Calamitic Nematic Liquid Crystal Phases from Zn^{II} Complexes of 5,15-Disubstituted Porphyrins

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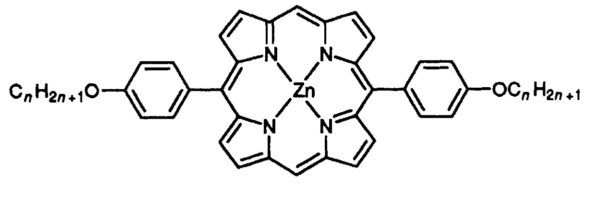
The liquid crystalline behaviour of porphyrins is normally associated with the formation of discotic mesophases, owing to stacking of the large, flat core; by extending the porphyrin along one axis *via* substitution at the 5 and 15 positions, the disc-like porphyrin can be made to behave as a rod, showing calamitic nematic and smectic A phases at elevated temperatures.

Metalloporphyrin compounds have been extensively studied in many functional chemistry fields such as photoelectronic conversion, non-linear optics and biomimetic studies in which control of orientation of porphyrin chromophores can play a very important role.[1] One of the methods for controlling the orientation of such species is by structural modifications that render the porphyrin liquid crystalline. While liquid crystalline phthalocyanines have been rather extensively studied,[2] the related porphyrins have received relatively little attention,[3] possibly due to the more involved synthetic chemistry.

In general, low molar mass thermotropic liquid crystals can be divided into two main classes according to the shape of the molecules which make up the mesophases. In so-called calamitic materials, the materials are rod-like and the mesophases (nematic and smectic) result from the organisation of the molecules *via* some correlation of the long molecular axes. In the so-called discotic systems, the materials are disc-shaped and the mesophases (discotic nematic and columnar) result from organisation of the short axis of the molecules.

In all of the studies of mesogenic porphyrins[4] and phthalocyanines,[5] the extended disc-like core has been peripherally substituted and therefore used as the basis for the construction of discotic materials. However, we recently reported on the synthesis of zinc complexes of 5,15-disubstituted porphyrins **1**[6] and in these systems, the 5,15 substitution proved sufficient to elongate the molecule in such a way that its behaviour became that of a rod-like liquid crystal, showing crystal smectic B and E mesophases.



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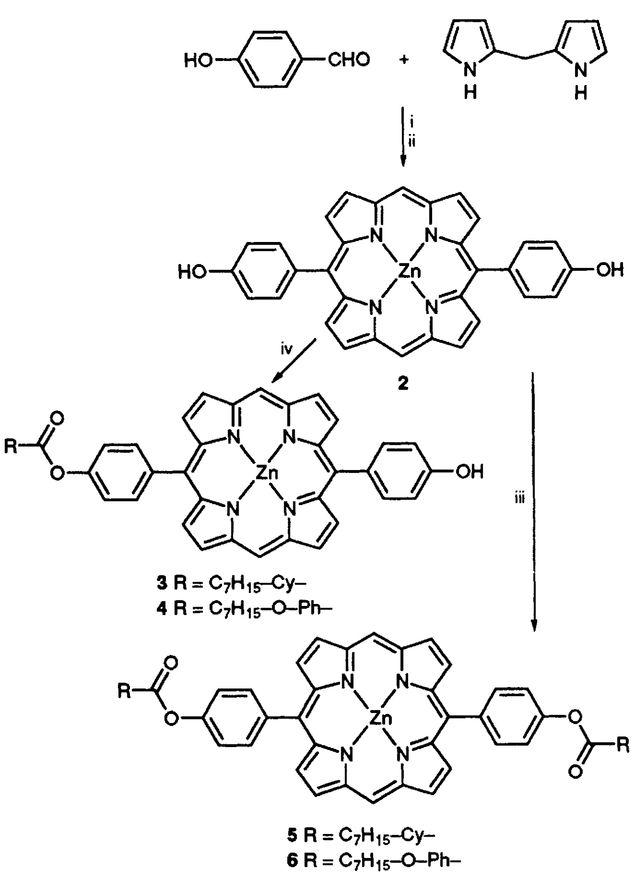
We have now extended these studies and have succeeded in generating new 5,15-disubstituted porphyrins, which exhibit fluid liquid crystal phases, in particular nematic and smectic A phases. The compounds, which are based on 5,15-di(4-hydroxyphenyl)porphyrins, were synthesised as shown in Scheme 1.

Thus, dipyrrylmethane[7] and 4-hydroxybenzaldehyde were cyclised by stirring in a mixture of dichloromethane and methanol, promoted by $BF_3 \cdot OEt_2$; the porphyrin was then obtained on oxidation with *p*-chloranil with concomitant metallation. The resulting di(hydroxyphenyl)porphyrin **2** was then esterified using dicyclohexylcarbodiimide and *N,N*-dimethylaminopyridine in THF; the production of the mono- or di-ester was simply controlled by the amount of the relevant acid used. The final porphyrins were purified by column chromatography and then by crystallisation to give unoptimised, isolated yields of 22–42%. Satisfactory analytical data were obtained for all new compounds.

The mesomorphism of the compounds was studied using polarised optical microscopy and differential scanning calorimetry; the results are quoted in Table 1.

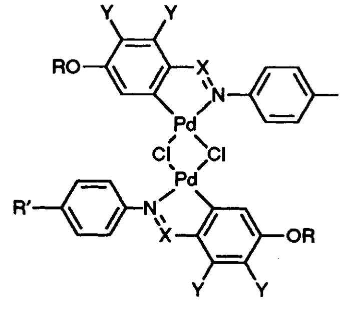
The phases were identified by their characteristic optical textures. Compound **3** melted at 315 °C to give a nematic phase which persisted until around 353 °C by which time the material had largely decomposed. The monoester **4** was similarly nematic, although it was not possible to obtain enthalpy data in this case as decomposition appeared to commence on melting. When the diester **5** was heated, the mesomorphism was different and a smectic A phase appeared



Scheme 1 *Reagents and conditions*: i, $BF_3 \cdot OEt_2$; ii, *p*-chloranil/$Zn(OAc)_2 \cdot 2H_2O$; iii, excess RCO_2H/DCC/DMAP/molecular sieves; iv, RCO_2H/DCC/DMAP

Table 1 Transition temperatures for the new porphyrins

Compound	Transition	T/°C	ΔH/kJ mol^{-1}
3	Cr–N	330	44.7
	N–I	353	—
4	Cr–N	298	—
	N–I	320	—
5	Cr–S_A	330	44.3
	S_A–I	384	—
6	Cr–N	309	47.6
	N–I	433	—



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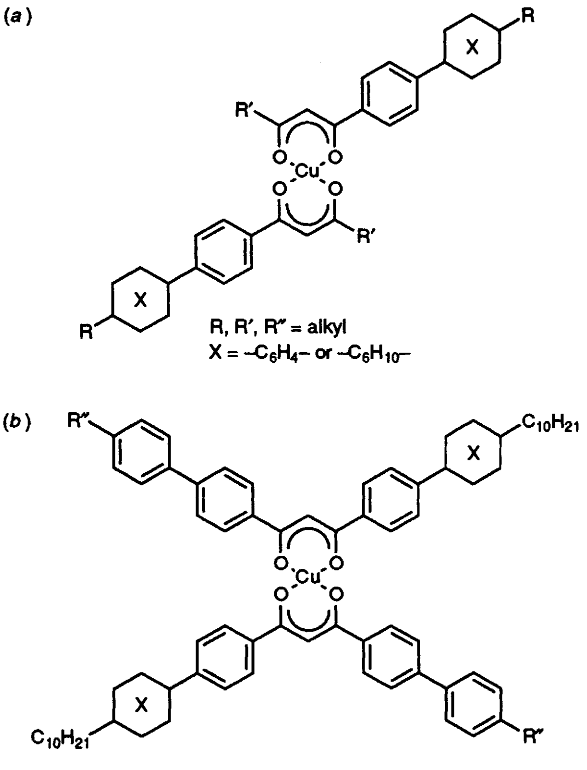

Fig. 1 Liquid crystalline Cu^{II} β-diketonates

on heating which persisted until clearing at around 384 °C, with decomposition setting in around 368 °C. Occasionally, a nematic phase would be observed in this compound, but its appearance was not in any way reproducible, leading to the view that it was due to the presence of some of the monoester **3** resulting from decomposition. The other diester, **6**, was different and, in common with the monoesters, melted to form a nematic phase at 309 °C which was observed to persist until around 433 °C when decomposition, which started around 410 °C, was finally complete.

That these inherently disc-like porphyrins can be persuaded to be rod-like in their behaviour is of interest, particularly in relation to the search for biaxial liquid crystals.[8] For some time it was simply considered that rod-like molecules would give rise to calamitic mesophases and disc-like molecules to discotic phases. However, there have always been interesting materials on the border of such 'rules', for example the dinuclear Pd^{II} mesogens described by Ghedini (**7** X = N, Y = H).[9] This motif is then made to show discotic phases by introducing further alkoxy groups on the periphery, **7**.[10]

In a more dramatic way, the β-diketonato complexes of Cu^{II} synthesised by Thompson *et al.*[11] (Fig. 1) illustrate a further complication in that the rod-like derivatives [Fig. 1(*a*)] show discotic phases while the more disc-like molecules [Fig. 1(*b*)] show calamitic phases.

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