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PREPARATION OF NON-CENTROSYMMETRIC LANGMUIR-BLODGETT FILMS WITH ALTERNATING MEROCYANINE AND STEARYLAMINE LAYERS

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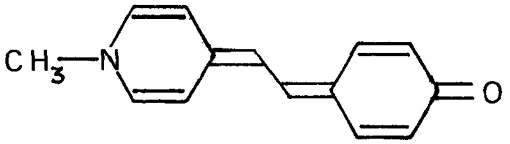
ABSTRACT

A route is described for the incorporation of a highly polarisable merocyanine dye into a non-centrosymmetric multilayer structure using the Langmuir-Blodgett thin film technique.

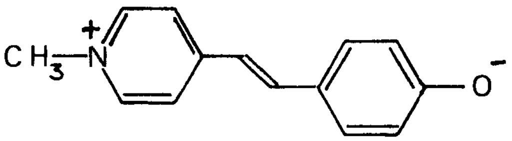
INTRODUCTION

Much interest has been shown in the merocyanine chromophore M since its synthesis was reported by Brooker and co-workers[1] who



M

demonstrated that pronounced colour changes could be achieved by changing solvent polarity *(solvatochromism)*. For example, a solution of M in pyridine is blue, absorption λ_{max} = 605 nm, but an ethanolic solution of M is red, λ_{max} = 513 nm. This was interpreted[1] as being due to changes in relative contributions of two resonance forms, the quinoidal form, M, and the charge-transfer, benzoidal form, M′.



M′

Gaines[2] has extended the solubility range of this chromophore by synthesising the n-hexadecyl homologue and, since the enolic oxygen is readily protonated (pK_a = 8.57 [3]) to give a yellow species, λ_{max} ~ 400 nm, he has suggested its use as an acid indicator in non-aqueous media.

Platt[4] has suggested that a significant shift in λ_{max} for this chromophore might be induced if an external electric field were to be applied (*electroabsorption*) Fisher[5] has shown that the optimum configuration for electroabsorption is one where the transition moments are oriented in a non-centrosymmetric, parallel fashion along the direction of the applied field.

Furthermore, M has the largest recorded second-order polarizability, $\beta = 10^{-27}$ esu[6], and therefore it is of interest for second-harmonic generation studies. A non-centrosymmetric structure is required here in order that the individual molecular polarizabilities do not cancel to zero.

We report here a route for the incorporation of this merocyanine chromophore into a non-centrosymmetric multilayer array using the Langmuir-Blodgett (L-B) film deposition technique[7]. These L-B films were visually of good optical quality but, as expected, the chromophores became protonated on standing in an air ambient due to the slightly acidic nature of dissolved CO_2. However, we have found that at least partial deprotonation is possible in a basic environment with no discernible degradation in optical quality.

EXPERIMENTAL

The surface-active n-hexadecyl and n-docosyl homologues of M were kindly supplied by Dr G L Gaines, Jr (General Electric Company) and we refer to them as M_{16} and M_{22} respectively. The ammonium sulphate (Analar grade) was obtained commercially from BDH Chemicals Ltd and stearylamine from ICN Pharmaceuticals Inc. The L-B trough (constant perimeter design) was purchased from Joyce-Loebl and was sited in a clean room. A Millipore Milli-Q system gave purified water and a n-hexane: ethanol mixture (~ 9:1 V/V) was used as the spreading solvent. All experiments were carried out at room temperature. Silica substrates (Thermal Syndicate Ltd, Spectrosil grade) were used for the UV/visible measurements and a 1 mm thick silicon prism (Harrick Scientific Corporation) was used for the multiple internal reflection (MIR) IR studies. Substrates were dipped at 5 mm min^{-1} (first cycle) and 10 mm min^{-1} (subsequent cycles).

RESULTS AND DISCUSSION

Since the main objective of this work was to demonstrate the incorporation of M into a non-centrosymmetric alternating layer (ABAB) structure, an optically inert material had to be found to act as the counter-layer which could be deposited using the same subphase conditions as M_{16} or M_{22}. Because M is acid-sensitive it was decided to investigate first the use of fatty amines[8,9] rather than, say, fatty acids.

Early experiments concentrated on the two dyes and figure 1 shows isotherm plots for M_{16} and M_{22} using subphase conditions which are known to give good quality films of stearylamine[9].

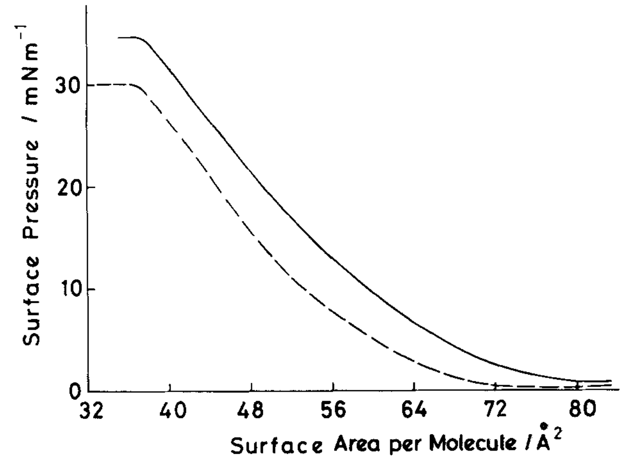


FIGURE 1 SURFACE PRESSURE-AREA ISOTHERMS FOR M_{16} (SOLID CURVE) AND M_{22} (DASHED CURVE) USING A 10^{-3} M $(NH_4)_2SO_4$ AQUEOUS SUBPHASE, pH ~ 7.5.

Note that both show expanded phases and that M_{16} has the larger collapse pressure. Both monolayers showed comparable stability ($-dA/dt \sim 0.25\%\ \mathrm{min}^{-1}$ at $\pi = 25$ mN m^{-1}) and both gave multilayer films which did not appear to scatter visible light (monolayer transfer pressure 28 mN m^{-1}). The as-deposited layers were red-orange, but turned yellow within one hour on standing in air due to protonation. Monolayer stability was reduced in the absence of ammonium sulphate suggesting that the chromophores are partially protonated at pH ~ 7.5 and the sulphate anions are promoting monolayer cohesion. Indeed evidence for the incorporation of sulphate anions into the multilayer film was obtained using IR spectroscopy which is discussed later.

It is, however, the unprotonated chromophore which is required for electro-optic measurements. We have found that it is possible, at least partially, to deprotonate the film by exposing it to a basic environment such as ammonia or methylamine vapour, or NaOH solution (pH $\gtrsim$ 12). Fifty three layers of M_{22} were transferred to both faces of a silica substrate which was then placed in a cuvette. A drop of ammonia solution was added and the film turned red. The cuvette lid was removed and the transformation back to the yellow form was followed by recording absorption data which are shown in figure 2.

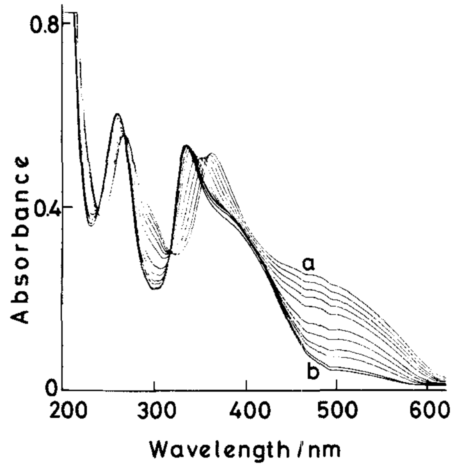


FIGURE 2 OPTICAL ABSORPTION DATA FOR AN M_{22} L-B FILM. CURVE a (RED FILM) WAS RECORDED AFTER EXPOSING THE FILM TO AMMONIA VAPOUR. THE REMAINING SPECTRA RECORD, AT ~ 5 MINUTE INTERVALS, PROTONATION OF M_{22} IN AIR TO CURVE b (YELLOW FILM).

Note the presence of isosbestic points which is consistent with the simple protolytic equilibrium of only two forms, M_{22} and $M_{22}H^+$. Repeated cycling between the yellow and red forms in the vapour phase resulted in negligible visual degradation of film quality for both M_{16} and M_{22}. However, care had to be taken when treating with NaOH solution to avoid excessive swelling of the multilayer film and its eventual lifting off from the substrate. Films successfully treated with NaOH solution took up to about two weeks to equilibriate back to the yellow form in air.

Confirmation of the reaction, $M_{22} + H^+ \underset{NH_3}{\overset{air}{\rightleftharpoons}} M_{22}H^+$, was achieved by making MIR IR measurements on a 37 layer film of M_{22} and spectra for $900 \leqslant \bar{\nu}/\mathrm{cm}^{-1} \leqslant 1800$ are shown in figure 3. Deprotonation on exposure to ammonia is confirmed by the decrease in absorption

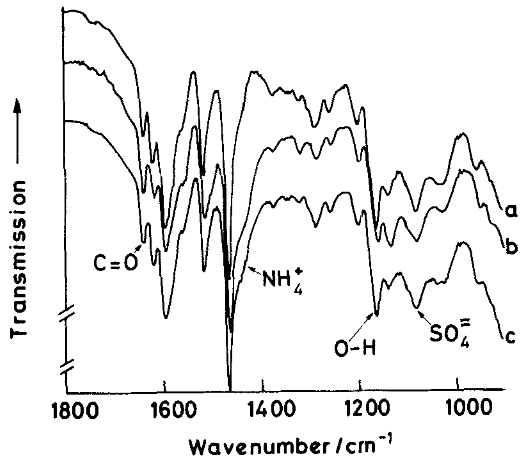


FIGURE 3 IR SPECTRA FOR AN M_{22} L-B FILM AT EQUILIBRIUM IN AIR (CURVE a), AFTER PROLONGED EXPOSURE TO AMMONIA VAPOUR (CURVE b) AND AFTER 2.5 HOURS EXPOSURE TO AN AIR AMBIENT (CURVE c).

of the phenolic O-H in-plane deformation mode at 1169 cm^{-1} and the concomitant increase in the quinoidal C=O stretching vibration at 1643 cm^{-1}. Also, note the presence of a $SO_4^=$ vibrational mode at 1091 cm^{-1} and the appearance of a NH_4^+ vibrational mode at ~1450 cm^{-1} (shoulder) as a consequence of exposing to ammonia. After standing for ~2.5 hours in an air ambient the spectrum closely resembles that recorded before exposure to ammonia except for the shoulder at ~ 1450 cm^{-1} which does not fully return to its original strength, indicating the retention of some NH_4^+ ions in the film.

The feasibility of constructing multilayer L-B films with alternating layers of stearylamine and M_{16} (or M_{22}) was confirmed by transferring the amine layers on the down strokes and the M_{16} (or M_{22}) layers on the upward stroke employing a common subphase (pH ~ 7.5, 10^{-3}M $(NH_4)_2$ SO_4). Many cycles could be performed and the optical quality of the resulting films, which protonated on standing in air, was indistinguishable to those with no amine layers present. Deprotonation using NaOH solution might well give the films adequate lifetime for electro-optic measurements, but we have not attempted this. Instead, because non-centrosymmetric structures are expected to possess a permanent dipole moment, we are now carrying out dielectric measurements with the objective of testing for pyroelectric behaviour. Structual studies are also underway.

Our observations reported here show that expanded monolayers can give L-B films of good optical quality. In contrast, materials which give condensed monolayers, such as certain fatty soaps, commonly produce L-B films which strongly scatter visible light from crystallite boundaries. It is clear that much important work remains to be done in trying to understand the detailed properties of precursor monolayers and the influence these properties have on the nature and quality of the deposited films.

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