

Deposition of Ordered Phthalocyanine Films by Spin Coating

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Thin films of octaalkyl-substituted phthalocyanines were prepared by spin coating. The films were remarkably smooth and showed optical absorption spectra with Davydov splitting, characteristic of crystalline order, similar to those of structurally related compounds prepared by the Langmuir–Blodgett technique. The crystallinity was confirmed by X-ray diffraction. The technique may have advantages for device fabrication.

Keywords: Phthalocyanine; Spin coating; Thin film

1. Introduction

The generation of high-quality, thin, continuous films is a major requirement for organic films to be utilised by the modern electronics industry. Such films can be incorporated into a wide variety of highly specialised and miniaturised components. The most common method of film deposition is sublimation, which has the advantages of ease and accuracy of deposition. The limitation of this technique is that it is only appropriate for those materials with a very high thermal stability, and in general films are rarely uniform in thickness or structure unless they have been epitaxially grown. Often, materials that have been functionalised to confer desirable electrical properties to the bulk are unsuitable for sublimation. An alternative approach is that of Langmuir–Blodgett (LB) film preparation. This generates highly ordered films but requires special conditions and normally demands specific functionalisation to allow the technique to work. The side groups needed are not necessarily desirable for bulk electrical properties.

The method of spin coating materials that have been functionalised to confer solubility is another approach to the deposition of high-quality thin films. Electrical properties of spin-coated and LB films of tetraalkylamido-derivatised phthalocyanines have been reported,¹ with the observation that spin-coated films may be less ordered than the corresponding LB films on the basis of conductivity measurements. Further thin and remarkably smooth phthalocyanine spin-coated films have been prepared² using derivatives solubilised by four neopentox groups. The films displayed a measurable photoconduction but no information about film crystallinity could be obtained. In this paper we report the preparation of equally smooth but thicker highly crystalline films using octa-substituted phthalocyanines.

2. Materials

The materials used in this study were organic-solvent soluble metal-free and metallated phthalocyanines bearing octyl chains at the 1,4,8,11,15,18,22 and 25 sites; the compound names are abbreviated as follows, octaoctyl metal-free phthalocyanine (1), octaoctyl copper phthalocyanine (2), and octaoctyl nickel phthalocyanine (3) (Fig. 1). Their synthesis has been described elsewhere.³ Attempts to deposit them by the LB technique were unsuccessful because they do not form stable Langmuir monolayers.⁴ However, in exhibiting discotic mesophases at elevated temperatures,^{5–7} they clearly show a propensity for self-ordering. It was anticipated that such a

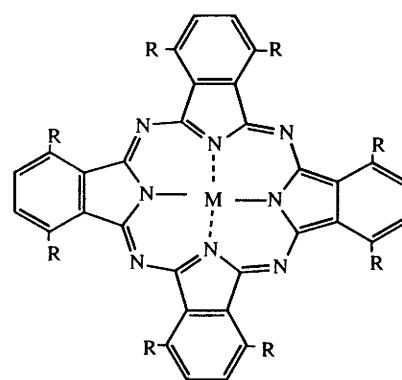


Fig. 1 Octa-substituted phthalocyanines. R = C₈H₁₇; 1, M = H; 2, M = Ni; 3, M = Cu

property would be conducive to generating ordered films by the spin-coating technique.

3. Film Deposition

Two main factors are critical to the production of high-quality films: the quality of the solution and the cleanliness of the substrate surface. A standard procedure was adopted in the preparation of both solution and substrate, and this was applied to all samples.

3.1 Solutions

A variety of solvents were used initially in the search for the most appropriate solvent for each sample. The two best solvents were tetrahydrofuran (THF) and toluene. Although THF proved a better solvent for one of the compounds (1), toluene had the advantage of being a good solvent for all the compounds used and was therefore used for the sake of consistency. The criterion for choice of solvent was whether the materials dissolved rapidly in a minimal volume, generating concentrated solutions without undissolved particles. Since it was desirable to use near saturated solutions, some particulate debris was inevitable. This along with any dust or foreign bodies was removed by passing the solution through a glass sinter (grade 3) fixed inside a glass pipette. Typical quantities of solution were (50–100) × 10^{−6} dm³ so the solutions needed to be used on the day of preparation to avoid evaporation of the solvent.

3.2 Substrates

Glass substrates were used throughout this study although other substrates such as silica and single-crystal silicon have been used successfully. Ordinary glass microscope slides were used and cut to an appropriate size, typically 20 mm × 20 mm. These were then scrubbed with detergent solution, rinsed with distilled water and left to soak in chromic acid for at least 5 h. After they had been soaked the substrates were again rinsed with distilled water and the surface water removed using a nitrogen jet directed through a thin glass nozzle. Once prepared, the substrates were stored individually in plastic boxes inside a desiccator cabinet to avoid contamination with dust.

3.3 Spin Coating

The basic principle of this method involves the rapid drying of a solution as it rotates and spreads on a surface revolving at speeds of *ca.* 2000 rpm. The apparatus comprises a rotating platform powered by a motor. In the centre of the platform is a small hole which acts as a vacuum chuck when connected to a rotary pump. The substrate is held firmly in position by atmospheric pressure and accelerated to a speed of *ca.* 2000 rpm by a variac. The speed of rotation is measured by a small light detector positioned beneath the platform, custom made for the purpose, which is connected to a frequency counter.

A single drop of solution is allowed to fall to the rotating substrate surface from a micropipette positioned not more than 5 mm from the platform. As the drop makes contact with the substrate, it spreads out across the substrate under the influence of centrifugal forces. As it moves, the solvent evaporates rapidly from the solution leaving, if conditions are correct, a smooth continuous film of phthalocyanine. Films deposited in this way are of the order of 500–1000 Å thick, depending on the particular material, and are clearly visible to the naked eye since they are coloured (usually blue or green). An assessment of thickness was made by comparing the absorption spectra of spun films with that of a solution of known concentration.

Films prepared in a similar way by first dropping solution onto a stationary substrate and then accelerating to the appropriate speed produced films of inferior quality. This was attributed to the very rapid evaporation of solvent before the centrifugal forces causing the spreading could act. Since smooth even films were desired, this method was not pursued further.

4. Results and Discussion

4.1 UV-VIS Spectroscopy

Spectra were recorded over the range 550–850 nm using a Hitachi V-3400 spectrometer.

In common with the related unsubstituted phthalocyanines, spectra of solutions of the metallated substituted phthalocyanines used in the present work show a strong Q-band absorption at *ca.* 700 nm. In the case of the metal-free compound the lower symmetry lifts the degeneracy of the excited state and the band is split, by *ca.* 50 nm, into a doublet. Spectra of the spin-coated films are quite different and, significantly, are also different from those of neopentoxo derivatives described in ref. 2. Although the neopentoxo phthalocyanine spun films have highly structured Q-bands, suggesting some order may have occurred, they do not show the clearly resolved splitting observed here (Fig. 2). Indeed the shapes of the Q-band absorption for the films of **1**, **2**, and **3** provide good evidence for molecular ordering.

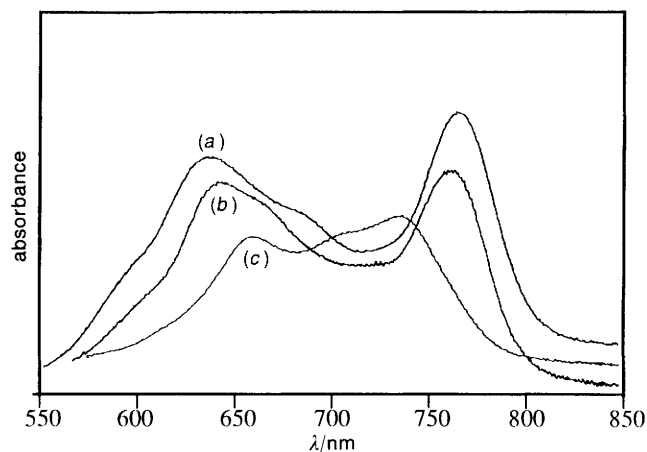


Fig. 2 Visible-region spectra of the spun films of (a) **1**, (b) **2**, (c) **3**

Aggregates of phthalocyanine molecules generally show a broad band, blue-shifted with respect to the solution phase Q-band.⁸ However the spin-coated films show both blue- and red-shifted bands, Fig. 2. This is consistent with Davydov splitting which occurs in a crystalline lattice containing translationally non-equivalent molecules.⁸ Comparison of the spectrum of the film of the metal-free compound, Fig. 2(a), with the spectrum reported⁹ for the same material crystallised from its mesophase is particularly informative; the two are very similar in terms of λ_{max} . The prominent bands observed at 635 and 765 nm for the film compare with λ_{max} 634 and 766 nm for the crystal state. The same band pattern is also observed in the spectra of the well ordered LB films prepared from closely related phthalocyanines having a hydrophilic group on two of the side chains.⁹ LB films of octaalkyl phthalocyanines substituted in the peripheral positions (2,3,9,10,16,17,23,24) have been deposited by the horizontal lifting method.¹⁰ The films also give rise to visible-region spectra with a Q-band structure similar to those presented here. The octadodecyl derivative gives a split Q-band with λ_{max} of 614 and 774 nm. Results obtained from polarised spectra suggest that the molecules are oriented parallel to the substrate surface. For the LB films of ref. 8 a columnar 'herringbone' arrangement of the molecules was proposed *cf.* the β -form of phthalocyanine itself,¹¹ with the columns aligned predominantly along the dipping direction. The spectral similarities discussed above imply that the spin-coated film of **1** has at least regions of similar columnar order. The question of the orientation of the columns will be addressed in future work.

The spectrum of the spin-coated film of **2**, Fig. 2(b), is similar to that of the metal-free derivative. However, that of **3**, Fig. 2(c), shows a definite blue-shifted peak at the higher wavelength end of the absorption envelope. Preliminary experiments with other octaalkyl phthalocyanines show that spectra appear to fall into these two categories. The differences may reflect variations in the orientations and/or packing of the molecules in the films.

4.2 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, $\lambda = 1.542$ Å. In this case, θ , the angle of tilt of the sample relative to the incident X-rays is fixed at an angle greater than zero (typically 1–2°) and the scan is described as 2θ scanning. The scattering vector always bisects the angle between incident and reflected rays thus

yielding information about layering in the plane perpendicular to the vector. This method is particularly sensitive for polycrystalline or very thin samples. The angle of tilt θ , and the width of the slit, ω are related to the active area of the sample. Setting $\theta=2^\circ$ and $\omega=0.1$ the irradiated area is *ca.* 16 mm^2 , this ensures maximum sample area without edge effects. With $\theta=2^\circ$, $2\theta=4^\circ$ and no information about the film can be resolved below this threshold.

The spectra obtained are presented in Fig. 3, spectra are displayed at a stacking tilt for clarity. It can be seen that small peaks occur at low angles, *ca.* $4\text{--}6^\circ$, which correspond to *d*-spacings of: 1, 17.8 \AA ; 2, 16.8 \AA ; 3, 18.2 \AA ; peaks occurring below 4° are below the cut off region of the instrument and should be ignored. These values are lower than the effective diameters of the molecules of 1 and 2 in their columnar mesophases, *ca.* $22\text{--}23\text{ \AA}$.⁵ This could reflect a more compressed structure within the film, a tilting of the molecular plane to the substrate or some factor which reduces the full extension of the side groups. Current work is being undertaken to investigate more fully the interaction of the side groups with respect to minimum-energy configurations and packing. For some of the films, a degree of variation in peak intensity was observed when the angle of rotation of the sample relative to the incident X-rays was varied; this could be related to differing crystalline domains over the area of the film.

4.3 Microscopy

Films were investigated using a scanning electron microscope (SEM). The films were found to be virtually featureless in agreement with results already reported for other soluble phthalocyanines,² indicating their smoothness. Experiments using an optical microscope with polarised light revealed that for some films, in particular the octaoctyl nickel derivative, small crystallites became apparent in an otherwise smooth film viewed under normal light. On close inspection of the crystallites, a preferred orientation in a radial direction was observed. Thus, despite the high degree of local order, the crystallite size is very small.

4.4 Film Growth

These results strongly suggest that the process of spin coating of the present soluble phthalocyanines leads to a film of

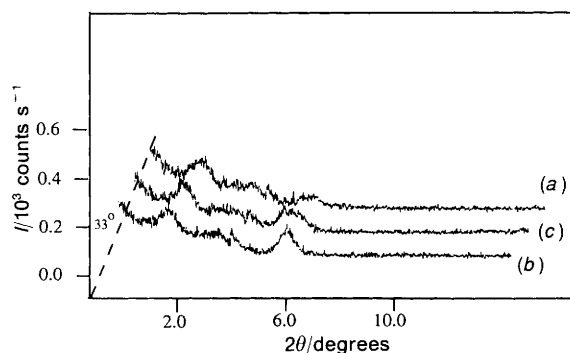


Fig. 3 X-Ray spectra of (a) 1 ($2\theta=4.96^\circ$ gives $d=17.8\text{ \AA}$), (b) 2 ($2\theta=5.25^\circ$ gives $d=16.8\text{ \AA}$), (c) 3 ($2\theta=4.86^\circ$ gives $d=18.2\text{ \AA}$). Spectra displayed at an angle of tilt as shown

uniform thickness possessing remarkably high crystalline order, apparently similar to that produced by the LB technique for amphiphilic analogues. The way in which order is achieved by spin coating is not fully understood but we may tentatively propose the following mechanism. As the film spreads out under the influence of centrifugal force, solvent evaporates and the molecules are progressively immobilised. A video recording of the spinning process was taken, which when slowed down to view the process step by step, showed the solution spreading in the way expected for a hydrophobic solvent on a hydrophilic substrate. The shape of the solution front, *i.e.* the outermost edge of the spreading drop, was convex; it is therefore assumed that it is under uniaxial compression due to the centrifugal forces acting upon it. The molecules will tend to pack in such a way as to achieve a 'closest packing' type arrangement along the spreading direction, which will be retained as the solvent evaporates. It appears that this process occurs from the centre outwards.

5. Conclusions

This paper has shown that spin coating can provide a quick and easy method of producing high-quality continuous films of uniform thickness which appear to have crystalline order similar to that of LB films of analogous compounds. The requirement is that the materials are significantly soluble in volatile solvents without the necessity for surface activity.

We would like to express thanks to SERC for research grants (S.M.C. and J.M.) and also IMS, Japan, for support (S.M.C.). Thanks are also due to Dr. S. Bandow, IMS, for help with the X-ray diffraction studies.

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