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Deposition and Characterisation by Surface Plasmon Resonance of Langmuir-Blodgett Monolayers of Three Macrocyclic Conjugated Tetrapyrrole Compounds Exposed to Chlorine Gas*

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Surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) studies are described for tetrakis-*tert*-butylphthalocyanatoCu(II) and two new tetrakis-5,10,15,20-(substituted phenyl)-21H,23H-porphines. The Langmuir isotherms of the porphines, coupled with the layer thickness and contact area of the LB monolayers, show that these two compounds are not forming regular monolayer LB films, but are exhibiting extensive clumping on the subphase and on the substrates. The optical spectra and SPR of the porphine films did not exhibit noteworthy sensitivity to chlorine. In contrast the phthalocyanine gave good quality monolayers, which showed promise for sensing chlorine in the 1–10 ppm range.

Key words: surface plasmon resonance, quartz crystal microbalance, Langmuir-Blodgett films, porphines

One of the first groups of researches to utilise Langmuir-Blodgett (LB) films of metallo-phthalocyanines to detect oxidising gases were collaboratively based at the Technical University of Wroclaw (Poland) and the Czecho-Slovak Academy of Sciences in Prague. Their principal contribution [1] focussed upon the utilisation of tetrakis-*tert*-butyl-phthalocyanato-Cu(II) (Fig. 1, **I**), in the form of a multi-layered LB film, to detect the reactive oxides of nitrogen by induced changes in electrical properties. Details of earlier related work on sublimed, relatively thick films of phthalocyanines can be found in the review by Snow and Barger [2] and references therein.

The pressure-area (π-A) isotherms of compound **I** have been studied by a number of research groups [3–10]. These isotherms, and the limiting molecular area estimated from them, show marked variations, although there is a consensus that the molecular area is of the order of 0.65 nm^2. An extensive range of other phthalocyanines

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* Dedicated to the memory of Professor Krzysztof Pigoń.
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and their metal complexes, rendered soluble in organic solvents by the attachment of up to eight identical (or disparate) alkyl- or alkoxy-bearing substituents [11], has been studied by the LB technique [12–15]. A number of these LB films have been studied to assess their potential as sensors for reactive oxidising gases (especially NO_2 but with little work on Cl_2) as well as a range of organic vapours. The sensing technologies used include electrical dark DC conductivity [12], optical absorption spectroscopy [13], voltammetry [14] and SPR [15]. The SPR of LB films of compound **I** has not been reported hitherto as a sensing technique for chlorine.

The phthalocyanines can be regarded as tetra-benzo derivatives of the archetypal tetrapyrrolic, biologically important pigment, porphin. Various research groups have utilised LB films of porphyrin free-bases and metal complexes (solubilised by the use of appropriate derivatives) in a range of gas-sensing regimes [16,17]. Richardson and his co-workers have recently given a detailed account of the use of LB films of a tetrakis-(4-alkylsulfonamidophenyl) porphyrin free base to detect chlorine by linear optical absorption [17]. We note that there are extensive similarities here to the oxidant-induced changes in optical spectra of solid films of simple tetrakis-(4-alkylphenyl) porphyrin and tetrakis-(4-alkoxyphenyl) porphyrin free bases as observed [18–19] and interpreted by Honeybourne [20].

In what follows, we present, for the first time, novel results for the SPR of LB monolayers of the following compounds: **I** tetrakis-*tert*-butyl-phthalocyanato-Cu(II), **II** tetrakis-5,10,15,20-(4-pentylphenyl)-21H,23H-porphine and **III** tetrakis-5,10,15,20(3,4-bis-(1-propylbutoxyphenyl))-21H,23H-porphine. Film thicknesses are evaluated from SPR data, and molecular areas in contact with the subphase or substrate respectively are estimated from the Langmuir isotherms and from data given by QCM. The effects of chlorine gas upon the optical absorption and SPR of the LB monolayers are described. Our isotherms and allied spectroscopic data for **II** and **III** are compared and contrasted with those for **IV** (tetrakis-5,10,15,20-(4-octadecylamidophenyl)-21H,23H-porphine [17] (see Figure 1) and with spectroscopic data for solid thin films.

EXPERIMENTAL

Materials: **I** was synthesised by the method of Michalenko [21] and **II** and **III** were obtained by cognate preparations of **IV** [22]. The glass slides for LB deposition were BDH (super premium grade) and were cleaned by repetitive cycles of washing with chloroform, isopropanol and ultra-pure water obtained by use of a combination of a Fistreem Cyclon distillation unit and a Millipore Milli-Q-185-Plus purification unit. The solvent for spectroscopy, and for the spreading phase in the preparation of Langmuir films, was Ultrafine UL grade chloroform. Solutions were prepared using an Ohaus GA200D microbalance and Volac volumetric flasks.

Cleaned glass slides were coated with a gold film (thickness *circa* 45 nm) in an Edwards E306A coating unit using 100 mg of gold (Aldrich, 99.9999%) at 10^{-6} mbar. The film thickness was controlled using an Intellimetrics IL150 thin-film deposition monitor.

Pressure-area Langmuir isotherms: The isotherms were produced using a NIMA Technology Langmuir-Blodgett trough in a dust-free (cleanroom) environment. The trough was cleaned with lint-free cleanroom wipes (Countdown, polycellulose, TX609) and the solvents and ultra-pure water mentioned above. The surface of the subphase was cleaned with an aspirator pump. After stabilisation of the surface

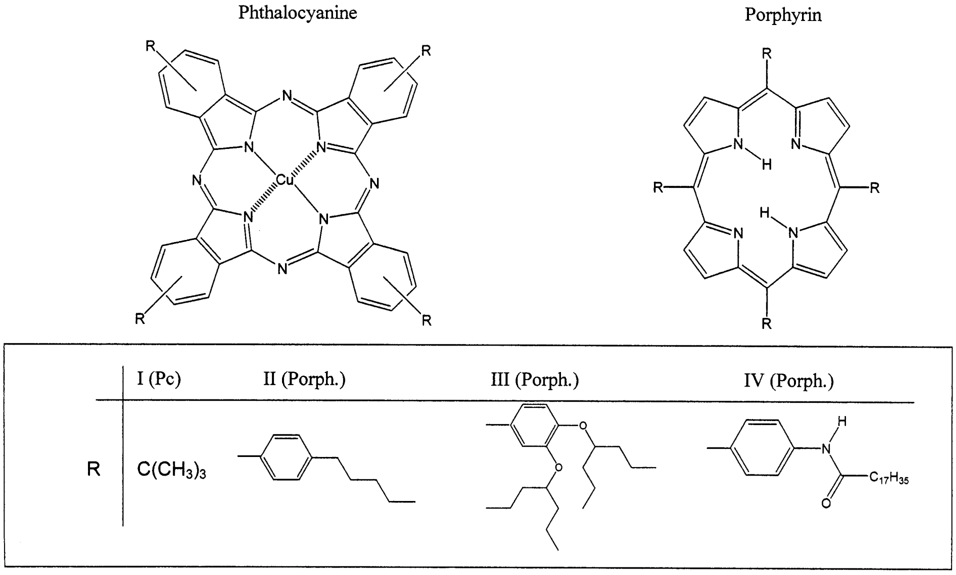

Figure 1. Molecular structures of macrocyclic tetrapyrrole compounds: **I**, tetrakis-*tert*-butyl-phthalocyanato-Cu(II); **II**, tetrakis-5,10,15,20-(4-pentylphenyl)-21H-23H-porphine; **III**, tetrakis-5,10,15,20-3,4,bis-(1-phenyl)-21H,23H porphine; **IV**, tetrakis-5,10,15,20-stearamido-21H,23H-porphine.

pressure (Wilhelmy plate), the pressure was zeroed and the spreading phase added, the solvent in which was allowed to evaporate for 10 minutes before compression at 25 cm^2 min^{-1}.

Langmuir-Blodgett film deposition: The standards of cleanliness observed for the production of Langmuir films were maintained for the production of LB films for which a NIMA 2000 trough with a vertical dipper mechanism was used. The glass, glass/Au or quartz-crystal substrates were fully submerged before the addition of the spreading phase. Once the required constant surface pressure was reached, the substrate was lifted through the surface at 5 mm min^{-1}.

Surface plasmon resonance: SPR experiments were performed on gold-coated glass plates (see above) by attenuated total reflection using the Kretschmann geometry [23]. A schematic of the apparatus is given in Figure 2. Reflectivities were obtained as a function of the angle of incidence, relative to the film, of a p-polarised laser (HeNe, 10 mW at $\lambda = 632.8$ nm). The data were corrected for reflections at the exit and entrance of a BK7 glass prism, in contact with the glass substrate using methyl benzoate as an index-matching fluid, and then were analysed by comparison with the Fresnel reflection formulas using the

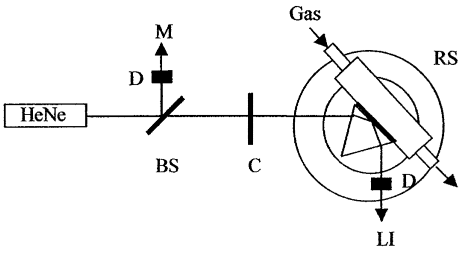

Figure 2. Schematic of SPR apparatus (M, Keithley 199 digital multimeter; RS, rotation stages; D, silicon detector; BS, 50:50 beamsplitter; C, optical chopper; LI Stanford Research Systems pre-amplifier and lock-in amplifier).

method of Barnes and Sambles [24]. The derived thicknesses of the metal film (*circa* 45 nm) and the real and imaginary parts of the dielectric permittivity (ε_r and ε_i respectively) were then used to assist the interpretation of the reflection data from the glass/Au/LB interfacial overlays. The refractive index (n) and the coefficient of absorption (κ) can be derived from the real and imaginary permittivities using the following equations: $n = \{[\varepsilon_r \pm (\varepsilon_i^2 - \varepsilon_r^2)^{1/2}]/2\}^{1/2}$; $\kappa = \varepsilon_i/2n$.

The influence of chlorine on the SPR of an LB monolayer was studied by using a controlled mix (mass flow controllers were Tylan General FC2900) of pure nitrogen (BOC) and chlorine (100 ppm Cl_2 in nitrogen, BOC Speciality Gases). The SPR gas cell is depicted in Figure 3.

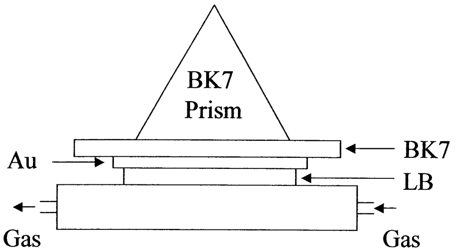

Figure 3. Schematic of gas cell for SPR.

Quartz crystal microbalance (QCM): The molecular areas in contact with the substrate were determined by monitoring the frequency change (ΔF) of an AT-cut quartz crystal substrate upon the deposition of an LB monolayer. The Sauerbrey equation [25] can be used to determine the corresponding mass increase (Δm) from the expression $\Delta F = -2F_o^2\Delta m/[A(\rho\mu)^{1/2}]$, in which F_o is the resonant frequency of the quartz crystal (10 MHz), ρ is the density (2.65 g cm^{-3}), μ is the shear modulus (2.95×10^{11} dyn cm^{-2}) and A the area of the metal film. The molecular area, A_o, is given by $A_o = 2AM_r/(L\Delta m)$, where M_r and L are, respectively, the relative molar mass and Avogadro's number.

RESULTS AND DISCUSSION

Compound I

Langmuir isotherm: The pressure-area isotherm (Figure 4a) shows that the limiting molecular area (*i.e.* at zero applied pressure) is 0.62 nm^2. Other workers have reported similar values [1,7], some cite rather lower values [6,9], whereas yet others have cited substantially higher areas [5,6,10]. The dimensions of the molecule, estimated by computer modelling (ChemOffice 2000, Chemsoft), indicate that, with a thickness of 0.35 nm (which is typical for quasi-planar molecules), the molecular area is *circa* 0.7 nm^2 if edge-on or *circa* 4.2 nm^2 if face-down on the subphase.

It has been shown that the packing and orientation of **I** are strongly influenced by the initial molecular density on the surface of the subphase before compression [26]. In addition, the rate of compression influences molecular packing. This latter is likely to be complicated and variable due to the fact that **I** consists of four randomers due to the geometrical non-uniformity of the tetra-substitution.

After evaporation of the solvent from the spreading phase, a single macrocyclic tetra-pyrrole such as **I** will tend to lie face down on the subphase in accord with the hydrophilic interaction between water and the nitrogen-atom lone-pairs perpendicular to the plane of conjugation. At low compression, this face-down regime is main-

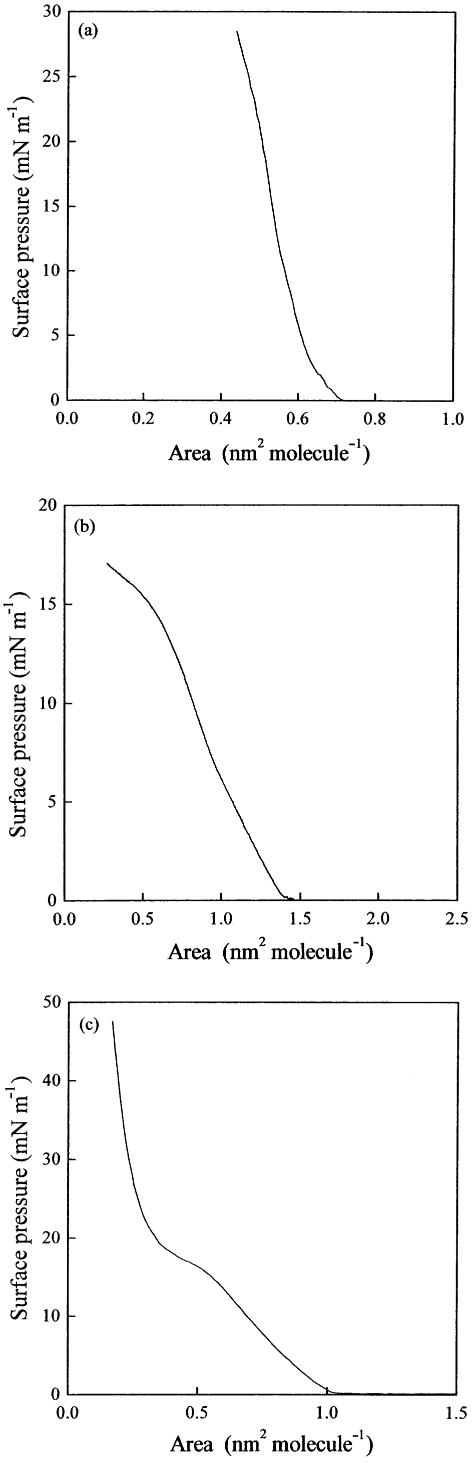

Figure 4. Langmuir pressure-area isotherms: (a) **I**; (b) **II**; (c) **III**.

tained. After a threshold value (*circa* 8–10 mN m^{-1}) [26], progressive contributions from edge-on orientated molecules set in. Our results show that the Langmuir films of **I** consist of molecules edge-on to the subphase at 10 mN m^{-1}. These films were used in the subsequent production of LB monolayers (see below).

LB films: LB films were deposited on quartz crystals for QCM measurements, glass slides for optical absorption spectroscopy, and gold-coated slides for the study of SPR. The area per molecule obtained from the QCM data was similar to that estimated from the π-A isotherm. The SPR data for each LB monolayer is given in Table 1. Noteworthy features are the relatively high values of ε_i and κ (the coefficient of absorption at the laser wavelength) for **I** compared to the values for the porphyrin species (**II** and **III**).

Table 1. Results obtained from the SPR for LB monolayers.

Parameter	LB of **I**	LB of **II**	LB of **III**
ε_r	2.1±0.2	2.4±0.2	2.4±0.2
ε_i	0.9±0.2	0.3±0.2	0.4±0.2
d	1.6±0.2	1.5±0.2	11.7±0.2
n	1.5	1.5	1.5
κ	0.3	0.1	0.1

Effects of chlorine upon optical absorption and SPR of LB films: The optical spectra of metallophthalocyanines show pronounced changes when exposed to oxidising gases [27]. For the LB monolayer, we obtain two bands, namely the B-band at 337 nm and the Q-band at 617 nm. Other workers have cited values of 340 nm and 620 nm [6]. The Q-band is "blue-shifted" from its in-solution value of 678 nm by solid-state packing effects. We find that, upon exposure of the LB film to chlorine, the Q-band region then consists of the original band and a new band at 675 nm, in agreement with Battisti and Aroca [28] (see Figure 5). These optical changes lie near to the operating wavelength of the laser. At low concentrations of chlorine (up to 10 ppm in nitrogen) the percentage response of the SPR to chlorine is approximately logarithmic (1.2%, 2.5%, 3.5% and 4.0% at 1 ppm, 2.5 ppm, 5 ppm and 10 ppm respectively). These responses did not reverse over a 24-hour period in nitrogen. At higher chlorine concentrations saturation effects are closely followed by destruction of the film.

Compound II

Langmuir isotherms: The isotherm consists of a shallow curve (Figure 4b), with the film beginning to break at 13 mN m^{-1}. The limiting molecular area is 1.28 nm^2, whereas we estimate that the molecule has an edge-on area of 0.65 nm^2 and a face-down area of 3.4 nm^2. These results show that the molecules are stacking up upon each other, rather than forming a simple monolayer; this is in accord with the suggestions of Bull and Bulkowski [29].

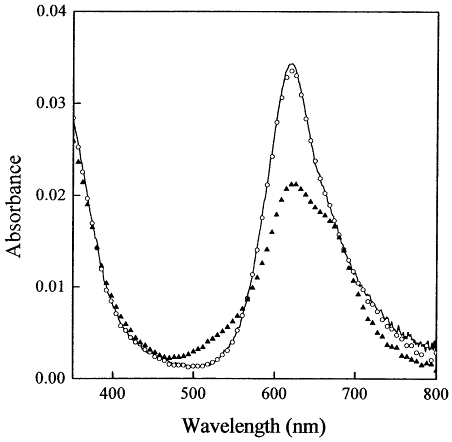

Figure 5. Optical spectrum of an LB film of **I** before (—) and after (▲) exposure to chlorine showing the extent of recovery (o) in air.

LB films: When **II** is deposited on a quartz crystal, the QCM results show that stacking is occurring again, because the area per molecule is now only 0.23 nm^2 if monolayer formation is assumed. The SPR results for an LB film on gold are shown in Table 1.

Effects of chlorine upon optical absorption and SPR of LB films: The monolayer of **II** displays a spectrum highly characteristic of all free-base porphyrins, with the Q-bands almost identical in position to those of simple free-bases in solution (Table 2). However, the expected changes upon exposure to 10 ppm of chlorine gas in nitrogen were not observed. This is in marked contrast to the behaviour of films deposited at low pressure by Richardson *et al.* [17]. However, the latter research group [17] found a much less pronounced response from LB films deposited at higher pressures, and our results are akin to these. Our SPR results, obtained from Langmuir-Blodgett films deposited under standard conditions, gave less than 1% response to 10 ppm of chlorine. We suggest that non-standard conditions of deposition are required in order to prepare films through the chlorine can readily diffuse.

Table 2. Optical absorption spectra of LB monolayers of **II** and **III**.

Sample	Soret region (λ_{max}/nm) (B – band)	Lower energy visible region (λ_{max}/nm) (Q – bands)
Solution spectrum of simple tetraphenyl analogue of **II** and **III**	419	515, 548, 592, 647
LB monolayer of **II**	447 (br.)	522, 551, 590, 646
LB monolayer of **II** post – Cl_2	450 (br.) falling	little observable change
LB monolayer of **III**	425 (sh,) 440, 446	520, 558, 600, 652
LB monolayer of **III** post – Cl_2	440 falling	little observable change

Compound III

Langmuir isotherms: The isotherm (Figure 4c) is of poor quality because there are no clear phase changes in the 2-16 mN m^{-1} region. Only an approximate estimate of limiting molecular area can be given, namely 1.28 nm^2. Due to the very large side chains (Figure 1), this molecule is far thicker than the others, with an edge-on area of 3.51nm^2 and a face-down area of 7.29 nm^2. These results, in common with those for **II**, are consistent with the fact that the molecules are exhibiting clumping and random stacking, rather than forming a simple, regular monolayer.

LB films: When **III** is deposited on a quartz crystal, the QCM results again confirm the presence of stacking because the apparent area of such a large molecule is found to be only 0.28 nm. The SPR results for an LB film on gold are shown in Table 1. The thickness is extraordinarily large (*i.e.* 11.74 nm) with the consequence that major changes to the SPR signal are observed upon deposition of this film (see Figure 6). This is yet further evidence for extensive clumping and multilayer formation.

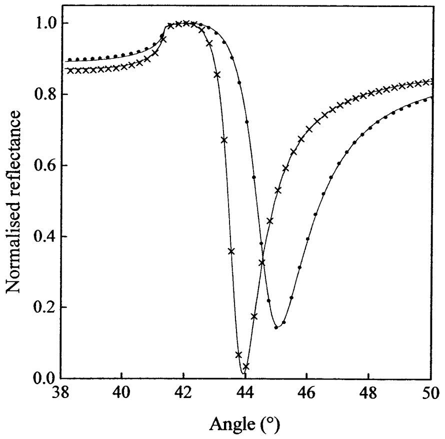

Figure 6. SPR of a gold film (x), a gold film with a thick clumped organic overlayer (**III**) (●) and their corresponding theoretical traces (—).

Effects of chlorine upon optical absorption and SPR of LB films: The monolayer of **III** gives an optical spectrum very similar to that of **II**, confirming the viability of the porphyrinoid structure (Table 2). However, exposure to chlorine causes little change to the spectrum of the monolayer, and does not influence the SPR signal sufficiently for gas-sensing purposes.

CONCLUSIONS

We have shown that compound **I** (a metallophthalocyanine) forms good quality LB monolayer films that offer potential for the detection of chlorine by SPR. There are substantial changes in the value of the imaginary part of the dielectric permittivity at the laser wavelength upon the ingress of chlorine. We suggest that, in the range 0–10 ppm, the applicability of the following expression should be investigated: R =

$R_{max} - B\exp(-t/\tau)$, in which R is the SPR response to chlorine, R_{max} is the maximum response, B is a constant and τ, the time constant, is a quadratic function of the ratio of the film thickness (l) to the Fick Diffusion Coefficient (D). It has been suggested by others that, for very thin films with a high value of D, $(l/D)^2$ is small and therefore only one pre-exponential factor(B) and one time constant are required [30].

The two porphyrin free bases, **II** and **III**, both of which lack bulky alkyl side-chains, give LB monolayers of poor quality. Our evidence indicates substantial clumping on the subphase and variations in thickness across the deposited film with the structure and stability of the films being governed by molecular packing rather than by hydrophobic/hydrophilic interactions [29]. The changes induced by exposure to chlorine appear to be inadequate to affect the SPR signal. One of us (CLH, ref. 20) has previously noted, in a similar context, the poor response of a related tetrakis-(4-alkoxyphenyl) porphin free base to chlorine, which complements our present findings for **III**. We suggest that the alkoxy groups are adversely affecting the molecular ionisation potential and/or the basicity of the pyrrole nitrogens of the porphyrins. The poor response of **II** to chlorine is surprising and more research is required before we can put forward an explanation.

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