CH₂)₂(CH₂)₆(CH₂)₂Br], 1.75 (m, 2H, OCOCH₂CH₂), 1.83 (m, 2H, CH₂CH₂Br), 2.58 (t, 2H, OCOCH₂), 3.38 (t, 2H, CH₂CH₂Br), 7.28 (d, 2H, 2,6-H_{Ar}), 7.92 (d, 2H, 3,5-H_{Ar}), 9.99 (s, H, CHO). IR (ν /cm⁻¹): 2926, 2848 [(CH₂)₅], 1676 (C=O), 1467 (Ar), 1160, 1138 (C–O), 642, 550 (C–Br).

General procedure for the preparation of porphyrins **3**, **4**. Pyrrole (100 mg, 1.42 mmol) and 4-(6-bromohexanoyloxy)benzaldehyde **1** (448 mg, 1.5 mmol) or 4-(11-bromoundecanoyloxy)benzaldehyde **2** (554 mg, 1.5 mmol) were dissolved in chloroform (50 ml). The reaction mixture was saturated with an inert gas under continuous stirring at room temperature for 5 min, and then BF₃·Et₂O (20 μ l, 0.15 mmol) and anhydrous ethanol (20 μ l) were added. The reaction mixture was stirred for 2 h at room temperature in a stream of an inert gas. After that, the inert gas stream was discontinued, DDQ (300 mg, 1.35 mmol) was added and the mixture was stirred for one more hour at room temperature. The reaction mixture was concentrated *in vacuo*. Oligomeric products were separated by flash chromatography on G 60 silica gel and eluted with chloroform. The target product was purified by column chromatography on G 60 silica gel and eluted with chloroform-hexane (4:1).

5,10,15,20-Tetra[4-(6-bromohexanoyl)oxyphenyl]porphyrin **3**: yield 148 mg (31%), mp 184 °C, $R_{\rm f}$ 0.8 (CHCl₃). Electronic spectrum ($\lambda_{\rm max}$ /nm): 419.8, 514.4, 549.8, 589, 645.6 (peak ratio: 63.4, 1.7, 1.4, 1.0, 0.9, respectively). ¹H NMR (CDCl₃) δ : 1.62 [m, 8H, OCO(CH₂)₂CH₂-(CH₂)₂Br], 1.77 (m, 8H, OCOCH₂CH₂), 1.94 (m, 8H, CH₂CH₂Br), 2.38 (t, 8H, OCOCH₂), 4.17 (t, 8H, CH₂CH₂Br), 7.18 (d, 8H, 2,6-H_{Ar}), 8.03 (d, 8H, 3,5-H_{Ar}), 8.81 (br. s, 8H, pyrrole).

5,10,15,20-Tetra[4-(11-bromoundecanoyl)oxyphenyl]porphyrin **4**: yield 208 mg (33%), mp 75 °C, R_f 0.8 (CHCl₃). Electronic spectrum (λ_{max} /nm): 418, 514.6, 549.8, 590.2, 645.8 (peak ratio: 68.4, 2.4, 1.7, 1.0, 0.86, respectively). ¹H NMR (CDCl₃) δ : 1.38 [m, 48 H, OCO(CH₂)₂(CH₂)₆-(CH₂)₂Br], 1.89 (m, 8H, OCOCH₂CH₂), 1.90 (m, 8H, CH₂CH₂Br), 2.76 (t, 8H, OCOCH₂), 3.43 (t, 8H, CH₂CH₂Br), 7.52 (d, 8H, 2,6-H_{Ar}), 8.22 (d, 8H, 3,5-H_{Ar}), 8.88 (s, 8H, pyrrole).



Figure 1 Results of optical polarisation microscopy: phase transition temperatures in the case of heating.



Figure 2 Results of optical polarisation microscopy: phase transition temperatures in the case of cooling.

[‡] *General procedure for the preparation of porphyrins* **5**, **6**. A starting porphyrin (**3** or **4**) was dissolved in pyridine and refluxed for 3 h. The reaction product was isolated by recrystallisation from diethyl ether. Yields 93–97%.

5,10,15,20-Tetra[4-(6-pyridylhexanoyl)oxyphenyl]porphyrin tetrabromide 5. Electronic spectrum (λ_{max} /nm): 415, 525, 580, 600, 640 (peak ratio: 51, 2.8, 1.45, 1.0, 0.5, respectively). ¹H NMR ([²H₆]DMSO) δ : 1.53 [br. m, 8H, OCO(CH₂)₂CH₂(CH₂)₂Py], 1.86 (m, 8H, OCOCH₂CH₂), 2.10 (m, 8H, CH₂CH₂Py), 2.82 (t, 8H, OCOCH₂), 4.72 (m, 8H, CH₂CH₂Py), 7.58 (d, 8H, 2,6-H_{Ar}), 8.23 (t, 8H, 3,5-Py), 8.28 (d, 8H, 3,5-H_{Ar}), 8.66 (t, 4H, 4-Py), 8.88 (br. s, 8H, pyrrole), 9.22 (d, 8H, 2,6-Py).

5,10,15,20-Tetra[4-(11-pyridylundecanoyl)oxyphenyl]porphyrin tetrabromide **6**. Electronic spectrum (λ_{max} /nm): 413, 512, 545, 589, 642 (peak ratio: 72.9, 3.2, 1.6, 1.0, 0.7, respectively). ¹H NMR (CD₃OD) δ : 1.26 [br. m, 48H, OCO(CH₂)₂(CH₂)₆(CH₂)₂Py], 1.72 (m, 8H, OCOCH₂CH₂), 1.93 (m, 8H, CH₂CH₂Py), 2.61 (t, 8H, OCOCH₂), 4.53 (m, 8H, CH₂CH₂Py), 7.21 (d, 8H, 2,6-H_{Ar}), 7.88 (d, 8H, 3,5-H_{Ar}), 8.01 (t, 8H, 3,5-Py), 8.48 (t, 4H, 4-Py), 8.69 (br. s, 8H, pyrrole), 8.91 (d, 8H, 2,6-Py).

General procedure for the preparation of metal complexes of cationic porphyrins 15–22. A metal acetate (chloride) (10 equiv.) in methanol was added to porphyrin 3 or 4 (1 equiv.) in methanol and the mixture was stirred for 3 h. The reaction completion was determined using spectral data. The reaction mixture was concentrated; the residue was dissolved in chloroform, filtered from inorganic salts and crystallised from diethyl ether to give compounds 7–14. Metal complexes 7–14 were dissolved in an excess of pyridine and refluxed for 3 h. The reaction completion was determined using TLC data in chloroform–methanol (1:1). The product was isolated from Et₂O. The yields of complexes 15–22 are 60–95%.

transition temperature $(T_{\rm pt})$ is lower in the cooling mode (mesophase–crystal transition temperature) than in the heating mode (crystal–mesophase transition temperature). Insignificant changes in the electron shell of the complex-forming metal result in considerable changes in the liquid crystal properties of these compounds.

Incorporation of a metal decreases the thermal stability of the crystal phase on heating; furthermore, the fewer electrons the metal has on the outer *d*-electron level, the lower the crystal-liquid crystal transition temperature. Moreover, the difference between the mesomorphic properties of the same metal complexes with 5 and 10 spacer methylene units manifests itself more strongly as the number of electrons on the outer *d*-electron level of the metal decreases.

On cooling, ligands 5 and 6 and their metal complexes with zinc (15, 16) and copper (17) undergo vitrification, which maintains the texture of the preceding liquid-crystal mesophase. Such compounds show promise for the development of materials for contemporary photonics.¹⁷

Compounds 5, 6, 16, 18, 21 and 22 show lyotropic mesomorphism and form a mesophase in binary mixtures with water and organic solvents, such as benzene, toluene, DMF and $CHCl_3$ at room temperature.

Thus, our study of the liquid crystal properties of cationic amphiphilic derivatives of 5,10,15,20-tetra-*meso*-aryl-substituted porphyrins and their metal complexes allowed us to find out that these compounds possess thermotropic mesomorphism that is considerably affected by the metal nature and the size of the aliphatic spacer.

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