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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

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To cite this Article Topacli, A. and Richardson, T.(1998) 'Fourier Transform Infrared Studies of Novel LB Films of Iridium Monoalkoxystilbazole', *Spectroscopy Letters*, 31: 2, 397 – 407

To link to this Article: DOI: 10.1080/00387019808003263

URL: <http://dx.doi.org/10.1080/00387019808003263>

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FOURIER TRANSFORM INFRARED STUDIES OF NOVEL LB FILMS OF IRIDIUM MONOALKOXYSTILBAZOLE

Key words : Stilbazole, Langmuir-Blodgett Films, infrared spectra

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ABSTRACT

Grazing Incidence Reflection Fourier Transform Infrared Spectroscopy (GIR-FTIR) has been applied to the determination of the structures of Langmuir-Blodgett (LB) films of iridium monoalkoxystilbazole on aluminised glass. Band assignments, peak positions and relative intensities are given for some characteristic groups. These results indicated that the hydrocarbon chains tend to orient perpendicular to the film surface. Further, the high relative intensity of C₄-O asymmetric stretch shows, in a qualitative way, that the transition moment of this vibration is oriented approximately perpendicular to the substrate surface.

INTRODUCTION

Infrared spectroscopy with polarized light is a well-known technique for determining molecular packing and molecular orientation. Reflection-absorption (RA) or grazing-angle spectroscopy, is a very useful technique that gives information about the direction of transition dipoles in a

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sample. The integrated intensity (I_i) of a vibrational absorption band i depends on the magnitude and orientation of the transition moment M_i with respect to the electric field vector E (Eq. 1), where θ is the angle between M_i and E .

$$I_i \approx |M_i E|^2 \approx \cos^2 \theta \quad (\text{Eq. 1})$$

The orientation of a molecular unit with attached transition moments on a substrate plane is schematically shown in FIG.1. The task is to determine the lateral and tilt angles, ψ and Φ , respectively.

A special sampling technique for monolayer studies involves the use of transparent substrate for transmission studies and evaporated metal mirrors on flat glass plates for the reflection studies. Only half of the substrate covered by the Langmuir-Blodgett (LB) film, the uncovered part served as reference.

In transmission experiments with normal incidence of the IR beam, the electric field vector E is oriented parallel to the layer plane. In this geometry the projection of the transition moments on layer plane is probed and the lateral orientation distribution of the molecules with respect to the transfer direction t of the substrate through the air-water interface of the Langmuir trough can be determined. The preferential orientation of rigid-rod polymer systems with respect to t during the transfer process was investigated with this method¹.

The geometry of the reflection experiment is shown schematically in FIG.2. Different names for the same experimental technique are used in literature: Grazing Incidence Reflection Fourier-Transform Infrared (GIR-FTIR) Spectroscopy or Infrared Reflection Absorption Spectroscopy (IR-RAS). The development of the technique goes back to the Greenler² and has become a very powerful experimental technique for several reasons^{3,4} due to the reflectivity conditions at the metal surface for light polarized parallel to the plane of incidence. The resulting electric field vector E is oriented perpendicular to the surface. If the IR beam is polarized perpendicular to the plane of incidence, E vanishes at the metal surface because of the phase change of π of the electromagnetic wave. As shown in FIG.2, GIR-FTIR spectroscopy offers the possibility to selectively observe molecular vibrations polarized parallel to the surface normal n .

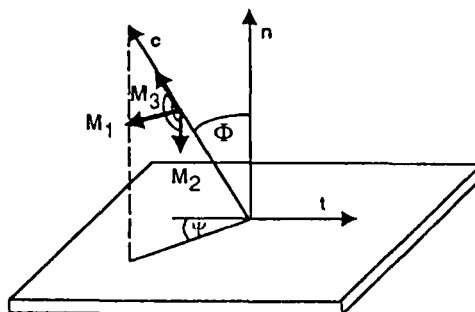


FIG. 1. Orientation of a set of transition dipole moments M_i of a molecule with the chain axis C with respect to the substrate geometry; n_i : surface normal, t : transfer direction, ψ : lateral angle, ϕ : tilt angle.

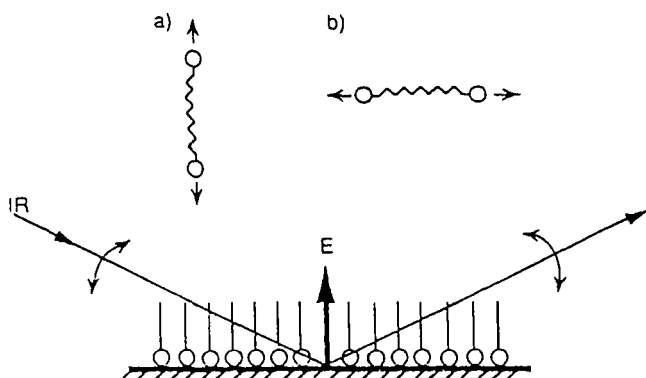


FIG. 2. Principle of infrared spectroscopy under grazing incidence conditions of the IR radiation. Only the molecular vibration a) can absorb light, b) is inactive.

Structural investigations with GIR-FTIR spectroscopy have become very useful for an understanding of the basic properties of LB films. Alkyl chains are frequently used as substituents of polymers for the LB technique, the structure of an alkyl chain end and the assignment of typical IR bands are presented in FIG.3. As shown in FIG.3, both the symmetric and asymmetric methylene vibrations ($\nu_s(\text{CH}_2)$ and $\nu_a(\text{CH}_2)$, respectively), are parallel to the metal plane, the symmetric vibration and both asymmetric vibrations of the methyl group (CH_3) have components that are perpendicular to the surface. Therefore, the methylene groups in a

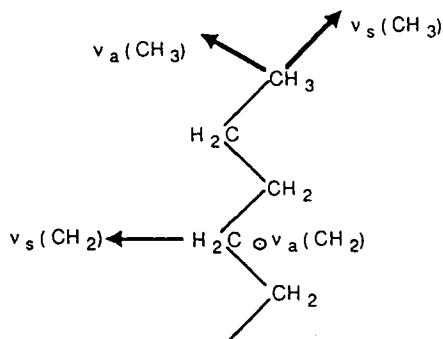


FIG. 3. Section of alkyl chain with characteristic IR vibrations bands and transition moments.

perpendicular, all trans alkyl chain will not be picked up by the p-polarized light. Of course, once the alkyl chain tilts from the normal to the plane, the symmetric and asymmetric vibrations of the methylene groups are no longer parallel to the surface and thus will appear in the grazing-angle spectra. The intensity of the methylene vibrations in the spectra is a direct function of the tilt angle of the alkyl chain. The intensity ratios in the CH stretching vibrations can be used as a qualitative measure of the molecular order in the alkyl-chain region. This unique property of the grazing-angle experiment enables the calculation of molecular orientation from FTIR⁵.

Metallo-organic materials often exhibit novel and interesting properties. Recently much attention has been focused on the alternate layer LB deposition technique to obtain noncentrosymmetric films which would possess spontaneous polarisation and give rise to second-order non-linear optical phenomena such as pyroelectricity. Iridium monoalkoxystilbazoles^{6,7} have been previously reported by our group whose structure is shown in FIG. 4.

EXPERIMENTAL

Alternate layer Langmuir-Blodgett (LB) film assemblies, consisting of *N* monolayers of the stilbazole complex codeposited with (*N*-1) monolayers of tricosanoic acid (TA) where 4, 8 and 12 were fabricated on an alternate-layer trough described previously^{6,7}.

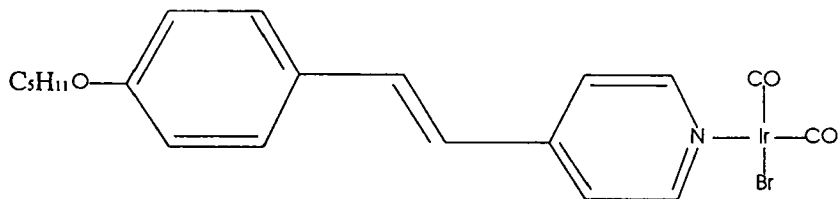


FIG. 4. Chemical Structure of the Iridium Monoalkoxystilbazole.

FTIR spectra were measured using a Perkin Elmer 1725X Spectrometer fitted with an MCT detector. Grazing incidence measurements were carried out using a Harrick reflection accessory.

RESULT AND DISCUSSION

The transmission spectrum of iridium monoalkoxystilbazole with KBr is given in FIG.5. As seen from this spectrum $\nu(\text{C}=\text{O})$ bands at 2075 cm^{-1} , 2051 cm^{-1} and 1982 cm^{-1} are greatly high intensity relative to the CH_2 stretching modes ($\nu_s(\text{CH}_2)$ at 2919 cm^{-1} and $\nu_a(\text{CH}_2)$ at 2851 cm^{-1}). Also 21-monolayers with iridium monoalkoxystilbazole (in chloroform) on the glass substrate have been made and recorded the transmission spectrum of this sample. The absorption spectrum of this film in the wave number region below 2000 cm^{-1} could not be obtained because of the strong absorption of the glass (FIG.6a). So, the film has been washed with a small amount of chloroform, after evaporating, the transmission spectrum of this sample has been recorded (FIG 6b). As seen from FIG. 6b, $\nu(\text{C}=\text{O})$ bands are greatly reduced in intensity relative to the CH_2 stretching modes as compared with the cast spectrum of iridium monoalkoxystilbazole (FIG.5). This effect can be interpreted as the result of the chemical changes of the head group of iridium monoalkoxystilbazole. In addition to a changing intensity, we also observed $\nu(\text{C}=\text{O})$ band at 1734 cm^{-1} (FIG.6b) which has not observed in the bulk spectrum of iridium monoalkoxystilbazole (FIG. 5). These result suggest that it may be new chemical arrangement for the head group after dipping.

FIG. 7a, 7b and 7c represent the grazing-angle spectra, respectively, of 4-, 8- and 12-monolayers of the alternate LB films of iridium monoalkoxystilbazole have also been recorded. The CH_2 scissoring and rocking bands of the hydrocarbon chains are known to be sensitive to

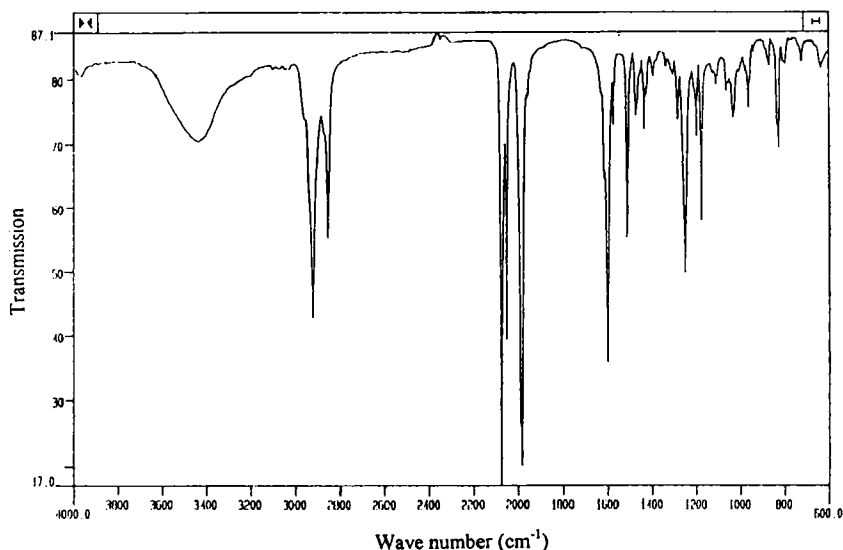


FIG. 5. Infrared transmission spectrum of Iridium Monoalkoxystilbazole in KBr.

the intermolecular interaction and are often used to distinguish the lateral packings of the chains^{8,9}. The presence of a single infrared peak indicates that the side chains are packed in a hexagonal-like manner whereas the presence of two peaks would indicate that orthogonal packing. The scissoring and rocking bands of the hydrocarbon chains appears as singlets at 1469 cm^{-1} and 721 cm^{-1} , respectively, indicating that the alkyl chains are in a hexagonal subcell packing where each chain is freely rotated around its long axis^{8,9}. As can be seen from the transmission spectrum of the cast LB film (FIG. 6b) these bands are not clear.

Assignments of the absorption bands are summarized in Table 1. Relative intensities of these bands are quite different between the transmission and reflection-absorption spectra. The intensity of CH_2 vibrations in the spectra is a direct function of the tilt angle of the alkyl chain. For completely perpendicular alkyl chains, the CH_2 vibrations, which have transition dipole moments perpendicular to the alkyl chain (i.e. parallel to the substrate surface, would be expected to approach zero intensity in the RA spectra).

If the CH_2 stretching modes ($\nu_s(\text{CH}_2)$ at 2919 cm^{-1} and $\nu_s(\text{CH}_2)$ at 2851 cm^{-1}) are compared (FIG. 7a, 7b and 7c) with the transmission spectrum of the random film (FIG. 6b), it can be

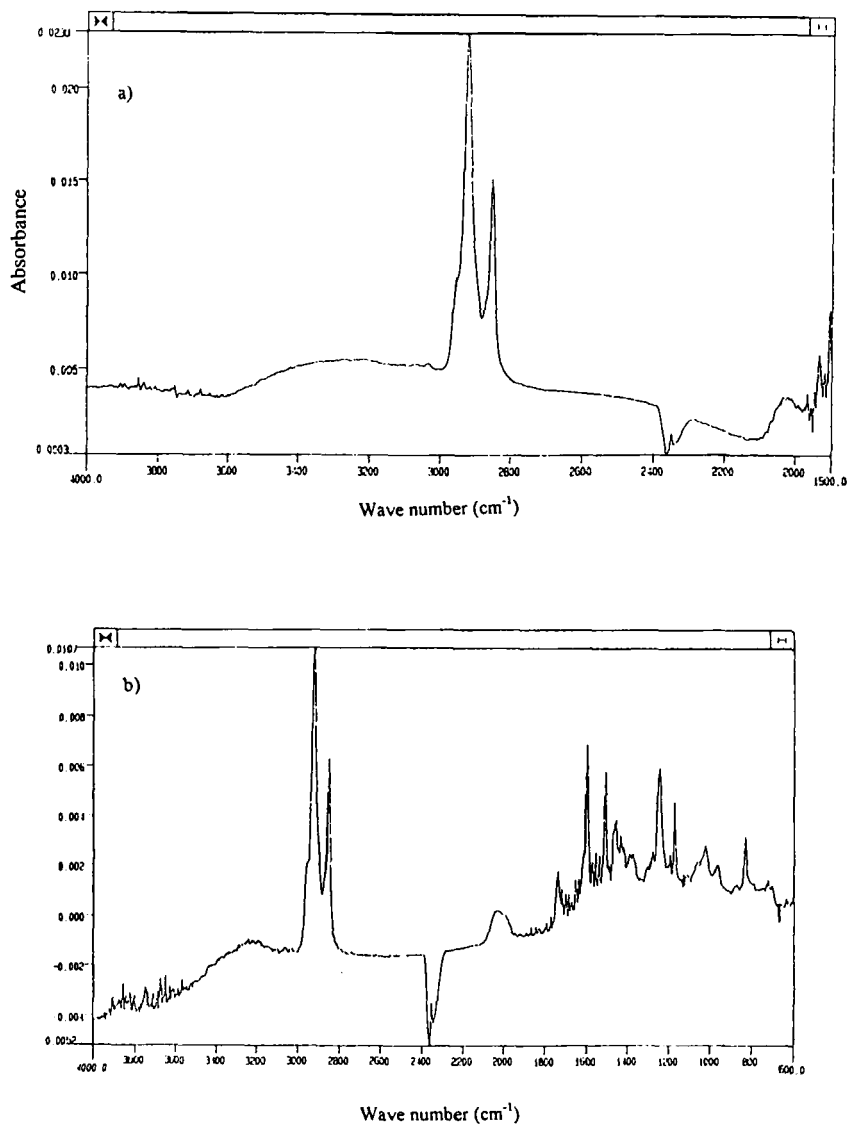


FIG. 6. Infrared transmission spectrum of 21-monolayers LB film of Iridium Monoalkoxystilbazole a) on a glass substrate b) after washing with the chloroform from the glass substrate.

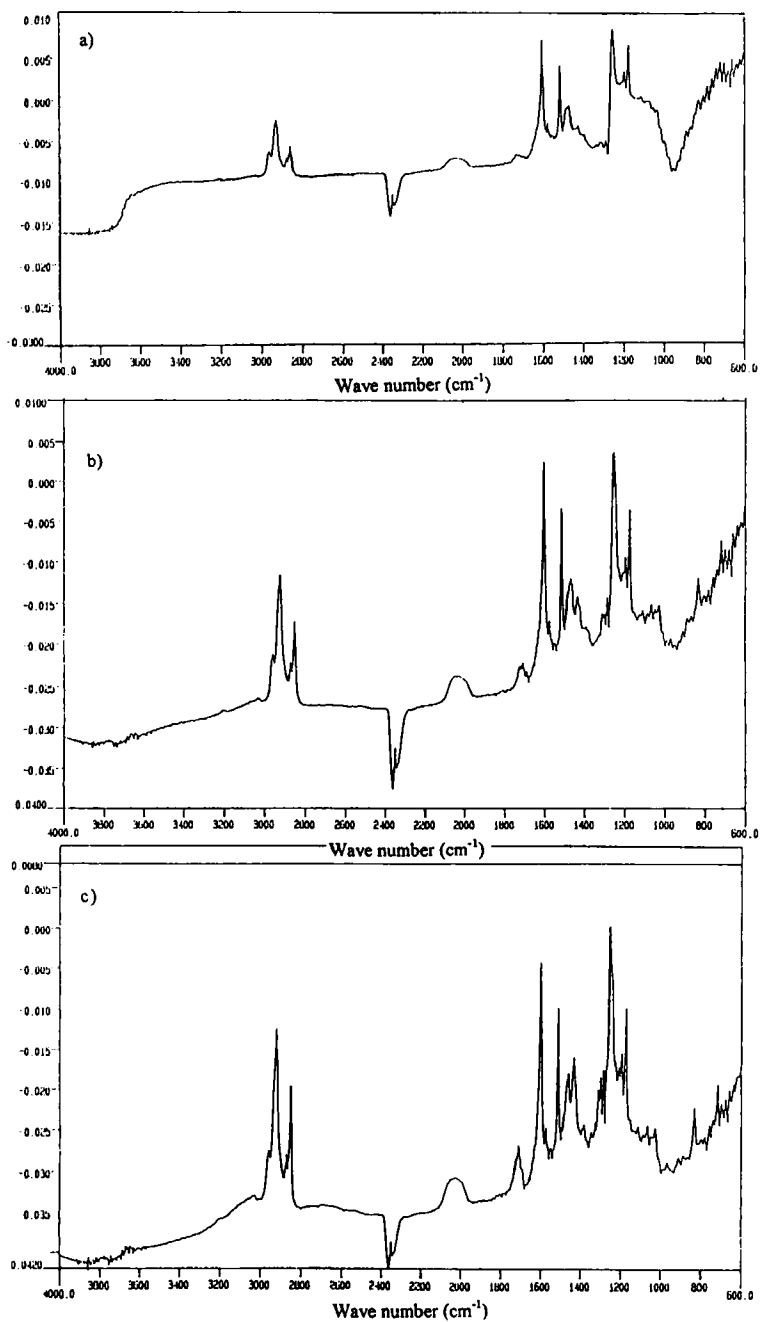


FIG. 7. Grazing -angle FTIR spectra of a) four b) eight c) twelve of alternate LB film of Iridium Monoalkoxystilbazole on an aluminized glass substrate.

TABLE 1.

Observed and Their Assignments of Iridium Monoalkoxystilbazole in LB Films.

Wavenumber (cm^{-1})		
Transmission	Ra	Assignment ^a
-	2957 sh ^b	$\nu_a(\text{CH}_3)$
-	2873 sh	$\nu_s(\text{CH}_3)$
2920	2919	$\nu_a(\text{CH}_2)$
2850	2850	$\nu_s(\text{CH}_2)$
1734	1714	$\nu(\text{C}=\text{O})$
1601 m	1604 s	benzene-ring
1512 m	1514 s	benzene-ring
1458 w	1469 w	$\delta(\text{CH}_2)$
-	1436 m	$\nu(\text{C}-\text{Ostr.}) + (\text{OHdef.})$
1250 m	1257 s	$\nu(\phi-\text{O})$
1175 w	1176 m	$\nu(\phi-\text{N})$
832 w	832 w	$\pi(\phi-\text{H})$
-	721 w	$\gamma(\text{CH}_2)$

^a ν , stretching; δ , bending; γ , rocking; π , out-of bending; α , asymmetric; s , symmetric^b s , strong; m , medium; w , weak; sh , shoulder

observed that the intensities of these bands are stronger in the transmission spectra than in the RA spectra. It indicates that the hydrocarbon chains, tend to orient perpendicular to the film surface. Also the 1257 cm^{-1} band we assign as a C-O-C asymmetric stretch¹⁰ note that it is shifted to a higher frequency by 7 cm^{-1} from the position in the cast spectrum (FIG. 6b). The high relative intensity of this band [(C₄-O)stretching band are much stronger in the grazing angle spectra than in the transmission spectrum], the transmission moment for this vibration in the LB film is roughly perpendicular to the surface. In addition, we assign this 1514 cm^{-1} band as an aromatic C=C stretching vibration (vibration 19a,¹¹) by comparison with assignments for

similar compounds¹² with a transition dipole moment, assuming C_{2v} symmetry of the phenyl ring, along to the C_{2v} axis. Like the C-O-C asymmetric stretching the high relative intensity of this band (compare with the transmission spectrum of the random film) indicates, in a qualitative way, that the transition moment for this vibration, and hence the C_{2v} axis of the phenyl ring, is oriented approximately, perpendicular to the substrate surface^{13,14}.

ACKNOWLEDGEMENT

This work was performed at the University of Sheffield. The author is grateful to thank Dr. Tim Richardson for the use of his Langmuir-Blodgett facilities and to Dr. Frank Davies for the use of the GIR-FTIR spectrometry. My thanks are also due to Dr. D.W. Bruce for supplying the iridium monoalkoxystilbazoles.

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Date Received: August 27, 1997

Date Accepted: October 8, 1997