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Characterisation of Langmuir–Blodgett assemblies of polyalkoxystilbazole complexes of iridium(I) and a cyclic polysiloxane in pyroelectric devices

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Abstract

Studies have been made of alternate layer (ABABA superlattices) multilayer Langmuir–Blodgett (LB) films using a cyclic polysiloxane (A) and an iridium(I) polyalkoxystilbazole metallo-organic complex (B). The electrically polar nature of the molecules studied suggests that they may be suitable candidates for new pyroelectric materials. The pyroelectric coefficient has been measured for alternate layer multilayer LB films built with various number of layers of the iridium(I) complex. We investigate the effect of chain length of the substitution and position of the substitution on the pyroelectric coefficient, capacitance and dielectric loss.

Keywords: Langmuir–Blodgett; Metallo-organic; Stilbazole; Pyroelectricity; Dielectric constant

1. Introduction

The pyroelectric effect occurs in non-centrosymmetric, polar crystals and thin films whose spontaneous polarisation changes as a function of temperature. Commonly pyroelectrics are inorganic compounds such as lithium tantalate and lithium niobate, but tremendous efforts have been made to incorporate organic materials in pyroelectric devices. However, in both cases, often electrical poling after the preparation of the thin film is necessary to render it pyroelectric. The alternate layer Langmuir–Blodgett (LB) [1,2] deposition technique provides an excellent mean to produce molecular assemblies which are polar at the macroscopic level. The advantages of using LB films as pyroelectric materials are: (i) precise control of the desired thickness; (ii) molecular architecture tailoring to impart non-centrosymmetry structure; (iii) low dielectric constant; (iv) low heat capacity for fast pyroelectric response; (v) ease to process film for devices without destruction of the orientation order of the molecules. LB films of metallo-organic materials [3] have received much attention and our group previously reported the study of complexes of monoalkoxystilbazoles [4,5]. This paper forms an extension to this earlier work by reporting the pyroelectric assessment of polyalkoxystilbazoles. Pyroelectric films were obtained by alternately depositing these metallo-organic complexes with a cyclic polysiloxane.

2. Experimental

2.1. Materials

The synthesis of the polyalkoxysubstituted iridium(I) complexes, whose chemical structures are shown in Fig. 1 has been described elsewhere [6]. The cyclic polysiloxane used in this work consists of a six Si–O units (hexahydrogenmethyl-

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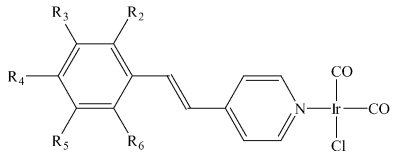

Complexes	R_2	R_3	R_4	R_5	R_6
Ir(8-3,4)	H	$C_8H_{17}O$	$C_8H_{17}O$	H	H
Ir(11-3,4)	H	$C_{11}H_{23}O$	$C_{11}H_{23}O$	H	H
Ir(14-2,4)	$C_{14}H_{29}O$	H	$C_{14}H_{29}O$	H	H
Ir(14-3,4)	H	$C_{14}H_{29}O$	$C_{14}H_{29}O$	H	H
Ir(14-3,5)	H	$C_{14}H_{29}O$	H	$C_{14}H_{29}O$	H
Ir(18-3,4)	H	$C_{18}H_{37}O$	$C_{18}H_{37}O$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

cyclohexasiloxane) which form the cyclic backbone, and has a spacer group containing 10 methylene groups between the polymer backbone (siloxane ring) and the carboxylic acid moiety.

2.2. Alternate Langmuir–Blodgett films

Solutions of the cyclic polysiloxane (A) and the iridium(I) complex (B) were made up to typical concentrations of 0.25–0.50 mg ml^{-1} using chloroform as solvent. Between 100 and 200 μl were spread over an ultra pure water (Elga System UHP) subphase, pH 6.0, in an alternate Langmuir trough possessing a central fixed barrier accommodating a rotating drum to which was clamped the substrate. In this way, two independently formed monolayers A and B were alternately deposited to form an ABABA. . . multilayer film. This technique enables the dipole moments associated with stilbazole molecules within individual monolayers to align in a preferred direction thus allowing a net macroscopic electric polarisation to build up. Transfer of the Langmuir film of the iridium(I) stilbazole complexes onto an aluminium-coated glass substrate was performed at a surface pressure of 25 mN m^{-1}.

2.3. Fabrication of pyroelectric devices

The bottom electrode is made up of 500 Å thick of aluminium thermally evaporated on a clean glass substrate at a rate of 3.0 Å s^{-1} from a tungsten filament in an Edwards 306A thermal evaporator at a pressure of 10^{-6} Torr. The thickness of the aluminium film was monitored by a quartz crystal microbalance. The organic layer was then LB-deposited using the alternate technique. A mask was used to shape three top electrodes over the LB film, and the evaporation was performed in two steps so as not to increase unnecessarily the temperature which could damage the organic layers. An initial evaporation rate of 1.0 Å s^{-1} was used for the first 50 Å thick of aluminium in contact with the organic layer, followed by a final evaporation rate of 2.0–3.0 Å s^{-1} until the required 500 Å thickness of aluminium was attained. Electrical contacts were made to the two electrodes using conducting silver paint, which was allowed to dry for at least 30 min prior to the evacuation of the sample chamber.

2.4. Pyroelectric assessment

Fig. 2 shows the temperature cycle imposed upon all the samples studied and the resulting pyroelectric current output. The current waveform approximates to a square-wave; the rounding effects are caused by the non-linear temperature variation which occurs at each heating/cooling transition point. In a typical experiment, at least 10 complete periods are used to yield an average pyroelectric coefficient and the amplitude of the temperature oscillation is restricted to a maximum value of 0.5 K. The mean temperature about which the oscillation is imposed is varied over the range 273–333 K with

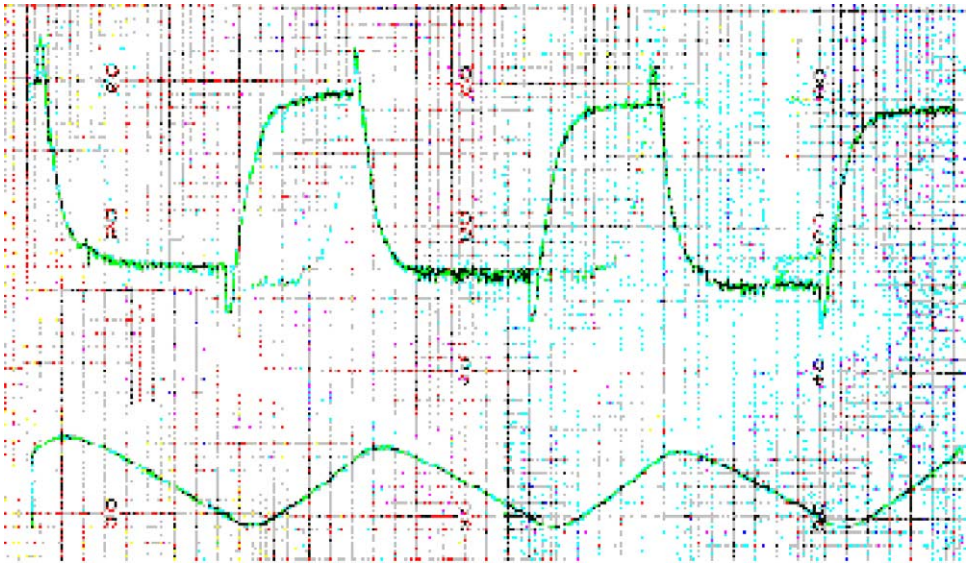

Fig. 2. The pyroelectric current response to a sawtooth temperature regime.