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Optical and structural studies of Langmuir–Blodgett films of polyalkoxystilbazole complexes of iridium(I)

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Abstract

Studies have been focused on Langmuir films of a family of iridium polyalkoxystilbazole metallo-organic complexes. We report that these polyalkoxystilbazole complexes form stable Langmuir monolayers on water as subphase, and are successfully transferred onto glass substrates for structural and optical characterisations using UV–vis spectroscopy. The area per molecule obtained for the polyalkoxystilbazole films is larger than that for the corresponding monoalkoxystilbazole films, and cannot simply be explained by the cross-sectional area of the $Ir(CO_2)Cl$ headgroup, which is common to all of them. The length of the alkoxy chains as well as their position of substitution have an influence on the orientation of the molecules.

Keywords: Langmuir; Langmuir–Blodgett; Organo-metallic; Stilbazole; Thin film

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1. Introduction

The Langmuir–Blodgett technique (LB) [1] is a simple and effective way to prepare ultrathin films with a controlled thickness at a molecular size level and with well-defined molecular orientation. It is essential that materials to be deposited by the LB technique be soluble in an organic solvent but insoluble in water. Such molecules must have a correct amphiphilic balance of hydrophilic and hydrophobic regions. Materials for LB films can be tailor-made via the design of both the head and the tail groups. Organo-metallic materials [2] often exhibit novel and interesting properties, such as non-linear optics [3], liquid crystals, and pyroelectric devices [4–9]. The organo-metallic compounds studied in this paper are polar molecules of polyalkoxystilbazole complexes of iridium(I). Our group previously reported studies on the same family of organo-metallic complexes [10], except that they were monosubstituted. In the present work, we report on the preparation and characterisation of Langmuir films of a series of polyalkoxystilbazole complexes of

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iridium(I) by measuring surface pressure–area (π–A) isotherms as well as UV–vis absorption spectroscopy.

2. Experimental

2.1. Materials

The synthesis of the polyalkoxystilbazole complexes of iridium(I) has been described elsewhere [11]. The chemical structures of the polyalkoxystilbazole complexes of iridium(I) and their abbreviations are shown in Fig. 1. To guide the reader through the different structures reported herein, we adopt the following nomenclature system. For the sake of simplicity, since the headgroup is identical for all the complexes, this will be simply referred to as Ir, the numbers between the brackets refer to the length of the alkoxy chains substituted, followed by the positions of the substitution.

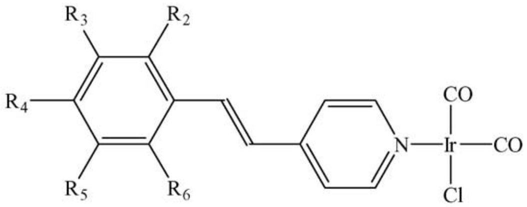
2.2. Langmuir films

All isotherms were measured in a clean room class 1000 at room temperature (20–24 °C). Solutions of typical concentration 5.0×10^{-4} mol l^{-1} in chloroform were prepared and a known volume, typically 100–150 μl, spread on the air–water interface. The spreading was performed by means of a microsyringe in such a way as to leave small droplets on the subphase, with each successive drop being as far away possible from the previous one, and the complete spreading carried out over a period of time of around 4–5 min. A fan was switched on for about 30 min to assist the evaporation of the spreading solvent. Prior to each experiment, the fan was switched off. The trough was placed in a house-made cabinet to minimise dust exposure. Formation of the air–water monolayer was carried out in a Langmuir trough of constant perimeter supplied with an electronic balance, which uses a Wilhelmy plate as the pressure sensor. Isotherms were produced by reducing the surface area available to the materials at a constant slow rate of 5 cm^2 s^{-1}.

3. Results and discussion

3.1. Surface pressure–area (π–A) isotherms

Fig. 2 shows the π–A isotherms for the polyalkoxystilbazole complexes of iridium(I). Equilibrium-spreading pressures of the polyalkoxystilbazoles on the subphase were measured, and the almost constant value of pressure attained over 3–8 h shows that they form very stable Langmuir films. At very slow rate of compressions, the molecules are allowed to reorganise themselves on the water surface, and thus, the isotherms obtained indicate the true average behaviour



Complexes	R_2	R_3	R_4	R_5	R_6
Ir(8-3,4)	H	$C_8H_{17}O$	$C_8H_{17}O$	H	H
Ir(11-3,4)	H	$C_{11}H_{23}O$	$C_{11}H_{23}O$	H	H
Ir(14-2,4)	$C_{14}H_{29}O$	H	$C_{14}H_{29}O$	H	H
Ir(14-3,4)	H	$C_{14}H_{29}O$	$C_{14}H_{29}O$	H	H
Ir(14-3,5)	H	$C_{14}H_{29}O$	H	$C_{14}H_{29}O$	H
Ir(18-3,4)	H	$C_{18}H_{37}O$	$C_{18}H_{37}O$	H	H
Ir(14-3,4,5)	H	$C_{14}H_{29}O$	$C_{14}H_{29}O$	$C_{14}H_{29}O$	H

Fig. 1. Chemical structures of polyalkoxystilbazole complexes of iridium(I).