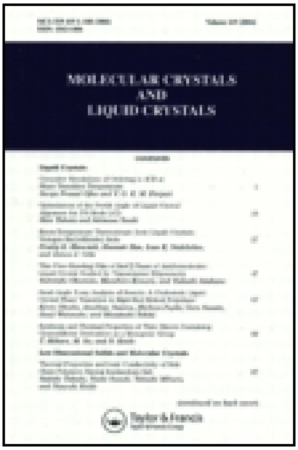

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Phthalocyanine and Its Polymers

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Phthalocyanine and Its Polymers

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Copper and metal free phthalocyanines are wide band gap semiconductors with remarkable chemical and thermal stability, giving them device potential. Extensive structural and chemical modifications are required to achieve the necessary improvement in carrier mobility, control of electronic properties, and processability.

In this paper some of the important developments in modifying the properties of phthalocyanines by chemical modification and polymerisation are reviewed. New results are reported in the μ-bridged phthalocyanines, including doping by ion implantation, band width determination by plasma absorption spectroscopy, and the influence of gases on the Seebeck coefficient. Infra-red photoconduction in two-dimensional polymers using light chopped at variable frequency is also reported.

INTRODUCTION

After forty years of research in many laboratories, the field of organic semiconductors may be on the verge of yielding a range of marketable devices.[1,2,3] A number of prototype devices have illustrated both the considerable potential of organic materials in electronic devices, and the formidable problems which still have to be overcome, most notably those of stability, mobility, and fabrication.

It is now possible, in general terms, to set out the required properties for a practical device material:

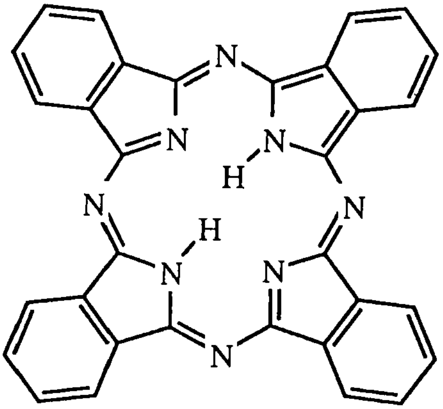
1. The band gap of the material must be controllable by chemical modification to optimise performance.
2. There must be a satisfactory electronic pathway through the material. This may require polymerisation to increase the interaction between monomer units.
3. The material must be in suitable form for device fabrication, which in the case of organics is likely to be in the form of either free standing or supported films.
4. For many devices the material must be able to be doped to control its electrical properties.
5. The material must be thermally and chemically stable under operating conditions.

It is highly appropriate that the very material which was chosen both by Eley in England[4,5] and Vartanian[6] in Russia to demonstrate for the first time that organic solids can show semiconductivity should now, forty years later, be recognised as forming the basis of one of the groups of materials most likely to satisfy the above criteria. Phthalocyanines are certainly some of the most stable organic materials known. The molecule can be modified by both substitution around the periphery and by exchange of the central metal atom. Polymerisation is possible by joining the rings cofacially or by edge-linking. Many of the materials are film forming and dopable.

The purpose of this review is to outline and discuss the various ways in which the electrical behaviour of phthalocyanines can be controlled by chemical modification and doping, and the way by which stable films of these materials, suitable for devices, may be obtained.

The Parent Phthalocyanines—Copper and metal free phthalocyanines [PCCu and PCH$_2$*].* A characteristic feature of monomeric phthalocyanines [Figure 1] is polymorphism. Two principal types are known which all have linear stacks, but differ in their angle of tilt [Figure 2]. The β form, which is normally found in large crystals, is the form most commonly studied. Evaporated films may be α or β, depending on conditions, and it follows that the polymorphs have very similar free energies. It is therefore to be expected that structural control can be achieved by minor modifications to the molecular shape, inter-molecular interactions, and by epitaxy on appropriate substrates.

It is convenient to use band theory for the discussion of electrical properties of phthalocyanines, not least because it is the most fully developed and readily applicable approach. Its applicability has been challenged,[7] but Simon and André[8]



(a)

FIGURE 1 Monomeric and Dimeric Phthalocyanines (a) Metal free Phthalocyanine, (b) Phthalocyanines of divalent metals, (c) Lithium Phthalocyanine, (d) Lutetium Phthalocyanine.

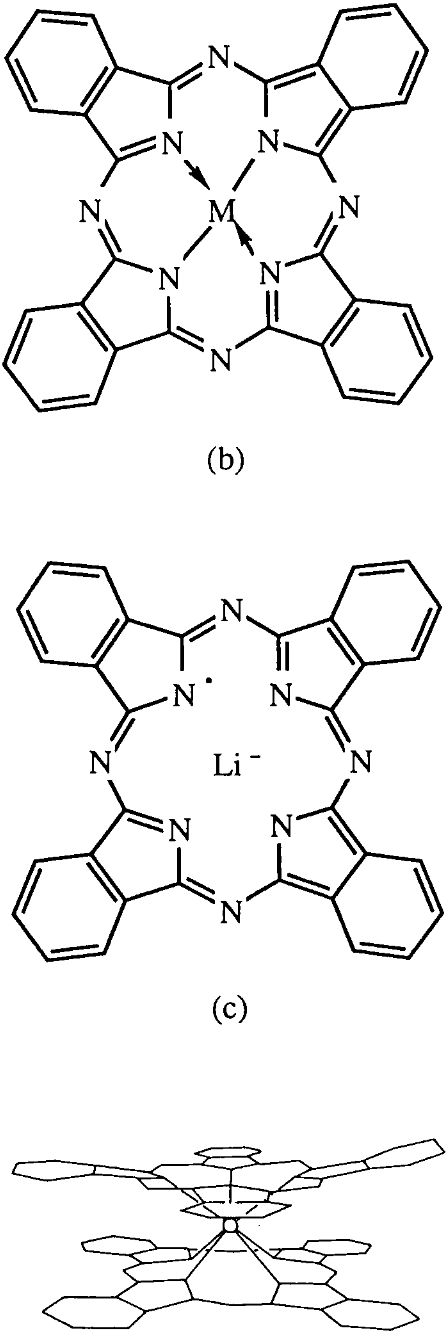


FIGURE 1 Continued.

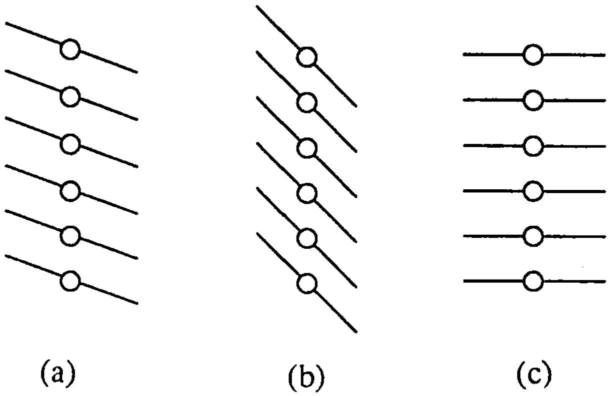


FIGURE 2 Principal stacking geometries of phthalocyanines (a) α-form, (b) β-form, (c) cofacial form.

conclude that it is appropriate for the b^{-1} direction of the reciprocal lattice in k space, but for the other directions a localised model, such as electron tunnelling,[9] may be preferable.

The accumulated evidence clearly points to an intrinsic band gap for metal free and copper phthalocyanines of approximately 2.0 ev.[8,10,11] The room temperature conductivities are strongly influenced by purity and crystal perfections, but $10^{-16}\Omega^{-1}cm^{-1}$ for metal free, and $10^{-10}\Omega^{-1}cm^{-1}$ copper phthalocyanine are typical values.

In general the most reliable mobility measurements in organic crystals have been obtained by the pulse photoconduction method pioneered by Kepler.[12] Values of 1.2 $cm^2\ V^{-1}s^{-1}$ and 1.1 $cm^2V^{-1}s^{-1}$ have been reported respectively for electron and hole draft mobilities in single crystals of PCH_2.[13] Much lower values ($10^{-2}-10^{-3}cm^2V^{-1}s^{-1}$) have been reported for polycrystalline samples of the same substance,[14] demonstrating clearly the role of a high trap density in reducing mobility. Similarly, whilst a mobility of 7 $cm^2V^{-1}s^{-1}$ has been observed[15] for PCCu, polycrystalline specimens give $10^{-3}-10^{-4}cm^{-2}V^{-1}s^{-1}$. The values reported for phthalocyanine single crystals are somewhat similar to the values reported in other organic single crystals where the molecules are separated by normal van der Waals distances.

MOLECULAR AND CRYSTAL ENGINEERING WITH PHTHALOCYANINES

If organic compounds are to be fully exploited as device materials full advantage must be taken of the opportunities that molecular materials offer for tailoring the material to the application. This requires not only fine tuning of the electrical and electronic properties but also optimisation of the mechanical properties relating to device fabrication such as film forming ability, film strength, adhesion to substrate, etc. The beauty of the phthalocyanine ring system is the vast scope for modification.

Exchange of the central atom, substitution around the periphery of the ring, and polymerisation can all bring about predictable and desirable changes in properties.

1. THE MOBILITY PROBLEM

The performance of devices based on the electrical properties of a semiconductor is strongly dependent on the carrier mobility. This can be illustrated by two examples where the use of organics has been explored.

e.g. (i) The field effect transister

The performance of a thin film transistor[16] can be judged from its figure of merit (η)

$$\eta = \frac{\mu V_G}{l^2}$$

where μ is the field effect mobility, V_G the gate voltage and l the channel length.

e.g. (ii) Conductivity gas sensors

The change in conductivity of a gas sensor ($\Delta\sigma$) is caused primarily by a change in the number of electrons (Δn) or holes (Δp) as a consequence of the interaction of the gas with the gas sensor.[17] Thus

$$\Delta\sigma = \Delta n e \mu_e + \Delta p e \mu_h$$

Again the response is directly dependent on carrier mobility.

The carrier mobilities in molecular crystals[18] (typically ~ $1 \mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$) and in polycrystalline and amorphous organic materials[19] (typically $10^{-3}-10^{-7}\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$) are far lower than those for inorganic electronic materials[20] such as Silicon (μ_e = 1350 and μ_h = 480 $\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$) and Gallium Arsenide ($\mu_e$ = 8000 and μ_h = 300 $\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$). It is therefore of major importance to produce organic materials with enhanced mobilities to reduce this disadvantage. The reason for the low mobilities in organics is twofold.

(a) Inter-molecular interaction

The adjacent atoms in the silicon lattice are covalently bonded, with an interatomic distance of 2.36 A, giving rise to broad conduction and valence bands and consequently the carrier mobilities are high. In organic materials such as phthalocyanines, the inter-molecular interaction is of the weak van der Waals type, and the separation is ~3.4 Å. Consequently the bands are narrow and the mobility low. The great sensitivity of the mobility to intermolecular interaction and distance can be illustrated by two experimental observations. The effect of high pressure[21,22] produces a massive enhancement in the conductivity of phthalocyanines which must

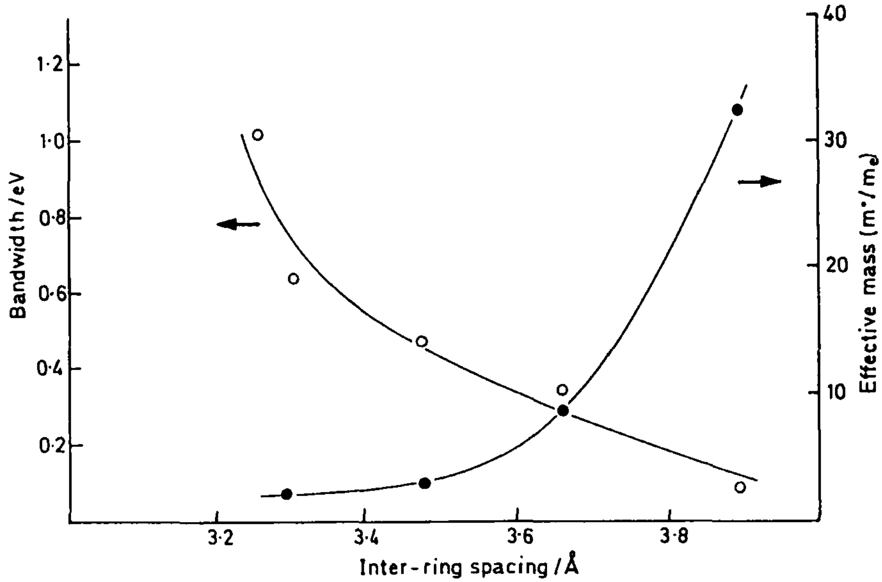


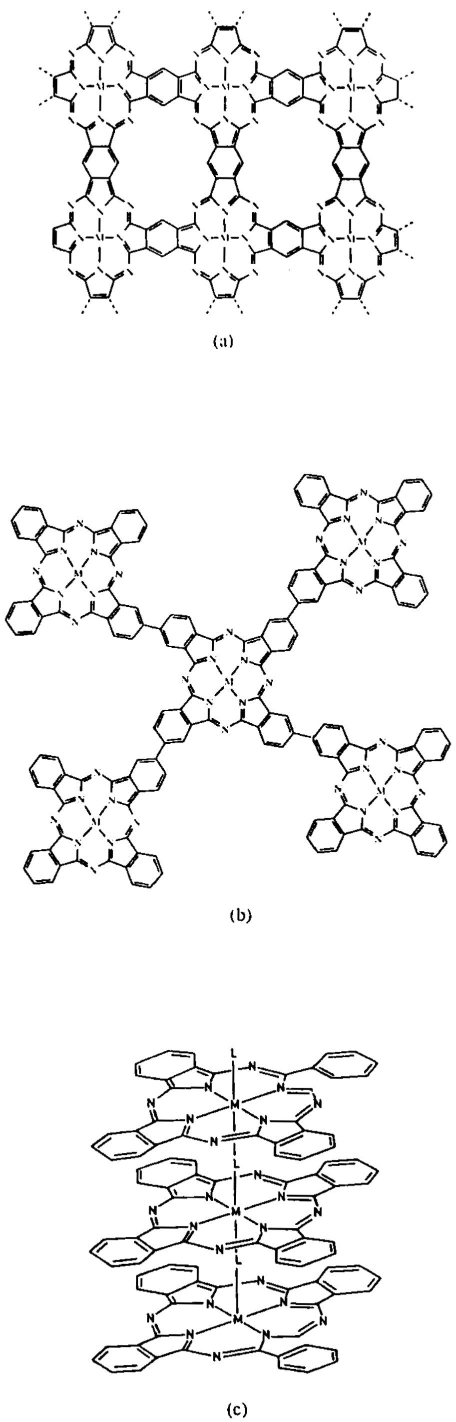
FIGURE 3 Band width and effective carrier mass in cofacially stacked phthalocyanines, derived from analysis of spectra of iodine doped materials.

be, in part, due to enhanced mobility. Furthermore, spectroscopic studies on cofacially linked with phthalocyanines (discussed later) show how the band width and effective mass vary strongly with the inter-molecular separations [Figure 3].

(b) Disorder

The lattice energy of a typical molecular crystal such as phthalocyanine is only a small fraction of that of a material with an infinite covalent lattice such as silicon. As a consequence the density of imperfections[23] (lattice vacancies, dislocation, etc.) tends to be high in molecular crystals, leading to a high trap density.[12,24] This density is even higher in polycrystalline materials such as evaporated films and polymeric materials. Consequently carriers suffer multiple trapping and the carrier mobility is low and activated.

To enhance carrier mobility is clearly necessary to either increase the intermolecular interaction or to minimise the disorder, or preferably both. Linking molecules by polymerisation reduces intermolecular distance and can produce greatly enhanced interaction. One of the earliest approaches was that of Epstein and Wildi[25,26] who synthesised a two dimensional conjugated polymer in which adjacent phthalocyanines share a benzene ring (Figure 4a). Hall measurements indicate an enhanced mobility (10 $cm^2V^{-1}s^{-1}$), which is presumably limited by the less frequent intermolecular barriers. In view of the impure[27] and poly-crystalline nature of the material this value is remarkably high. Edge-linking has also been achieved by polymerising phthalocyanines in a plasma discharge[28] [Figure 4b]. It appears that

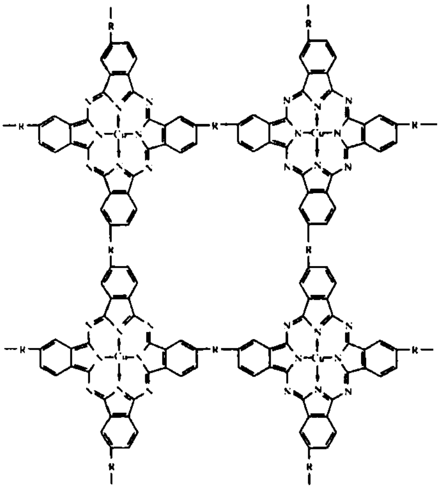


(a)

(b)

(c)

FIGURE 4 Phthalocyanine Polymers (idealised structures).



(d)

FIGURE 4 Continued.

the highly stable ring system remains intact and that polymerisation occurs by predominantly σ-bands formed following the loss of H-atoms.

Cofacial linking to yield a one-dimensional conduction pathway has been achieved in a number of ways [Figure 4c]. Using Group IV atoms such as Silicon and Germanium, a series of phthalocyanine polymers have been synthesised with an oxygen bridge.[29] Transition metal phthalocyanines have been linked by bi-dentate ligands such as pyrazine.[30] Where the central atom is a Group III metal such as Aluminum or Gallium,[31] the fluoro compound forms a linear stack (as in Figure 2c) with a metal-Fluorine-metal bridge. This fluorine bridge is weak compared with a covalent bond but is nevertheless sufficient to modify the crystal structure, thus providing a striking example of crystal engineering. The carrier mobility in such systems has still to be fully established.

An alternative approach to increasing intermolecular interaction has been used with great success by Turek *et al.*[32] The Lutetium and mono-Lithium derivatives of phthalocyanine, PC_2Lu and PCLi [Figure 1(c) & (d)] have free radical character. Intermolecular interaction via the incompletely occupied HOMO gives rise to a remarkably low intermolecular distance of 3.24 Å for PCLi, in contrast to the van der Waals distance of 3.4 Å. A high mobility is to be expected for these materials and these authors report a value from space charge limited currents of 1.3 $cm^2V^{-1}s^{-1}$ for a thin film sample of PC_2Lu. This method yields the effective mobility $\theta\mu$, where θ is the fraction of carriers free to move, and thus represents a lower limit for the true mobility. Even so it claimed to be the highest value reported for a thin film at room temperature.

2. CONTROLLING THE ELECTRICAL PROPERTIES

(a) Control of the band gap

The chemist's approach to structure property relations, which involves making carefully planned modifications to the molecular structure and evaluating the change in electrical and related properties has been remarkably successful in the development of new materials, particularly organic metals and organic superconductors. It is also fraught with difficulties, particularly in wide gap semiconductors such as phthalocyanine. Whilst changes in molecular structure may modify the intrinsic band gap and mobility, the new material may well have a different crystal structure, different purity and different trap concentration. Thus the observed changes in electrical properties may be entirely or partly due to extrinsic factors.

This problem is illustrated by the apparent effect of crystal structure on the electrical properties of PCCu. Early workers[33] reported a significantly lower band gap and significantly higher conductivity for the α-form than was observed for the β-form. It soon became apparent, however, that oxygen traps[34] play a significant role in phthalocyanine and particularly in the α-form. Later work pointed to a similar band gap for both forms indicating that the role of crystal structure is unimportant.[35] This result is somewhat surprising, on theoretical grounds. Lyons[36] has shown that in weakly interacting systems the energy gap, ΔE, is given by

$$\Delta E = I_g - E_g - 2P_i$$

where I_g and E_g are the gas phase ionisation potential and electron affinity respectively. P_i is the polarisation energy due to an ion in the lattice. Inokuchi[37] as shown that the polarisation energy is different in the α and β forms indicating that ΔE for the α form would be expected to be 0.5 ev greater than for the β form.

Whilst the electrical properties of a number of chemical variants of phthalocyanine have been studied it is, in many cases, not clear whether the observed behaviour reflects intrinsic conduction. Establishing that the behaviour is intrinsic requires either a study of space change limited currents,[38] or of the thermoelectric power.[39] In the case of changes in the π system, spectral shifts can give an indication of the band gap, since there is a strong similarity between band gap and the first electronic absorption band. Although the near equality is to some extent fortuitous, nevertheless since the spectral process involves transfer of an electron from the HOMO to the LUMO in the same molecule and the generation of change carriers involves transfer of an electron from the HOMO to the LUMO of a distant molecule, some correlation is to be expected.[10] Despite the absence of confirmatory evidence, it does appear that changes in the central metal atom do affect the band gap,[40] and conductivity. Perhaps the most dramatic illustration of the effect on the band gap of increasing the extent of conjugation is provided by the two dimensional polymer [Figure 4a]. The conductivity is very much increased over that of the monomer and a band gap of 0.26 ev has been reported.[26] If this reflects a reduction in the intrinsic band gap then the optical absorption should be broadened and shifted into the near infra red. The material might be expected to be an infra-red photoconductor, and indeed this proves to be the case.

The two dimensional corrugated polymer described by Epstein and Wildi[26] is a powder. A related but higher quality product can be made as a film by the reaction between tetracyanobenzene vapour and pure copper at 350°C.[41] Using chopped light and phase sensitive detection to reduce the dominance of the significant dark current it is possible to observe measurable photoconduction in these films. By using variable frequency chopping it is possible to separate the relatively slow heating (bolometric) effect from the true photoconduction.[42] The photocurrent is found to be virtually independent of wavelength from 300 to 4000 nm, is linearly dependent on intensity, and is only weakly dependent on temperature.[43] It thus possesses some of the qualities required for a cheap high area infra-red detection. Figure 5 shows the photoresponse which closely follows the monochrometer output.

(b) Creating a partially filled band

Eley[44] recognised at a very early stage that the way to make an organic metal is to create an array of identical open shell molecules. Subsequent studies have established the correctness of the postulate[45] but have shown that other conditions must also be satisfied to observe the high conductivity, which decreases with increasing temperature, characteristic of a metal. These conditions are:

(i) That there is sufficient intermolecular interaction between the HOMOs of adjacent molecules that the band width ϵ is greater or equal to the Coulomb repulsion (C) such that the Mott-Hubbard relation[46,47]

$$\Delta E = C - \delta$$

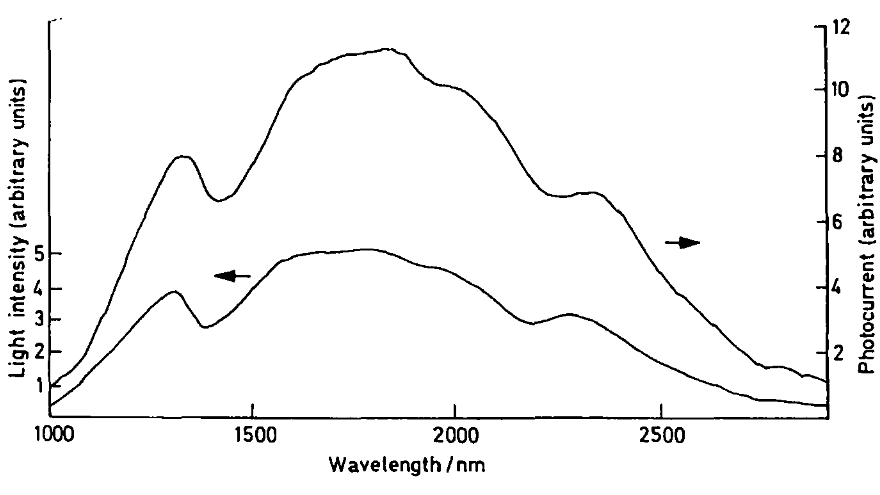


FIGURE 5 Photoconductive response of eka-conjugated phthalocyanine polymers. (a) Monochrometer output, (b) Photoresponse.

gives rise to a zero band gap.

(ii) That the molecules are equally spaced. Unequal spacing results in semiconductor behaviour. Furthermore, in truly one dimensional systems there is a tendency to undergo a Peierls[48] transition to a non-metallic state.

(iii) That the mobility is controlled by lattice scattering.

Phthalocyanines, with their favourable intermolecular overlap and tendency to stack are good candidates for conversion to organic metals if the necessary order and open shell character can be achieved. PCLi is a phthalocyanine radical, but the solid although remarkably highly conducting ($\sigma_{RT} = 2 \times 10^{-3}\Omega^{-1}cm^{-1}$) and with a high mobility,[32] is nevertheless a semiconductor with an apparent band gap of 0.2ev. Presumably the band width (50meV) is less than the Coulomb repulsion term, or the mobility is activated.

An alternate but related approach is to partially oxidise a phthalocyanine with an electron acceptor such as iodine.[49–53] This has the effect of removing electrons from the conduction band leaving it incompletely occupied. Some of these materials are stoichiometric and crystalline, such as $PCNiI_{1.0}$. This material[54] crystallises with the molecules in a linear stack with a spacing of 3.244 Å, indicating strong interaction. The room temperature conductivity is 270–750 $\Omega^{-1}cm^{-1}$ with the negative temperature coefficient characteristic of a metal. Other materials such as the cofacially stacked phthalocyanines,[51,52] which are normally only available as powders, can be partially oxidised by exposure to iodine vapour or solution. [The process is often described as doping, but in view of the high concentration of iodine employed the term is rather misleading.] The conductivity is increased dramatically, but it is normally weakly activated, perhaps reflecting the temperature dependence of mobility in a polycrystalline sample. For example, the cofacially stacked, oxygen bridged phthalocyanine, $[(PCSiO)I_{1.55}]_n$, has a room temperature conductivity of $1.4\Omega^{-1}cm^{-1}$ and with an activation energy of 0.04ev[55].

Treatment of films by iodine and other acceptors is a very convenient way of modifying their conductivities. It is however difficult to control and tends not to be permanent. Recently we have shown[56,57] that accurate control of electrical properties of films of the stacked phthalocyanines can be achieved by ion implantation. Figure 6 shows the conductivity-temperature relations for different doses of iodine in $[PCALF]_n$. The depth profile of the iodine can be determined by Rutherford Back Scattering. When allowance was made for the concentration profile the highest conductivity achieved in the implanted region was $0.1^{-1}cm^{-1}$. The achievement of metallic conductivity by this method would require a much higher degree of molecular order than is present in polycrystalline films. The implanted films show long term stability indicating that the implanted iodine reaches sites inaccessible by diffusion. Although some surface damage occurs the original conductivity can be restored by heat treatment showing that the effect is not due to graphitisation. Cofacially stacked phthalocyanines, when treated with iodine, show metal-like reflectance and the broad plasma absorption characteristic of highly conducting materials. Kramers-Kronig analysis of the reflectance spectrum enables the band width and effective mass to be deduced. A summary of our work[58] and that of others[59] is shown in Figure 3, in which the expected variation with inter ring spacing is clearly seen.

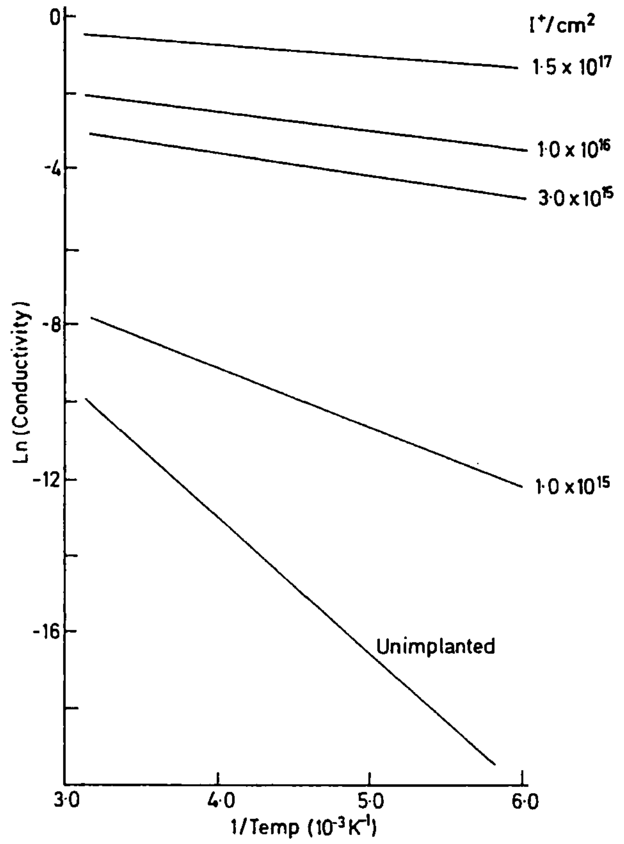


FIGURE 6 The dependence of the semiconducting properties of $[PCALF]_n$ on the dose of implanted iodine.

In an attempt to further control the electrical properties the films were implanted with a series of different ions[60] (Figure 7). The expected increase in conductivity with dose is seen as well as the effect of electronegativity. Initially there is the expected increase of conductivity with electron affinity, reflecting an increasing degree of change transfer. The subsequent decline in the curve may be attributed to the fact that these species tend to aggregate and the atomic value is no longer appropriate.

The sensitivity of the electrical properties of phthalocyanines, particularly those which are cofacially stacked, makes them particularly suitable for use as gas detectors.[61] Acceptor gases such as NO_2 act as dopants and produce a significant increase in conductivity. Figure 8 shows a band theory calculation[62] of the effect of acceptor concentration on both the conductivity and thermoelectric power of a phthalocyanine. The conductivity is unaffected until the material starts to become extrinsic (p type). The change is even more sudden for the thermopower, which also changes sign. A rather similar situation is predicted for the influence of donor

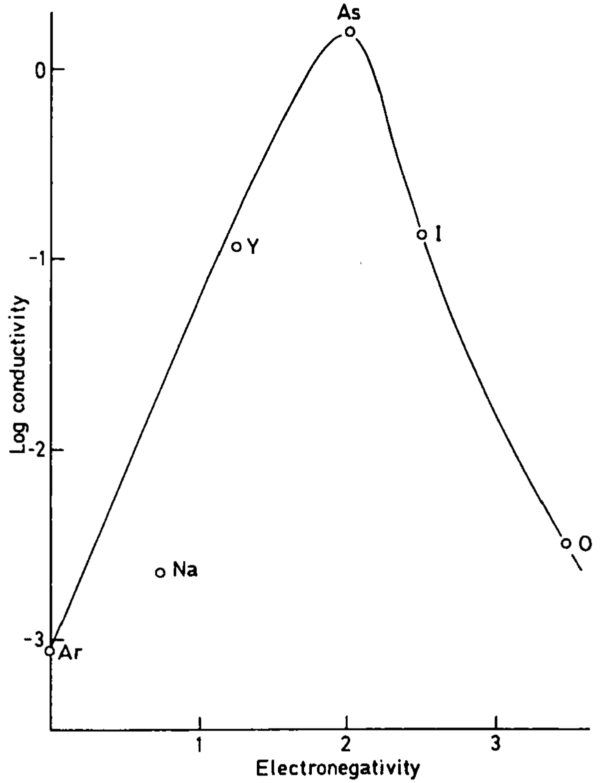


FIGURE 7 The conductivity of $[\mathrm{PCALF}]_n$ films implanted with a dose of 3×10^{16} atom cm^{-2} of different elements.

gases. To maximise the sensitivity of a sensor using these effects controlled doping is required to achieve a material with the critical impurity level. That the thermopower of phthalocyanines is indeed sensitive to NO_2 concentration is shown in Figure 9. However, critical doping levels have still to be achieved.

3. THE FABRICATION PROBLEM

Organics in general, and phthalocyanines in particular, offer immense opportunities for structural modification to tailor the physical properties to the needs of the device, both for its fabrication and its performance. For instance, a phthalocyanine has been synthesised with long alkoxy side chains, which shows liquid crystal behaviour.[63] A curable polymer has been synthesised[64] in which the rings are linked in a two-dimensional array, bridged by a conjugated para or meta dianil structure [Figure 4(d)]. The pre-polymers melt and can be moulded and cast before curing. The electrical properties can be controlled by heat treatment. The product is a

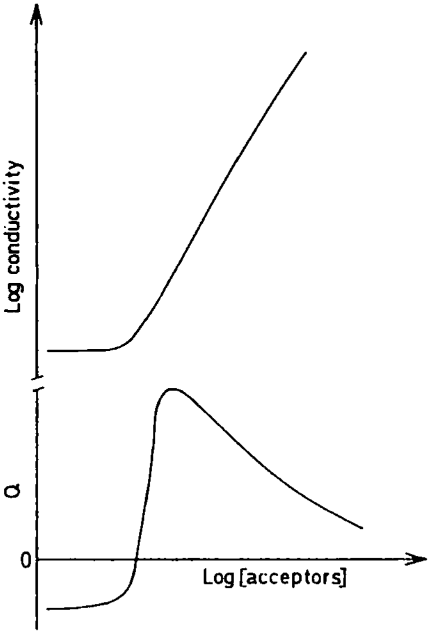


FIGURE 8 Computer modelled response of conductivity and thermoelectric power (Q) of an intrinsic phthalocyanine to increase of acceptor concentration.

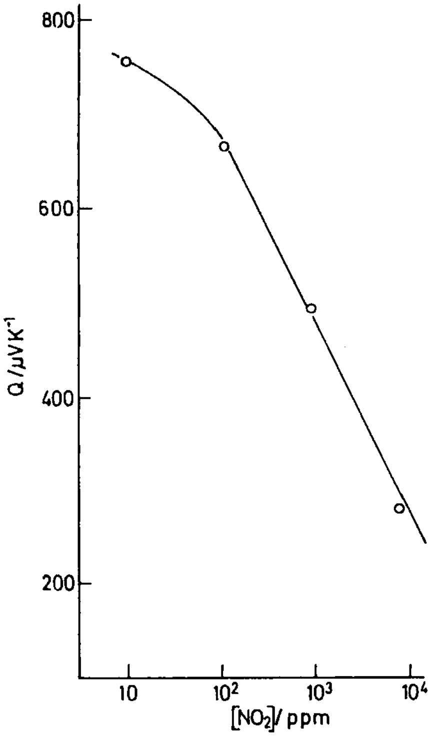


FIGURE 9 Effect of NO_2 gas on the Seebeck effect in $[PCALF]_n$ in films.

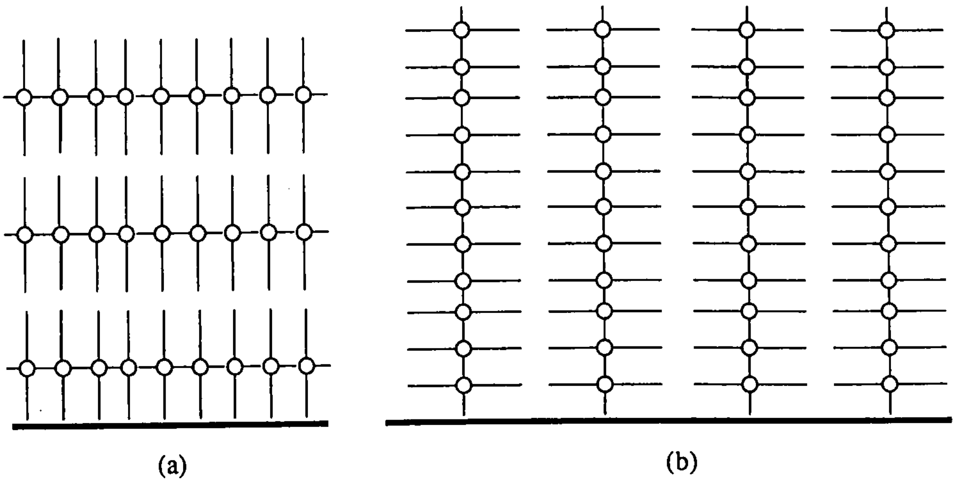


FIGURE 10 Idealised structure of films of $[PCALF]_n$. (a) sublimed onto silicon, (b) grown epitaxially on KCl single crystal.

very strong solid with electrical properties ranging from those of a good insulator to a good conductor (0.2 $\Omega^{-1}cm^{-1}$).

Whilst the most desirable physical form of the material may vary from device to device the most general useful form is likely to be that of a thin film, since single crystals so far produced are too small and too fragile. Bearing in mind the mobility problem discussed earlier, the most desirable phthalocyanine films are likely to be those in which the intermolecular interaction is high, or the degree of order is high, or preferably both.

Many methods of deposition have been employed, particularly:

1. Vacuum sublimation

When the material is a stable monomer films of good optical quality can be deposited by vacuum sublimation.[65] The product is normally polycrystalline. Transmission electron micrographs[66] of films of PCAlF on a silicon substrate show regions of crystallinity in which the stack lies parallel to the substrate surface [Figure 10a]. The method is, however, unsuitable for most other polymeric phthalocyanines and also some peripherally substituted materials.

2. Spin coating

The solubility of phthalocyanines can be increased by the use of suitable, peripheral substituents.[67] Preliminary observations[68] show that films of these compounds suitable for sensor applications may be prepared by spinning, but the surface is rougher than of those prepared by sublimination. The method may have advantages for less thermally stable materials (eg PCCrF) and where the material has been doped in solution.

3. Plasma polymerisation

The plasma polymerised phthalocyanines, referred to earlier,[28] form amorphous smooth films which adhere to glass, silica and ceramic substrates.

4. Chemical reaction

The two dimensional polymer[26,41] formed by reaction of tetracyano-benzene with a copper film, or bulk copper, adheres well to the substrate but has a rough surface.

5. Langmuir-Blodgett films

The Langmuir-Blodgett technique enables the preparation of highly ordered films. The technique normally requires long alkyl chains as substituents to give the molecule amphiphilic character, but in the case of phthalocyanines both substituted and unsubstituted materials have been used.[69,70] Of particular interest is the recent report by Orthmann and Wegner[71] who have successfully deposited polymeric films by this method. The cofacially stacked polymer $[\mathrm{PLSiO}]_n$ was unsymmetrically substituted with a methoxy and an octyloxy group at the 5 and 6 positions of each benzene ring. The chains lie along the substrate with the macrocycle normal to the substrate surface. This method offers a route to an ordered film with good intermolecular interaction.

6. Organic molecular beam epitaxy

Uyeda[72] has obtained remarkably highly resolved transmission electron micrographs of various phthalocyanines from films deposited on single crystals of potassium chloride. The films showed small regions of epitaxial growth. Using a similar technique Fryer[73] has observed epitaxy with both the two dimensional polymer derived from tetracyano-benzene, and with $(\mathrm{PCALF})_n$. In both cases the macro cyclic ring lies parallel to the surface [Figure 10b]. If such epitaxy could be achieved on a macroscopic scale, then the twin objectives of order and molecular interaction could be achieved. One report shows that a Schottky diode prepared by deposition from a molecular beam has improved performance.[74] Current experiments in Japan[66] aimed at defining the conditions for optimum growth have produced larger crystalline areas (~1000Å × 1000 Å), and shown that further progress depends on the development of improved substrates.

FUTURE PROSPECTS

It is becoming apparent that whilst the low mobility in molecular materials can be significantly increased it is likely to remain well below that of inorganic materials. It therefore seems unlikely that organics will compete directly with many of the silicon based devices. Applications must therefore be sought in areas where the special properties of organics give them a significant advantage.

Organics do have some significant advantages. Firstly, work on phthalocyanines has shown that significant control of the electrical properties can be achieved and is likely to be further improved. Thus tailoring the electrical properties to the specific needs of the device seems to be a realistic possibility. Where organics really score is in their physical properties which can be varied and controlled to a far greater degree than is possible with silicon or related materials.

The most urgent need now is for a range of devices, however simple, to be produced and marketed which will establish the credibility of organics as device materials. Such applications are likely to utilise the varied physical properties of the materials. Already a solid state capacitor[75] has been produced and marketed which incorporates a TCNQ salt. This material is unusual in that it is soluble, meltable and highly conducting, properties which are utilised in the fabrication of the device. In the case of phthalocyanine based materials perhaps the best prospects in the short term are those where the advantages of being able to produce large area films cheaply, outweigh the efficiency of the device itself.

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