Synthesis and Columnar Mesomorphism of Octa(dodecyl)tetrapyrazinoporphyrazine and its Copper(II) Complex

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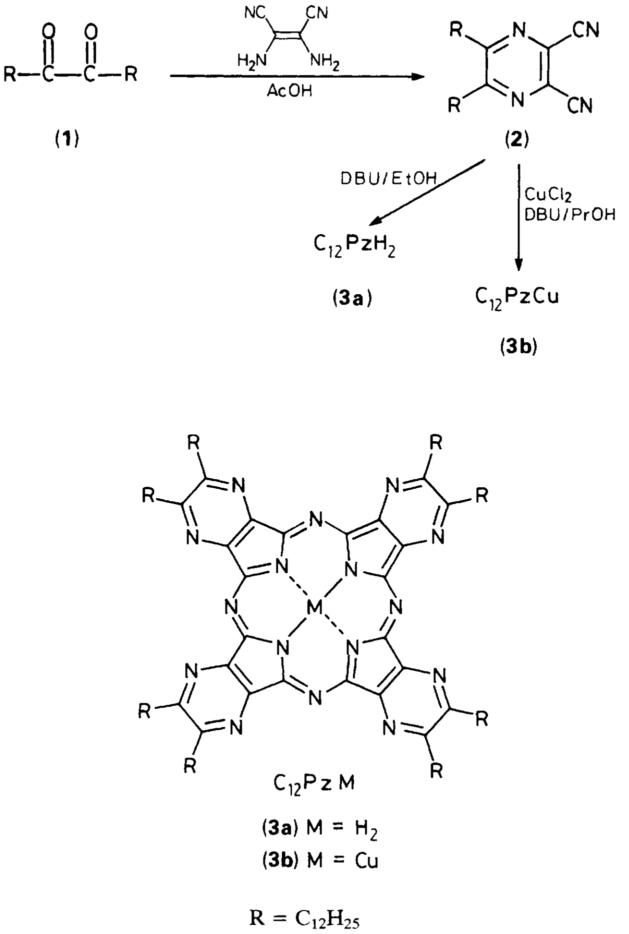
The disc-like compounds, 5,6,5′,6′,5″,6″,5‴,6‴-octadodecyltetrapyrazino[2,3-*b*:2′,3′-*g*:2″,3″-*l*:2‴,3‴-*q*]porphyrazine ($C_{12}PzH_2$) and the copper(II) complex ($C_{12}PzCu$), which have now been synthesized, exhibit different columnar mesomorphism (D_{hd} for $C_{12}PzH_2$, D_{rd} for $C_{12}PzCu$).

Long chain-substituted phthalocyanine derivatives are well known macrocyclic compounds which exhibit columnar mesomorphism.[1] Phthalocyanine is able to co-ordinate to various metals, and the resulting complexes have potential for use in a variety of applications.[2] The present macrocyclic compounds, $C_{12}PzH_2$ (**3a**) and $C_{12}PzCu$ (**3b**), are phthalocyanine (PcH_2) and PcCu analogues with nitrogen replacing carbon at positions 1,4,8,11,15,18,22,25. We have investigated the synthesis and the columnar mesomorphism of (**3a**) and (**3b**).

Compounds (**3a**) and (**3b**) were synthesised by the method in Scheme 1. The substituted diketone (**1**) was prepared by a literature method.[3,4] The dicarbonitrile (**2**) was obtained from



Scheme 1. Synthesis of the long chain-substituted tetrapyrazinoporphyrazine (**3a**) and the copper(II) complex (**3b**).

(**1**) in 85% yield by refluxing in glacial acetic acid with an excess of diaminomaleonitrile.[5] $C_{12}PzH_2$ (**3a**) was synthesized from (**2**) by refluxing in ethanol with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[6] $C_{12}PzCu$ (**3b**) was synthesized by refluxing a solution of (**2**) in n-propanol with DBU and copper(II) dichloride.[7] Compounds (**3a**) and (**3b**) were soluble in $CHCl_3$ and/or CH_2Cl_2. $C_{12}PzH_2$ (**3a**) was purified by column chromatography (silica gel, CH_2Cl_2, R_f 0.86) and recrystallization from tetrahydrofuran (THF); yield: 14%; $\lambda_{max.}$ (log ε) ($CHCl_3$) 340 (5.06), 564 (4.38), 571 (4.38), 605 (4.72), 618 (5.06), and 654 nm (5.18). $C_{12}PzCu$ (**3b**) was purified by column chromatography (silica gel, CH_2Cl_2, R_f 0.36) and recrystallization from ethyl acetate and a small amount of dichloromethane; yield: 8%; $\lambda_{max.}$ (log ε) ($CHCl_3$) 300 (4.71), 340 (4.99), 574 (4.50), and 634 nm (5.25). Satisfactory C, H, and N analyses were obtained for (**3a**) and (**3b**).

Interestingly, gelation of a THF solution of $C_{12}PzH_2$ took place on recrystallization from THF at −20 °C.[8] Microscopic observation of the gel revealed that it consisted of cotton-like long fibres and the solvent; it was destroyed by heating at >54 °C. In contrast, $C_{12}PzCu$ did not show the gelation in THF.

$C_{12}PzH_2$ and $C_{12}PzCu$ both exhibit columnar mesomorphism.[9] The phase transition temperatures and the enthalpy changes are summarized in Table 1. They were determined by using a polarizing microscope equipped with a hot plate, and by differential scanning calorimetry (DSC). The K_1 crystals of $C_{12}PzH_2$ transform into K_2 crystals at 94 °C and then change into the columnar mesophase at 118 °C; on further heating, decomposition occurs at 238 °C without clearing. The K_1 crystals of $C_{12}PzCu$ transform into K_2 crystals at 71 °C and then change into another crystalline phase K_3 at 92 °C; transformation into a columnar mesophase occurs at 114 °C, and decomposition at 288 °C without clearing.

Table 1. Transition temperatures (T_t) and enthalpy changes (ΔH_t) of $C_{12}PzH_2$ and $C_{12}PzCu$.[a]

Compound	Phase	$\xrightarrow[\Delta H_t/\text{kcal mol}^{-1}]{T_t/°C}$	Phase						
$C_{12}PzH_2$	K_1	$\xrightarrow[6.2]{94}$	K_2	$\xrightarrow[8.8]{118}$	D_{hd}	$\xrightarrow{238}$	Decomp.		
$C_{12}PzCu$	K_1	$\xrightarrow[4.9]{71}$	K_2	$\xrightarrow[0.74]{92}$	K_3	$\xrightarrow[10.2]{114}$	D_{rd}	$\xrightarrow{288}$	Decomp.

[a] Phase nomenclature: K = crystal, D_{hd} = hexagonal disordered columnar mesophase, D_{rd} = rectangular disordered columnar mesophase.

These columnar mesophases were identified by powder X-ray diffraction. $C_{12}PzH_2$ has a hexagonal disordered columnar mesophase (D_{hd})[9] at 150 °C, whereas $C_{12}PzCu$ has a rectangular disordered columnar mesophase (D_{rd})[9] at 150 °C. $C_{12}PzH_2$ gave two diffuse bands at *d* 4.7 and 3.5 Å in the X-ray wide-angle region, corresponding to the melt of the alkyl chains and the fluctuations of the interdisc-distance, respectively; a narrow reflection corresponding to the order of the interdisc-distance in this X-ray region is absent. It also gave three narrow reflections at *d* 27.8, 16.1, and 13.6 Å in the low-angle region, which correspond to (100), (110), and (200) respectively in a two-dimensional hexagonal lattice, lattice constant a = 32.2 Å. Therefore, $C_{12}PzH_2$ has a D_{hd} mesophase. $C_{12}PzCu$ also gave two diffuse bands at *d* 4.7 and 3.4 Å, corresponding to the melt of the alkyl chains and the fluctuations of the interdisc-distance at 150 °C, respectively. It gave five narrow reflections at *d* 28.9, 26.3, 16.4, 14.7, and 13.2 Å, which correspond to (200), (110), (310), (020), and (220) in a two-dimensional rectangular lattice, respectively, lattice constants a = 57.5, b = 29.6 Å.

Thus, the columnar mesophases D_{hd} in $C_{12}PzH_2$ and D_{rd} in $C_{12}PzCu$ could be identified from the X-ray powder diffraction patterns.

It has recently been reported that metals have the ability to modify the mesomorphism of ligands on co-ordination.[10,11] However, in most cases, the molecular shapes of the complexes are very different from those of the corresponding ligands.[10] For the examples reported here, it should be emphasized that the small change from H_2 to Cu in the centre of the same Pz core causes a drastic change of the mesomorphic structure from D_{hd} to D_{rd}.

The half-wave potentials for the reduction of $C_{12}PzH_2$ and $C_{12}PzCu$, determined by cyclic voltammetry, are −0.41 V for $C_{12}PzH_2$ and −0.55 V for $C_{12}PzCu$ (*vs.* saturated calomel electrode in dichloromethane solution). Thus, both these Pz derivatives are π-acceptors whereas all long-chain-substituted phthalocyanine derivatives are π-donors. To date, π-acceptor columnar mesogens have not been reported, so far as we know.

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