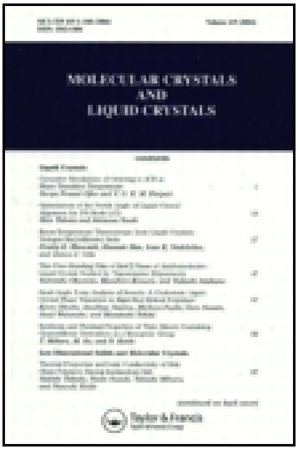

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Investigating the Orientations of Langmuir Blodgett Films of Copper Tetra-t-Butyl Phthalocyanine Using Polarised, Ultra-Soft Xanes Spectroscopy

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INVESTIGATING THE ORIENTATIONS OF LANGMUIR BLODGETT FILMS OF COPPER TETRA-*t*-BUTYL PHTHALOCYANINE USING POLARISED, ULTRA-SOFT XANES SPECTROSCOPY.

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Abstract Phthalocyanines have long been of special interest as essentially organic molecular conductors with properties that can be modulated by varying the central atoms. Soluble phthalocyanines have recently been developed enabling the production of Langmuir-Blodgett films, of interest to the electronics industry. Data are presented for the determination of the orientation of a Langmuir-Blodgett film of copper tetra-t-butyl phthalocyanine using XANES spectroscopy and showing that the molecules in the films are oriented normal to the substrate surface.

INTRODUCTION

Metal phthalocyanines are well established, industrially, due to their structural and thermal stability. They are widely used as dyes[1] and can also be used as simple models for the more complex biological molecules chlorophyll and haemoglobin[2]. However, they are of particular interest due to their electrical and optical properties; phthalocyanines are essentially organic molecular conductors with properties which can be modulated by varying the substituent atom. Therefore, there has been considerable interest in growing orderly thin films of such materials.

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Baker et al[3] worked on the preparation of Langmuir-Blodgett (LB) films on the surfaces of semi-conductors in an effort to simplify the structures of various devices, such as field effect transistors, photo voltaic cells and light emitting diodes. The thermal stability of the phthalocyanines - an essential attribute in such an application - makes them useful as insulators in the first truly practical electronic LB devices[4].However, until recently, their usefulness was unable to be exploited, due to their general insolubility in organic solvents, which makes them unsuitable for the LB technique. Baker and co-workers[3] were the first to produce LB films of solubilized phthalocyanines e.g. dilithium phthalocyanine, which is unusual in being soluble in some organic solvents, and some lightly substituted phthalocyanines, such as tetra-*t*-butyl phthalocyanine (TBP). The latter combine the desired solubility with all the properties of the unsubstituted species. The films were found to be very hard and abrasion resistant. However, in spite of their intrinsic interest, these films have received little further study, as they are present as multilayers, both on the water surface and after deposition as LB films.

LB films of asymmetrically substituted copper phthalocyanines (Cu-pt's) have been found to make very sensitive gas detectors, e.g. for NO_2[1]. Work by Hann et al[5] showed that the copper and zinc derivatives of TBP form monolayers on the water surface. CuTBP is the more suitable for practical purposes, since Zn-TBP photo-oxidises in air. It is with this copper derivative that this study is concerned.

Albouy[6] investigated the structures of Cu-pt LB thin films using x-ray diffraction. It was reported that the molecules form columns lying flat on the substrate surface, and it was proposed that this would account for the high degree of "in-plane" orientation. However, it is known that the orientation of metal-phthalocyanine is strongly substrate dependent, and that the orientation strongly influences the electrical and optical properties.

In order to understand, and thereby modify and refine, the properties of such films, it is necessary to probe the molecular structure. Diffraction techniques provide a useful tool for investigating well ordered LB films, but it is also important to have detailed information where the films are less well ordered[5].

X-RAY ABSORPTION SPECTROSCOPY

In principle, X-ray Absorption Spectroscopy (XAS) provides the capability to probe the structure of interfaces without recourse to the use of ultra-high vacuum (UHV)-based analytical tools, such as electron microscopy and surface analysis (e.g. XPS/SIMS). Significantly, XAS does not demand long-range order or ultra-clean surface preparative methods. In addition, the high intensity provided by synchrotron radiation (SR) enables interfaces to be examined "in-situ" and structural changes to be probed dynamically.

However, in practice, the use of XAS at the ultra-soft energies (ca 150-1000 eV) around the C,N, and O K-edges, necessary for the study of organic materials, has, until recently, been dominated by pure surface scientists working on single crystal surfaces in UHV. Now, advances in window materials and detectors have opened up the possibility of applying the technique to a range of real surfaces with widespread industrial relevance.

X-ray absorption spectra of condensed materials exhibit an oscillatory structure which can extend up to 1000 eV or more beyond the absorption threshold. The features appearing close to the absorption edge (near-edge structure) can be attributed to transitions to localised molecular orbitals, and this is known as X-ray Absorption Near-Edge Structure (XANES)spectroscopy.

The application of this technique at ultra-soft energies has been dominated by the surface science community, principally Stohr[7] and co-workers. Much of this seminal work involved the determination of the structural orientation of small molecules on idealised metal or semi-conductor surfaces. XAS studies at these energies have been mostly concerned with the near-edge structure and its variation with the electric vector of the polarised SR beam. For example, Stohr's group was able to examine the surface organisation of long chain carboxylic acids. The technique is sensitive to molecular π or σ orbitals, with a strong resonance when the electric field vector of the radiation is parallel to the bond being probed. Thus, by varying the angle of incidence, the molecular orientation can be determined. The position and intensity of the resonances reflect the nature of the intra-molecular interactions involved, thus conferring the ability to discriminate between the same atoms involved in different bonding configurations.

Thus XAS is ideal for probing the structures of those organic materials forming the LB films.

PREVIOUS WORK

Hann et al[5] and Fryer et al[8] made studies of Cu-TBP. In the former study, electron microscopy was used to probe the structure of LB films of Cu-TBP on carbon coated grids. It was found that the order in Cu-TBP is very short, much of the film being amorphous. This was deemed to be consistent with the variability of electrical measurements and change in the electrical properties on storage and thermal cycling of LB films on glass or tin oxide-coated glass. Molecular modelling based on these results, produced a structure in which the t-butyl groups on each molecule are interleaved with those of neighbouring molecules. The latter study, using electron diffraction and high-resolution electron microscopy, refuted the notion of molecular interleaving and furthermore, suggested that the phthalocyanine molecules were oriented normal to the substrate, not tilted as suggested by the modelling.

It was the aim of the present study to verify the orientation of the copper tetra-*t*-butyl phthalocyanine Langmuir-Blodgett film using synchrotron, polarised, ultra-soft, x-ray absorption near edge structure spectroscopy (XANES) as described above.

EXPERIMENTAL

Langmuir-Blodgett Film Preparation

The Cu-TBP was dispersed in xylene and the solutions (1 $\mathrm{mgml^{-1}}$) were spread onto the surface of an ICI Langmuir trough (Pitt and Walpita 1980[9], Roberts, McGinnity, Barlow and Vincett 1980[10]), filled with water, de-ionised to 18 mΩ resistivity and Milli-Q filtered. The barriers were compressed to obtain a surface pressure of 20 $\mathrm{mNm^{-1}}$. The monolayer was then deposited on a glass slide.

Data Acquisition

The spectra were recorded over the regions 275-320 eV (C K-edge) and 395-430 eV (N K-edge) on beamline U1A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using an extended range grasshopper (ERG) monochromator. The experimental chamber provides for measurements to be made in electron yield mode while the sample is maintained under vacuum conditions. A conventional channeltron electron yield detector was used. The sample chamber, which is separated from the UHV beamline by a differentially pumped aluminium window (typically 0.1-0.4 μm thick) is maintained at moderate pressures (ca 1×10^{-6} mbar) and is thus suitable for examination of high molecular weight organic thin films. Spectra were obtained at angles of x-ray incidence ranging from glancing angle (10°) to normal (90°) with respect to the substrate in increments of 10°.

Data Reduction

The spectra were normalised to an edge step of 1.0 using the plotting/analysis program PLOTEK (Daresbury Laboratory). The approximate orientations were determined visually and by comparison of peak intensities.

RESULTS & DISCUSSION

Copper tetra-*t*-butyl phthalocyanine is a planar molecule. From its structure (figure 1) the N=N and C=C double bonds should show the same maximum and minimum with respect to the angle of x-ray incidence. Figure 2 illustrates that this is indeed the case. Peaks A in both spectra arise due to the C=C and N=N π^* transitions respectively. We can see that these peaks have their maxima at 90° and their minima at 10°. This means that at x-ray incidence 90°, the electric field vector of the synchrotron beam is aligned with the π bonds, and thus the beam itself is at right angles to those bonds Hence the π bonds are parallel to the substrate (figure 3). Since these bonds are perpendicular to the plane of the molecule, therefore, the Cu-TBP molecule is oriented normal to the substrate.

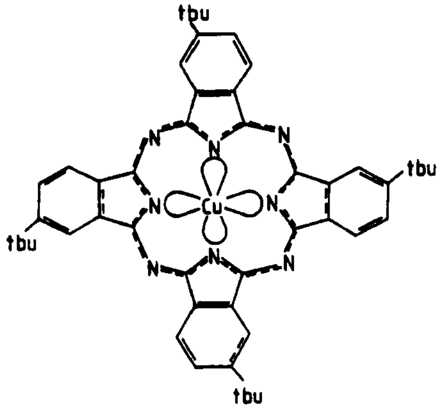

FIGURE 1 Model of copper tetra - *t* - butyl phthalocyanine[11].

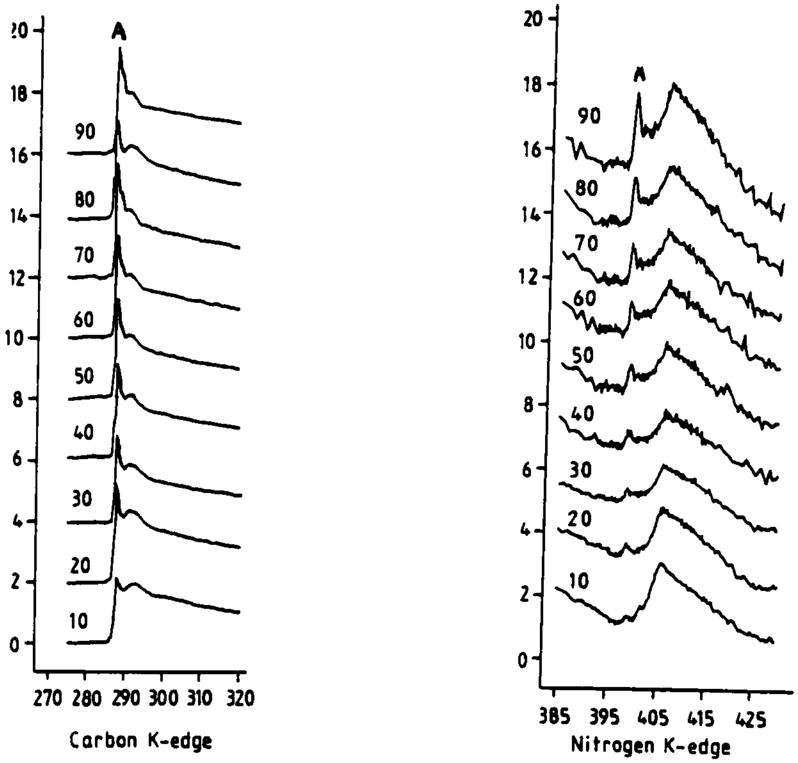

FIGURE 2 Spectra showing the orientation dependence of Cu-TBP; (a) C K-edge and (b) N K-edge.

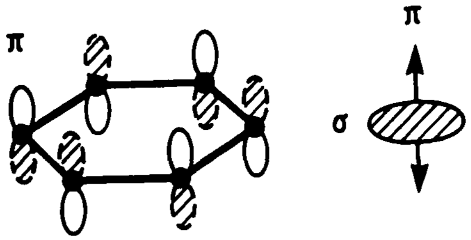

FIGURE 3 Schematic illustration of spatial orientation of π* and σ* orbitals in the aromatic ring.The π* orbitals point in a specific direction (vector type) but the σ* orbitals span a plane[7].

CONCLUSIONS

Our results confirm those of Fryer et al[5] in suggesting that the molecules in the LB film are oriented normal to the substrate. The results also show the potential of the ultra-soft, polarised XAS technique for the structural characterisation of condensed organic interfaces.

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