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PRELIMINARY COMMUNICATION

Phase transitions of long chain esters of meso-tetrakis(para-carboxyphenyl)porphyrin

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Several long chain esters of meso-tetrakis(*para*-carboxyphenyl)porphyrin, and two of their metal complexes (Cu, Zn) have been prepared and characterized. Each of them exhibits at least one thermotropic phase transition below the clearing point to the isotropic liquid, but no definitive evidence of liquid crystallinity has been found by differential scanning calorimetry, optical microscopy, or X-ray diffraction.

Supramolecular stacks of porphyrins and metalloporphyrins bearing long alkyl chains at the macrocycle periphery are the focus of current interest due to their potential utilization in molecular electronic devices as columnar liquid crystalline materials for one dimensional charge or energy migration [1]. Several octa-ß-substituted porphyrins and some of their metal complexes have been claimed as exhibiting discotic liquid crystalline phases [1–4]. Recently the general ease of synthesis of tetraphenylporphyrins has prompted investigations of the thermotropic behaviour of meso-phenyl-substituted porphyrins bearing *para-n*-alkoxy [5–6] or *para-n*-alkyl [6] substituents. Discotic mesomorphism has been claimed in some instances, although the evidence presented so far for their mesomorphic nature has been equivocal. We describe herein the synthesis, and differential scanning calorimetry (DSC) and small and wide angle X-ray diffraction (XRD) investigations of long chain esters derived from meso-substituted tetra-*para*-carboxyphenylporphyrin and some of their metal complexes.

Esters of *para*-carboxybenzaldehyde **2a–c** were obtained (see the figure) by reaction of **1** with long chain alcohols in the presence of dicyclohexylcarbodiimide (DCC) and of a catalytic amount of dimethylaminopyridine (DMAP). Condensation with pyrrole according to the Lindsey method [7] gave porphyrins **3a–c** in 35–50 per cent yields. Metallation of **3b** with $Zn(OAc)_2$ and $Cu(OAc)_2$ gave **4b**, Zn and **4b**, Cu in quantitative yields. All compounds were recrystallized from CH_2Cl_2–*n*-heptane, and gave satisfactory analytical data. All of the materials **3a–c**, **4b**, Zn and **4b**, Cu were examined for thermal decomposition using the Mettler TA 3000 Thermogravimetric Analysis

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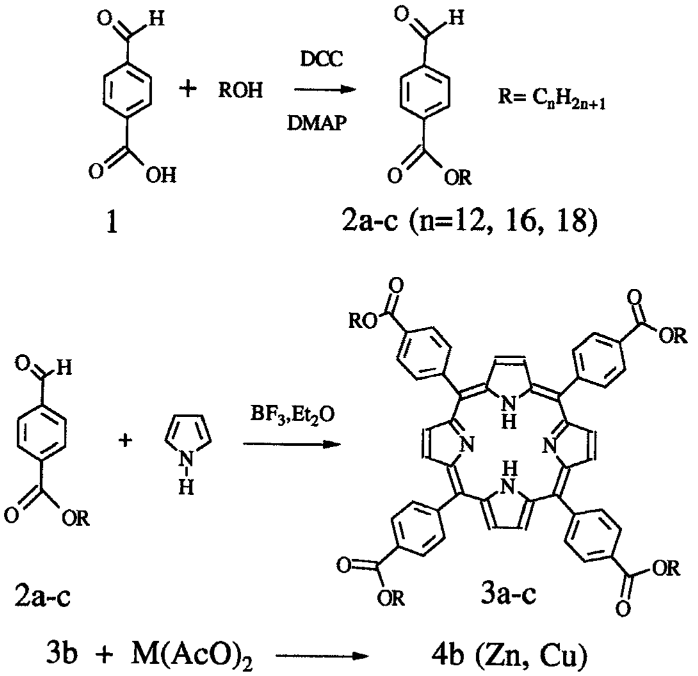

Synthetic route for the preparation of the porphyrins.

system. In each case, on heating to 300°C from room temperature, a weight loss of less than 2 per cent was observed, indicating the thermal stability of these materials up to 300°C.

Phase transition temperatures and enthalpies were determined by DSC (Perkin–Elmer DSC 7) and polarizing microscopy (Leitz Orthoplan microscope and Mettler FP 80/FP 82 heating stage). X-ray diffraction studies were performed on all materials using a Marconi Elliott GX 20 rotating anode source ($Cu–k_{\alpha 1}$) and detected using a flat film camera. Temperature control *in situ* on the X-ray camera was via a Mettler FP 5 controller and FP 82 hostage.

All of the materials **3** and **4** were crystalline at room temperature. The phase transition temperatures and enthalpies for compounds **3** and **4** are given in the polymorphic scheme. Phase transition temperatures were determined from the DSC peak onset temperatures, and are given in degrees centigrade, with an error of 0·5°C. Enthalpies of each transition are given in parentheses, in $kJ\,mol^{-1}$. In every case the heating and cooling rates were $10°C\,min^{-1}$. The symbols C, ? and I have been used to denote crystalline solid, unknown and isotropic liquid phases, respectively. Polarizing light microscopy confirmed the temperature of the transition to the isotropic phase (on heating, at $<1°C\,min^{-1}$) and was also used to observe the birefringent textures developed in each phase of the materials **3** and **4**. In the phases marked unknown in the scheme, no texture typical of liquid crystal phases (nematic, layered or discotic columnar) [8, 9] could be developed.

As can be seen in the scheme, in each material there is a hysteresis between the isotropic temperatures on heating and cooling, which is very much greater than any error in the temperature measurement. Such hysteresis of transition temperatures on heating and cooling is indicative of a transition (respectively) from or to a crystalline

3a	C	30·8	?	137·9	?	143·8	I	Heating
		(19·6)		(4·1)		(21·1)		
	C	24·2	?	117·6	I			Cooling
		(20·5)		(29·6)				
3b	C	85·0	?	101·9	?	123·4	I	Heating
		(8·1)		(6·6)		(29·9)		
	C	60·0	?	97·1	I			Cooling
		(25·5)		(19·1)				
3c	C	106·2	?	117·3	I			Heating
		(99·8)		(30·0)				
	Isotropic phase supercools to <40°C.							
4b, Zn	C	115·8	?	138·2	I			Heating
		(58·2)		(30·3)				
	C	95·2	?	118·9	I			Cooling
		(68·3)		(25·9)				
4b, Cu	C	96·8	?	132·9	I			Heating
		(56·9)		(42·0)				
	C	89·2	?	116·4	I			Cooling
		(57·6)		(39·7)				

Polymorphic behaviour (temperatures in °C, enthalpies in parentheses, in kJ.mol^{-1}) of the porphyrin derivatives.

phase. The isotropic temperatures reported here for the non-metal porphyrins **3a–c** are comparable with those reported by Shimizu in his study of alkylphenyl and alkoxyphenyl substituted porphyrins [6], and show the same trend of decreasing isotropic temperature with increasing chain length. The enthalpies of transition from the unknown to the isotropic phases are similarly comparable with the 'discotic lamellar' to isotropic enthalpies that Shimizu measured for the alkylphenyl substituted porphyrins. The enthalpies of the crystal–isotropic transition of the alkoxyphenyl substituted porphyrins that Shimizu investigated were, by contrast, approximately twice those of the materials reported here.

The main spacings (most intense reflections) calculated from the diffraction images obtained for each material in various phases are presented in the table. Spacings could be calculated with an estimated accuracy of 1 Å for the small angle region, and 0·2 Å for the wide angle region. The diffraction images from the unknown and the crystal phases showed similar features. At low angles, typically 3 or 4 concentric rings were seen in all materials, corresponding to a spacing of between 31 and 43 Å. This spacing increased with alkyl chain length, and may correspond to the length of the molecular 'side' (from the end of one alkyl chain to the end of an adjacent alkyl chain) [6]. Within the error of measurement, diameters of the rings were always in the ratio 1:2:3:4, indicating a layered structure in both the crystal and unknown phases.

At wide angles, one intense sharp reflection was seen for each material from both their known crystal and their unknown phases. This reflection corresponded to a spacing of 4·6 to 4·8 Å, and was possibly greater in the metal-free porphyrins **3a–c** (4·8 Å) than in the two metallated porphyrins **4b** (4·6 Å), although the difference could be just due to measurement error. A second intense wide angle reflection at 4·2–4·3 Å was also observed in some cases.

In 5-10-15-20-alkylphenyl substituted porphyrins, 'lamellar discotic' mesophases have been claimed [6] from microscopy, DSC and XRD evidence. In the same paper, Spacings as determined by X-ray diffraction.

Material	Phase temperature/°C	Spacings/Å		
		Low angle	Wide angle	
3a	? (135)	31	4·8	
	? (141)	31	4·8	
3b	? (115)	38	4·8	4·3
3c	? (110)	43	4·8	4·3
4b, Cu	C (90)	34	4·6	
	? (125)	35	4·6	
4b, Zn	C (110)	31	4·6	4·2
	? (130	31	4·6	4·2

the same techniques were used to demonstrate the absence of mesophases in 5-10-15-20-alkoxyphenyl substituted porphyrins (previously claimed as showing mesophases [5]). For octa-substituted porphyrins, hexagonal discotic phases have been claimed on the basis of XRD evidence [4] and also on the basis of microscopy and DSC alone [1, 3]. Structurally similar to the porphyrins, the phthalocyanines have been shown by XRD to exhibit hexagonal columnar phases when octa-substituted with alkyl, alkoxy and alkoxymethyl chains [10–12].

In the light of the literature reports just described, either a hexagonal discotic or a lamellar discotic mesophase may have been expected to be formed by the materials presented here. The small angle diffraction images with the 1 : 2 : 3 : 4 ratio of diameters suggest a lamellar structure: a hexagonal structure (such as a hexagonal array of columns) would have presented small angle diffraction circles with diameters in the ratio $1:\sqrt{3}:2:\sqrt{7}$: this is not observed here. Fluid discotic phases have been observed to present diffuse diffraction rings in the wide angle region due to the disordered ('melted') alkyl chains. Typically this diffuse ring gives spacings between 4·5 Å [4] and 4·8 Å [10, 11]. Furthermore, a second diffuse ring in the same region is sometimes observed due to the disordered packing of the discotic molecules within a column. No such diffuse rings are seen here: sharp rings only were observed, except when samples were heated into the isotropic phase, when diffuse rings at typically 30 Å and 5 Å were seen. These observations lead to the conclusion that the unknown phases denoted by ? above must either be crystalline or of an ordered smectic type.

In this short note, the synthesis and characterization of some meso-substituted tetra-*para*-carboxyphenylporphyrins and some of their metal complexes have been described. In contrast with the reported mesomorphic behaviour of similar tetra- and octa-substituted porphyrins, no clear evidence of liquid crystallinity in the phases between the room temperature crystal phase and the isotropic liquid phase has been found.

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