

Phthalocyanine thin films*

Michael J. Cook

School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

Abstract: Liquid crystalline phthalocyanines which are formally amphiphilic, with substituents which between them provide hydrophilic headgroups and hydrophobic tailgroups, deposit as well-ordered films by the Langmuir–Blodgett method. A comparison of normal incidence transmission Fourier transform infrared (FTIR) spectra and Reflection absorption infrared (RAIR) spectra shows that the molecules are arranged with the cores essentially perpendicular to the surface. Atomic Force Microscopy (AFM) of the surface of films of the compounds reveals columnar structures which are anisotropically aligned. Spin-coated films of various phthalocyanines and analogues, which contain either a thiophene or pyridine ring in place of one of the benzenoid rings, also contain columnar assemblies. Phthalocyanine derivatives incorporating a thiol or disulfide unit at the end of an alkyl chain substituent can be deposited by self-assembly from solution onto a thin gold film supported on a glass slide or silicon wafer. FTIR measurements of the self-assembled monolayer (SAM) films demonstrate that orientation of the macrocyclic ring within these films is dependent upon the length of the mercaptoalkyl tethering chain. Evanescent wave stimulated fluorescence can be detected from the films when the support is used as a waveguide. The potential applications of examples of these films in the area of gas sensing is discussed.

INTRODUCTION

Phthalocyanines (Pcs) (Fig. 1) are well-known commercial blue–green pigments, the colour arising from an intense absorption in the visible region spectrum, the Q-band. Examples of Pcs have also been used as catalysts for several manufacturing processes [1]. However, Pcs also show interesting photophysical properties, redox properties, and both photo and dark semiconductivity, which render them particularly interesting for use in more technologically advanced applications. They are used in photocopiers, laser printers [2] and in optical data storage systems [3], and research into their potential as photosensitizers in photodynamic therapy is well advanced [4]. There is further active research into exploiting these materials in, for example, photovoltaic (PV) cells [5] and fuel cells [6] and as the active component in gas sensing systems [7,8]. A number of potential devices which may arise from this research rely upon the fabrication of the Pc compounds as thin films. Accordingly, there is continuing interest in depositing these compounds in this type of formulation, with research focused on the design of suitable derivatives for providing ordered and reproducible films.

Sublimation is a standard method for forming films of unsubstituted compounds, not least because their usual insolubility in common solvents leaves them rather intractable for other types of formulation work. In the 1980s, however, the pioneering work from Roberts' group [9] and Snow and Barger [8], working with derivatives rendered soluble in organic solvents through the introduction of substituents, demonstrated that such compounds can be deposited by the Langmuir–Blodgett (LB) technique. The present paper summarises some of the contributions made by the group at the University of East Anglia, UEA, in the area of Pc LB films, and also reviews subsequent work on films generated by spin-coating and self-assembly methods.

* Lecture presented at the 4th International Symposium on Functional Dyes—Science and Technology of Functional π -Electron Systems, Osaka, Japan, 31 May–4 June 1999, pp. 2009–2160.

Correspondence: E-mail: M.cook@uea.ac.uk

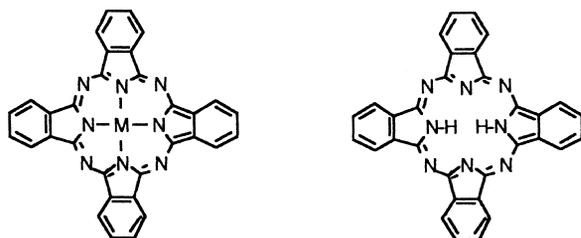


Fig. 1 The structure of the phthalocyanine ring system. M can be one of *ca.* 70 elements of the Periodic Table. These are primarily metal or metalloid elements, but can also be H (right-hand side), to give 'metal-free phthalocyanine'.

LANGMUIR–BLODGETT FILMS

There are two principal stages in the LB procedure [10]. The first is the formation of a compressed molecular monolayer at the air–water interface. The compound of interest is administered as a dilute solution in a low boiling organic solvent to the surface of high purity water, contained in a trough. The trough is fitted with a movable barrier; once the organic solvent has evaporated, the barrier is slowly closed to reduce the surface area. As the surface area is reduced, the molecules are compressed together to form a close packed monolayer. The second step is the transfer of the molecules, one molecular monolayer at a time, onto a solid substrate. This is achieved by dipping the substrate into the supporting water through the surface monolayer. In Y-type deposition, a second layer is deposited as the substrate is withdrawn. Accordingly, a molecular bilayer is deposited during one cycle. Subsequent dipping cycles build up thicker films. The original studies by Langmuir and Blodgett used simple amphiphilic compounds, such as stearic acid, and many multimolecular layers could be built up. Early work in the 1980s on the deposition of Pcs by the LB method used organic solvent soluble tri- and tetra-substituted derivatives. Subsequently, many further examples, especially of tetra-substituted compounds, have also been successfully deposited [11]. Despite the fact that the materials are normally used as mixtures of isomers and apparently lack the conventional amphiphilic character of simple stearic acid, the compounds generally give LB films having some degree of molecular order and uniformity. A commonly observed feature of the visible region spectrum of the LB films of these compounds is a blue shift (relative to the solution phase spectrum) of the Q-band absorption, attributed to cofacial alignment of the Pc molecules stacked in columnar assemblies within the deposited monolayers.

Research at UEA has focused on the design and synthesis of octa-substituted Pc derivatives for LB deposition [11]. An advantage of this number of substituents is that compounds can be prepared as a single isomer. The strategy has been to develop compounds which are formally more amphiphilic than the tetra-substituted compounds referred to above. Extensive studies have shown that compounds particularly suitable for generating LB films are those which incorporate six hydrophobic alkyl groups and two hydrophilic hydroxyalkyl substituents, the $R_6(OH)_2Pc$ s depicted in Fig. 2. Examples have been prepared with alkyl chains, R, from hexyl through to decyl; typical side-chains bearing the hydrophilic headgroups contain four or six methylene groups. Metal-free and metallated derivatives have been examined [12]. The combination of substituent groupings has ensured adequate solubility in organic solvents for transfer to the water surface and insolubility in the water subphase. The substituents also sustain mesophase behaviour, whereby the molecules generate discotic columnar liquid crystal phases. The latter implies a degree of spontaneous self-organisation which may assist in the formation of columnar stacks at the water surface which are then transferred as such to the substrate surface.

The compounds are synthesised using a lithium alkoxide catalysed cross-condensation of a 3,6-dialkyl phthalonitrile and a 3,6-dihydroxyalkylphthalonitrile [12] (Fig. 2). The precursor phthalonitriles are themselves synthesised *via* the Diels–Alder reaction of fumaronitrile and a 2,5-dialkylthiophene-1,1-dioxide and a 2,5-bishydroxyalkylfuran respectively. For the cross-condensation reaction, a ratio of 9:1 in favour of the 3,6-dialkylphthalonitrile ensures that there are only two main products formed, namely the required $R_6(OH)_2Pc$ and the simpler octa-alkyl derivative, R_8Pc . After work-up, the two components are present as metal-free derivatives and are readily separated by chromatography. Metallation is achieved by reaction with a metal salt.

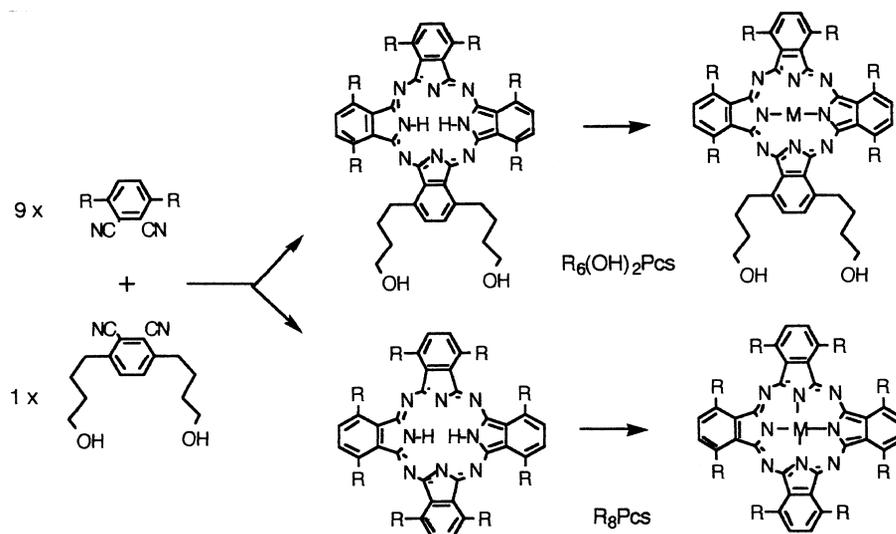


Fig. 2 Scheme showing the synthesis of $R_6(OH)_2Pcs$ with R_8Pcs formed as by-products.

The R_8Pcs do not form simple monolayers at the water surface, the molecules apparently stacking on top of each other to some extent. They cannot be deposited as LB films by the conventional dipping procedure described above [13]. However the $R_6(OH)_2Pcs$ behave very satisfactorily. Surface area measurements indicate that the compounds are standing more or less vertically at the surface of the water in the compressed monolayer. LB deposition from the compressed monolayer proceeds Y-type onto substrates whose surfaces are first rendered hydrophobic.

Fourier transform infrared (FTIR) spectroscopy provides a powerful means of probing molecular orientation within a film. Two experiments are particularly important (Fig. 3). A normal incidence transmission spectrum of a film can be obtained providing it is supported on an IR transparent substrate such as silicon. The electric field vector then interacts with the vibrational modes polarized parallel to the surface. In reflection absorption infrared spectroscopy (RAIRS), a film supported on a gold surface is probed at a grazing angle, *ca.* 85° . Through the metal-surface selection rule, only modes polarized perpendicular to the surface are active. Spectra have been acquired for films of various examples of $R_6(OH)_2Pcs$ deposited on both silicon and gold. A significant difference in the two types of spectra is a strong out-of-plane stretching mode at 760 cm^{-1} in the transmission spectra which is virtually absent in the RAIRS spectra. The data thus indicate that the molecules are oriented with the plane of the ring approaching the perpendicular to the surface [12,14].

Confirmation of this conclusion is forthcoming from measurements of film thickness. The thicknesses of very thin films formed by one, two and three dipping cycles of $R_6(OH)_2Pc$, $R = C_{10}H_{21}$, have been investigated using Atomic Force Microscopy (AFM), the tip being used to remove material down to the substrate surface [15]. The depth of the hole provides a measure of the film thicknesses which for one, two and three bilayers are *ca.* 40, 80 and 120 \AA respectively. This demonstrates a uniform build up of the films as further monolayers are added. The thickness of a bilayer is almost twice the estimated width of the molecule from the polar headgroups across to the end of the alkyl groups on the opposite side of the molecule and thus confirms the near-vertical orientation of the molecules. Low angle X-ray reflectivity measurements, typically of 15 dip films, show two or three orders of diffraction and a bilayer spacing of *ca.* 41 \AA [16].

Investigation of the surface topography of the films by AFM reveals that the molecules are deposited as columnar stacks. The homogeneity of the columnar assemblies and the orientation of the column axes within the outermost monolayer have been analysed by AFM for the one, two and three bilayer films of the compound discussed above. The lateral extent of the ordered areas covers at least $10\text{ }\mu\text{m}^2$ and there is very clear evidence of a predominant alignment. Of 82 images taken at different regions of the film surface, *ca.* 83% show columns whose axes are aligned to within $\pm 30^\circ$ of the dipping direction [15].

Films have also been deposited onto glass substrates bearing interdigitated platinum electrodes to

investigate their potential for gas sensing [16,17]. The films were exposed to gas blends of 1–5 ppm NO_x gas in air for 2 min. The devices were then left in an air flow for 2 min to recover, and the sequence repeated. Changes in conductivity during these cycles were proportional to the concentration of the NO_x gas. Significantly, the magnitude of the change is dependent upon how the device is constructed. The sensitivity of the device is greater when the arms of the electrodes are perpendicular to the dipping direction rather than parallel to it. This result is consistent with the anisotropic packing of the columnar assemblies referred to above. In the former case, the columnar assemblies straddle the shorter distance between the electrodes and thus the greater response implies conduction along the axis of the column. There is good evidence of selectivity in the response to gases. Thus there are no responses upon exposure to 10–30 ppm of ammonia, 1–5 ppm of sulfur dioxide and 0.2–1 ppm of chlorine.

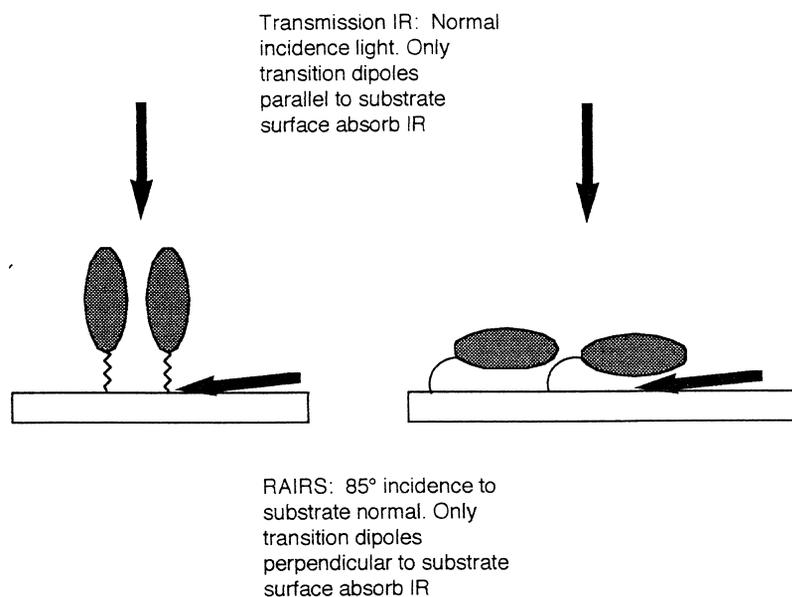


Fig. 3 The distinction between normal incidence transmission infrared and RAIR spectroscopy.

SPIN-COATED FILMS

Evaporation of solutions of any of the Pcs in Fig. 2 leaves the material as a thin film. If the solution is on a substrate rotating at, typically, 2000 rpm, a 'spin-coated' film is generated. X-Ray reflectivity measurements show diffraction peaks consistent with layering within the spin-coated film structure with the d spacing approximately that of the width of the molecules in the case of the R_8Pcs [18] and twice the width for the molecules of an example of an $\text{R}_6(\text{OH})_2\text{Pc}$ [19]. The evaporation process has been investigated by transmission electron microscopy (TEM). In these experiments, solutions of R_8Pcs in tetrahydrofuran (THF) have been evaporated onto carbon-coated copper grids and observed as they gel. The micrographs show the formation of 'molecular wires', corresponding to the generation of columnar assemblies of the molecules during the evaporation process [20]. The spin-coated films undergo molecular reorganisation on heating and this can be monitored by changes in the visible region absorption spectrum. The transition temperatures correspond very well to phase and mesophase transitions observed in the bulk solid [21].

The simplicity of spin-coating as a film-forming method is attractive and the UEA group has extended the work to other Pc-type derivatives in which a heterocyclic ring replaces one of the benzenoid structures (Fig. 4). All the compounds form smooth even films, apparently free of crystallites. Films of the thiophene analogues show a very broad red-shifted band over the region 600–800 nm [22]. In contrast, but with one exception, films of the pyridine-containing compounds show visible region absorption band envelopes similar to those of the corresponding spectra of films of the R_6Pcs . The exception is the film of the zinc derivative. There is good evidence that, in the solution phase, this compound forms an 'edge-to-face' dimer through coordination of the pyridine nitrogen atom of one molecule with the zinc at the centre

of a second [23]. The film spectrum is very similar to the solution phase spectrum; electron microscopy of the gel formed during evaporation of a solution of the compound confirms that no columnar structure is formed during the evaporation process.

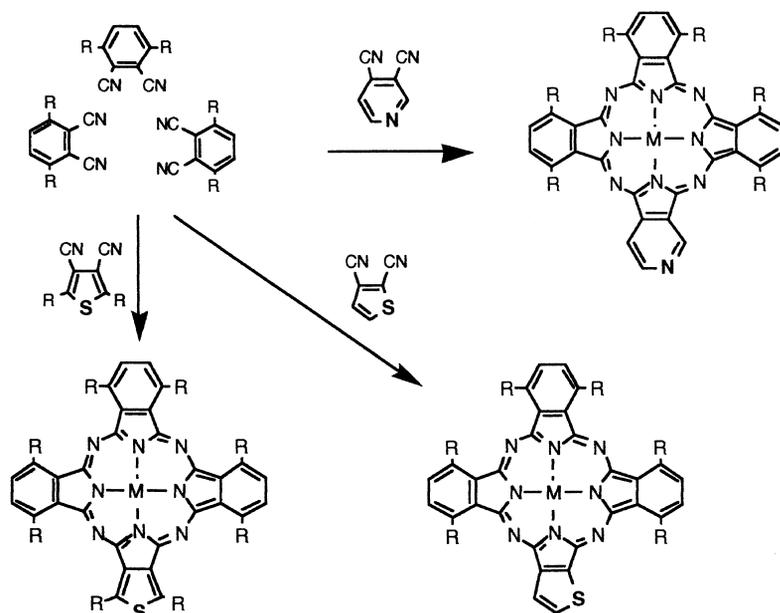


Fig. 4 Examples of thio- and pyridino-tribenzoporphyrazines, M = H, Ni, Zn.

SELF-ASSEMBLED MONOLAYER (SAM) FILMS

SAM films are formed *via* reaction of a functional group within a molecule with the surface of a solid substrate. SAMs are of interest because the chemically bound monolayer is intrinsically more robust than, for example, LB films. Furthermore, from the point of view of sensor technology, response times to analytes are expected to be fast when the film is particularly thin. Typical approaches for the formation of SAMs include the reactions of thiols and disulfides at gold or silver surfaces and of trichlorosilylalkyl derivatives with hydrophilic groups at the surface of glass or silicon. Much fundamental work has been undertaken with simple functionalised alkane derivatives [10]. In the case of alkylthiols on gold, it has been established that the monolayer films are densely packed with a high degree of order, with chains typically oriented at *ca.* 65° to the substrate surface.

Research at UEA has been concerned primarily, although not exclusively [24], with SAMs deposited onto gold-coated glass slides [25–27]. For these studies, a single ‘tether chain’ has been included in the molecule to connect the Pc to the surface. Accordingly, syntheses analogous to that depicted in Fig. 2 have been devised to form the corresponding series of R₇(OH)Pcs (Fig. 5). These have been converted into the corresponding thiol derivatives, R₇(SH)Pcs, or disulfide derivatives, R₇PcSSR₇Pc [28] (Fig. 5). The thiols and disulfides all readily form SAM films on gold surfaces. The films can be characterised by the FTIR techniques referred to above [25–27]. RAIR spectra have been measured of SAMs typically supported on a gold film *ca.* 500 nm thick. However, it has also been possible to obtain normal incidence transmission spectra when the SAM is deposited onto a very thin gold coating, *ca.* 100 nm thick. For these studies, the gold is deposited onto a silicon wafer. The two types of spectra obtained for the SAM derived from a disulfide with a short, (CH₂)₃, tether are very different. There are absorptions assignable to the N—H and aromatic C—H stretching frequencies in the normal incidence transmission spectrum, but they are apparently absent in the RAIR spectrum. In view of the ‘selection rules’ depicted in Fig. 4, these observations are consistent with the Pc core aligned parallel to the gold surface.

Experiments with further examples of R₇(SH)Pcs with longer tethers, (CH₂)₈ and (CH₂)₁₁, have revealed that, as the tether length is increased, the core of the Pc is no longer parallel to the surface and, in the case of the compound with the longest tether, apparently approaches the normal to the surface [29].

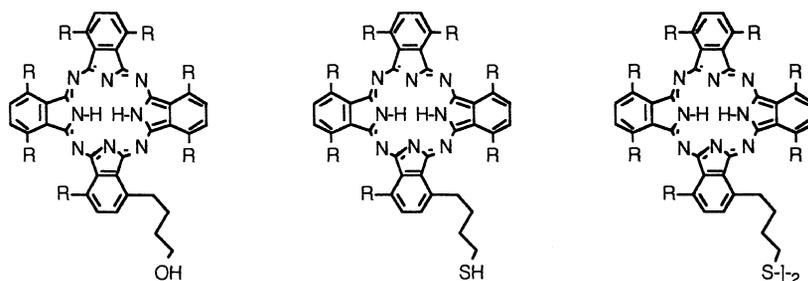


Fig. 5 Left, precursor $R_7(OH)Pc$ s for synthesis of Pc derivatives for SAM deposition; middle, $R_7(SH)Pc$ s; right, R_7PcSSR_7Pc s.

In a further set of experiments, the glass slide bearing the gold coating and SAM film has been used as a waveguide; 670 nm light from a laser diode has been waveguided down the longitudinal axis of the slide and the evanescent wave emanating from the surface has been shown to photoexcite the Pc molecules in the SAM, leading to their fluorescence. Comparisons of SAMs with Pcs bound to the gold with a short, $(CH_2)_3$, and a long, $(CH_2)_{11}$, tether have shown that the fluorescence from the latter is by far the greater. This can be attributed, at least in part, to reduced quenching of the excited state by the gold surface which is clearly further away with the longer tether [27].

Fluorescence quenching by external molecules can, in principle provide the basis for an optical sensing device. Exposure of the SAM with the longer chain tether to 200 ppm NO_2 gas showed that the fluorescence is indeed reversibly quenched. In further experiments, changes in the surface plasmon resonance (SPR) reflectivity signal were observed when the SAM was exposed to NO_2 in proportion to concentration, pointing to a further optical method for the detection of this gas [26].

CONCLUSION

Research at UEA has demonstrated that Pc derivatives designed with self-organising properties can generate well-ordered molecular assemblies. Mesogenic compounds which contain both hydrophobic tailgroups and hydrophilic headgroups, eg the $R_6(OH)_2Pc$ series, deposit as LB films which contain a good degree of ordering. Layer spacing experiments indicate that the molecules stack more or less perpendicularly to the surface, while AFM studies of the surface topography have identified columnar structures which are aligned predominantly along the 'dipping direction'. This anisotropy is also manifested in conductometric experiments in which the films are deposited onto interdigitated electrodes with the dipping direction parallel or perpendicular to the electrodes arms and then exposed to NO_x gas. Examples of the same compounds and the simpler mesogenic octaalkyl derivatives, R_8Pc s, also form even spin-coated films. They contain layer spacing and presumably the molecules self assemble into columnar structures as the solvent evaporates. This supposition is supported by TEM studies of evaporating solutions on a TEM grid. The spin-coated films show reversible molecular reorganisation upon heating, with transition temperatures the same as, or similar to, those for phase and mesophase changes exhibited by the bulk materials. Thiopheno-tribenzoporphyrines and pyridino-tribenzoporphyrines can also be spin-coated. The films of the former exhibit a broad band absorption envelope in the visible region spectrum.

Highly substituted Pcs bearing a mercaptoalkyl group, the $R_7(SH)Pc$ series, and the corresponding disulfide derivatives form self-assembled monolayer films on gold surfaces. The latter are formed by vacuum deposition of gold onto a solid substrate, usually appropriately treated glass slides. The SAM films can be detected by RAIR spectroscopy and by transmission IR spectroscopy if the gold layer is sufficiently thin and supported on an IR transparent material such as a silicon wafer instead of glass. Experiments indicate conclusively that the molecular packing in the SAM is dependent upon the structure of the molecule and especially the length of the mercaptoalkyl linkage used to tether the molecules to the gold surface. A short tether leads to a SAM in which the core of the Pc molecule is essentially parallel to the gold surface. However, if the tether is long, the cores are aligned with their planes closer to the normal to the surface. When the glass slide is used as a waveguide, the evanescent wave at the surface of the substrate excites the molecules and fluorescence can be detected, the fluorescent intensity being higher when the tether to the Pc ring is longer.

ACKNOWLEDGEMENTS

This work has been performed with the help of post-doctoral assistants Drs Isabelle Chambrier and Jim McMurdo and a number of research students, in particular Richard Poynter, Carmine Ruggiero, Geoff Bryant, Denise Mayes, David Miles, John Simmons, and Ali Jafari-Fini. Their contributions and enthusiasm are much valued. I am also especially grateful for the major contributions made by Dr David A. Russell, Tim Simpson and David Revell at UEA in developing the SAM work, and to others for particular measurements, notably Dr Robert M. Richardson (Bristol) for the X-ray reflectivity work, Dr Steve Thorpe at the HSE laboratories in Sheffield for help with gas sensing and Dr Marisela Vélez (Madrid) for the AFM studies. Finally, this work would not have been possible without the financial support received from the EPSRC, the CEC HCM contract CHRX-CT94-0558, DERA and ICI.

REFERENCES

- 1 F. H. Moser, A. L. Thomas. *The Phthalocyanines*, Vol. 2, *Properties* p. 87. CRC Press, Boca Raton, FL (1983).
- 2 P. Gregory. *High-Technology Applications of Organic Colorants*, p. 759. Plenum Press, New York (1991).
- 3 R. Ao, L. Kilmert, D. Haarer. *Adv. Mater.* **7**, 495 (1995).
- 4 L. Milgrom, S. MacRobert. *Chem. Br.* **45**, (1998).
- 5 D. Wöhrle, D. Meissner. *Adv. Mater.* **3**, 129 (1991).
- 6 A. B. P. Lever, M. R. Hempstead, C. C. Leznoff, W. Lui, M. Melnik, W. A. Nevin, P. Seymour. *Pure. Appl. Chem.* **58**, 1467 (1986).
- 7 J. D. Wright. *Prog. Surf. Sci.* **31**, 1 (1989).
- 8 A. W. Snow, W. R. Barger. In *Phthalocyanines—Properties and Applications* (C. C. Leznoff, A. B. P. Lever eds), p. 341. VCH Publishers, NY (1989).
- 9 S. Baker, G. G. Roberts, M. C. Petty. *Proc. Inst. Electr. Eng., Part 1* **130**, 160 (1983).
- 10 A. Ulman. *An Introduction to Ultrathin Films: from Langmuir–Blodgett to Self-Assembly*. Academic Press, San Diego/London (1991).
- 11 M. J. Cook. *J. Mater. Chem.* **6**, 677 (1996).
- 12 M. J. Cook, J. McMurdo, D. A. Miles, R. H. Poynter, J. M. Simmons, S. D. Haslam, R. M. Richardson, K. Welford. *J. Mater. Chem.* **4**, 1205 (1994).
- 13 M. J. Cook. *J. Mater. Sci. Mater. Electr.* **5**, 117 (1994).
- 14 R. H. Poynter, M. J. Cook, M. A. Chesters, D. A. Slater, J. McMurdo, K. Welford. *Thin Solid Films* **243**, 346 (1994).
- 15 M. Vélez, S. Vieira, I. Chambrier, M. J. Cook. *Langmuir* **14**, 4227 (1998).
- 16 A. Cole, R. J. McIlroy, S. C. Thorpe, M. J. Cook, J. McMurdo, A. K. Ray. *Sens. Actuators B* **13–14**, 416 (1993).
- 17 D. Crouch, S. C. Thorpe, M. J. Cook, I. Chambrier, A. K. Ray. *Sens. Actuators B* **18–19**, 411 (1994).
- 18 S. M. Critchley, M. R. Willis, M. J. Cook, J. McMurdo, Y. Maruyama. *J. Mater. Chem.* **2**, 159 (1992).
- 19 G. C. Bryant, M. J. Cook, C. Ruggiero, T. G. Ryan, A. J. Thorne, S. D. Haslam, R. M. Richardson. *Thin Solid Films* **243**, 316 (1994).
- 20 A. Jafari-Fini. PhD Thesis, UEA, Norwich, UK (1998).
- 21 M. J. Cook, D. A. Mayes, R. H. Poynter. *J. Mater. Chem.* **5**, 2233 (1995).
- 22 M. J. Cook, A. Jafari-Fini. *J. Mater. Chem.* **7**, 5 (1997).
- 23 M. J. Cook, A. Jafari-Fini. *J. Mater. Chem.* **7**, 2327 (1997).
- 24 M. J. Cook, R. Hersans, J. McMurdo, D. A. Russell. *J. Mater. Chem.* **6**, 149 (1996).
- 25 T. R. E. Simpson, D. A. Russell, I. Chambrier, M. J. Cook, A. B. Horn, S. C. Thorpe. *Sens. Actuators B* **29**, 353 (1995).
- 26 T. R. E. Simpson, M. J. Cook, M. C. Petty, S. C. Thorpe, D. A. Russell. *Analyst* **121**, 1501 (1996).
- 27 T. R. E. Simpson, D. J. Revell, M. J. Cook, D. A. Russell. *Langmuir* **13**, 461 (1997).
- 28 I. Chambrier, M. J. Cook, D. A. Russell. *Synthesis* **10**, 1283 (1995).
- 29 D. J. Revell. PhD Thesis. UEA, Norwich, UK (1999).