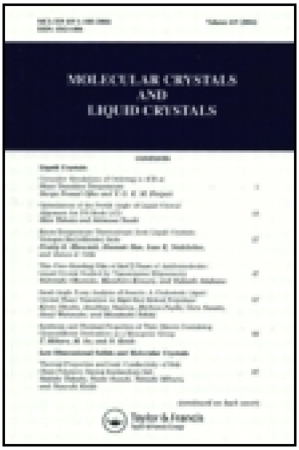

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# Synthesis and Properties of Novel Octasubstituted Metallophthalocyanines

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# SYNTHESIS AND PROPERTIES OF NOVEL OCTASUBSTITUTED METALLOPHTHALOCYANINES

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Abstract A series of novel metallophthalocyanines $(OC_{12}H_{25})_8MPc$, where M = Zn, Cu, Ni and Co have been prepared. These compounds are based upon the known metal-free (2,3,9.10,16,17,23,24) octakis(dodecyloxy)-phthalocyanine. These compounds all display discotic mesophases, and have been fully characterised.

## INTRODUCTION

Phthalocyanines and metallophthalocyanines have a great deal of chemical and thermal stability resulting from their highly delocalised π electron system. They are now widely used as photoconductors[1], gas sensors[2] and in molecular devices.

15 years ago, a new type of liquid crystal, the 'discotic' mesophase[3] was discovered. This was observed in organic molecules, whose structure was characterised by planar aromatic cores surrounded by flexible hydrocarbon chains. The molecules stack in columns and the individual columns form a hexagonal array. The ability of these molecules to assemble themselves in stacks confers on them one-dimensional properties arising from the anisotropy of these systems. For example the electrical conductivity of the material can be different when measured parallel to or perpendicular to the stacking direction. Thus metallophthalocyanines substituted with

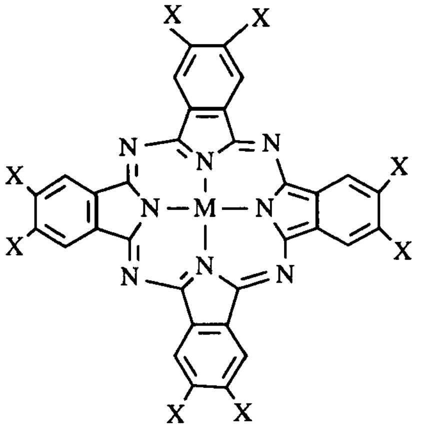
long aliphatic chains are not only important because of their liquid crystal properties, but also because of those properties arising from the one-dimensional nature of the system.

The first phthalocyanines of this type were described by Simon and co-workers[4] and Hanack *et al*[5]. They were octasubstituted in the peripheral (2,3,9,10,16,17,23,24) positions with long chained alkoxmethyl[6]groups. (Fig 1. series **1.**) More recently discotic behaviour has been reported for other metal-free and metallophthalocyanines, peripherally substituted with alkyl[7] and alkoxy[8,9] groups. (Fig 1 Series **2,3**)

**Fig. 1**

1. X = $CH_2OAlkyl$
2. X = Alkyl
3. X = OAlkyl

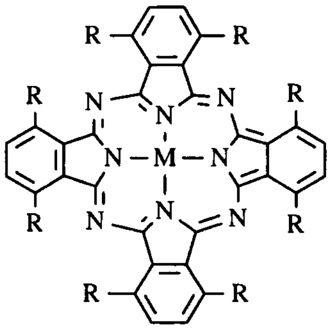
M = 2H or Metal



Cook and co-workers are carrying out an extensive study of non-peripherally (1,4,8,11,15,18,22,25) octasubstituted phthalocyanines, which runs parallel to the 2,3 octasubstituted work mentioned above. The non-peripheral substututed work has produced a series of alkyl[10] alkoxy[11] and alkoxymethyl,[12] octasubstituted phthalocyanines. (Fig 2 series **4, 5 & 6**).

**Fig. 2.**

4. R = Alkyl, $C_4$- $C_{10}$
5. R = OAlkyl
6. R = Alkoxymethyl
7. R = $C_7H_{15}$ M = Zn, Cu



It was discovered that the non-peripherally substituted alkoxyphthalocyanines display no mesomorphic behaviour and melt directly into the isotropic liquid[12] unlike their peripherally substituted analogues. More recently[14] research has been carried out into the effect of inserting a central metal (zinc or nickel), on the mesophase temperature range for the non-peripherally octaalkyl substituted phthalocyanine (series **4**).

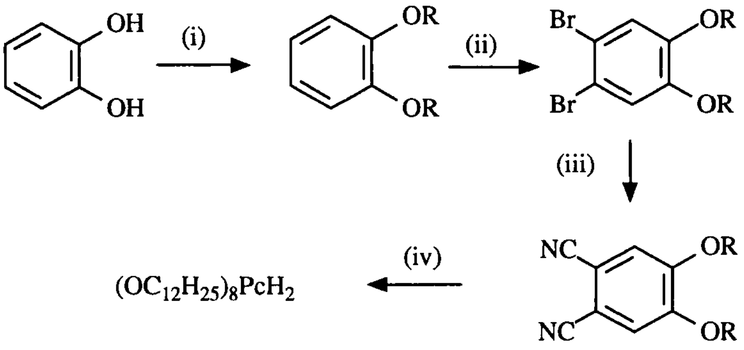
This paper is concerned with novel metallophthalocyanines based upon the known peripherally substituted ocktakis(dodecyloxy)phthalocyanine[13], where M = Cu, Ni, Zn & Co, and describes the synthesis, characterisation and examination of their melting behaviour.

## SYNTHESIS

### Metal-free Phthalocyanine

The metal-free phthalocyanine was prepared according to the method proposed by Van der Pol *et al*[13] and illustrated in scheme 1.

**Scheme 1**



(i) $K_2CO_3$, DMSO, RBr (ii) $CH_2Cl_2$, $Br_2$ (iii) CuCN, DMF,
(iv) Dimethylaminoethanol.

Various problems arose in step (iii) and optimum conditions were found to involve 4.5 molar equivalents of copper cyanide and very dry solvents and apparatus. Step (iv) the conversion of the phthalonitrile to the phthalocyanine was only successful when freshly distilled dimethylaminoethanol and pure phthalonitrile (min. quantity 7g) were used. Purification of the phthalocyanine is of paramount importance if the discotic mesophase is to be observed. The methods used were soxhlet extraction, and recrystallisations, followed by flash chromatography. The product, obtained as an intense green powder, was insufficiently pure to observe mesophase behaviour and was therefore further purified by the following methods;

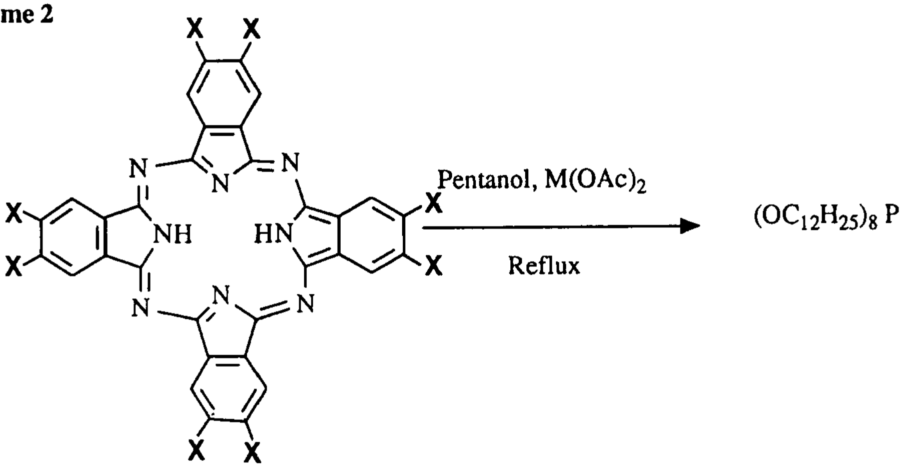
1. Column chromatography on a 1g. scale using flash silica and toluene as eluent.
2. Triple recrystallisation, by dissolving the phthalocyanine in boiling hexane and allowing it to crystallise at out at room temperature.
3. Column chromatography using gravity silica and chloroform as eluent.

At this stage the phthalocyanine was pure enough to undergo metal insertion reactions.

## Metallophthalocyanines

The metallophthalocyanines were prepared, in a one pot reaction, by refluxing the metal-free phthalocyanine in pentanol, followed by the addition of the metal acetate.

**Scheme 2**



The reaction was monitored by UV spectroscopy to ensure complete insertion of the metal(Scheme 2). Table 1 summarises the characterisation of the MPc's.

## RESULTS AND DISCUSSION

### Characterisation

The elemental analysis of each derivative was satisfactory (Table 1). The $^1$H NMR of the $(OC_{12}H_{25})_8$MPc's were broadened but the spectra of the alkyl chains could be assigned. The metal-free phthalocyanine gave very clear peaks and in this case the aromatic and benzylic protons could be assigned. The UV spectra of the $(OC_{12}H_{25})_8$MPc confirmed the successful insertion of the metal into each $(OC_{12}H_{25})_8PcH_2$. A characteristic singlet was found in the 700nm region of the spectra, which replaced the doublet normally observed in that region and characteristic of the metal-free Pc. (Table 1 )

Table 1

| Phthalocyanine | Yield % | Analysis C | Analysis H | Analysis N | $\lambda_{MAX}$. nm |
|---|---|---|---|---|---|
| $(OC_{12}H_{25})_8PcH_2$ | 26 | 76.09<br>(77.29) | 10.33<br>(10.64) | 4.53<br>(5.63) | 700.9<br>663.8 |
| $(OC_{12}H_{25})_8PcCo$ | 63 | 74.29<br>(75.20) | 9.21<br>(10.25) | 4.93<br>(5.45) | 669.2 |
| $(OC_{12}H_{25})_8PcNi$ | 60 | 74.87<br>(75.17) | 9.70<br>(10.33) | 5.34<br>(5.48) | 669.3 |
| $(OC_{12}H_{25})_8PcZn$ | 65 | 74.82<br>(75.00) | 10.74<br>(10.20) | 4.54<br>(5.40) | 678.4 |
| $(OC_{12}H_{25})_8PcZn$ | 55 | 72.57<br>(74.90) | 10.33<br>(10.20) | 4.84<br>(5.40) | 675.3 |

## Thermotropic Behaviour

The melting behaviour of the metallophthalocyanines was investigated by microscopy and observing the mesophases both with and without cross polarisers (Table 2). The metal-free phthalocyanine underwent a transition from crystal to mesophase at 95°C, and underwent a transition to isotropic liquid at 333°C. These values differ from those recorded for this molecule in the literature[13] (K - M 85°C, M - I 309°C). The $(OC_{12}H_{25})_8CuPc$ had also been previously prepared, but was reported to decompose when heated above 300°C. The $(OC_{12}H_{25})_8CuPc$ synthesised in the present study from carefully purified phthalocyanine formed, however, an isotopic liquid (310°C).

Table 2

| Phthalocyanine | Temperature °C K | | M | I |
|---|---|---|---|---|
| $PcH_2$ | 95-110 | [62.5] | - | 333 |
| PcCo | 85-91 | [52.5] | - | 345 |
| PcNi | 96-98 | [51.0] | - | 254 |
| PcCu | 105 | [68.0] | - | 310 |
| PcZn | 99.3 | [-] | - | 375 |

K = crystalline solid, M = Mesophase, I = isotropic liquid

[ ] = represents temp. of crystallisation

The thermal effect of cobalt, nickel, copper and zinc on the thermal behaviour of the octakis(dodecyl)oxyphthalocyanine were also investigated. In each case one mesophase was observed on cooling the $(OC_{12}H_{25})_8MPc$'s from the isotropic liquid phase. The mesophase of each $(OC_{12}H_{25})_8MPc$ aligns homeotropically. A series of fern-like crystals grow covering the entire slide. The resultant pattern does not show birefringence until pressure is applied to the surface of the slide. When the optical textures of the $(OC_{12}H_{25})_8PcH_2$ and $(OC_{12}H_{25})_8CuPc$ were first studied[13], needle-like structures were reported. However, the present study shows that these needle-like structures are in fact the spines of the ferns.

Initial examination of results show the $(OC_{12}H_{25})_8NiPc$ to have a lower mesophase-isotropic(M-I) transition temperature than the metal-free phthalocyanine and the other $(OC_{12}H_{25})_8MPcs$. The $(OC_{12}H_{25})_8ZnPc$ has the highest M - I transition of all four $(OC_{12}H_{25})_8MPcs$ studied at 372°C. This is maybe due to the fact that the zinc within the $(OC_{12}H_{25})_8ZnPc$ is more likely to be five coordinate. This would have a stabilising effect within the column and hence increase the transition temperature[14].

## SOLID STATE PROPERTIES

The formation of thin films of these $(OC_{12}H_{25})_8MPcs$ is being studied[15] by both the Langmuir-Blodgett technique and by spin-coating. The electrical conduction properties of these films are currently under investigation.

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