1,4,8,11,15,18-Hexa-alkyl-22,25-bis(carboxypropyl)phthalocyanines: Materials designed for Deposition as Langmuir–Blodgett Films

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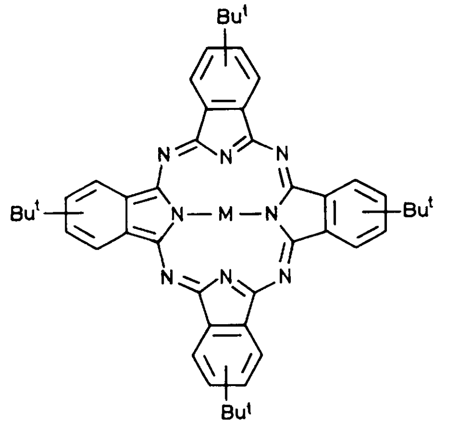
Examples of the title compounds form stable monolayers on a water surface and are transferred onto hydrophobic silica as Langmuir–Blodgett films, which are highly ordered as judged by polarised absorption spectroscopy.

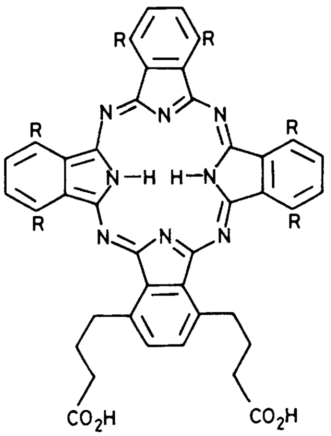
Roberts and his co-workers[1] were the first to demonstrate that phthalocyanine can be deposited as a thin film using the Langmuir–Blodgett technique. The prospect of obtaining highly ordered films of phthalocyanines has pointed a new way forward for exploiting the interesting properties of the phthalocyanine ring in sensors and electronic devices. In turn, this has led to a quest for derivatives with properties suited for the Langmuir–Blodgett method, notably solubility in an organic spreading solvent.[2—5] The tetra-t-butylphthalocyanines (**1a**—**c**) have attracted particular attention[1,2] but others, including the tris(isopropylaminomethyl),[3] and tetracumylphenoxy derivatives,[4] have also been developed and evaluated. However, these materials are obtained as mixtures of isomers, and this is likely to disrupt structural ordering in the film. The isomer problem is absent for octasubstituted phthalocyanines obtained from symmetrically substituted precursors; a 2,3,9,10,16,17,23,24-octasubstituted phthalocyanine has recently been successfully deposited as an L–B film.[5] We describe here the preparation of novel phthalocyanines (**2a**—**c**) designed specifically for the Langmuir–Blodgett technique, and report some unexpected properties of the films prepared with them.

The structure of the present series of metal-free phthalocyanines was designed bearing in mind the beneficial effects on molecular ordering at the air–water interface expected for a compound having both hydrophilic and hydrophobic side chains. The substituents are located at what we term the non-peripheral sites; this distinguishes the series from previous phthalocyanines deposited as Langmuir–Blodgett films. This substitution pattern was chosen for the compactness of the molecular structure and with a view to two longer-term ambitions for 'tuning' the properties of the films. First, we reasoned that inter-ring spacing of ordered phthalocyanine molecules should be highly susceptible to chain branching when the chains are located in the non-peripheral sites. Second, substituents at these sites have a greater effect upon the electronic transition energy of the Q-band than at the 2,3,9,10,16,17,23, and 24 (peripheral) sites. In choosing the length of the hydrophilic chain, consideration was given to making the distance L_p (Figure 1) as similar as possible to the distance L_a in 9-alkyl-10-carboxyethylanthracenes. The latter are deposited as ordered Langmuir–Blodgett films.[6]

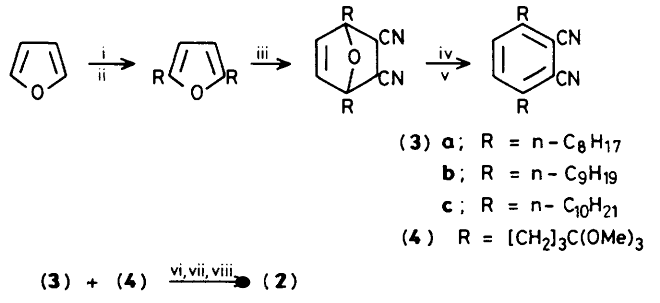
The series (**2**) was prepared by condensing together a 3,6-di-n-alkylphthalonitrile (**3**) with the chain-elaborated analogue (**4**) with the aim of hydrolysing the ortho ester groups in the initially formed phthalocyanine product to the carboxylic acid functionality. Compounds (**3a**—**c**) were prepared as outlined previously[7] and (**4**) by adaptation of the same route (Scheme 1). The desired phthalocyanines were obtained *via* condensation ($LiOC_5H_{11}$, $C_5H_{11}OH$) of (**3**) and



(**1**) a; M = Cu
b; M = H,H
c; M = SiCl$_2$



(**2**) a; R = n-C$_8$H$_{17}$
b; R = n-C$_9$H$_{19}$
c; R = n-C$_{10}$H$_{21}$



Scheme 1. *Reagents:* i, BuLi, RBr; ii, BuLi, RBr; iii, (CHCN)$_2$; iv, LiN(SiMe$_3$)$_2$, THF −78 °C; v, H$_2$O; vi, LiOC$_5$H$_{11}$, HOC$_5$H$_{11}$; vii, AcOH; viii, OH$^-$, H$_2$O then H$_3$O$^+$.

(**4**) in 9 : 1 ratio, chosen to simplify the product mixture to essentially the required material and the octa-alkylphthalocyanine from which it is easily separated.

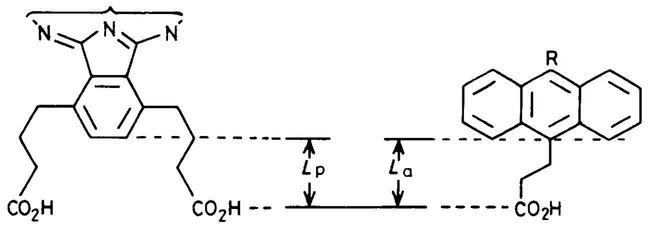


Figure 1. Comparison of the distances between the hydrophilic centre and the aromatic nucleus in (a) the phthalocyanines (**2**) and (b) 9-alkyl-10-carboxyethylanthracenes.

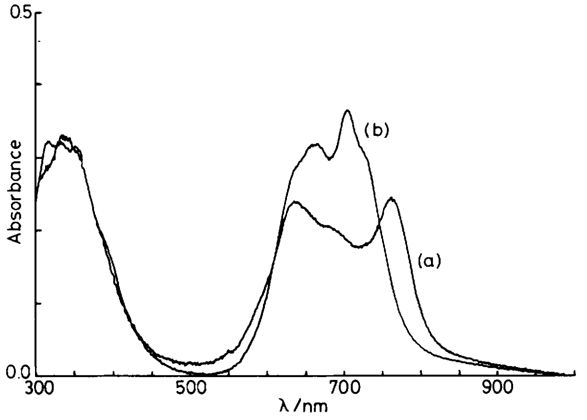


Figure 2. (a) Visible absorption bands from the Langmuir–Blodgett film of (**2a**); (b) as (a) but after warming the film.

Films were prepared by using a Joyce–Loebl constant perimeter design trough. Compounds were transferred onto the surface of the water (pH 5.6) as solutions in xylene–tetrahydrofuran (5 : 1). The pressure/area isotherms show minimal hysteresis and are characterised by a steep condensed-phase region. Values for the surface area per molecule, calculated from the isotherms by the normal procedure, are 120 Å^2 for each phthalocyanine. This value is in reasonable agreement with the minimum area calculated from the breadth [~28 Å for (**2a**), ~31 Å for (**2c**)] and width (~4 Å) as estimated from CPK space-filling models, and suggests that the molecules are arranged with their faces approximately perpendicular to the water surface. The monolayers show excellent stability. Thus at a surface pressure of 35 mN m^{-1} the surface area of the film of (**2a**) decreased by 3% over 6 h. For each compound, consecutive monolayers were deposited onto hydrophobic silica slides (Spectrosil B) at a pressure of 35 mN m^{-1} and a dipping speed of 15 mm min^{-1}. Deposition was of the *Y*-type. A detailed u.v.–visible spectroscopic study of (**2a**) showed that the absorbance varies linearly with the number of dips.

The visible spectra of films of (**2**) differ from those reported of Langmuir–Blodgett films of other phthalocyanines.[1,2,5] A typical absorption spectrum [Figure 2(a)] shows sharp bands at 636 and 762 nm. This type of spectrum arises from intermolecular interactions giving rise to exciton transitions.[8] When warmed the films undergo a change in their molecular assembly, characterised by a change of colour to a greener shade. Thus the spectrum of the film of (**2a**) changes to that depicted in Figure 2(b). The transition is a sharp one and occurs at 127.5 °C, well below the m.p. (185 °C). The change is not reversed during cooling. Polarised absorption spectra for the original and the modified film are shown in Figure 3. The substantial variation of the spectra as a function of the direction of the electric field vector of the light with respect to the dipping direction of the film implies anisotropy in the ordering of molecules in both films.

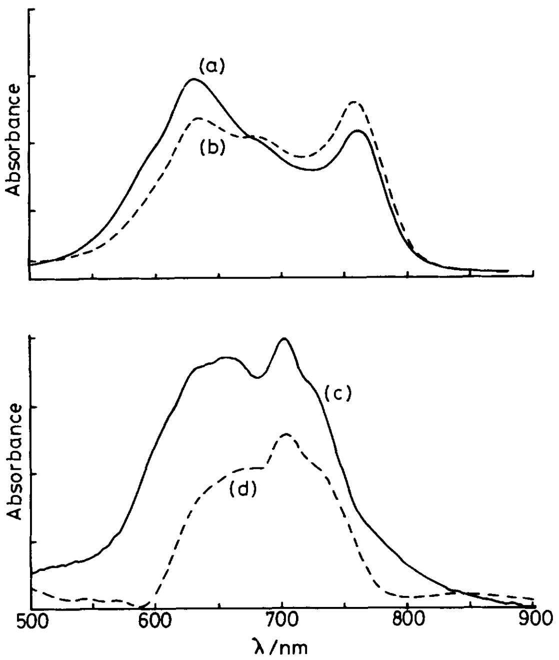


Figure 3. (a) The polarised absorption spectrum of the Langmuir–Blodgett film of (**2a**) with the transmission axis of the polariser perpendicular to the axis of dip; (b) as (a) but the transmission axis parallel to the axis of dip; (c) and (d) as (a) and (b), respectively, but after warming the film.

In conclusion, the purpose-designed phthalocyanine derivatives (**2**) show excellent stability as films at the water–air interface and give pressure/area isotherms with little hysteresis. The materials deposit very well in the *Y*-mode onto silica substrates to give multilayer Langmuir–Blodgett films. Optical properties of the films suggest a high degree of ordering. The films undergo changes at elevated temperature, but below the m.p., apparently due to molecular reorientation in the film.

The degree and nature of ordering in the films is currently under investigation.

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