Control of intermolecular porphyrin π–π interactions: low-melting liquid-crystal porphyrins with calamitic mesophases

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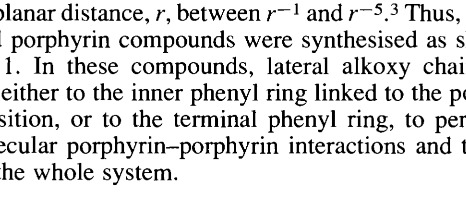
By control of intermolecular π–π interactions using 'fly-over' chains, calamitic nematic mesophases are observed in 5,15-disubstituted zinc porphyrins with greatly reduced melting and clearing points.

We have previously shown that inherently disc-like porphyrins could be persuaded to be rod-like liquid crystals with the synthesis of 5,15-disubstituted porphyrins (**1**).[1,2] In these porphyrins, three rings plus the porphyrin core appeared to define the minimum structural modifications to elongate the molecule in such a way that the reduction of the geometric anisotropy of the molecules owing to the incorporation of the bulky porphyrin moiety into a rod-like mesogenic system could be compensated. Thus, for example, we reported the compounds **1a** as showing crystal smectic mesophases,[1] while compounds **1b** and **1c–1e** were found to show a smectic A and nematic phases, respectively.[2] Because the porphyrin core is rigid and at least two rings were linked to it, it was perhaps inevitable that melting points were found to be very high. For example, prphyrin **1c** melted at 305 °C, showing a nematic phase which persisted to 433 °C, with decomposition setting in around 410 °C. Therefore, the question inevitably arose as to whether the melting points could be brought down to more manageable temperatures.

It is known that porphyrins usually aggregate *via* electrostatic attractions.[3] Such attractions can considerably increase intermolecular interactions and therefore enhance the thermal stability of both the crystal state and the mesophases.

In order to reduce these attractions, one of the strategies identified is to increase the face-to-face distance by including a 'soft' fragment(s) between the π-electron clouds to produce a large interplanar separation, as the π–π interaction varies with the interplanar distance, r, between r^{-1} and r^{-5}.[3] Thus, laterally branched porphyrin compounds were synthesised as shown in Scheme 1. In these compounds, lateral alkoxy chains were attached either to the inner phenyl ring linked to the porphyrin *meso* position, or to the terminal phenyl ring, to perturb the intermolecular porphyrin–porphyrin interactions and thus 'lubricate' the whole system.



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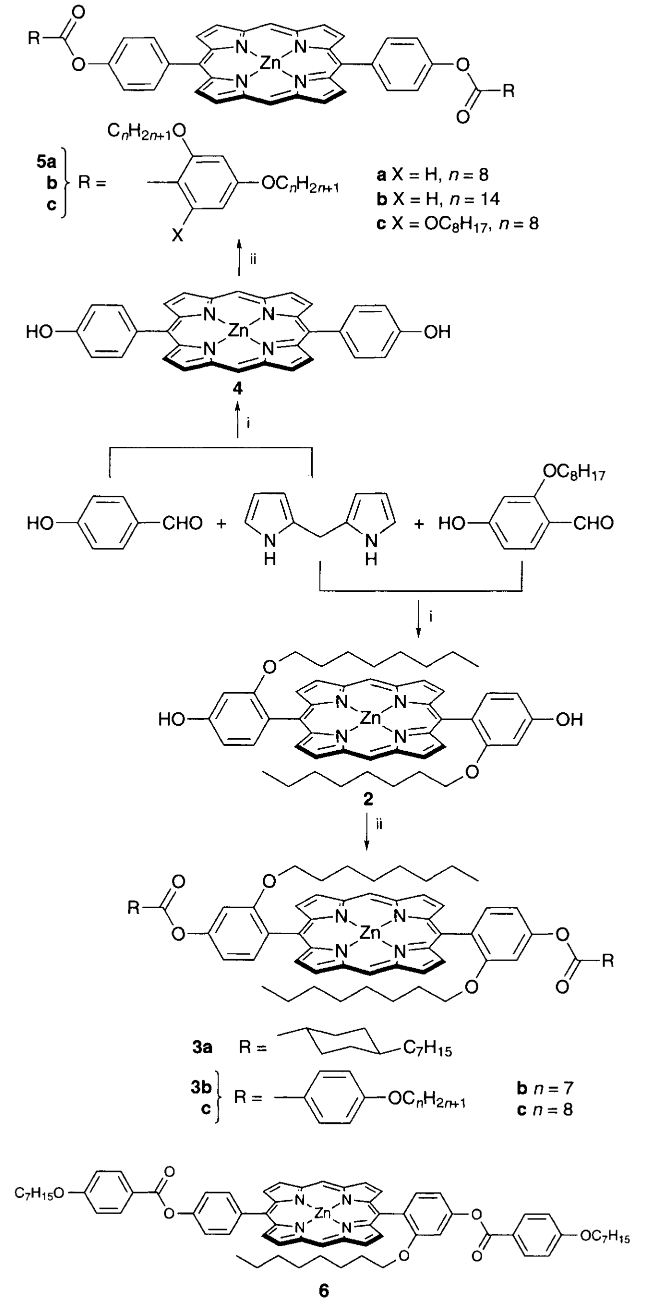
a R = C_nH_{2n+1}
b R = $C_7H_{15}O–C_6H_{10}–CO$
c R = $C_7H_{15}O–C_6H_4–CO$
d R = $C_8H_{17}O–C_6H_4–CO$
e R = $C_{14}H_{29}O–C_6H_4–CO$

Table 1 Upfield shifts (Δδ) of the terminal methyl protons of lateral chains in $CDCl_3$ solution

Compound	2	3a	3b	3c	5a	5b	5c
Δδ[a] (ppm)	0.60	0.64	0.60	0.60	0.02	0.17	0.08

[a] Δδ = δ(parent aldehyde or acid) −δ(porphyrin).

The target porphyrins, **3** and **5**, were obtained *via* the intermediate porphyrins **2** and **4** as shown in Scheme 1, using dipyrromethane obtained by a new, modified procedure.[4] In addition, porphyrin **6** was synthesised by the cyclisation of 2



Scheme 1 Synthesis of the new porphyrins. *Reagents and conditions*: i, a, $BF_3·OEt_2$, N_2, 20 h, room temp., CH_2CO_2–MeOH; b, *p*-chloranil, $Zn(OAc)_2·2H_2O$, reflux, 1 h; ii, excess RCO_2H, DCC, DMAP, activated molecular sieves.

Table 2 Transition temperatures for the new porphyrins and the relevant parent porphyrins

Porphyrin	Transition[a]	T/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	Parent porphyrin[b]	Transition[a]	T/°C
3a	$K_{\alpha\beta}$–$K_{\alpha\alpha}$	129	45.9	114	**1b**	K–S_A	316
	($K_{\alpha\beta}$ + $K_{\alpha\alpha}$)–I	178	48.4	107		S_A–I	383
	(I–N)	138	−2.0	−5			
3b[b]	$K_{\alpha\beta}$–N	141	—	—	**1c**	K–N	305
	N–I	177	—	—		N–I	433
	$K_{\alpha\alpha}$–I	192	—	—			
3c[b]	$K_{\alpha\beta}$–N	122	—	—	**1d**	K–N	300
	N–I	160	—	—		N–I	431
	$K_{\alpha\alpha}$–I	176	—	—			
5a	K–I	177	34.8	77	**1d**	K–N	300
						N–I	431
5b	K–K′	37	41.7	134	**1e**	K–K	228
	K′–I	143	33.6	81		K′–N	297
						N–I	356
5c	K–K′	126	3.8	10	**1d**	K–N	300
	K′–I	130	44.1	110		N–I	431
6	K–N	212	31.1	64	**1c**	K–N	305
	N–I	244	0.9	1.7		N–I	433

[a] K, crystalline smectic K phase; I, isotropic phase; N, nematic phase; S_A, smectic A phase. [b] Transition temperatures from Q. M. Wang, PhD Thesis, University of Sheffield, 1996, or ref. 3. [b] The phase transition temperatures were observed by microscopy. On heating, the α,β-atropisomers exhibited nematic mesophases, while the α,α-atropisomer were not mesomorphic; on cooling (> 10 °C min^{-1}), only the α,β-atropisomers were found, showing nematic mesophases, which remained in the glassy state and eventually crystallised to give a mixture of α,β- and α,α-atropisomers once more.

equiv. of dipyrromethane with 1 equiv. of 4-hydroxybenzaldehyde and 1 equiv. of 2-octyloxy-4-hydroxybenzaldehyde. As expected, a mixture of products was obtained and the designed porphyrin was isolated by chromatography. All porphyrins were fully characterised by ^{1}H NMR, FAB mass spectrometry and elemental analysis, for which satisfactory results were obtained.

The ^{1}H NMR spectra of porphyrins **3** and **6** in $CDCl_3$ solution showed upfield shifts for the lateral alkyl chain(s) as compared to the δ values of the reference compounds (*i.e.* the precursor aldehyde and acids used in the syntheses), as shown in Table 1. Since these δ values remained almost the same on tenfold dilution of solutions of **3b** and **5b**, intermolecular association can be excluded and the upfield shifts can therefore be explained as a result of the porphyrin ring current. Therefore, the lateral chains in porphyrins **3a–c** were folded over the faces of the porphyrin, one above and one below (α,β-atropisomer). However, a second set of peaks for the folded alkyl chains in porphyrins **3a–c** was found in the ^{1}H NMR spectra. Thus, the α,α-atropisomer was formed in the reaction as well as the α,β-atropisomer.[5] Although not discussed here in detail, variable-temperature proton NMR studies showed the transformation of the α,α-atropisomer into the α,β-atropisomer on cooling, suggesting the latter to be the more stable state. For porphyrins **5a, b**, however, only one conformation was observed by ^{1}H NMR, and, in addition, the shielding effect on the lateral chains in porphyrins **5a, c** was very weak when compared with porphyrin **3**. This suggested that the lateral octyloxy chains placed on the *ortho* position of the terminal benzene rings were not long enough to reach the out-of-plane, high π-electron density area. However, the lateral tetradecycloxy chains in porphyrin **5b** were affected by the porphyrin ring current to a greater degree than those of **5a, c**, although to a much lesser degree than for porphyrins **2** and **3**. This is consistent with the chains being much further away from the porphyrin ring system (shielding falls off with distance[6]) and therefore acting to broaden the molecules, hence destablising their mesophases. Porphyrin **6** showed only one isomer, as expected.

The mesomorphism of all the new porphyrins was studied using polarised optical microscopy and differential scanning calorimetry. The results are collected in Table 2.

Comparison of porphyrins **1b–d** with porphyrins **3a–c** showed that the melting points of porphyrin **3** were markedly reduced from over 300 °C (**1b–d**) to below 150 °C (**3a–c**), while clearing points were reduced by up to 271 °C. Mesophase ranges were now about 40 °C, but at much more accessible temperatures. Porphyrin **6** represented a sort of 'halfway house', reducing the melting point by about 100 °C and the clearing point by 200 °C, thus reducing the mesomorphic range to about 20 °C. However, porphyrins **5a–c** were not mesomorphic although they had relatively low melting temperatures. For example, the melting point of porphyrin **5c** was reduced to 130 °C. It is noted that porphyrins **3c** and **5a** are isomers, the only difference between them being the position of the lateral long chains. Thus, the position of these chains is clearly crucial in determining mesomorphism.

These are remarkable results which support the assertion that π–π interactions were primarily responsible for both the high melting and clearing temperatures of these porphyrins. Comparison between **1b** and **3a** is particularly interesting as the former showed only a smectic A phase (which we attribute to the tendency of the non-aromatic parts of the molecule to partition themselves together) while the latter showed a monotropic nematic phase. Thus, the lateral chain(s) have also suppressed the intermolecular interactions necessary for the formation of smectic phases.

In conclusion, we have demonstrated that having identified intermolecular π–π interactions as being largely responsible for high melting and clearing temperatures in 5,15-disubstituted metalloporphyrins, these can be screened out by appropriate molecular design to give much lower-melting and -clearing compounds.

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