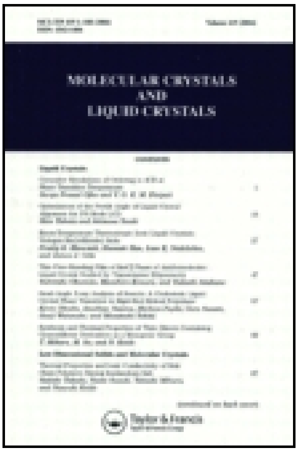

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Switching Phenomena in Thin Films of Lead Phthalocyanine

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SWITCHING PHENOMENA IN THIN FILMS OF LEAD PHTHALOCYANINE

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Abstract Further experiments are reported relating to the reported switching phenomenon in lead phthalocyanine thin films including cyclic voltammetry, of both the oxidation and reduction of the thin films on ITO glass, and the influence of vapours on the asymmetry of the current-voltage relationship. The possible mechanisms are reviewed and a mechanism proposed involving a field induced electron transfer to an electron acceptor such as oxygen. The switching may be localised leading ultimately to hot spots and breakdown.

INTRODUCTION

Molecular scale electronics requires molecules which change their properties in response to an external stimulus such as electromagnetic radiation or an electric field. The switching phenomenon in thin films of lead phthalocyanine (PbPc), reported by several groups[1-4] may be just such a phenomenon. Indeed, it has been attributed by Hamann et al to a disorder-order transition dependent upon a field induced molecular inversion[1,2,5].

This interpretation has been questioned by Göpel[6] and co-workers who suggests that the formation of inter-electrode shorts could be responsible.

In this paper the possible effects which could give rise to a field induced enhancement of the conductivity are considered in the light of the behaviour of other phthalocyanines. A model is proposed involving a field induced redox process, with oxygen or other impurity (such as water) as counter-ion. Supporting evidence is provided by cyclic voltammetry of PbPc thin films and the influence of vapours on the asymmetry of conductivity of thin sandwich cells of PbPc.

EXPERIMENTAL

Lead phthalocyanine was synthesised as described by Kroenke and Kenney[7] and subsequently purified by entrainer sublimation.

For cyclic voltammetry (CV) studies films of thickness ca 0.3µm were deposited on small (3mm x 4mm) conducting plates (ITO glass) at an evaporation rate of 1.5-2.5 Å/s and formed the working electrodes for CV studies. A cell solution of propylene carbonate containing 0.1M tetraethylammonium perchlorate (TEAP) as supporting electrolyte was employed as the cell solution.

For conductivity measurements sandwich cells were deposited on glass substrates with gold film electrodes (400Å) and a PbPc film thickness of approximately 0.3µm. The cells were mounted in an evacuable chamber, to which organic vapours could be admitted, and the current-voltage characteristic recorded.

RESULTS AND DISCUSSION

In principle, field induced changes in conductivity could be caused by

(a) A structural change resulting in a reduction in the band gap energy giving rise to near-metallic behaviour.

(b) A structural change resulting in a dramatic increase in mobility.

(c) An increase in carrier concentration by an extrinsic process.

(d) An intermittent electrical short.

These possibilities will be discussed in the light of the new results.

The Band Structure

Closed shell phthalocyanines, typified by CuPc and H_2Pc, are believed to be narrow band materials with a band gap of approximately 2.0eV. They have a strong tendency to bind oxygen rendering them extrinsic semiconductors. Although the non-planarity of the PbPc molecule may have some influence on the molecular packing and interaction, the properties are expected to be broadly similar.

The band gap in narrow band materials may be estimated from the Lyons equation[8].

$$E_g = I_g - A_g - P^+ - P^- \qquad (1)$$

where I_g and A_g are the gas phase ionisation potential and electron affinity, respectively, and P^+ and P^- are the polarisation energies resulting from the formation of positive and negative molecular ions in the lattice. Using available experimental data[9], equation (1) yields 1.71eV for CuPc and 2.0eV for H_2Pc in line with expectation. A similar calculation for PbPc yields a band gap of 1.26eV.

An alternative approach, based on redox potentials, has been applied with considerable success by André and Simon[10]. They propose that

$$E_g = E_{ox}^{½} - E_{red}^{½} \qquad (2)$$

It is assumed that the polarisation effects in the crystal and in solution are similar. Using published solution values[9] this calculation gives E_g=1.39eV which is in remarkably good agreement with the previous calculation.

The significant features of the band structure of PbPc are that it is both a better electron donor and electron acceptor than CuPc and H_2Pc. This may explain why switching is observed in PbPc but not in H_2Pc and CuPc.

Structural Changes (Disorder-Order Phase Transition).
Since the non-planarity gives the molecule an electric dipole, and since phthalocyanines frequently have several structural modifications of similar free energy[11], a field-induced phase change is a possibility. In the Lyons model[8] this would appear as a change in the polarisation energies P^+ and P^-. To account for the observed conductance changes, probably occurring in small regions of the solid, a large change in P^+ and P^- would be required. Such a change would need to be much greater than has been observed in phthalocyanine phase changes to yield near metallic conduction - a rare occurrence in closed shell systems.

The model proposed by Hamann[2,5] involves a field-induced inversion leading to the formation of a one-dimensional stack with metallic conduction. Whilst the mechanism remains an attractive possibility, the metal phase has not been fully characterised. However, the requirement for air to be present suggests an extrinsic process.

Extrinsic Effects
The only well established way to induce high conductivity in normally closed shell molecular systems is by partial oxidation or reduction. For instance, iodine will cause cofacially stacked phthalocyanines to show near-metallic behaviour.

It is proposed that electron transfer to or from an impurity molecule is responsible for the conductivity enhancement. Supporting evidence comes from cyclic voltammetry measurements, figures 1 (a) and (b).

The voltammograms are consistent with those observed in solution, adding support to the band gap calculation. The large and sudden conductivity surge in the oxidation voltammogram is strongly suggestive of a process rendering the film conductive (a similar effect has been observed in thin film studies of $Lu(Pc)_2$[12]).

Such a process could equally well occur in the solid state provided oxygen molecules are available to form a stable counter-ion.

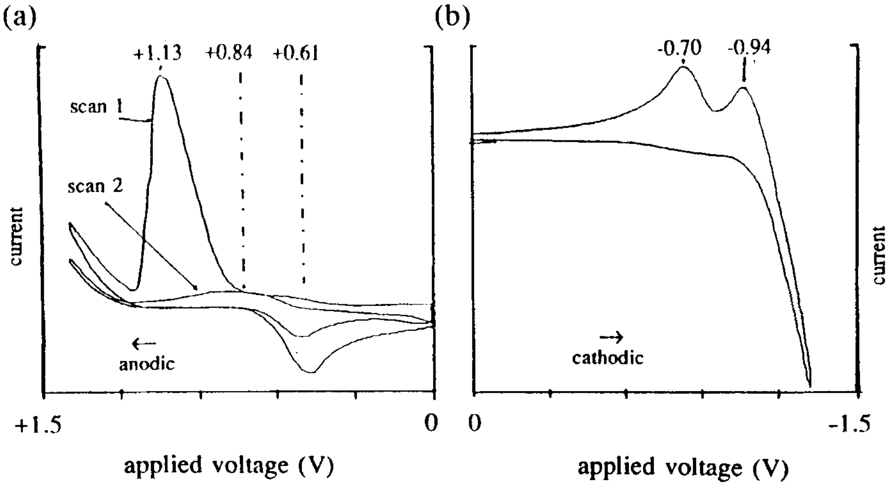


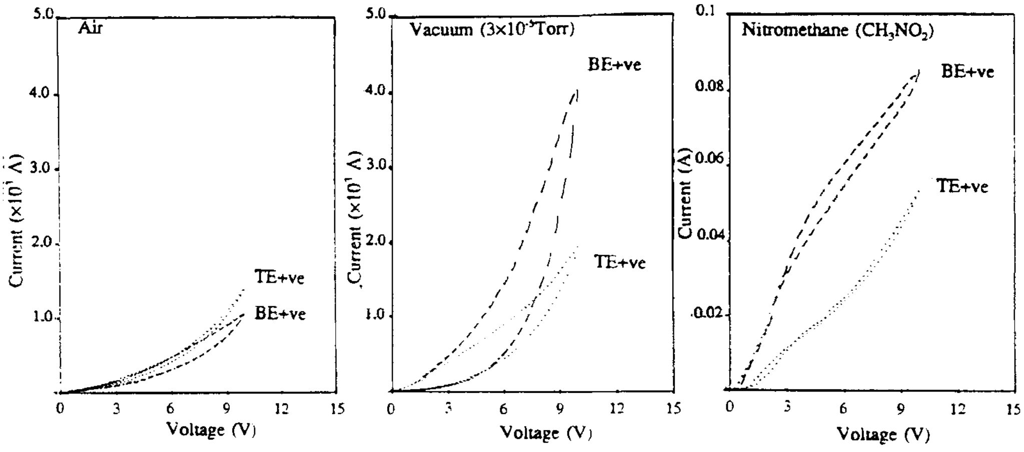
FIGURE 1: (a) Oxidative sweep and (b) reductive sweep of PbPc/ITO electrode system and measured peak potentials (referenced against ferrocene $(E_p)_a$=0.47V).

The report by some workers[2,3] that switching only occurs in air provides further support for this observation. Furthermore, such a process could be reversed by changing the polarity of the applied field.

Of interest is the inherent asymmetry in the conductivity of PbPc films on reversal of electrode polarity, as illustrated by figure 2(a)-(c). The asymmetry of conductivity has also been observed by the Matsushita Research Group[3,4] and attributed to two crystalline phases. It could equally well be associated with greater access of oxygen to one electrode interface, permitting some field-induced oxidation. The observation of a change in the asymmetry on admission of nitromethane (acceptor), figure 2(c), provides strong evidence for this.

Intermittent shorts

The switching phenomena is only likely to occur in small areas within the film. The Joule heating occurring is likely to give rise to electrical shorts and ultimately physical hole formation.



(a) (b) (c)

FIGURE 2: Asymmetry in a virgin PbPc thin film exposed to (a) air (b) vacuum (3×10^{-5}Torr) (c) nitromethane vapour.

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