Synthesis and Phase Behaviour of β-Octaalkyl Porphyrins

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A homologous series of three octakis-alkyl-substituted porphyrin (OAP) derivatives with alkyl chain lengths of C8, C10 and C12 has been synthesised. For each compound, both the free-base (i.e. two H-atoms) and the fourfold coordinated zinc complex were investigated, where the latter for each chainlength was found to exhibit liquid crystalline mesophase behaviour (1). At low temperatures all three metal coordinated compounds formed a solid phase with a structure based on a square packing of columns with a stacking periodicity of approximately 4.5 Å. At increased temperatures the square packed solid S phases undergo phase transitions to liquid-crystalline columnar phases (Figure 1) based on centered rectangular lattices of C2/m symmetry, with the ratio of the lattice parameters, a/b, ranging between 1 and 1.732. The a/b ratio exhibited two discontinuous jumps with increasing temperature prior to melting to the isotropic phase for Zn-OAP-C₈, implying the existence of three columnar phases denoted Col_{r1}, Col_{r2} and Col_{r3}. For the longer chainlength compounds, the number of mesophases formed was reduced, first to two for Zn-OAP-C₁₀, then to one for Zn-OAP-C₁₂.

Reference

(1) G. C. Shearman, G. Yahioglu, J. Kirstein, L. R. Milgrom, J. M. Seddon J. Mater. Chem. 2009, 19, 598.



Figure 1. Optical texture of the C_8 Zn porphyrin compound after cooling slowly from the isotropic phase into the columnar liquid crystal phase.