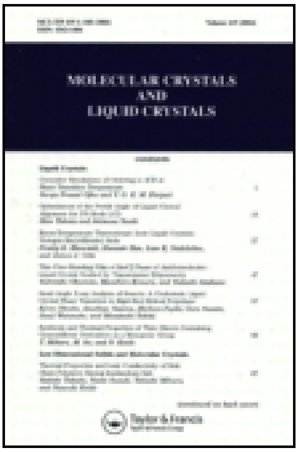

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Cofacially Stacked Phthalocyanine Copolymers

Richard Elliott-martin [a] , Nazar Hussein [a] & Martin Willis [a]

[a] Department of Chemistry, University of Nottingham, U. K.

Version of record first published: 04 Jun 2010.

To cite this article: Richard Elliott-martin , Nazar Hussein & Martin Willis (1993): Cofacially Stacked Phthalocyanine Copolymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 229-234

To link to this article: http://dx.doi.org/10.1080/10587259308032202

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 229–234
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Printed in the United States of America

COFACIALLY STACKED PHTHALOCYANINE COPOLYMERS

RICHARD ELLIOTT-MARTIN, NAZAR HUSSEIN, MARTIN WILLIS
Department of Chemistry, University of Nottingham, U.K.

Abstract

The successful synthesis and characterisation of μ-bridged stacked copolymers based on Fluoroaluminium phthalocyanine is reported. Modification of the d.c., a.c. and photoelectric properties of this material have clearly been demonstrated. Furthermore, iodine doping leads to high conductivity, limited by disorder and resembles the behaviour of classical alloys.

INTRODUCTION

Fluoroaluminium phthalocyanine, $[PcAlF]_n$ has received much attention due to its inherent high thermal stability and its low dimensional structure. High quality thin films can be produced on a variety of substrates, and can be systematically doped with acceptors such as I_2 giving rise to near metallic behaviour. The aim of this work is to carefully "tune" the properties of this material by introducing modified phthalocyanine molecular sub-units into the chain. Although chemically similar, $[PcAlF]_n$ and fluorogallium phthalocyanine, $[PcGaF]_n$ have rather different electrical conductivities as a result of differing degrees of π-orbital overlap between stacking Pc ligands and differing tendency to bind oxygen. We have shown that copolymers, constituting GaPc and AlPc repeat units, cofacially linked with fluorine bridges, can be prepared covering a range of compositions.

SYNTHESIS

$[PcAlF]_n$ and $[PcGaF]_n$ were prepared by literature procedures[1]. By adopting the methodology of Kenney et al[1], varying molar proportions of PcAlCl and PcGaCl were hydrolysed and fluorinated together to form copolymers of integral ratio compositions. All materials were entrainer sublimed in a flow of nitrogen.

FILM FORMATION

Approximately 1μ thick films were formed on quartz substrates using an evaporation unit operating at a base pressure of 10^{-5} torr. The evaporation rate never exceeded 1Å s^{-1}. This gave rise to good quality continuous films. However, preliminary XPS experiments show Al:Ga ratio in the 1:1 copolymer at 60:40 rather than 50:50 suggesting some fractionation. Depth profiling studies using Ar ion bombardment show that this composition remains constant as surface layers are eroded and thus the films are homogeneous.

PHYSICAL PROPERTIES

Thin layers obtained by sublimation were characterised by I.R. and U.V. spectroscopy. Broad bands (500-550 cm^{-1}) are observed for copolymers assigned to ν(M-F) suggesting the polymeric nature has been retained. Unresolved Davydov splitting (Q-band) is observed for all compounds indicating limited crystalline order. A thick film consisting of two equal layers ($[AlPcF]_n$ on $[GaPcF]_n$) gave a spectrum showing that the ratio of intensities of absorption at 645 and 700 nm which differed from that of the

1:1 copolymer.

Powder diffraction data (Table I) gives good evidence for a copolymeric structure. A 1:1 mixture of the parent $[GaPcF]_n$ and $[AlPcF]_n$ isomorphous compounds has all the peaks present that are characteristic of the individual components. The corresponding copolymer pattern indicates a new inter-ring separation intermediate to that of the parent molecules.

TABLE I Powder XRD data

Material	d spacings / Å
$[AlPcF]_n$	12.62, 3.59, 5.71, 9.07
$[GaPcF]_n$	12.62, 3.67, 3.82, 5.63, 8.83
{1:1 mixture}	12.62, 5.63, 3.82, 3.67, 3.59, 8.83
{1:1 copolymer}	12.62, 3.70, 5.71, 8.83

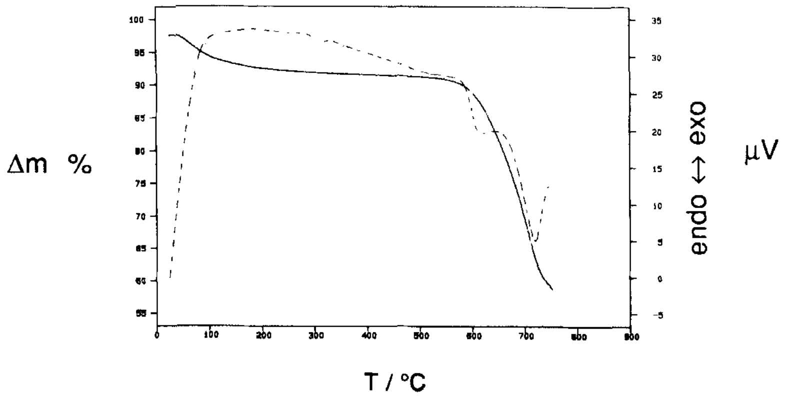

FIGURE 1 DTA/TG trace for 1:2 copolymer in atmosphere of N_2. Dotted line represents DTA curve solid line represents TG curve

A typical simultaneous DTA/TG thermal analysis (Figure 1) illustrates a small amount of fractionation observed for copolymers in the region 500-700 °C. The DTA trace for a 1:2 {Al:Ga} mixture differs enormously from that of the copolymer in this region. For such a mixture, onset of sublimation takes place at 505 °C. A pure sample of $[GaPcF]_n$ was also found to sublime at 505 °C. The 1:2 {Al:Ga} copolymer analysis shown here infers onset of sublimation at 530 °C.

Figure 2 shows Arrhenius behaviour in the d. c. conductivity of compressed powders. Similar behaviour is observed in evaporated copolymer films. Clearly intermediate behaviour is evident in the copolymer. The decrease in activation energy of the 1:1 mixture compared with copolymer is typical of the case where one phthalocyanine acts as a dopant towards another as observed for CuPc/VOPc mixtures[2].

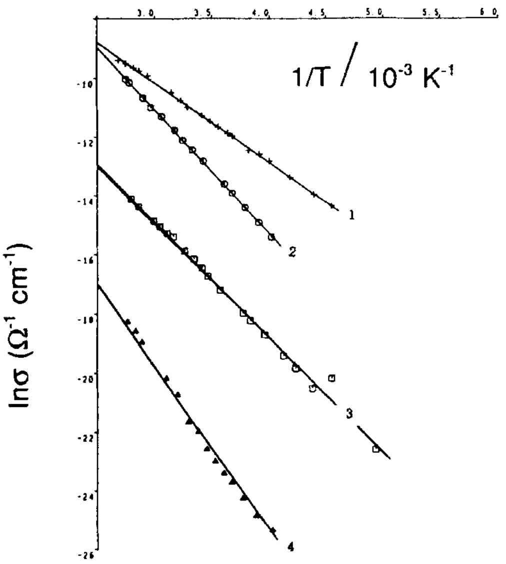

FIGURE 2 Temperature dependent d.c. conductivity data. 1, 1:1 mixture. 2, $[AlPcF]_n$. 3, 1:1 copolymer. 4, $[GaPcF]_n$

Likewise a.c. conduction of the 1:1 copolymer is intermediate[3] which indicates that the concentration of random hopping sites is not increased on copolymerisation.

Photoconduction experiments using the chopped light technique[4] show the 1:1 copolymer to have enhanced response compared with either homopolymer.[3] The structural changes within a chain appears to favour the formation of the charge-transfer exciton in accordance with the Noolandi-Hong model[5].

DOPING WITH IODINE

Conductivity is dramatically increased on partial oxidation with I_2 vapour. However, these mixed valence compounds still exhibit Arrhenius type conductivity albeit with a much reduced activation energy. Molecular disorder plays an important role and it has been found that the results are consistent with Matthiessens Rule[6], where the resistivity of a metal containing small amounts of impurities may be written:

$$\rho = \rho_o + \rho(T)$$

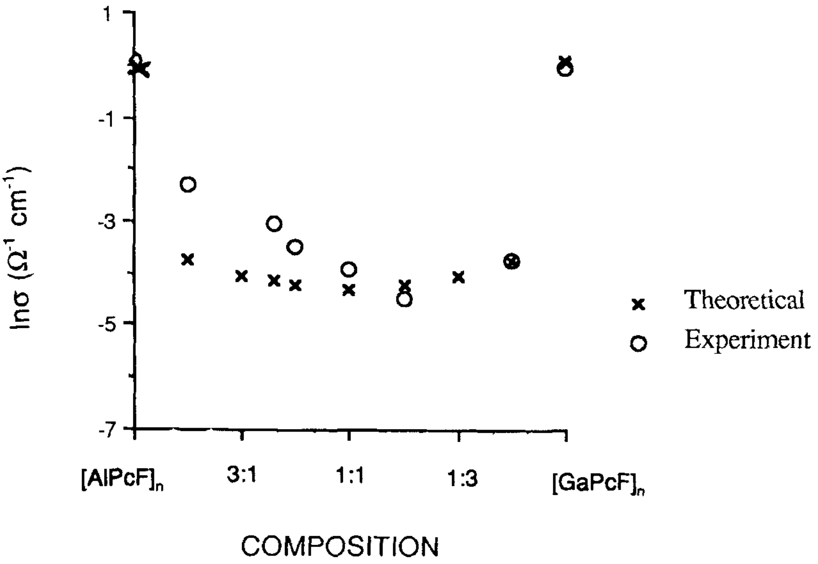

FIGURE 3 Experimental and calculated conductivity as a function of copolymer composition for iodinated samples.

ρ_0 is a constant which increases with increasing impurity concentration and $\rho(T)$ is the temperature dependent resistivity due to phonon scattering. By definition ρ_0 is temperature independent. However, it is expected that for organics this parameter will have some temperature dependence. Extending the model to the full concentration range gives:

$$\rho = \text{const. } x\ (1-x) + \rho(T)$$

where x is the mole fraction of one component and (1-x) the mole fraction of the other component. Copolymer composition was plotted vs. $\ln\sigma$ at 298K (Figure 3) by taking $\rho(T)$ to be the value for iodine doped $[\text{AlPcF}]_n$ and assuming a value of 300 Ω cm for the constant. Clearly the experimental data is in good agreement with the theoretical data. Similar behaviour, with different values of constant and $\rho(T)$, is also observed at 166K.

ACKNOWLEDGEMENTS

We would like to thank the SERC for financial support.

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