Ordered Langmuir–Blodgett multilayers of a new porphin free base with a purpose-built enlarged hydrophobic edge

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Abstract. By a modification of the Jackson–MacDonald condensation reaction between two dipyrromethanes, a new porphin as a model for mesoporphyrin IX dimethyl diester has been synthesized. The new compound has the n-Pr Et Et n-Pr sequence along its hydrophobic edge in place of the Me, Et, Me, Et sequence found in the naturally occurring compound. This purpose-built increase in the volume of the hydrophobic constituents leads to improved phobic–phobic contact between bilayers so that Y-type dipping takes place on hydrophobic substrates (such as freshly etched silicon wafer) to produce Langmuir–Blodgett films displaying first- and second-order peaks in their LAXRD spectra. Angles-of-tilt and bilayer thicknesses are thereby determined.

1. Introduction

Honeybourne *et al* (1979) designed a synthetic route to new amphiphilic porphins as models for naturally occurring porphyrins in order to study the interactions between the enzyme ferrochelatase and porphins and porphyrins. This early work targeted porphins with a smaller hydrophobic edge (i.e. at the 2, 3, 7, 8 positions) than the methyl–ethyl–methyl–ethyl sequence in mesoporphyrin IX. In the title compound, I, of our current work, the substituents along the hydrophobic edge are n–propyl–ethyl–ethyl–n–propyl.

In the work described later we present results for the new porphin which has a hydrophobic edge of slightly larger bulk than that in the naturally occurring compound. We report the influence of the different substituents upon the formation of monolayers upon pure water, and the formation of Langmuir–Blodgett (LB) multilayers on hydrophobic substrates. In contrast to other work (Tredgold *et al* 1985, Luk *et al* 1988) we have produced multilayers of pure porphin of sufficiently high order to give diffraction maxima from low-angle x-ray diffraction.

2. Experimental details

2.1. The synthesis of the new porphin free base (I), 2,8-di-n-propyl-3,7-diethyl-12,18-dimethyl-13,17-di(2'-methoxycarbonylethyl)porphin

The structure of the title compound, I (see figure 1 and caption), is identical to that of the naturally occurring mesoporphyrin IX dimethyldiester (II), except for the
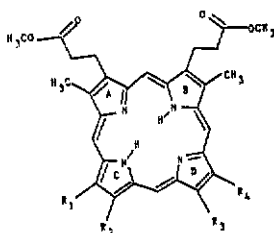
Figure 1. General structure of class IX porphyrins. Mesoporphyrin IX, $R_1 = R_3 =$ methyl, $R_2 = R_4 =$ ethyl: Model porphyrin IX, $R_1 = R_4 =$ propyl, $R_2 = R_3 =$ ethyl.

substituents at the 2, 3, 7, 8 positions. In II the latter comprise 2,7-dimethyl-3,8-diethyl.

The synthesis of I was achieved by the Jackson–McDonald condensation (Honeybourne and Jackson 1980) between a 5,5'-pyrrodimethane-dialdehyde and a dipyrrodimethane with no substituents at the 5,5-locations. The condensation took place in the presence of hydriodic acid and a large volume of acetic acid. A deep burgundy red indicated the formation of the partially conjugated macrocyclic porphodimethene. After adjusting the pH to 7 by the addition of sodium acetate, atmospheric oxidation using an air-bubbler produced the required compound in 24% yield (melting point 164–166 °C). The structure was confirmed by elemental microanalysis, by proton NMR and UV-visible spectroscopy, and by mass spectrometry. Full details of this synthesis have been submitted elsewhere, and the details of three cognate preparations have been published (Honeybourne and Jackson 1980).

2.2. Sample preparation

The free-base porphin was dissolved in Aristar-grade chloroform to give an accurately known concentration in the region of 1 mg ml^{-1}. To avoid decay, it proved to be essential to store the solution in tightly sealed containers in the dark at a temperature below 4 °C.

2.3. Substrate preparation

The substrates chosen were glass microscope slides (Richardson), optically flat quartz (UQG Ltd) and silicon wafer (University of Bristol and Plessey, Caswell). The surfaces of these substrates were rendered hydrophobic as described later.

The surfaces of glass or quartz slides were first treated with chromic acid and then washed thoroughly with dust-free water (Millipore) followed by washing with HPLC-grade iso-propyl alcohol (IPA). They were then further cleaned by the rinsing action of IPA using a specially designed Soxhlet extractor to facilitate cleaning a large number of substrates at one time. After drying in dust-free air, the substrates were rinsed with a 2% (v/v) solution of dimethyl-dichloro-silane in 1,1,1-trichloroethane, using the same bulk Soxhlet technique. The substrates were then washed with water (Millipore) to remove any residual hydrochloric acid.

The hydrophobic nature of the substrates was checked by pulling them through the surface of pure water. A completely dry surface indicated that the substrates were uniformly hydrophobic.

The preparation of hydrophobic silicon surfaces was carried out on a small scale, with each sample being treated individually. The slice of silicon wafer was cleaned in a Soxhlet extractor with high-purity chloroform, and then by HPLC-grade IPA. After drying in a stream of dust-free air, the sample was subjected to further cleaning in an ultrasonic bath containing pure water (Millipore). The surface of the water was removed by suction (to avoid contamination). The sample was then removed from the water, and emerged completely dry if the cleaning process had been successful. Using plastic utensils, the cleaned silicon was chemically etched in 5% hydrofluoric acid for approximately 25 s. Copious rinsing with pure water then produced a totally hydrophobic silicon substrate without the use of hydrophobizing chemical agents.

The hydrophobic nature of freshly etched silicon has been a point of contention (Petty 1988), because silicon forms a new oxide layer by atmospheric oxidation of the freshly etched surface, thereby rendering it hydrophilic. To overcome the effect of this oxide layer, hydrophobizing, silylating agents are usually employed.

We wish to present evidence which proves that the formation of the oxide layer on freshly etched silicon proceeds sufficiently slowly to permit the use of such material as a hydrophobic substrate.

Using the technique of x-ray photoelectron spectroscopy (XPS), the extent of oxidation approximately 10 min after chemical etching was determined. The spectrum obtained of the chemical shift of the Si(2p) electrons is shown in figure $2(a)$, in which only a signal from elemental silicon appears. However, the extent of oxidation slowly increases over a period of 11 days as shown by the spectra in figures $2(b)$ and $2(c)$, in which the smaller of the two peaks represents the chemical shift of Si(2p) electrons in silicon dioxide.

2.4. The Langmuir–Blodgett trough

The apparatus used was supplied and designed by Nima Technology Ltd. It consisted of a circular boro-silicate glass trough, with a triangular-sector barrier constructed of polytetrafluoroethylene. Control of the equipment was by Nima Technology software implemented on a BBC microcomputer. Changes in the surface pressure (surface tension) of a floating Langmuir monolayer were monitored by a feed-back loop consisting of a linear voltage differential transducer and a Wilhelmy plate comprising a piece of filter paper 10 mm in width. The temperature of the subphase was maintained by a thermostatically controlled water bath, and the pH monitored by a pH probe. The dipper mechanism was equipped with controls for selecting dipping speed and length of dipping stroke.

Between each experiment, the trough and barrier were scrupulously cleaned. This was carried out by drying, rinsing with chloroform and then with IPA, followed by drying in dust-free air. Finally, the equipment was thoroughly rinsed with pure water (Millipore).

To ensure that contamination by air-borne particles was kept to a minimum, the equipment was housed in a microbiological cabinet (Hepaire). This latter was fitted with a fan such that a positive internal air-pressure could be maintained, with air being drawn through a microbiological filter.
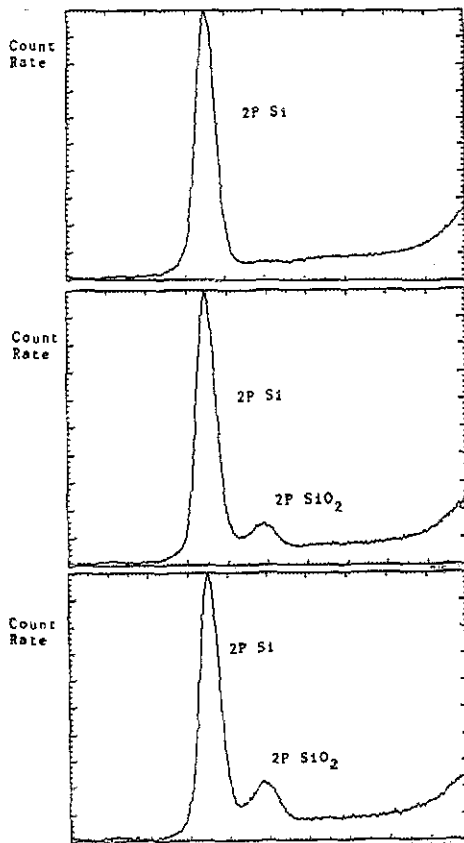
Figure 2. Growth of oxide layer on fresh, chemically etched silicon. XPS (carbon 1s) results are given for time-lapse from cleaning.

2.5. Preparation of Langmuir and Langmuir–Blodgett films

The subphase for all the work on spreading of floating monolayers (i.e. Langmuir layers) consisted of pure water (Milli-Q grade) at 20 °C. The pH was 5.8 due to the buffering action of dissolved carbon dioxide. The porphin molecules were spread from a solution in chloroform onto the clean surface of the subphase. The solution was added dropwise in close proximity to the surface of the subphase. Sufficient time was allowed for each drop to evaporate before adding the next drop. Usually, 25 μl of solution, added using a graduated syringe, was adequate.

The molecules were then compressed between the fixed and moveable barriers: the rate of movement of the latter was 100 cm min^{-1}.

Good quality pressure–area (PA) isotherms were produced for the formation of Langmuir monolayers. The stability of the Langmuir monolayers at a predetermined surface pressure was monitored with respect to time: a dipping pressure of 35 mN m^{-1} was thereby found to be the most suitable.

To obtain LB films, layers were transferred consecutively on to solid substrates at dipping speeds ranging from 5–10 mm min^{-1}. Multi-layer formation proceeded via a modified Y-type deposition (vide infra), with material being deposited on to the solid substrate on both the up-stroke and the down-stroke. Deposition was executed without intervening pauses for the films to drain because the films emerged completely dry when pulled from the aqueous subphase.

2.6. Low-angle x-ray diffraction (LAXRD)

The application of LAXRD to the study of the structure of LB films has been described by Tredgold (1987). The x-ray measurements were taken on a Philips Diffractometer PW 1700 (by courtesy of Rolls Royce, Bristol). The quasi-chromatic source was a chromium target x-ray tube equipped with a vanadium filter. Divergence and scatter slits were used that possessed angular apertures of 0.25°. The divergence slit ensured that small angles could be scanned without saturation of the signal by the x-ray beam. A receiving slit (0.2 mm) defined the width of the reflected beam.

The sample was rotated by and the counter tube was rotated by 2°. To obtain maximum resolution, a 0.25°, 10 s step scan was used. The substrate used for these measurements was hydrophobic silicon: the LB film facing the moveable barrier was chosen because this was of higher visual quality.

3. Results and discussion

3.1. Pressure–area isotherms of Langmuir monolayers

The title compound, I, produced PA isotherms of high quality on the aqueous subphase. The isotherms (see figure 3) displayed the characteristic features of 'solid', 'liquid' and 'gas' phases, and became reproducible after two compression–decompression cycles. By subtending the long linear region to zero pressure, an estimate for the molecular area of 71 Å^2 was obtained. The plane of the porphin ring is thus making an angle of 22° to the normal to the solid substrate, on the basis of the molecular area being approximately 250 Å, as estimated from a space-filling model. A collapse-point of approximately 50 mN m^{-1} was observed for these films.
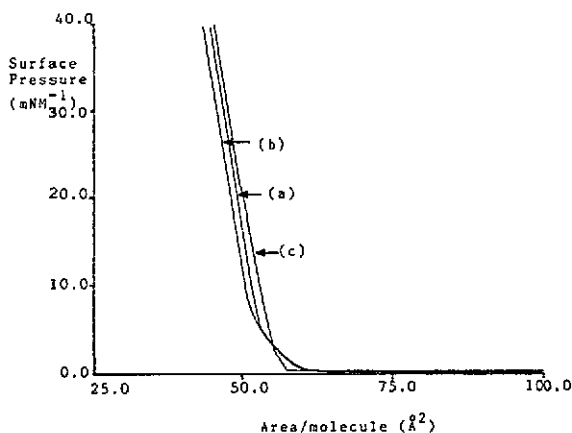

Figure 3. Isotherm for a Langmuir monolayer of model porphyrin IX. (*a*) First compression, (*b*) second compression, (*c*) third compression.

3.2. The deposition of Langmuir–Blodgett multilayers

The optimum dipping pressure was determined from the PA isotherms and the stability of the area reading when a particular pressure was maintained for a period of some

15 min. In the case of compound I, the optimum dipping pressure was evaluated as 35 mN m^{-1}. The dipping speed was in the range 5–10 mm min^{-1} for the hydrophobic substrates used in this work. The behaviour of compound I with regard to multilayer deposition was intermediate between Y-type and Z-type, because the percentage coverage was greater on the up-stroke than on the down-stroke. The down-stroke gave an average 62% coverage, whereas the up-stroke gave virtually 100% coverage. It has been reported (Jones *et al* 1983), that meso-porphyrin IX dimethyl ester(II) produced only Z-type deposition (i.e. 100% coverage on the up-stroke, with zero coverage on the down-stroke). Thus, the increase of the bulk of the hydrophobic edge from diethyldimethyl(in II) to diethyldipropyl(in I) has produced a hydrophobic–hydrophobic contact more compatible with Y-type deposition.

In accord with our earlier enzyme-compatibility work (Honeybourne *et al* 1979, Honeybourne and Jackson 1980), small changes in the volume of the hydrophobic edge produces distinct changes in inter-molecular interactions.

3.3. Characterization of LB multilayers

The satisfactory quality of the LB films obtained by multilayer deposition on hydrophobic glass was confirmed by the linearity of the plot of absorbance against number of layers. The principal optical absorption band (the Soret band) was used to obtain these results (figure 4) (Baker *et al* 1983).
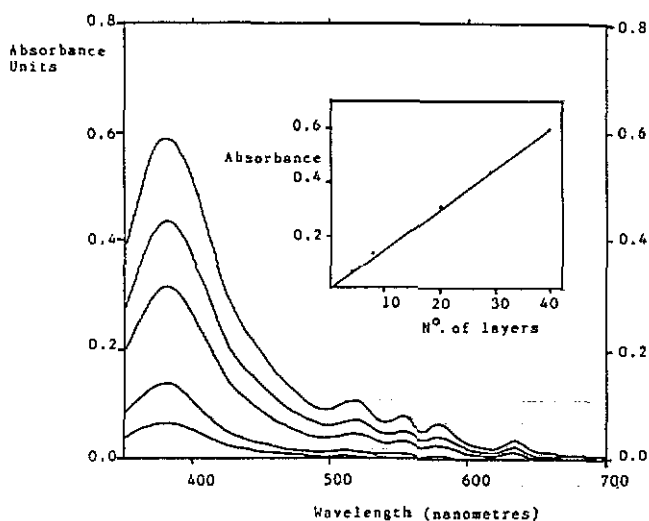

Figure 4. Plot of optical absorbance against number of LB layers of model porphyrin IX.

In accord with the work of Luk (*et al* 1988), the Soret band was broadened by solid-state interactions from the 'full width at half height' value obtained from solution spectra. A further change, characteristic of solid state interactions, is the red shift of the bands in the 500–600 nm region (figure 5).

If diffraction maxima occur in the LAXRD of LB films, then it is possible to obtain a value for the *d* spacing because of the ordering perpendicular to the surface of the substrate. In the case of films that deposit in the Y-type mode, the *d* spacing will provide an estimate of the thickness of the bilayer. If the number of layers is known
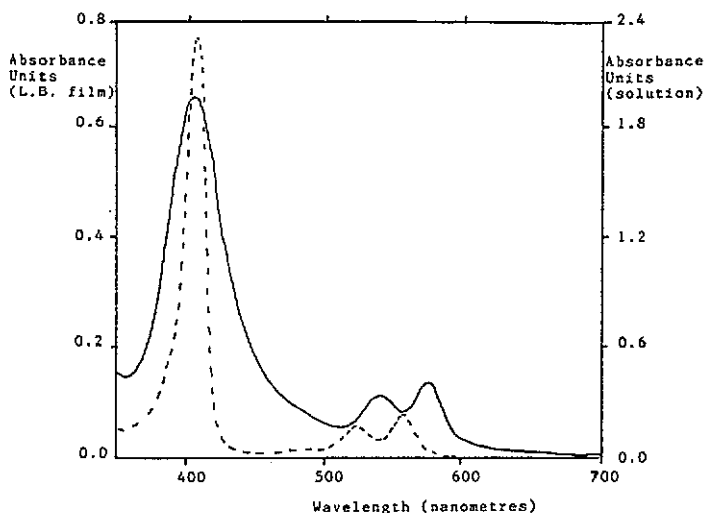
Figure 5. Comparison of a solution spectrum with a solid-state spectrum to illustrate the solid-state red shift in model porphyrin IX.

then the thickness of the film can be calculated (Tredgold 1987). The LAXRD of the silver and gold complexes of mesorphyrin IX dimethyl diester (Tregold *et al* 1985) did not show diffraction maxima. However, the LAXRD of our compound, I, gives two maxima (figure 6) which shows that, even in the absence of either long alkyl substituents or co-deposition with a long-chain fatty acid, it is possible to obtain some degree of ordering with relatively inflexible molecules. We estimate an angle of tilt of 36°, and a bilayer thickness of 29 Å. There was close agreement between the *d* spacings estimated from the first and second diffraction maxima.
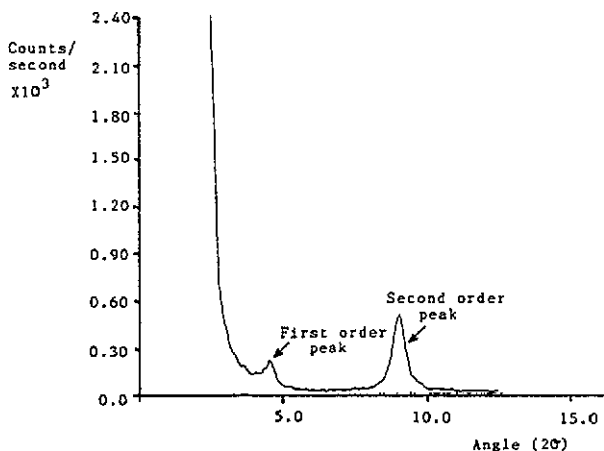

Figure 6. Low-angle x-ray diffraction of a thick LB multilayer of model porphyrin IX.

4. Conclusion

A new porphin free-base dimethyldiester, custom-synthesized to have a slightly larger

volume of hydrophobic edge than the corresponding location in the related natural product mesoporphyrin IX dimethyl diester(II), has been shown to give LB multilayers by a deposition sequence intermediate between Z-type and Y-type. The substrate employed was clean hydrophobic silicon wafer, and new evidence is presented to confirm that freshly etched silicon is indeed hydrophobic.

The results from LAXRD show that the LB multilayers are sufficiently well ordered to give two distinct diffraction maxima from which a bilayer spacing of 29 Å has been estimated. The tilt angle of 36° to the normal in the LB multilayers is greater than the corresponding angle in the floating Langmuir monolayer films (i.e. 22°).

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