Langmuir–Blodgett Films of Porphyrins containing a Metal–Metal Sigma Bond

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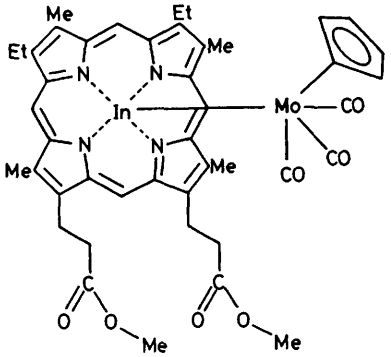
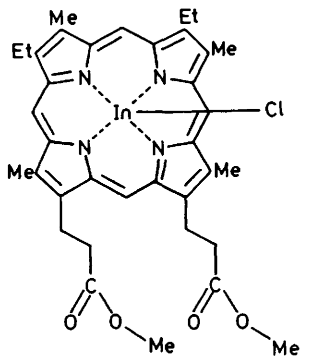
Mono- and multi-layer Langmuir–Blodgett (LB) films of a newly synthesised porphyrin derivative, indium mesoporphyrin-9-dimethyl ester cyclopentadienyltricarbonyl molybdenum containing a metal–metal (In–Mo) σ-bond, have been prepared on hydrophobic and indium tin oxide-coated glass; a combination of n.m.r., i.r., and u.v. absorption spectroscopies has been employed for the characterisation of the molecule and the LB films.

Langmuir–Blodgett (LB) films are of considerable scientific and technological importance.[1,2] Much early work was performed on the long chain fatty acids[3] and their derivatives[4] but recently, in the quest for more thermally and mechanically robust films, attention has turned to certain polymers, *e.g.* diacetylene,[5] phthalocyanine,[6] and porphyrin[7,8] derivatives. Recently Baker *et al.*[6] reported the syntheses of metal-free and asymmetrically substituted copper phthalocyanine films. Snow and Jarvis[9] also succeeded in depositing LB films of various metal phthalocyanine compounds with cumylphenoxy peripherals substituted, and Tredgold *et al.*[10,11] have reported extensive studies on porphyrin LB films. Electrochromism was recently reported in metal-free phthalocyanine LB layers.[12]

In parallel with these studies on LB films, several research groups have reported the existence of dimeric[13] and polymeric[14] porphyrins and units containing hetero-atomic metal–metal σ-bonds have been synthesized.[15] In this communication we report for the first time the preparation and characterisation of porphyrin LB films containing a metal–metal σ-bond. The presence of the metal–metal bond offers possibilities for modifying the light absorption–emission characteristics of LB films and further enhances their capabilities in catalysis.



(1)



(2)

MPixDMEIn–Mo(CO)$_3$C$_5$H$_5$ (**1**) (where MPixDME is mesoporphyrin-9-dimethyl ester) was prepared by reaction of MPixDMEInCl (**2**) (esterification of mesoporphyrin IX followed by reaction with InCl$_3$) with the Mo(CO)$_3$C$_5$H$_5$$^-$ anion [reaction of Mo$_2$(CO)$_6$(C$_5$H$_5$)$_2$ with Na–Hg] according to a previously reported procedure.[15] Characterisation was achieved by i.r. [ν(CO) 1975, 1910, 1890 cm^{-1}], ^{1}H n.m.r. in CDCl$_3$ (δ CHCl$_3$ 7.27); [2.58, (s, C$_5$H$_5$), 10.17 (s, arom-H), 3.63 (s, ring-Me), 4.41 (t, ester-CH$_2$), 3.21 (t, ester-CH$_2$), 3.63 (s, ester-Me), 4.09 (q, ethyl-CH$_2$), 1.77 (t, ethyl-Me)], and u.v.–visible spectroscopy [406 (Soret), 443, 536, and 572 nm]. Using standard conditions similar to those employed for dipping stearic acid, a stable monolayer was prepared from chloroform solutions of the compound at surface pressures greater than 45 mN m^{-1}. Multilayers could be prepared on hydrophobic glass and indium tin oxide-coated glass (ITO) at relatively high surface pressures (40 mN m^{-1}). Z-type deposition was observed with transfer ratios of unity.

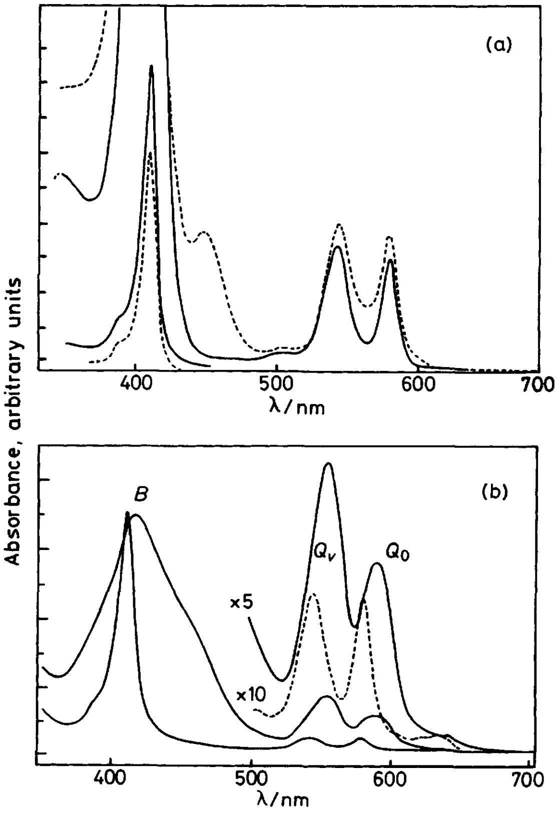


Figure 1. U.v.–visible spectra of THF solutions (a) and for LB layers (b) of MPixDMEInMo(CO)$_3$C$_5$H$_5$ (**1**) (----) and MPixDMEInCl (**2**) (——).

Figure 1 shows u.v.–visible absorption spectra of (**1**) and its precursor (**2**) in tetrahydrofuran (THF) solution and as LB films deposited on ITO hydrophobic glass. The significant difference in the solution spectra is the appearance of a band at *ca.* 450 nm attributable to the In–Mo bond. This band decreases in intensity when the THF solution is allowed to stand in air consistent with the slow dissociation of (**1**). For LB films of the two molecules there are differences in the two band systems Q and B observed in the regions 500—600 and 380—500 nm, respectively. System Q, comprising two pronounced maxima Q_0 and Q_v, is common to both films but shows a blue shift for (**1**) of *ca.* 10 nm as well as a change in the intensity ratio of Q_v relative to Q_0. System B is markedly narrower for (**1**) with the maximum again blue-shifted by *ca.* 6 nm. This broadening may reflect interaction between electron systems of neighbouring molecules in LB films of MPix DMEInCl which is not present for (**1**) because of the protruding $Mo(CO)_3C_5H_5$ ligand system.

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