Molecular Thin Films of Porphyrin Dimers prepared by the Langmuir–Blodgett (LB) Technique

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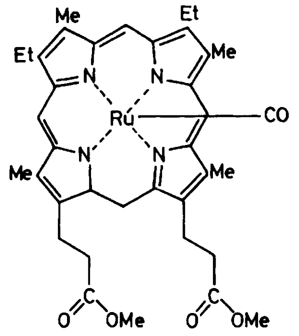
Molecular thin films of the porphyrin derivative ruthenium mesoporphyrin-9-dimethyl ester carbonyl have been prepared on a range of substrates including hydrophobic glass, polyethylene, and silver bromide by the Langmuir–Blodgett (LB) technique; irradiation of the films yields dimers, containing Ru=Ru bonds, which have been characterised by u.v. and i.r. spectroscopy.

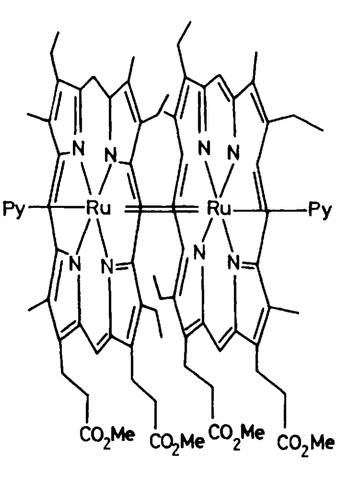
Molecular thin films are of interest because of their potential uses in molecular electronics.[1] We have recently described the preparation of such films comprising monomeric porphyrin moieties by the Langmuir–Blodgett (LB) technique and have demonstrated how metal–metal σ bonds may be incorporated into the structures.[2] Since this publication further interest has been shown in porphyrin- and phthalocyanine-based thin films primarily because of their gas sensing,[3] electrical,[4] and optical[5] characteristics. In this communication we report on a novel porphyrin dimer formed *in-situ* by u.v. irradiation of monomeric LB films. This dimer involves a π-bonded metal–metal centre.

RuMPixDMECO(**1**) (where MPixDME is mesoporphyrin-9-dimethylester) was prepared using a literature technique[6] and purified by column chromatography over neutral alumina using CHCl$_3$ as eluent. The molecular structure of the resulting porphyrin has been confirmed by u.v. and i.r. spectroscopy. (**1**) was then converted to the pyridate (**2**) (RuMPixDMECOPy) by dissolution in pyridine and removal of excess solvent under vacuum. Irradiation of (**2**) with light from a medium pressure mercury lamp produces a photodimer (RuMPDMEPy)$_2$ (**3**) with the elimination of CO.[7]



(**1**) RuMPixDMECO

(**2**) RuMPixDMECOPy (Py=pyridine)



(**3**)

LB films of the monomeric porphyrin (**2**) were prepared by casting a solution in CHCl$_3$ (10^{-3} mol dm^{-3}) on to a subphase of purified water (Milli-Q: resistivity 18 MΩ cm) to which CdCl$_2$ at a concentration of 10^{-4} M was added.[8] The pH was adjusted to 5.8 using NH$_3$(aq) where necessary. The isotherm for (**2**) is given in Figure 1. An area per molecule of 60 Å^2 is obtained which is consistent with stacking of the porphyrin ring perpendicular to the water surface.[8] Transfer of the porphyrin on to glass made hydrophobic by trichloromethylsilane was effected at a surface pressure of 23 mN m^{-1}. Transfer was also successful on to carbon-coated glass slides, polyethylene, and silver bromide substrates. Irradiation of 30 layers of the monomeric porphyrin (**2**) using a medium pressure mercury lamp results in a gradual spectral change (see Figure 2). The Soret band at 403 nm exhibits a bathochromic shift of *ca.* 14 nm, is broadened and reduced in intensity by 50%. The Q bands at 553 and 522 nm disappear. This behaviour is similar to the spectral change reported on dimerisation of RuOEPCOPy to (RuOEPPy)$_2$ (OEP = octaethylporphinato).[7] The observed changes of the Soret band are consistent with other literature reports of cofacial dimerisations and probably result from exciton coupling.[9,10] The i.r. spectrum of 60 layers of (**3**) on silver bromide indicates that the CO ligand ($\bar{\nu}_{CO}$ = 1940 cm^{-1}) is eliminated upon

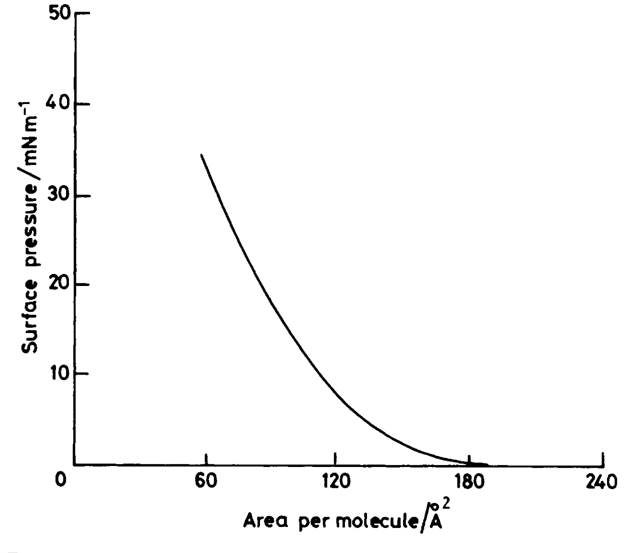


Figure 1. Pressure–area isotherm for RuMPixDMECOPy at 20 °C.

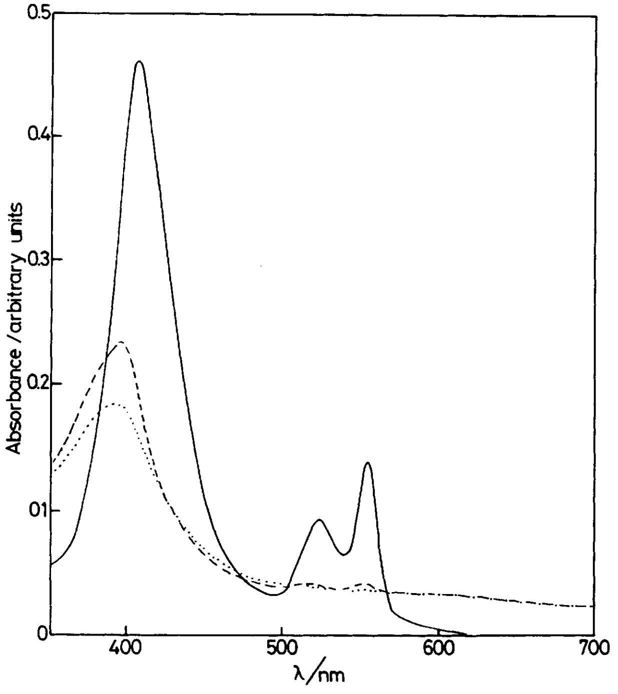


Figure 2. Visible absorption spectra for 10 layers of RuMPixDME-COPy (**2**) (——), after irradiation for 10 min (- - -) and 20 min (· · ·) with ultraviolet light.

irradiation of (**2**). The far i.r. spectrum of 60 layers of (**3**) on polyethylene contains an absorption at 112 cm^{-1} attributable to the Ru=Ru bond.[11]

The *in-situ* formation of the Ru=Ru porphyrin dimer is, in principle, the first step in our objective of preparing polymers of cofacially oriented porphyrin moieties linked together through a central metal atom. The properties of these films should be significantly different from those of preformed polymers based on Si-phthalocyanines which we[12] and others[13] have also prepared since the unique layer structure inherent in LB films should be preserved. Clearly, dimerisation of (**2**) only occurs if the monomers possess a well defined geometry for the porphyrin rings and there is an optimum separation distance for the reaction centres.[14,15]

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