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Synthesis and axial ligation behaviour of sterically hindered Zn(II)–porphyrin liquid crystals

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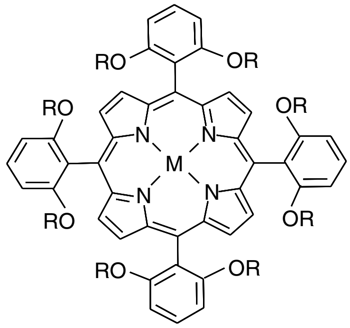
Abstract—A new class of low melting liquid crystalline octaalkyloxyporphyrins have been synthesised. Their Zn(II)-complexes display an interesting ligation behaviour towards amines (of varying shapes and sizes), ascribed to the steric hindrance or hydrophobic pockets on both the faces of the porphryin as evidenced from the crystal structure of Zn(II)–octabutyloxyporphyrin.

The synthesis of functionalised porphyrins is of growing interest for their use as model compounds.[1] Such substituted porphyrins have also been employed in various materials applications.[2] Notably, sterically hindered metalloporphyrins were used as model compounds of heme proteins[1,3] including the shape-selective oxidation of organic substrates by cytochrome P_{450}.[4] *meso*-Tetraarylporphyrins are widely used due to their synthetic versatility, easy functionalisation, large extended π-system, high thermal stability and diverse coordination chemistry. There are several reports available on the synthesis and properties of sterically unhindered liquid crystalline porphyrins.[5] The synthesis and properties of sterically hindered liquid crystalline porphyrins largely remained unexamined. In an effort to determine the role of the shape of the mesogen on the liquid crystalline properties of the porphyrin mesogen, we have examined a new family of sterically hindered porphyrins (Scheme 1). Their Zn(II)-complexes show an interesting shape-selective ligation behaviour with nitrogenous bases of varying shapes and sizes.



MT(2',6'-OC$_n$P)P
M = 2H, Zn(II), Cu(II); R = C_nH_{2n+1}
n = 4,8,12,16,20.

Scheme 1. Molecular structures of the octaalkyloxyporphyrins.

Sterically hindered porphyrins were synthesised using 5,10,15,20-tetrakis(2′,6′-dihydroxyphenyl)porphyrin, **H_2T(2′,6′-DHP)P**[6] as the precursor. Alkylation with *n*-bromoalkanes in dimethylformamide in the presence of anhydrous K_2CO_3 and 18-crown-6 at 85 °C under nitrogen atmosphere over a period of 48 h produced very good yields (80–95%) of **H_2T(2′,6′-OC$_n$P)P** ($n = 4, 8, 12, 16$ and 20) derivatives (Scheme 1). Their Zn(II)-complexes were prepared by conventional metallation procedures[7] in excellent yields. All the synthesised sterically hindered porphyrins were characterised by UV–visible, ^{1}H NMR and mass spectral methods.[8]

To determine the liquid crystalline behaviour of the octaalkyloxyporphyrins, the chain length of the alkyloxy groups were varied from C_4 to C_{20}. The **MT(2′,6′-OC$_n$P)-Ps** ($n = 4, 8$) derivatives are non-mesogenic. Representative differential scanning calorimetric thermograms of octaalkyloxyphenylporphyrins are shown in Figure 1a. The temperature ranges of these mesogens are from room temperature to high temperatures (<100 °C)

Keywords: Porphyrins; Sterically hindered porphyrins; Liquid crystals; Crystal structure; Axial ligation; Porphyrin mesogens.

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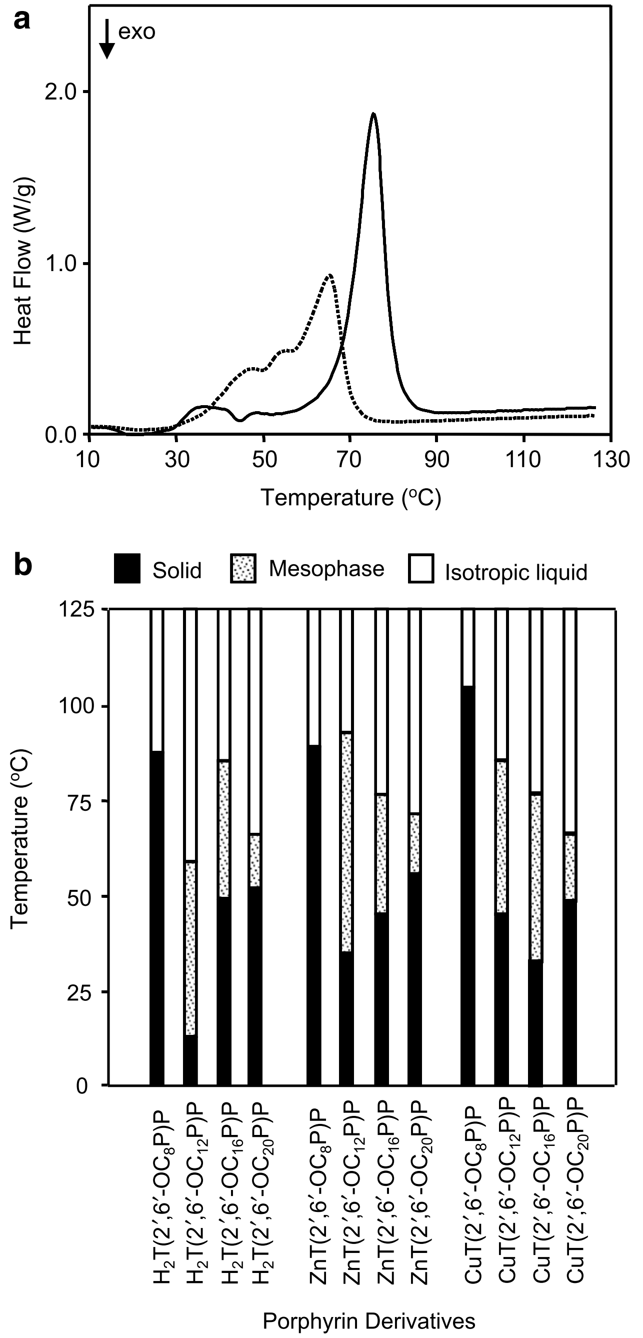

Figure 1. (a) Differential scanning calorimetric (DSC) thermograms (heating curves) of **ZnT(2′,6′-OC$_{16}$P)P** (heavy line) and **CuT(2′,6′-OC$_{20}$P)P** (dotted line). (b) DSC data of sterically hindered porphyrin liquid crystals. The heating rate was maintanied at 10 °C/min.

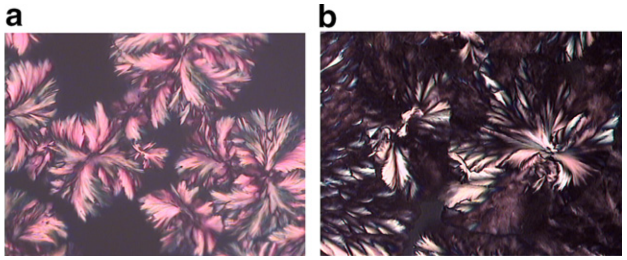

Figure 2. Optical microscopic images of (a) **CuT(2′,6′-OC$_{16}$P)P** and (b) **H$_2$T(2′,6′-OC$_{20}$P)P** viewed between cross polarisers. The domains (40–100 μm size) were obtained upon annealing the sample from the isotropic phase.

(Fig. 1b). The differential scanning calorimetric data (Fig. 1b) and birefringes from the optical microscopic images (Fig. 2) indicates the existence of mesophases in these sterically hindered porphyrin derivatives. Interestingly, with the increase in chain length, the mesophase is narrower and shifted to higher temperatures. The mesophase range of these porphyrins are lowered from the lower alkyl chain to higher ones and the trend is comparable to reported literature for less sterically hindered 3,5-disubstituted alkoxycarbonylporphyrins.[9] Interestingly, the enthalpies of melting for **H$_2$T(2′,6′-OC$_n$P)P** ($n = 12, 16, 20$) are decreased by four to sevenfold relative to those reported for *meta*-alkoxycarbonylporphyrins.[9] A similar trend in clearing temperatures was observed for **H$_2$T(2′,6′-OC$_n$P)Ps** ($n = 12, 16, 20$) relative to octaesterporphyrins. **H$_2$T(2′,6′-OC$_n$P)Ps** ($n = 12, 16, 20$) show melting points which are substantially lower compared to those of the α,β-isomers of 5,15-di(2′,4′-alkoxyphenyl) porphyrins.[10] Adding alkyloxy chains at the *ortho*-phenyl positions of H$_2$TPP could prevent π–π interactions and induce weak van der Waals/hydrophobic interactions between the porphyrins leading to lower melting[10] and lower clearing points (mesophase to isotropic liquid temperatures). The observed enthalpy data seems to suggest the decreased π–π interactions in **MT(2′,6′-OC$_n$P)Ps** ($n = 12, 16, 20$) derivatives. The crystal structure discussed later indicates that the changes of shape of the mesogen influence the intermolecular interactions in the solid state and hence the mesophase structure. Further characterisation of the mesophases of these porphyrin mesogens is in progress.

In an effort to probe the size and shape selectivity of the Zn(II)-centres of Zn(II)–octaalkyloxyporphyrins, axial ligation studies with various Lewis bases of different shapes and sizes (alkylamines) were carried out in toluene at 298 K. Zn(II)–porphyrins were chosen since they exhibit simple five-coordination behaviour in solution. The equilibrium constant, K_{eq}[11] and stoichiometry of the binding of Lewis bases to Zn(II)–porphyrins were evaluated using literature procedures.[12] In all cases, the stoichiometry of the binding of the Zn(II)–porphyrin with the Lewis bases was found to be 1:1. For comparison, the ligation of bases with ZnTPP and Zn(2′,6′-DMP)P porphyrins were also performed under similar conditions. The observed K_{eq} of ZnTPP with dodecylamine and cyclododecylamine in toluene are quite similar to the reported values.[13b] Figure 3 shows the data of K_{eq} for the ligation of various alkylamines of differing shapes and sizes. The K_{eq} data can be summarised as follows: (1) for linear alkylamines, irrespective of their chain length, the K_{eq} values are fairly similar for **ZnT(2′,6′-OC$_n$P)P** ($n = 4$–20) complexes. (2) Among the cyclic amines, similar K_{eq} values for cyclohexyl-, cyclooctyl- and cyclododecylamines were observed for **ZnT(2′,6′-OC$_n$P)P** ($n = 4$–20) complexes, except for cyclobutylamine. (3) The least sterically hindered ZnTPP showed higher K_{eq} values for different Lewis

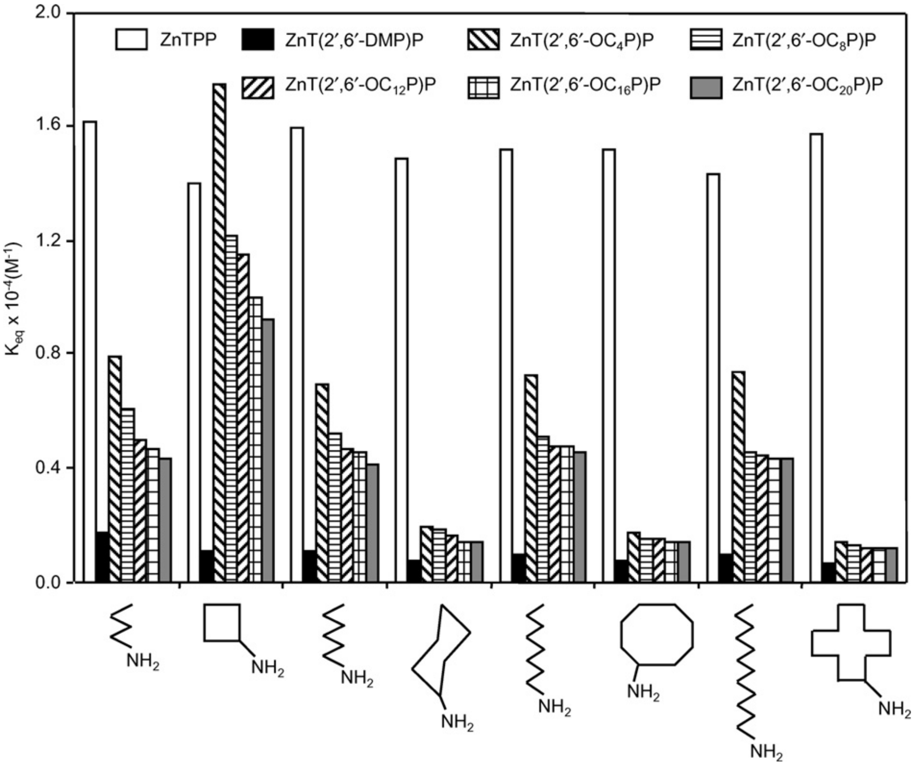

Figure 3. Plot of K_{eq} versus alkylamines for various Zn(II) porphyrins. Error in K_{eq} values: ±10%.

bases. (4) The moderately hindered pocket of the **Zn(2′,6′-DMP)P** complex showed the least K_{eq} values for all the alkylamines. (5) In general, the observed trend in ligation behaviour of alkylamines follows the order: **ZnTPP** > **Zn(2′,6′-OC$_4$P)P** > **Zn(2′,6′-OC$_n$P)P**($n > 4$) > **Zn(2′,6′-DMP)P**. (6) Interestingly, cyclobutylamine showed its highest K_{eq} value for the **ZnT(2′,6′-OC$_4$P)P** complex and remained fairly similar for other **ZnT(2′,6′-OC$_n$P)P** ($n = 8, 12, 16$ and 20) complexes.

One would anticipate an increase in steric hindrance with an increase in alkyl chain length on open faces of the porphyrin. However, an increase in K_{eq} values was observed for the ligation of bases with **Zn(2′,6′-OC$_n$P)P** complexes relative to the moderately hindered **ZnT(2′,6′-DMP)P** complex. The increased K_{eq} values of **Zn(2′,6′-OC$_n$P)P** complexes cannot be ascribed to increase in steric hindrance on both faces of the porphyrin. It was reported earlier that an increase in steric hindrance induces a decrease in K_{eq} values.[13] Furthermore, the increase in the K_{eq} values of **Zn(2′,6′-OC$_n$P)P** complexes cannot be due to the electron deficiency of the porphyrin π-system since the first ring redox potentials of **ZnT(2′,6′-OC$_n$P)P** ($n = 4, 8, 12, 16$ and 20) were shifted 200–350 mV cathodically. For example, redox potentials (vs Ag/AgCl) in CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate for **ZnT(2′,6′-OC$_4$P)P** were shifted cathodically ($E_{1/2}$: 0.61 V, 1.10 V, −1.75 V) relative to ZnTPP under similar conditions ($E_{1/2}$: 0.82 V, 1.13 V, −1.37 V and −1.75 V).[14] The trend in ligation behaviour of **Zn(2′,6′-OC$_n$P)P** complexes relative to **ZnT(2′,6′-DMP)P** was ascribed to possible attractive interactions between the bases with the alkyl chains present on both faces of the porphyrin. In general, Zn(II)–octaalkyloxyporphyrins showed a greater selectivity towards linear amines relative to cyclic amines (except for cyclobutylamine) and in some cases selectivity differences were as high as 10-fold.

The crystal structure[15] of **ZnT(2′,6′-OC$_4$P)P** complex was determined in order to probe the extent of steric hindrance on the faces of the porphyrin. The Zn(II) ion shows a four-coordinate geometry and lies almost in the plane, of the four nitrogens (±0.0070 Å). The ORTEP representation of the complex is shown in Figure 4. The observed 24-atom core structure is comparable to that reported for ZnTPP.[16] The structure shows the two different conformational features for the alkyloxy groups. Two of the four alkyloxy groups of the opposed aryl groups on the same face of the porphyrin are pointing towards the porphyrin plane while the other two are pointing in an upward direction. The van der Waals packing diagram of the structure shows access from above or below (~4.0 Å by 5.5 Å, excluding van der Waals radii) with limited side-on access for the incoming bases. The size of the cyclobutylamine[17] (~4.0 Å by 6.5 Å including van der Waals radii) is quite comparable to the size of the pocket on both faces as in the **ZnT(2′,6′-OC$_4$P)P** structure. In the case of the reported **H$_2$T(2′,4′,6′-TMeOP)P**[18] structure, there was a pocket size ~6.0 Å by 6.0 Å (excluding van der Waals radii) on both the faces of the porphyrin. The effective increase in K_{eq} values of the **ZnT(2′,6′-OC$_n$P)P**s is probably due to a highly flexible hydrophobic pocket on the faces of the porphyrins.

In summary, a series of sterically hindered porphyrins have been synthesised and these porphyrins show

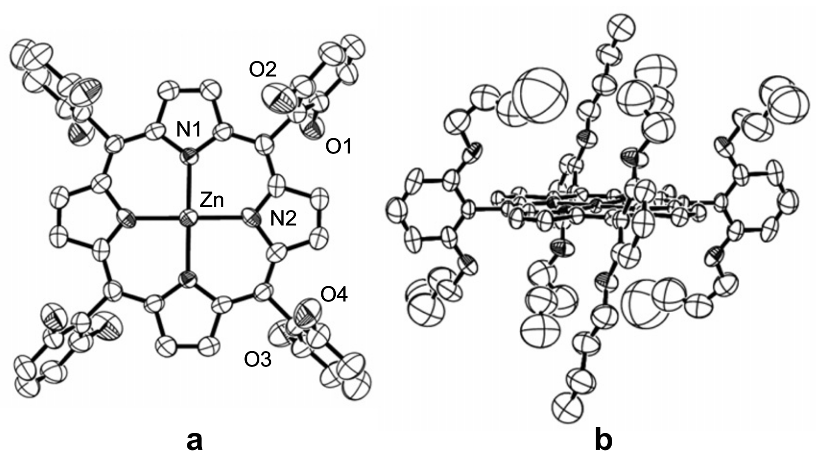

Figure 4. ORTEP diagram showing (a) the top view of **ZnT(2′,6′-OC$_4$P)P** complex (alkyl carbons and hydrogens are omitted for clarity), (b) the side-on view. Thermal ellipsoids are shown at 50% probability level.

considerable lowering of mesophase temperatures, possibly due to decreased intermolecular π–π interactions. The shape-selective ligation of Lewis bases to Zn(II)–octaalkyloxyporphyrins shows an increase in K_{eq} values indicating the possible attractive interactions between the bases with the hydrophobic pocket on the faces of the porphyrin.

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8. Spectral data for selected compounds. UV–vis data of **H$_2$T(2′,6′-OC$_4$P)P** in toluene: $\lambda_{max,}$ nm (log ε): 420 (5.67), 514 (4.33), 546 (3.72), 593 (3.79), 649 (3.14). ^{1}H NMR in CDCl$_3$: δ_H in ppm (400 MHz, TMS): 8.68 (s, 8H, β-pyrrole-H), 7.65 (t, 4H, $J = 8.40$ Hz, *p*-phenyl-H, 6.97 (d, 8H, $J = 8.48$ Hz, *m*-phenyl-H, 3.79 (t, 16H, $J = 6.64$ Hz, α-CH$_2$), 0.97 (q, 16H, $J = 7.04$ Hz, β-CH$_2$), 0.62 (q, 16H, $J = 7.42$ Hz, γ-CH$_2$), 0.32 (t, 24H, $J = 7.32$ Hz, –CH$_3$), −2.53 (s, 2H, imino–H). MALDI-TOF mass spectrum (in α-cyanohydroxycinnamic acid) (*m*/*z*): 1190.35 (Calcd. 1191.60). Elemental analysis calcd. for $C_{76}H_{94}N_4O_8$: C, 76.61; H, 7.95; N, 4.70. Found: C, 75.78; H, 8.36; N, 4.76. **ZnT(2′,6′-OC$_4$P)P**: $\lambda_{max,}$ nm (log ε): 424 (5.68), 550 (4.42), 582 (sh). ^{1}H NMR in CDCl$_3$: 8.66 (s, 8H, β-pyrrole-H), 7.61 (t, 4H, $J = 8.38$ Hz, *p*-phenyl-H), 6.95 (d, 8H, $J = 8.37$ Hz, *m*-phenyl-H), 3.77 (t, 16H, $J = 6.49$ Hz, α-CH$_2$), 0.87 (quin, 16H, $J = 6.92$ Hz, β-CH$_2$), 0.40 (quin, 16H, $J = 7.31$ Hz, γ-CH$_2$), 0.15 (t, 24H, $J = 7.33$ Hz, –CH$_3$). FAB mass spectrum (*m*/*z*): 1254.00 (Calcd. 1254.97). **CuT(2′,6′-OC$_4$P)P**: $\lambda_{max,}$ nm (log ε): 419 (5.71), 541 (4.53), 571 (sh). MALDI-TOF mass spectrum (*m*/*z*): 1252.09 (Calcd. 1253.13). The other **MT(2′,6′-C$_n$P)P** (M = 2H, Zn(II) and Cu(II); $n = 8, 12, 16$ and 20) derivatives were characterised as described above.
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15. Crystal structure of ZnT(2',6'-OC$_4$P)P complex: $C_{76}H_{92}N_4O_8Zn$, $M_r = 1254.91$. Crystal dimensions: 0.3 ×

$0.2 \times 0.2\ \mathrm{mm}^3$, dark pink, triclinic, P-1, $a = 13.646(2)$ Å, $b = 13.754(7)$ Å, $c = 20.765(7)$ Å and $\alpha = 72.45(4)°$, $\beta = 81.32(2)°$, $\gamma = 68.94(3)°$, $V = 3464\ (2)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.203\ \mathrm{Mg/m}^3$, $F(0\,0\,0) = 1340$. Diffractometer: Enraf-Nonius CAD4 single crystal X-ray diffractometer equipped with graphite monochromated Mo K_α (0.71073 Å), $T = 293(2)$ K. Data collection: $2\theta = 25°$, range of *hkl*: $h = 0$–16, $k = -15$ to 16, $l = -24$ to 24. Number of reflections collected, 12,736, 12,175 independent reflections ($R = 0.0702$), Refinement on F^2 with the results $R1 = 0.0665$, $wR2 = 0.1672$. SIR92 (WINGX) program was used to solve the structure by direct methods. The structure was completed by successive Fourier synthesis. The structure was refined using full matrix least squares techniques. The crystallographic data for the **ZnT(2′,6′-$\mathbf{C_4}$P)P** complex, (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 614498. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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