Synthesis and Phase Behaviour of β -Octaalkyl Porphyrins

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Received (in XXX, XXX) 1st January 2007, Accepted 1st January 2007

First published on the web 1st January 2007

DOI: 10.1039/b000000x

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. At low temperatures all three metal coordinated compounds formed a solid S phase with a structure based on a square packing of columns with a stacking periodicity of 4.7 Å. At increased temperatures the square packed solid S phases undergo phase transitions to liquid-crystalline columnar phases 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.

Introduction

Since the discovery of discotic mesogens¹, a large number of disc-shaped molecules have been found to exhibit liquid crystalline phases (columnar and/or nematic mesophases) as a function of temperature. In recent years there has been renewed interest in designing and synthesizing discotic liquid crystals due to their potential application in several fields including charge transport², photoconductivity³, optical sensors⁴, nonlinear optics⁵ and organic light-emitting diodes⁶. Generally speaking, most discotic mesogens have flat or nearly flat central cores surrounded by six or eight (rarely four) long chain substituents. The porphyrin framework provides an ideal core structure for synthesizing new materials like liquid crystalline porphyrins, which have received considerable attention as uni-dimensional conductors⁷ and semiconductors^{8,9}. The first study of mesogenic porphyrins was on uroporphyrin-I octa-*n*-decyl ester which exhibited a monotropic discotic mesophase¹⁰. Since then, numerous porphyrin derived mesogens have been reported. These can broadly be divided into two categories depending upon the location and the number of side chains around the macrocyclic ring; octa- β -substituted porphyrins, which tend to exhibit a discotic columnar mesophase but are synthetically challenging¹¹ and the simpler to prepare *meso*-aryl substituted porphyrins which depending on the number and nature of substituents form narrow-range discotic lamellar¹², nematic/smectic¹³ and hexagonal columnar phases¹⁴. The mesophase behaviour of both metallated and free-base octa- β -substituted porphyrins has been examined for a variety of substituent groups. The metallated compounds have generally been found to display much more diverse liquid-crystalline phase behaviour due to the stronger electrostatic

interactions between the porphyrin rings, which can be considered as negatively charged due to the delocalised π electron systems, and the positively charged metal cores of neighbouring porphyrins¹⁵. Interestingly, the stabilisation of liquid crystalline mesophases has also been achieved by decreasing the symmetry of the discotic molecules, i.e. having a variety of different peripheral substituents, as well as tuning the length of the side chains⁸. There are several columnar mesophases, ranging from the highly symmetric hexagonal (Col_h), through to the rectangular (Col_r) and finally the lowest symmetry oblique columnar phase (Col_{ob}). Stronger core-core interactions are needed for lower symmetry mesophases, resulting in the oblique columnar phase rarely being observed¹⁶. Three different plane group symmetries are known to exist for the 2-D rectangular columnar lattice: P2₁/a, P2/a and C2/m; exact determination of these, and other, columnar mesophases is usually carried out by X-ray diffraction. Transitions between columnar mesophases have been widely reported, with those of higher symmetry, e.g. Col_h, generally occurring at higher temperatures¹⁷ although other competing processes such as dimerization can reverse this trend¹⁸. A transition between two centered rectangular phases, both of space group C2/m, has also been reported¹⁸ though this is rare, and to the best of our knowledge, no detailed analysis has been carried out on such systems. This paper aims to redress this by examining a homologous series of β -octaalkyl porphyrins, where the number of mesophases is related to the alkyl chain length.

Results and discussion

Discussions and experimental data will concentrate on the synthesis of 3,4-didodecylpyrrole and the corresponding β -

octadecylporphyrin **1** and its zinc complex **2**. Both the

Scheme 1. Synthesis of octadecylporphyrin and its zinc complex

Scheme 2. Synthesis of 3,4-dialkylpyrroles

octaalkylporphyrins requires 3,4-disubstituted pyrroles as
starting material. Their preparation is outlined in Scheme 2

Figure 1. Optical textures for the Zn porphyrin compounds with differing chain lengths observed after cooling slowly from the isotropic phase. (a) The dendritic texture of the C₈ compound, (b) flower-like texture of the C₁₀ compound, and (c) spherulitic texture of the C₁₂ compound.

and is based on the work of Chamberlin and LeGoff^{19,22} and involves the synthesis of an electrophilic alkene (α,β -unsaturated ketone **11**, **12**, **13**) and its reaction with tosylmethyl isocyanide to give the corresponding ketopyrrole **14**, **15**, **16**. These were reduced in high yields to give the desired 3,4-dialkyl pyrroles **17**, **18**, **19**.

Figure 2. DSC heating scans of the C₈, C₁₀ and C₁₂ zinc porphyrin compounds, at a heating rate of 5 °C min⁻¹.

Table 1. Transition temperatures, enthalpies and entropies for the various thermal transitions observed in the free base (FB) and zinc (Zn) porphyrin derivatives.

Compound	Transition	T (°C)	ΔH (kJmol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
Zn C ₈	S→Col _{r1}	172.5	38.7	86.8
Zn C ₈	Col _{r1} →Col _{r2}	180.8	2.2	4.8
Zn C ₈	Col _{r3} →I ₁	220.4	16.1	32.6
Zn C ₁₀	S→Col _{r2}	145.6	52.4	125.1
Zn C ₁₀	Col _{r3} →I ₁	182.3	13.5	29.6
Zn C ₁₂	S→Col _{r2}	124.5	57.2	143.8
FB C ₈	S→I	137.0	70.5	171.9
FB C ₁₀	S→I	115.4	95.9	246.8
FB C ₁₂	S→I	106.6	107.9	284.1

Thermal behaviour

The samples were first examined by polarising microscopy, and it was found that, for the Zn derivatives, characteristic optical textures indicative of discotic columnar phases were most clearly obtained by slow cooling at 1 °C/min from the isotropic melts. Initially, nuclei formed that developed into dendritic or flower-like textures, observed for the C₈ and C₁₀ porphyrin compounds respectively (Figures 1(a) and 1(b)), both of which have previously been reported for hexagonal ordered columnar phases²³. The C₁₂ Zn compound displayed a spherulitic texture (Figure 1(c)), which is also characteristic of a columnar phase^{16,24}. With further cooling, these birefringent regions coalesced and although broadly the patterns remained the same, the dendritic and flower-like textures displayed increasing angularity and the degree of birefringence decreased markedly at the discotic-solid transition.

In the DSC scans, the free bases all showed single sharp peaks on heating and cooling, corresponding to the melting of the solid to the isotropic liquid, without any liquid crystal phase formation. On the cooling scans, the measured transition temperature fell from 137 °C for the C₈ compound, to 107 °C for the C₁₂, and the transition enthalpy increased from 71 kJ mol⁻¹ to 108 kJ mol⁻¹. DSC scans of the Zn derivatives of the C₈, C₁₀ and C₁₂ porphyrin compounds showed multiple sharp transitions both on heating and on

cooling (Figure 2).

The melting points and clearing points of the zinc

Figure 3. Chainlength-dependence of the melting points and clearing points, as well as their associated transition enthalpies, of the free-base and zinc porphyrin derivatives, as measured from DSC cooling scans. The filled triangles represent the free-base derivatives, while the open symbols refer to the zinc derivatives where the open circles and the open squares depict the melting and clearing points respectively.

derivatives as a function of chainlength are shown in Figure 3, and the thermal data from the DSC cooling curves for both the free bases and the zinc porphyrin derivatives are summarized in Table 1. The melting points are some 35 °C higher than those of the free base compounds, showing that the presence of the zinc at the centre of the molecule tends to stabilise the packing. The crystallization temperature, as determined from DSC cooling scans, decreases steeply with chainlength, from 173 °C for the C₈ compound, to 124 °C for the C₁₂ compound. This trend of lower melting temperatures for substituents with progressively longer chain lengths has often been reported previously e.g. for octaalkylphthalocyanines²⁵. Conversely, the transition enthalpy increases from 39 kJ mol⁻¹ to 57 kJ mol⁻¹ for the C₁₂ compound. These melting enthalpies are rather low, considering that eight alkyl chains per molecule are involved, and thus, for example, for the C₁₂ porphyrin it amounts only to some 7 kJ mol⁻¹ per alkyl chain. For comparison, the C₁₂ alkane *n*-dodecane has a melting enthalpy of 36.5 kJ mol⁻¹.²⁶ This difference is too large to be accounted for by the fact that the zinc porphyrin compounds are first forming liquid crystal phases before transforming to the isotropic liquid: it implies that the low temperature 'crystal' phase must already contain a considerable degree of disorder. The clearing point also falls steeply with chainlength, from 220 °C for the C₈ compound, to 152 °C for the C₁₂ zinc

Figure 4. A continuous X-ray diffraction scan of the C_8 compound, from 260°C – 160 °C, at a cooling rate of 10 °C / hour.

Figure 5. Typical X-ray powder diffraction patterns for the C_8 compound of (a) the isotropic (I) phase, (b) the Col_{r3} mesophase, (c) the Col_{r2} mesophase, (d) the Col_{r1} mesophase, and (e) the solid (S) phase.

derivative (obtained by polarising microscopy). Interestingly, the enthalpy for this transition *falls* with chainlength, to approx 16 kJ mol⁻¹ for the C_8 compound, to 13.5 kJ mol⁻¹ for the C_{10} derivative. The clearing point for the C_{12} zinc derivative was not observed by DSC, implying that this transition has a negligible energy change associated with it. The DSC scans yield the same values for the clearing points upon heating as on cooling, whereas the melting points are

Figure 6. The X-ray powder diffraction patterns of the solid S phase for the C_8 , C_{10} and C_{12} porphyrin compounds.

shifted approximately 5 °C higher on the heating scans than the crystallization temperatures measured from the cooling scans.

X-Ray Diffraction

X-ray diffraction measurements confirmed that the free base compounds melt directly to the isotropic phase, whereas the zinc derivatives have a rich liquid crystal phase behaviour. For example, an X-ray continuous-temperature scan for the C_8 zinc porphyrin is reproduced in Figure 4, and shows that three different mesophases, denoted Col_{r1} , Col_{r2} and Col_{r3} , are formed between the high temperature isotropic liquid (I) and the low temperature solid phase (S). Transitions between the various phases are sharp, within the resolution of the X-ray diffraction temperature scans.

The characteristic X-ray powder diffraction patterns of all five phases (I, Col_{r3} , Col_{r2} , Col_{r1} , and S) of the C_8 compound are shown in Figure 5. A relatively large number of fairly sharp X-ray reflections are seen for the S phase, spanning from the low-angle region through to the wide-angle region. For the Col_{r1} , Col_{r2} and Col_{r3} mesophases, the sharp multiple reflections are localised in the low-angle region, and only weak diffuse scatter is observed in the wide-angle region, centred at a reciprocal spacing of 0.212 Å⁻¹, corresponding to a real space value of 4.7 Å. For the isotropic liquid phase, only low-angle and wide-angle diffuse scattering is seen, centred at reciprocal spacings of 0.049 Å⁻¹ and 0.21 Å⁻¹, corresponding to real space values of 20 Å and 4.8 Å, respectively.

The X-ray patterns of the solid (S) phase of the C_8 , C_{10} and C_{12} porphyrin compounds are compared in figure 6. It is clear that the patterns are qualitatively identical, indicating that all three compounds have the same basic structure. Similar comparison of the diffraction patterns of the Col_{r2} phase also show that they arise from a liquid crystal mesophase with the same underlying structure. The Col_{r3} mesophase is only observed for the C_8 and C_{10} derivatives, and the Col_{r1} mesophase only for the C_8 compound.

Table 2. Reciprocal spacings and indexing of the solid and liquid crystal phases of the zinc derivatives of the C₈, C₁₀ and C₁₂ porphyrin compounds.

Mesophase	Miller indices (<i>hkl</i>)		C ₈			C ₁₀			C ₁₂	
			Spacing / Å			Spacing / Å			Spacing / Å	
		Phase lattice constants	<i>d_{obs}</i>	<i>d_{calc}</i>	Phase lattice constants	<i>d_{obs}</i>	<i>d_{calc}</i>	Phase lattice constants	<i>d_{obs}</i>	<i>d_{calc}</i>
S	100	a=20.4Å	20.41	20.40	a=22.4Å	22.35	22.40	a=24.3Å	24.32	24.30
	110		14.47	14.42		15.83	15.84		17.25	17.18
	200		10.26	10.20		11.20	11.20		12.18	12.15
	210		9.20	9.12		10.04	10.02		10.88	10.87
	320								6.82	6.74
Col _{r1}	110	a=34.46Å;	20.41	20.37						
	200	b=25.26Å	17.21	17.23						
	020		12.59	12.63						
	310		10.47	10.46						
	220		10.18	10.19						
Col _{r2} (low T)	110	a=35.45Å;	20.46	20.49	a=36.94Å;	22.63	22.54	a=39.49Å;	24.26	24.31
	200	b=25.10Å	17.69	17.73	b=28.46Å	18.44	18.47	b=30.85Å	19.75	19.75
	020		12.55	12.65		14.15	14.23		15.47	15.43
	310		10.77	10.69		11.29	11.30		12.15	12.16
	220		10.26	10.24		11.29	11.27		12.15	12.11
Col _{r2} (high T)	400					9.18	9.24		9.99	9.95
	110	a=36.95Å;	20.36	20.27	a=37.61Å;	22.59	22.54	a=40.05Å;	24.18	24.26
	200	b=24.25Å	18.40	18.48	b=28.16Å	18.78	18.81	b=30.05Å	20.06	20.02
	020		11.99	12.13		14.03	14.00		15.30	15.25
	310		11.07	10.98		11.46	11.45		12.20	12.23
Col _{r3}	220		10.18	10.14		11.26	11.27		12.20	12.13
	400					9.43	9.40			
	130					9.12	9.11			
	110	a=38.51Å;	20.06	19.93	a=41.86Å;	22.59	22.59			
	200	b=23.29Å	19.22	19.25	b=26.83Å	20.93	20.93			
	020		11.48	11.65		12.70	13.41			
	310					12.70	12.38			

The reciprocal spacings and the deduced indexing of the crystal and liquid crystal phases observed for the three different chainlength zinc porphyrin compounds are listed in Table 2. For the solid S phase, only a selection of the observed peaks are listed for simplicity, however all of the peaks indexed perfectly. Essentially all of the observed peaks from the solid S phase can be indexed as (*hk*) reflections arising from a 2-D square lattice, with a lattice parameter *a* increasing from 20.6 Å for the C₈ compound, to 24.5 Å for the C₁₂ derivative, with only a wide-angle peak at approximately 4.5 Å being associated with the periodicity of the stacking along the columns. From these data we are strictly speaking unable to determine whether the columns are completely untilted with respect to the x-y plane of the square lattice (tetragonal symmetry) or slightly tilted (monoclinic symmetry). In the latter case reflections such as (100) and (010) etc. are no longer coincident in the powder pattern. We estimate from the resolution of our X-ray experiments that the deviation away from tetragonal symmetry can be no more than approximately 5°, or else we would see a splitting of the peaks. This low temperature S phase which we are loosely denoting as a ‘solid’ phase, since it appears to lack general (*hkl*) reflections, should perhaps more accurately be described as an ‘ordered columnar’ phase. It seems to be less ordered than one would expect from a normal crystal, and this conclusion is supported by the relatively low enthalpy of

melting to the liquid crystal phase (see Table 1).

The Col_{r1}, Col_{r2} and Col_{r3} phases all exhibit only diffuse scattering in the wide angle region, whose maximum occurs around a reciprocal spacing of 0.212 Å⁻¹, corresponding to a spacing of approximately 4.7 Å. This peak presumably arises from a combination of the liquid-like alkyl chains, and a liquid-like stacking of the cores along the columns. Remarkably, the liquid-crystalline phases of the three compounds can all be indexed convincingly as 2-D rectangular lattices, where the Bragg peaks denoting the interplanar spacings, *d_{hkl}*, are related to the unit cell parameters *a* and *b* as:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} \quad (1)$$

It should be noted that if $b = a/\sqrt{3}$ i.e. an *a/b* ratio of 1.732 for then the lattice arrangement is hexagonal rather than rectangular. Similarly, for the centered rectangular phase (C2/m), if *a* = *b* i.e. a ratio of 1, then a square lattice is observed, although with smaller lattice constants since the ‘centered square’ lattice that would theoretically be obtained is not a true 2-D lattice. For the reflections obtained for each mesophase of the three metallated compounds, the reflection condition $h + k = 2n$ held true,

Figure 7. Lattice parameters as a function of temperature for the C₈, C₁₀ and C₁₂ zinc derivatives, where the symbols for the lattice parameters *a* and *b* are empty squares and circles respectively and their ratio (*a/b*) is shown as filled circles.

per CH₂ group for the end-end length of the fully-extended molecule (remembering that there are alkyl chains on opposite sides of the molecule). The discrepancy seems too large to be attributed only to chain interdigitation: most likely some chain disorder and/or out of plane tilting is also responsible.

The lattice parameters of the liquid-crystalline columnar phases (Col_{r1} – Col_{r3}) are plotted as functions of temperature in Figure 7. Focusing on the data for the C₈ compound, we see that the lattice parameters *a* and *b* have constant values of 34.4 Å and 25.2 Å respectively in the liquid-crystalline Col_{r1} phase, then to 35.1 Å and 25.0 Å in the Col_{r2} phase, climbing to 37.0 Å and 24.3 Å, and finally jumping to values of 38.5 Å and 23.3 Å in the Col_{r3} phase. Concomitantly, the *a/b* ratio starts with a value of 1.37 in the Col_{r1} phase, then to 1.40 in the Col_{r2} phase, rising gradually to 1.52, before reaching a value of 1.65 in the Col_{r3} phase. This last value is close to the *a/b* ratio of 1.73 which is characteristic of 2-D hexagonal packing.

Experimental

The microscopy experiments were performed with a Nikon Eclipse E600 polarising microscope equipped with a Linkam TMS94 temperature programmer coupled with a liquid nitrogen pump and an LTS350 heating stage. The calorimetric measurements were carried out using a Perkin-Elmer Diamond DSC. 2 - 5 mg samples were weighed into aluminium sample pans then heated and cooled several times at a rate of 5 °C/min. The reference cell contained an empty aluminium pan. Transition temperatures and enthalpies were calibrated against indium (melting point 156.6 °C; Δ*H*_{fusion} = 3.28 kJ mol⁻¹).

For the X-ray experiments a Phillips PW 2231/20 X-ray generator was used, fitted with an AEG Cu fine-focus X-ray tube operating at 40kV and 30mA. The diffraction patterns were obtained using a Guinier camera (R. Huber, Rimsting Germany) fitted with a bent quartz monochromator to isolate Cu K_{α1} radiation (λ = 1.54 Å). The camera is fitted with a motor driven film holder which can slowly translate the film vertically behind a 3 mm horizontal masking slot. By simultaneously scanning the sample temperature, using electrical heating in conjunction with a Eurotherm controller, diffraction patterns can be recorded as continuous functions of temperature, either as heating and/or cooling scans. The patterns were recorded on Kodak X-OMAT AR X-ray film, scanned using an Epson Perfection 4990 Photo scanner, and analysed using the AXcess software program developed in our laboratory (A. Heron, PhD. Thesis²⁹). Commercial CrystalMaker / CrystalDiffract software was used to aid indexing of the diffraction patterns.

Synthesis

Experimental

Chemicals and solvents were obtained from various commercial sources and used without further purification unless otherwise stated. Tlc was performed on glass-backed silica-gel 60 F₂₅₄

indicating that all three mesophases, Col_{r1}, Col_{r2} and Col_{r3} belong to the C2/m space group. For the C₈ compound, which displayed all three columnar mesophases, the *a/b* ratio was found to be smallest for phase Col_{r1} (approximately 1.37), larger for Col_{r2}, and increasing to close to 1.65 by phase Col_{r3}. Thus the symmetry of the in-plane packing varies between square for phase S, to almost 2-D hexagonal for the Col_{r3} phase. These liquid-crystalline columnar phases are tilted with respect to the basal plane, however as the *a/b* ratio of the C2/m phase becomes closer to that of the hexagonal lattice i.e. the Col_{r3} phase, the demand for an offset geometry and therefore the tilt is reduced.

For the solid S phase, the lattice parameter is much smaller than the fully-extended molecular length (estimated to be 27.3 Å, 32.3 Å and 37.4 Å for the C₈, C₁₀ and C₁₂ compounds respectively, from the methyl endgroup on one alkyl chain to the methyl group at the end of the opposing chain on the other side of the porphyrin core^{27,28}). This implies that the molecules are packed with the chains extensively interdigitated, as previously deduced by Liu *et al.*²⁷ in a previous study of zinc octakis(β-decoxyethyl)porphyrin, where a similar square packing in the crystal phase was found. The lattice parameter of the S phase increases by 2 Å between C₈ and C₁₀, and 1.9 Å between C₁₀ and C₁₂, corresponding to a linear incremental increase of 0.5 Å per CH₂ group. This value may be compared with the expected increase of 1.25 Å

and/or neutral aluminium oxide plates. Column chromatography was performed on silica gel 60A. ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 unless otherwise stated on either a Jeol JNM FX 200 MHz or a 400 MHz Bruker DMX 400 spectrometer.

All chemical shifts are reported in δ (ppm) using the residual proton impurities of the NMR solvent as an internal reference and J values are reported in Hz. Mass spectra EI, FAB and MALDI mass spectra were obtained by the chemistry department at Imperial College London. UV-absorption spectra were measured on a HP 8453 diode-array spectrometer using spectroscopic grade chloroform or dichloromethane. Infrared spectra were measured as KBr discs or as thin-films between NaCl plates using a Perkin Elmer FTIR 1720 spectrometer.

Octadodecylporphyrin (1)

A solution of the the 3,4-didodecylpyrrole **17** (3.7 g, 9.2 mmol) fresh 37% aqueous formaldehyde (43 ml) and aqueous 48% hydrobromic acid (2 ml) in absolute EtOH (300 ml) was refluxed for 24 h under nitrogen then refluxed a for a further 24 h open to the atmosphere. The resulting solution was allowed to stand a room temperature open to the atmosphere for 8 days during which the porphyrin precipitated out of solution. The EtOH was removed, the residue neutralised with saturated aqueous sodium carbonate and extracted with DCM (3x 200 ml). The DCM was removed and the residue chromatographed on silica gel with a 1:1 mixture of chloroform/hexane as the eluant (R_f 0.74) to give the porphyrin as a red/brown paper-like solid (0.57 g, 15% yield). ^1H NMR (CDCl_3): δ_{H} 10.08 (s, 4 H, *meso*-H), 4.1 (m, 16 H, pyrrole- CH_2 -), 2.31 (m, 16 H, $-\text{CH}_2$ -), 1.82 (m, 16 H, $-\text{CH}_2$ -), 1.55 (m, 16 H, $-\text{CH}_2$ -), 1.28 (m, 112H, $-\text{CH}_2$ -), 0.86 (m, 24 H, $-\text{CH}_3$), - 3.72 (s, 2H, N-H); ^{13}C NMR (CDCl_3): δ_{C} 144.19, 140.25, 96. 90, 34.04, 31.96, 30.50, 29.89, 29.85, 29.80, 29.72, 29.42, 26.73, 22.71, 14.14; MS (MALDI) 1658 ($M + 1$, 100%); UV/Vis (CHCl_3) λ_{max} (log ϵ) 400 (5.3), 500 (4.1), 536 (4.0), 567 (3.8), 620 nm (3.6).

Zn-Octadodecylporphyrin (2)

To a refluxing solution of the free-base porphyrin **1** (26 mg, 0.016 mmol) in chloroform, a saturated solution of zinc acetate dihydrate in methanol was added drop-wise resulting in an immediate colour change from deep-red to fuschia. The reaction was followed spectroscopically and was over within 1 hour. The solvent was removed and the residue triturated with methanol, filtered and washed repeatedly with methanol to remove any zinc salts. Final purification was achieved by column chromatography on silica gel eluting with a 1:1 mixture of DCM/hexane (R_f 0.97) to give a deep burgundy solid (22 mg, 80%). ^1H NMR (CDCl_3): δ_{H} 10.13 (s, 4 H, *meso*-H), 4.05 (m, 16 H, pyrrole- CH_2 -), 2.38 (m, 16 H, $-\text{CH}_2$ -), 1.81 (m, 16 H, $-\text{CH}_2$ -), 1.56 (m, 16 H, $-\text{CH}_2$ -), 1.28 (m, 112H, $-\text{CH}_2$ -), 0.86 (m, 24 H, $-\text{CH}_3$); ^{13}C NMR (CDCl_3 + 1% pyridine): δ_{C} 147.6, 140.50, 97.09, 34.23, 31.91, 30.55, 29.89, 29.86, 29.83, 29.78, 29.38, 26.86, 22.67, 14.09; MS (MALDI) 1720 (M , 100%); UV/Vis (CHCl_3) λ_{max} (log ϵ) 404 (5.4), 534 (4.2), 570 (4.3).

Figure 8. Illustrations showing (a) the 2-D square packed columnar structure of the solid (S) phase and (b) the centered rectangular (C2/m) columnar structure of the Col₁, Col₂ and Col₃ mesophases.

Conclusions

We have synthesized a series of porphyrin derivatives and demonstrated that the zinc coordinated compounds exhibited novel phase behavior. At low temperatures, X-ray diffraction revealed that the solid S phase was composed of square packed columns (Figure 8(a)). The observed equivalence of the reciprocal spacings of the ($h00$) and ($0h0$) reflections in the indexing of the diffraction patterns implied that the columns were untilted with respect to the x - y plane. The relatively low values of the in-plane lattice parameter a , and the fact that it increased linearly by only 0.5 Å per CH_2 group, also indicated an interdigitation of the neighbouring chains in the x - y plane. The melting points and clearing points of the zinc octaalkyl porphyrin derivatives both fell progressively with increasing length of the alkyl chains. For the Zn-OAP-C₈ compound, three discotic phases of space group C2/m (Figure 8(b)) were observed between the solid S phase and the isotropic liquid, however for increasing chainlengths, the number of liquid crystalline phases was decreased, culminating in only one discotic phase for Zn-OAP-C₁₂. The highest temperature Col₁ phase has a packing that is close (but not identical) to 2-D hexagonal. The rich liquid crystalline phase behavior of the metal coordinated compounds reported here suggests that they may have applications in several developing fields such as optical sensors.

Acknowledgements

We thank the EPSRC for the award of the Platform grant GR/S77721.

Notes and references

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† Electronic Supplementary Information (ESI) available: Characterisation data for intermediate compounds. See DOI: 10.1039/b000000x/

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Graphical Abstract

Zinc metallated octakis-alkyl-substituted porphyrin derivatives can form multiple liquid-crystalline columnar phases based on centred rectangular lattices of $C2/m$ symmetry.