

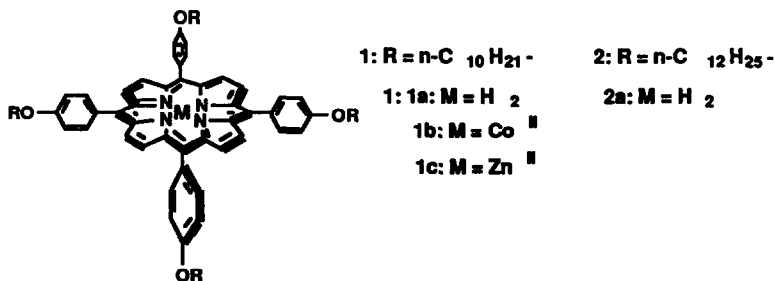
Novel Liquid Crystals Consisting of Tetraphenylporphyrin Derivatives

Shin-ichi Kugimiya* and Motoko Takemura

Department of Chemistry, College of General Education, University of Tokushima, Josanjima, Tokushima, 770 Japan

Abstract: Tetrakis(p-n-alkyloxyphenyl)porphyrin, **1**, has been found to form mesophases with a wide range of temperature (from 45.3 to 144.5°C: **1a**).

Control of orientation of porphyrin chromophores in condensed phase has been studied intensively¹⁻². One of the promising ways is utilization of Langmuir Blodgett (LB) techniques¹) or liquid crystallines²). In literature, some liquid crystalline porphyrins (LCP for discotic LC³)) have been previously reported; however all of them have *six to eight* alkyl chains on the porphyrin rings^{2,4}). Recently, Bard et al. reported that *octasubstituted* porphyrin derivatives and their zinc complexes showed mesophases and interesting optical properties of the ordered porphyrin chromophore. There is a simple question raised. Is *six to eight* alkyl chains with a plane core in a molecule necessary for forming discotic liquid crystalline? How many alkyl chains per a porphyrin ring are required for showing liquid crystalline properties? Tetrakis(p-n-alkyloxyphenyl) porphyrins have been found to form monolayer assemblies by LB techniques¹). In a viewpoint of structural analogy (discotic structure) between *tetrasubstituted* porphyrins and *octasubstituted* porphyrins, tetrasubstituted porphyrins might be good candidates for LCP. In this communication, we would like to report the liquid crystalline properties of *tetrakis*(p-n-alkyloxyphenyl) porphyrins and their metal complexes.



Meso-tetrasubstituted porphyrins **1a** and **2a** were prepared by usual procedure from corresponding *p*-n-alkyloxybenzaldehyde and pyrrole in propionic acid⁵). They were purified by column chromatography (silica gel; eluant: hexane + 30 % dichloromethane) and crystallized from a dichloromethane-hexane). Treatment of the free base with metal (cobalt or zinc) acetate in chloroform-methanol yielded corresponding metal complexes (**1b** and **1c**). The spectral (u.v.-vis., ¹H-NMR, FAB mass) data are in agreement with the assigned structures. The thermal and optical properties have been studied by differential scanning calorimetry (DSC: Simadzu DSC-50) and with a polarizing microscope (x60) equipped with a variable temperature stage. The calorimetric data are given in Table 1.

Table 1 Calorimetric Data^a for Compounds 1-2

compound		T/°C ($\Delta H/kJ\ mol^{-1}$)					
1a	C	45.3 (-6.79)	LC ₁	88.6 (-1.70)	LC ₂	144.5 (-53.56)	IL
1b	C	-24.8 (-6.65)	LC ₁	-13.8 (-1.10)	LC ₂	187.6 (-75.55)	IL
1c	C	-16.0 (-2.5)	LC ₁	91 (+9.1)	LC ₂	116.5 (-9.9)	LC ₃ 170.1 (-57.65) IL
2a	C	5.9 (-8.38)	LC ₁	77.2 (-2.46)	LC ₂	90.2 (-2.64)	LC ₃ 136.8 (-60.55) IL

a: Heating rate 10°Cmin⁻¹, C: crystal; LC₁ : liquid crystal phase; IL: isotropic liquid

p-n-Decyloxy compound **1a** has two LC phases (LC₁: 45.3-88.6°C; LC₂: 88.6-144.5°C; see Figure 1)⁶). Folding fan -like highly viscous texture obtained on cooling from the isotropic liquid of **1a** is shown in Figure 2. On cooling from LC₂ to LC₁, clefts in the texture grew gradually. Increasing alkyl chains from decyl to dodecyl, decreasing T_{C-CL1} while not so decreasing melting point. Cobalt complex **1b** displays LC phases extending a wide range of 210°C before melting to the isotropic liquid. On cooling from the isotropic liquid of **1b**, a large board-like texture was obtained. This texture is much more clear than that of free base **1a**. On continuing the cooling, the texture changed into the creviced one.

Thermal property of zinc complex **1c** is very different from that of other compounds as shown in Table 1. On heating other compounds at a rate of 10°C min⁻¹, endothermic peaks were observed during phase transitions. And these endothermic peaks in DSC are quantitatively reversible on a cycle of heating-

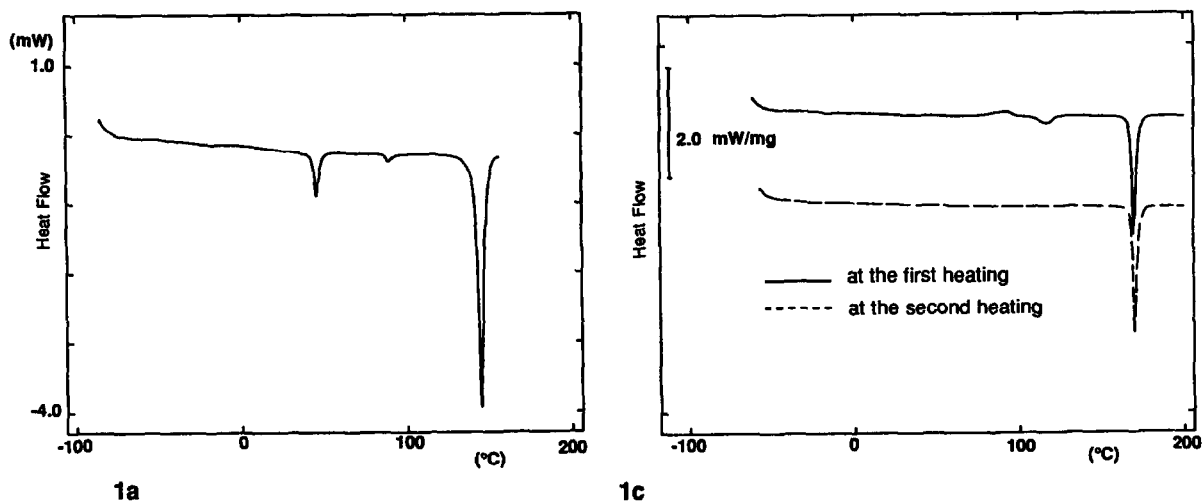


Figure 1. Differential scanning calorimogram of decyloxy compound **1a** and corresponding zinc complex **1c**; heating rate $10^{\circ}\text{Cmin}^{-1}$.

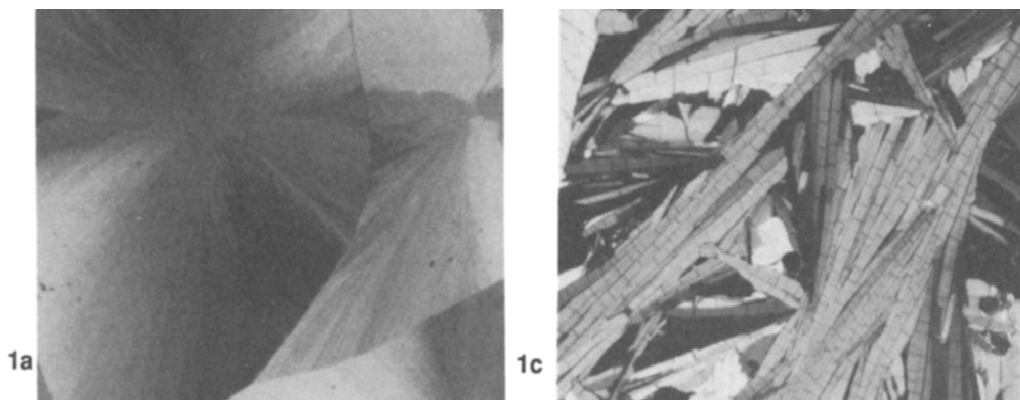


Figure 2. Optical texture of decyloxy compound **1a** and corresponding zinc complex **1c**; obtained on cooling from the isotropic liquid.

cooling-heating. However, for zinc compound **1c**, an exothermic peak at 91°C ($+9.1 \text{ kJ/mol}$) in DSC was observed. Moreover, peaks of zinc complex **1c** in DSC was irreversible on a cycle of heating-cooling-heating (see Figure 1). Angled stick-like texture of zinc complex **1c** was also different from that of cobalt complex **1b** and other free base porphyrin compounds **1a** and **2a**.

Detailed structure of LC phase of these compounds must await the results of EPR or X-ray analysis which are now underway.

In conclusion, porphyrins with *four* long alkyl chains per a porphyrin ring, such as **1a** and others, have been found to have LC properties with a wide range of temperature. For LC properties, *four* alkyl chains are sufficient. Because of meso-substitution (protecting meso-positions) of all compounds described here, these compounds might be more stable and easy to prepare than Bard's *octasubstituted* porphyrins.

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References and Notes

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- 6) m-n-Decyloxy compound was also prepared as a comparison. Meta-substituted compound was highly viscous liquid even at 10°C. Above 10°C upto 200°C, no texture of the compound was observed. This indicated that para substitution of tetraphenylporphyrin is essential for LC properties.

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