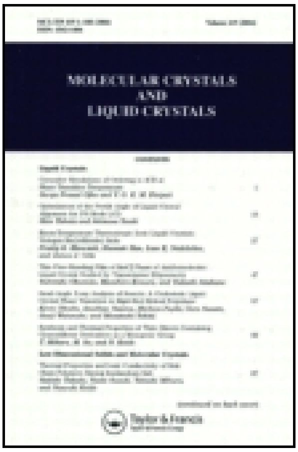

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Preparation of Smooth Crystalline Phthalo-cyanine Films by Spin Coating

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PREPARATION OF SMOOTH CRYSTALLINE PHTHALOCYANINE FILMS BY SPIN COATING

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Abstract Smooth thin films of soluble, octa-alkyl phthalocyanines have been prepared by spin coating. Optical spectroscopic studies showed strong splitting of the Q band, very similar to that observed in LB films and attributed to Davydov splitting. This indicates a highly ordered structure with two different crystal sites. The very high degree of order was confirmed by electron diffraction and X-ray diffraction. The technique offers a useful method of preparing films for STM studies, preliminary studies of which are consistent with a columnar structure.

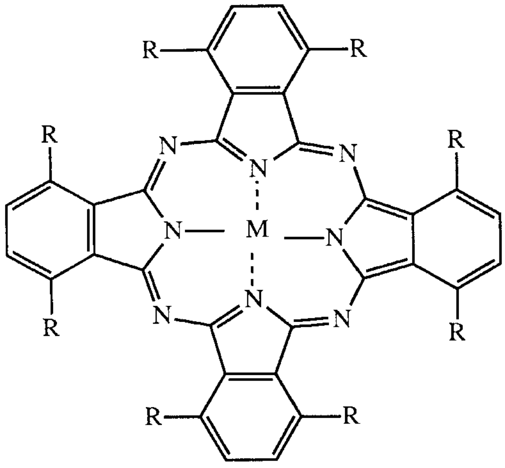
INTRODUCTION

Most electronic devices exploiting the electronic properties of phthalocyanines are likely to require thin films. Furthermore the films must be of uniform thickness to give uniform field, and be ordered to maximise the carrier mobility, which determines the device performance. For thermally stable phthalocyanines, epitaxial growth from the vapour phase shows considerable promise. Functionalised phthalocyanines are not normally sublimable, but with suitable side groups the Langmuir Blodgett technique is appropriate. Spin coating offers a quick and easy method of producing uniform crystalline films of soluble phthalocyanines, avoiding the requirement of polar side groups and polar (normally aqueous) subphase.

The materials chosen were a range of 1,4,8,11,15,18,22,25 octa substituted metal free and metal phthalocyanines which are known to show discotic liquid crystal properties. Films were spun on glass substrates rotating at 2000 rpm using saturated solutions in toluene. Scanning electron microscopy showed that, provided that the solutions had been filtered to remove particulate matter, then the film was exceptionally smooth and featureless [1,2]. The film thickness was estimated to be 200-1000Å on the basis of comparison of the optical absorption with that of a standard solution.

MATERIALS

The materials used in this study were analogous to those already reported [1,2] and are shown in figure 1. Their synthesis has been described elsewhere [3]. The visible spectroscopy studies were confined to metal free materials (1a,1b,1c) although there is no evidence currently to suggest that the metal constituent has any effect on molecular ordering of these materials. The materials used for the X-ray diffraction studies were octa-hexyl metal free (1a) and octa-octyl cobalt (1b) phthalocyanines.



Compound	R	M
a	C6	H_2
b	C8	Co
c	C8	H_2
d	C6	H_2
e	C4	H_2

FIGURE 1 Functionalised phthalocyanine molecule.

EXPERIMENTAL

The phthalocyanines were deposited from toluene by the spin coating method. The details of the deposition and substrate preparation have been described elsewhere [2]. Films of mixtures of phthalocyanines were prepared from equimolar amounts of the two components dissolved in toluene. The u.v./visible spectra of the solutions were the sum of those of the two components, indicating the absence of complexation.

RESULTS AND DISCUSSION

(a) X-ray Diffraction

Experiments were carried out using a MAC Science MXP3V powder diffractometer using the goniometer arrangement for thin film analysis, with a Cu target, x = 1.542Å. The spectra obtained are presented in figures 2 and 3, the spectra in each figure are displaced horizontally to compare repetitive scans. The spectra refer to single component films of (1a) and (1b). Strong peaks occur for both materials and in the case of (1a) the peak is particularly sharp. The value of 2θ at which the peaks occur is quite low ca. 4-5Å. The actual values and their corresponding α-spacings, calculated assuming a first order peak, are shown in table 1.

Compound	2θ/degrees	d/ Å
1a	4.56	19.36
1b	4.18	21.12

TABLE I

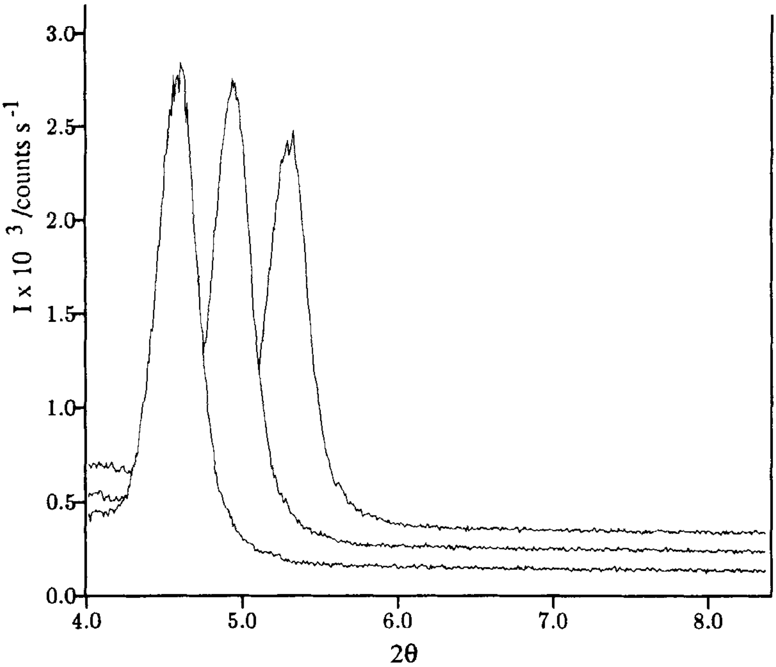


FIGURE 2 X-ray diffraction scan of octahexyl metal free phthalocyanine.

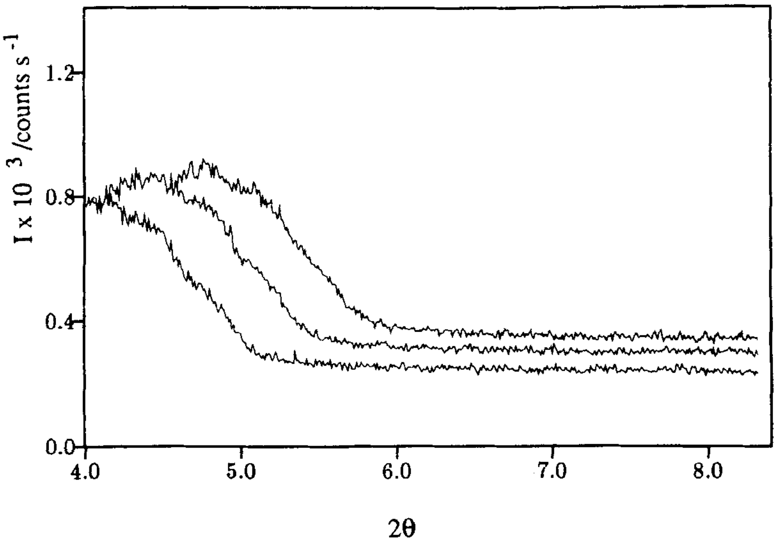


FIGURE 3 X-ray diffraction scan of octaoctyl cobalt phthalocyanine.

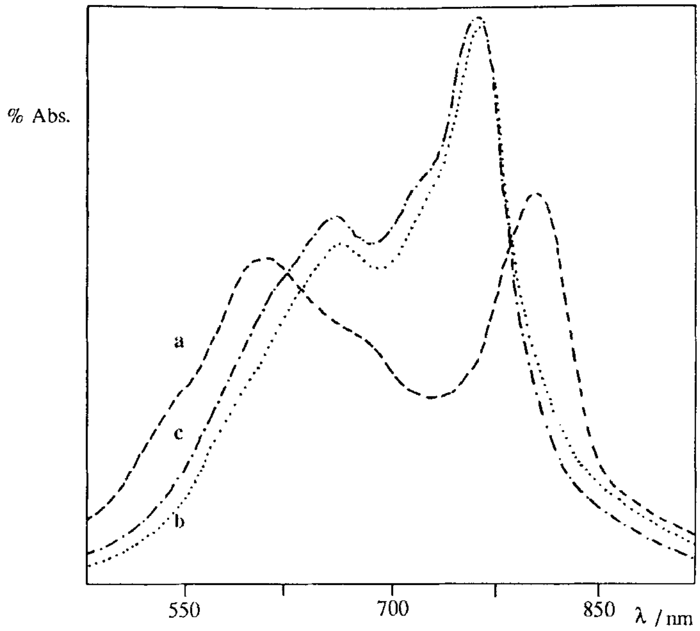


FIGURE 4 Visible region spectra of (a) octaoctyl metal free Pc, (b) octahexyl metal free Pc and (c) a 1:1 mixture of the two components.

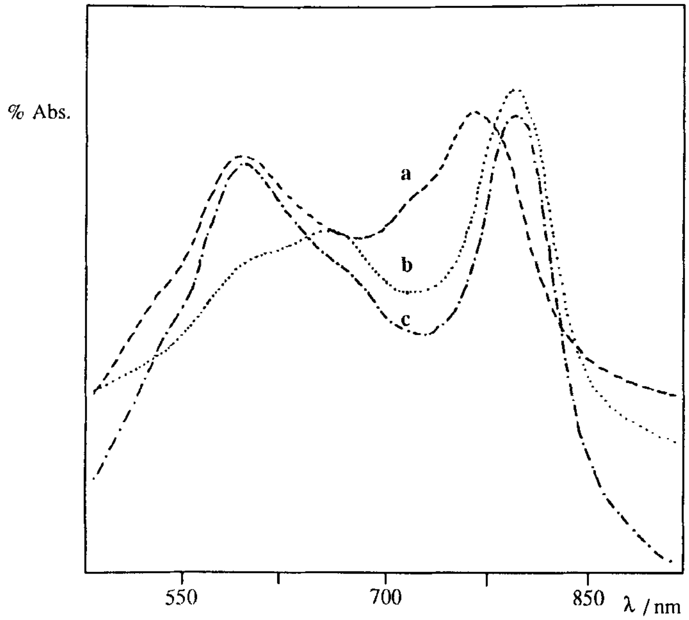


FIGURE 5 Visible region spectra of (a) octaoctyl metal free Pc, (b) octabutyl metal free Pc and (c) a 1:1 mixture of the two components.

The d values obtained are smaller than the effective diameters of analogous materials in their columnar mesophase, ca. 22-23Å [4], though this is still indicative of considerable crystalline ordering and may suggest a tilting of the molecular stacks. That such ordering occurs in a film deposited in less than one tenth of a second is very remarkable.

(b) Visible Region Spectroscopy

Film spectra were recorded over the range 550-850 nm using a Hitachi -3400 spectrometer. The spectra are presented in figures 4 and 5. In both cases, spectra of the parent molecules are presented for comparison. In figure 4, the two compounds vary be their chain length from C_8 (4.a) to C_6(4.b). It can be seen that even though this seems to be a slight chemical variation, the spectra are clearly different in shape and intensity. Similarly in fig. 5 the two single component films, with chain length C_8(5a) to C_4(5b), vary considerably. In both instances the visible region spectra of the mixed component films resemble very closely the spectra of one of their parents. In fig. 4 the mixture resembles the spectrum of the octahexyl component (4.b) whereas in fig.5 the mixture spectrum resembles that of the octaoctyl component. It thus appears that a solid solution is formed with one component dictating the crystal structure.

(c) High speed photography

A video film taken at 200 frames per second shows that during the deposition process the liquid solution advances radially in the form of an annulus, with solvent evaporation and crystallisation occurring in its wake. It appears that the forces associated with the circular motion and viscous flow exert an ordering effect as the solvent molecule evaporates.

GENERAL CONCLUSIONS

The experiments show that uniform, crystalline films of solubilised phthalocyanine can be prepared by spin coating. Experiments are in progress to determine the size and orientation of the crystallites, and the relationship between the film morphology and its electrical properties.

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