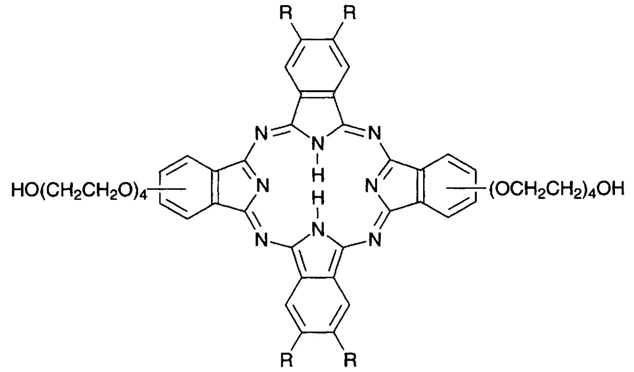
Solvent cast films derived from amphiphilic phthalocyanines: an alternative to the Langmuir–Blodgett technique for the preparation of ordered multilayer films

Kevin E. Treacher, Guy J. Clarkson, Ziad Ali-Adib and Neil B. McKeown*

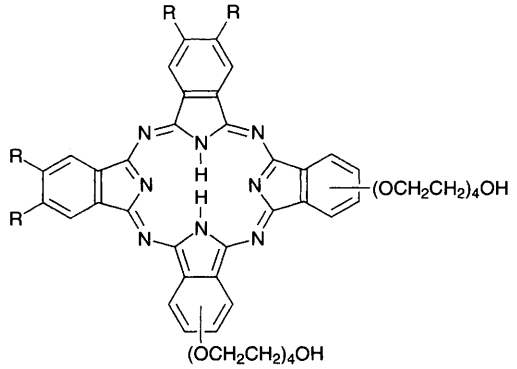
Department of Chemistry, University of Manchester, Manchester, UK M13 9PL

Solvent cast films of novel amphiphilic phthalocyanine derivatives are described which possess highly ordered multilayer structures analogous to Langmuir–Blodgett films.

The Langmuir–Blodgett (LB) technique has been successfully applied to the fabrication of thin films composed of phthalocyanine (Pc) derivatives.[1,2] Such films have been investigated for application within gas sensors,[3] electrooptical devices[4,5] and as non-linear optical materials.[6] Presently, LB film deposition has a number of limitations which make their commercial exploitation unlikely. These include slow speed of deposition, the small area of substrate which can be covered, the high cost of equipment and the need of a highly controlled environment free from dirt and vibration.[2] In addition, the order within most LB films formed by Pc derivatives is questionable, with the assumption of a layered structure often unverified by a low-angle X-ray diffraction study.[7] Alternatives to the LB technique for the preparation of ordered, layered organic films includes sublimation of appropriate amphiphiles,[7] covalent self-assembly[2] and the formation of solvent cast multilayers derived from amphiphilic compounds.[8] This communication reports our preliminary results on the formation of solvent cast films formed by novel amphiphilic Pc derivatives.



1; R = $C_{16}H_{33}$



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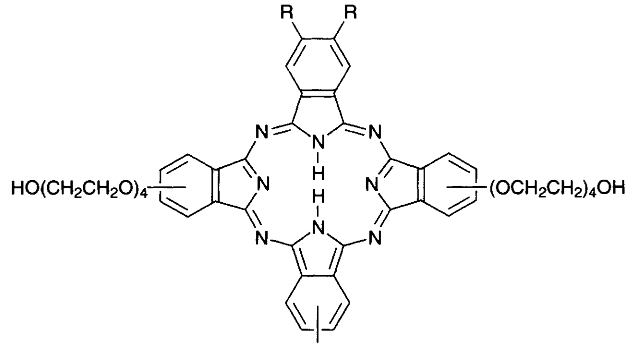
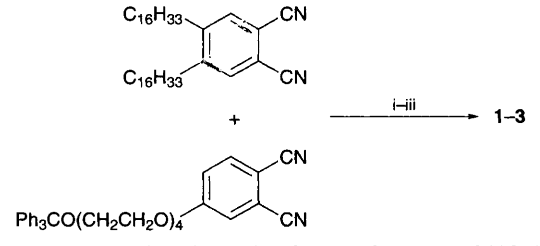


3; R = $C_{16}H_{33}$

The amphiphilic Pcs **1–3** used in this study were prepared by the route shown in Scheme 1, based upon the mixed reaction between 4,5-bis(hexadecyl)phthalonitrile and 4-(14,14,14-triphenyl-1,4,7,10,13-pentaoxatetradecyl)phthalonitrile. The resultant complex Pc product mixture was separated by simple column chromatography and finally, the trityl protecting groups were removed using acidic conditions. The other product obtained from this synthetic scheme, 2,3,9,10,16,17-hexadecyl-23-(12-hydroxy-1,4,7,10-tetraoxadodecyl)phthalocyanine, is insoluble in cold organic solvents and thus unsuitable for the formation of cast films. The structures of Pcs **1–3** were confirmed by fast atom bombardment mass spectrometry (FABMS), high resolution ^1H NMR and UV–VIS absorption spectroscopy.† The Pcs also gave satisfactory elemental analyses and were pure (> 99%) as assessed by HPLC.

NMR analysis shows that Pcs **1** (the *opposite* isomer) and **2** (the *adjacent* isomer) are composed of a statistical mixture of two and three regioisomers, respectively. The separation of similar *opposite* and *adjacent* isomers containing both oligo(oxyethylene) and alkyl chains have been reported recently.[9,10] Phthalocyanine **3** is obtained as a mixture of four isomers.

X-Ray diffraction studies (Fig. 1 and Table 1) show that Pcs **1–3** give highly ordered lamellar films when cast from chloroform solution (0.2 mg ml^{-1}) onto clean, hydrophobic substrates (clean silicon or glass microscope slides pretreated with hexamethyldisilazane vapour). The degree of layered order shown by these films appears greater than that exhibited by even



Scheme 1 *Reagents and conditions*: i, $LiOC_5H_{11}$–$C_5H_{11}OH$, 135 °C, 4 h; ii, acetic acid, separation by chromatography; iii, HCl (aq), THF, reflux, 4 h

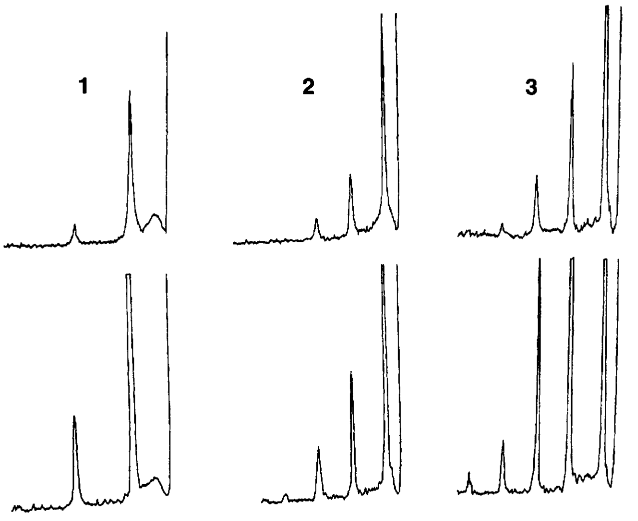


Fig. 1 X-Ray diffractograms from the solvent cast films of Pcs **1–3** on a hydrophobic silicon substrate. The upper diffractograms are obtained from the films as cast and the lower from the same films after heating at 200 °C. The most intense peaks are truncated to emphasise the presence of higher order diffractions.

Table 1 X-Ray diffraction data for cast films of Pcs **1–3**, at 20 °C[a]

Pc	Lamellar *d*-spacing (Å)	Orders of diffraction	Intensity[b] (arbitrary units)
1	29.7 (29.5)	2 (2)	140 (838)
2	48.7 (49.7)	3 (4)	217 (458)
3	49.1 (51.3)	4 (5)	285 (813)[c]

[a] Values in parentheses refer to data collected at 20 °C from films which have been annealed for a short period of time at 200 °C. [b] Intensity of first-order diffraction peak. [c] Second-order diffraction peak is of greater intensity (856 arbitrary units).

the best LB films derived from Pc derivatives.[11–13] Films cast onto hydrophilic substrates give no evidence of lamellar structure, suggesting that in the ordered films the non-polar hexadecyl chains of the first monolayer are in contact with the hydrophobic substrate. Phthalocyanines **2** and **3** give a large lamellar spacing consistent with the formation of a bilayer structure in which the Pc molecules are oriented perpendicular to the substrate, whereas Pc **1** gives a film with a smaller lamellar spacing consistent with a monolayer structure. The formation of a bilayer film from Pc **1** would be disfavoured by the position of substituents of similar polarity on opposite benzo-portions of the Pc. Visible absorption spectra of the films (Fig. 2) give, in each case, a single broad band at 620 nm, blue shifted as compared to the Q-band absorption in dilute solution (≈ 700 nm), which is characteristic of exciton coupling between cofacial aggregates.[14] This indicates that the molecules are in a columnar arrangement within the lamellar plane.

The cast film forming properties of Pcs **1–3** appears to be related to segregation of the non-polar hexadecyl side-chains from the polar hydroxy-terminated tetraoxyethylene side-chains. Phthalocyanines which contain only one type of side-chain do not give films with layered ordering. Evidence of a lamellar structure in bulk samples of Pcs **2** and **3** was obtained by powder X-ray diffraction studies. In addition, Pcs **1–3** all form columnar thermotropic mesophases (Table 2) with Pc **2** exhibiting a rare example of a discotic lamellar mesophase (D_L).[15] The large lamellar spacing of 55 Å within the D_L mesophase of **2**, as measured by powder X-ray diffraction, is also consistent with a bilayer structure formed by side-chain segregation. A detailed examination of the mesophase properties of these materials will be reported in a future publication.

It has been reported that the order of LB films derived from amphiphilic Pc derivatives can be increased by heating.[11] Thus the cast films of Pcs **1–3** were annealed for a short time at 200 °C, at which temperature the Pcs are in a columnar mesophase. Table 1 shows the resultant increase in intensity of the X-ray diffraction peaks of the films on cooling to room temperature.

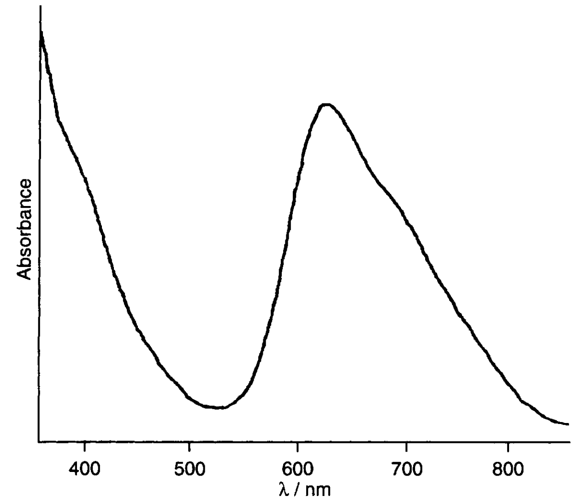


Fig. 2 Representative UV–VIS spectra obtained from a solvent cast film of Pc **3**. The strong absorption at 620 nm is indicative of exciton coupling between cofacial Pcs.

Table 2 Mesophase transition temperatures (°C) with enthalpy changes (ΔH/J g^{-1}) in parentheses[a]

Pc	$K–D_{rd}$	$K–D_L$	$D_{rd}–D_{hd}$	$D_L–D_{rd}$	$D_{rd}–I$	$D_{hd}–I$
1	30 (29.5)	—	109 (2.5)	—	—	234 (5.0)
2[b]	—	79 (87.7)	—	132 (0.9)	194 (3.6)	—
3	80 (16.1)	—	252 (0.8)	—	—	273 (0.8)

K = crystal, D_L = discotic lamellar, D_{rd} = discotic rectangular, D_{hd} = discotic hexagonal disordered. [a] Transition temperatures and enthalpies are for heating cycle. [b] Also displays a monotropic D_{hd} mesophase of narrow thermal range on cooling from the isotropic phase.

Pcs **1–3**, despite forming stable monolayers at the air–water interface, could not be deposited as uniform, ordered multilayers. It is possible that the strong intermolecular interactions, responsible for the well-ordered cast films, result in monolayers which are too viscous for smooth deposition.

The cast films formed by Pcs **1–3** are much easier to prepare than LB films derived from Pc derivatives and appear to possess better layered ordering. Polarising microscopy indicates that no cracking of the films occurs during deposition or as a result of subsequent heat treatment although there are distinct birefringent domains. However, other desirable structural properties associated with Pc-based LB films, namely in-plane anisotropy[11] (absent presumably due to the random orientation of the domains) and thickness uniformity are not obtained in the cast films. Experiments to induce in-plane anisotropy using suitable substrates for surface alignment and to produce films of a uniform thickness by spin-coating[16] are planned.

Footnote

† *Spectroscopic data*: Pc **1**. UV–VIS (toluene, λ_{max}/nm) 704, 668, 642, 606, 394, 340. ^1H NMR (500 MHz, C_6D_6) −1.8 (2 H, br s), 1.00 (12 H, t), 1.3–1.9 (104 H, m), 2.1–2.3 (8 H, m), 3.0–3.4 (8 H, m), 3.50 (4 H, t), 3.67 (4 H, m), 3.71 (4 H, m), 3.78 (4 H, m), 3.81 (4 H, m), 3.89 (4 H, m), 4.06 (4 H, m), 4.45 (4 H, m), 7.85 (2 H, m), 8.8–9.5 (8 H, m) (signal due to hydroxy protons is hidden by alkyl resonances). FABMS; found: *m/z* 1796. $^{13}CC_{111}H_{178}N_8O_{10}$ (M + H)$^+$ requires 1796.

Pc **2**. UV–VIS (toluene, λ_{max}/nm) 706, 670, 638, 608, 384, 344. ^1H NMR (500 MHz, C_6D_6) −1.4 (2 H, br s), 1.00 (12 H, t), 1.3–1.9 (104 H, m), 2.1–2.3 (8 H, m), 3.2–3.4 (8 H, m), 3.55 (4 H, t), 3.65 (4 H, m), 3.69 (4 H, m), 3.77 (4 H, m), 3.81 (4 H, m), 3.86 (4 H, m), 4.02 (2 H, m), 4.07 (2 H, m), 4.40 (2 H, m), 4.50 (2 H, m), 7.6–7.8 (2 H, m), 8.7–9.5 (8 H, m), (signal due to hydroxy protons is hidden by alkyl resonances). FABMS; found: *m*/*z* 1796. $^{13}CC_{111}H_{178}N_8O_{10}$ (M + H)$^+$ requires 1796.

Pc **3**. UV–VIS (toluene, λ_{max}/nm) 706, 670, 638, 608, 384, 344. ^1H NMR (500 MHz, C_6D_6) −3.3 (2 H, br s), 1.00 (6 H, t), 1.3–2.2 (56 H, m), 2.8–3.3 (4 H, m), 3.65 (6 H, m), 3.74 (6 H, t), 3.78 (6 H, m), 3.86 (6 H, m), 3.95 (12 H, m), 4.05–4.20 (6 H, m), 4.25–4.6 (6 H, m), 7.6–7.8 (3 H, m), 8.0–9.2 (8 H, m), (signal due to hydroxy protons is hidden by alkyl resonances). FABMS; found: *m*/*z* 1541. $^{13}CC_{87}H_{130}N_8O_{15}$ (M + H)$^+$ requires 1540.

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