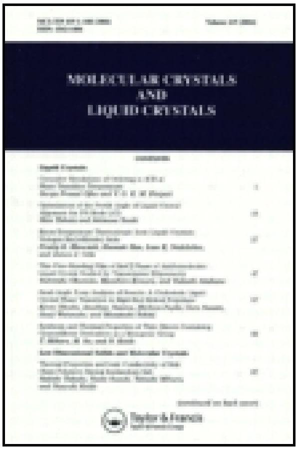

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P-Type Doping of Stacked Phthalocyanines. Synthesis and Properties of $[(MPcF)(z)_y]_x$ WHERE M=A1 or Ga and Z=BF_4^- or PF_6^-.

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P-TYPE DOPING OF STACKED PHTHALOCYANINES. SYNTHESIS AND PROPERTIES OF $[(MPcF)(Z)_y]_x$ WHERE M=Al or Ga and Z=BF_4^- or PF_6^-.

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Nitrosonium salts, NO[Z] where Z = BF_4^- or PF_6^-, have been used to oxidize the stacked, fluorine bridged metal phthalocyanines $(PcMF)_x$ where M = Al or Ga. The oxidized products give pressed pellet conductivities as high as 0.3 $(\text{ohm-cm})^{-1}$. These materials are stable for months in air and only begin to decompose in vacuo at temperatures exceeding 115-125°C. No unpaired spins are observed in the neutral polymers but the oxidized products have highly mobile electrons with spin densities of 0.003 to 0.3 e/anion.

INTRODUCTION

Two important factors in the ultimate uses of any materials are air and thermal stability. Most conducting polymers behave poorly in these areas although often the undoped polymers are themselves quite stable. Such is the case with the stacked fluoroaluminum and fluorogallium phthalocyanine polymers $(PcAlF)_x$ and $(PcGaF)_x$. These polymers are stable in air and are unaffected in vacuo when heated to temperatures in excess of 400°C.[1] On the other hand, the conducting materials obtained directly from reaction with

I_2 are unstable.[2]

A third important factor in the characterization of doped polymers is the fate of the dopant. Knowledge of the structure of the dopant helps define the polymer-dopant interaction and guides the quantitative interpretations of physical measurements. Dopants often used for polymers (Br_2, I_2, and particularly AsF_5) have caused controversy and confusion in the literature.[3-8] Because of uncertainties in preparative reproducibility, considerable effort has been expended in mapping out the chemistry of these polymer dopant interactions. In spite of these efforts, use of these dopants continues to hamper the interpretation of physical data because sample histories usually critically affect the dopant form. Consequently, syntheses using other dopants were undertaken in an attempt to reproducibly prepare stable conducting polymers which are more amenable to characterization. The work described involved oxidation of the stacked, fluorine-bridge metal phthalocyanines $(PcAlF)_x$ and $(PcGaF)_x$[1,9] with nitrosonium salts NO[X] where X = BF_4^- or PF_6^-. These salts are excellent one electron oxidizing agents[10,11] which provide a ready pathway for the incorporation of stable, well characterized anions into the product.

EXPERIMENTAL

The $(PcAlF)_x$ and $(PcGaF)_x$ were prepared and purified as described previously.[1] The nitrosonium salts $NOBF_4$ and $NOPF_6$ were purchased from Alfa Inorganics and were stored at -10°C prior to use. The general preparative method is as follows. Portions of the phthalocyanine and nitrosonium salt were weighed and transferred, along with a magnetic stirring bar, into a Schlenk tube or other airless vessel. Dry, degassed nitromethane or dichloromethane was then vacuum distilled onto the reactant mixture.

In all cases, reaction began when the solvent began to melt and was complete within 10 to 30 minutes. After standing at room temperature for a half hour or more, the product was filtered (more than once) washed with portions of methanol, acetone, dichloromethane, and diethylether, and then dried in vacuo. Product yields were always greater than 90%. Products were analyzed by infrared (IR), electron spin resonance (ESR) spectroscopy, Faraday method magnetic susceptibility, thermogravimetric analysis (TGA), mass spectrometry (MS), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction patterns, and elemental analyses (Galbraith Analytical Labs., Knowville, TN). Conductivities of pressed pellets were measured by the Van der Paaw four point probe method.[6]

RESULTS AND DISCUSSION

The nitrosonium salts react with the stacked phthalocyanines, according to eqn. (1) below:

$$(\mathrm{PcMF})_x + y\ \mathrm{NO}[\mathrm{Z}] \rightarrow [(\mathrm{PcMF})(\mathrm{Z})_y]_x + y\ \mathrm{NO}_{(g)} \qquad 1$$

The intact PF_6^- anions were unambiguously identified in the product of IR (fig. 1), MS and XPS. Most analytical spectroscopic evidence thus far supports the presence of BF_4^- in the samples doped with $NOBF_4$. However the evidence is not unambiguous. For the sake of simplifying this brief discussion, samples doped with $NOBF_4$ will be referred to as BF_4^- salts.

Anion concentrations (y) were determined from elemental analyses and from TGA and XPS results. The values of y vary over the range from 0 to 0.6 or 0.7 in the case of PF_6^- and from 0 to ca. 0.9 for BF_4^-. The stoichiometries prepared are given in Table I. Stoichiometries for heavily oxidized products ($y > 0.5$) were achieved under the conditions where the molar ratio of NO[Z] to (PcMF) was always initially greater than one.

In these instances unreacted nitrosonium salt remaining in the filtrate after collection of the solid product decomposed with gas evolution on exposure to air. The limiting stoichiometries increase with decreasing size of the anion and with increased intrastack monomer

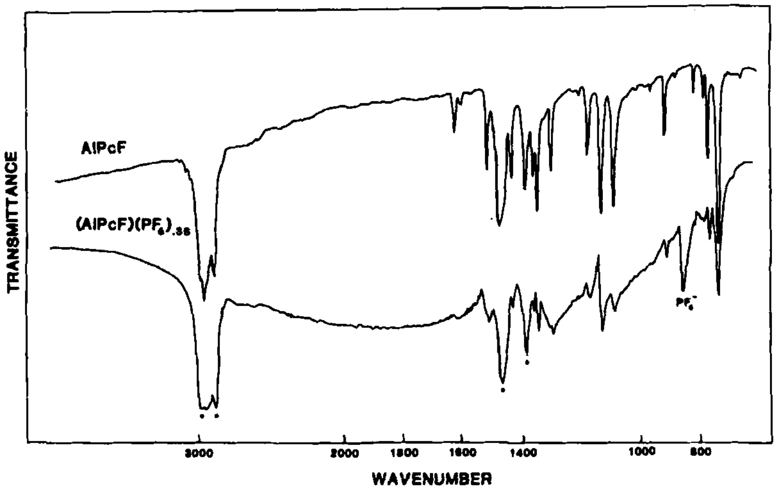

Figure 1. IR spectra of pure $(PcAlF)_x$ and $[(PcAlF)(PF_6)_{0.38}]_x$. Asterisks denote nujol oil bands. The new band at 845 cm^{-1} in the oxidized product is due to PF_6^-.

repeat distance (3.4-3.5Å for PcAlF and 3.7-3.8Å for PcGaF).

Table I. Anion PcMF Stoichiometries for Phthalocyanines Oxidized with Nitrosonium Salts

	BF_4^-	PF_6^-
PcAlF	0.44	0.38, 0.59
PcGaF	0.9	0.42, 0.66

X-ray powder diffration patterns were obtained for all products. These materials exhibited diffraction lines nearly identical in position and relative intensity to the lines recorded for the unoxidized materials. However, in all cases the lines were somewhat weaker in the photographs of the oxidized products than in the starting material so oxidation apparently has introduced some disorder into the system.

Four point probe conductivity measurements were made in air at room temperature on pressed pellets of the oxidized phthalocyanines. The conductivities are summarized in Table 2. All measurements showed the conductivities of the products are greater than those of the precursors. The most oxidized samples $(PcAlF)(PF_6)_{0.59}$, $(PcGaF)(PF_6)_{0.66}$, and $(PcGaF)(BF_4)_{0.9}$ had the highest conductivities and were in the 0.1 to 0.3 $(ohm\text{-}cm)^{-1}$ range.

Table 2. Conductivities of $(PcMF)_x$(M=Al or Ga) Oxidized with Nitrosonium Salts

Compound	Conductivity $(ohm\text{-}cm)^{-1}$ [a]
$(PcAlF)_x$	~ 10^{-7} [b]
$[(PcAlF)(BF_4)_{0.44}]_x$	3.0×10^{-2}
$[(PcAlF)(PF_6)_{0.38}]_x$	4.2×10^{-3}
$[(PcAlF)(PF_6)_{0.59}]_x$	0.3
$(PcGaF)_x$	~ 10^{-9} [b]
$[(PcGaF)(PF_6)_{0.42}]_x$	4.1×10^{-3}
$[(PcGaF)(PF_6)_{0.66}]_x$	2.0×10^{-2}
$[(PcGaF)(BF_4)_{0.9}]_x$	0.2

[a] Conductivities measured on pressed pellets using a four point probe technique [6]

[b] Ref. 2.

The air stability of the oxidized products is exceptional. Products stored in air at room temperature give reproducible spectra and conductivity measurements after periods as long as one year. Oxidized products likewise exhibit moderate thermal stabilities. TGA and MS studies demonstrate that the products are stable up to temperatures of 115-130°C. A typical TGA is shown in figure 2. From MS data it is known that volatile decomposition products over the temperature range 115-300°C are largely from the anions

BF_4^- or PF_6^-.

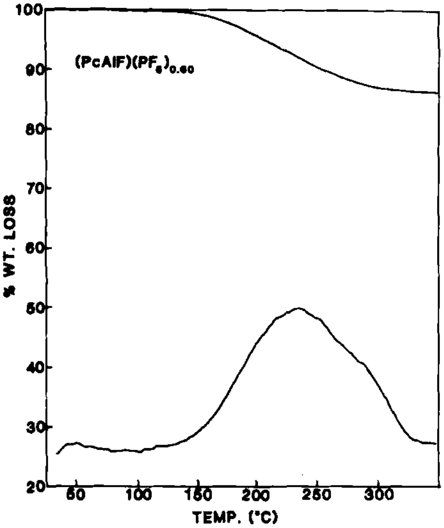

Figure 2. Weight loss as a function of temperature for $[(PcAlF)(PF_6)_{0.59}]_x$

As a consequence of the incorporation of well characterized anions into the products and knowledge of the anion/PcMF ratio (Table 1), we are afforded the opportunity to examine the changes in magnetic properties as a function of oxidation. Pure $(PcAlF)_x$ and $(PcGaF)_x$ are diamagnetic but, like other organic conductors[7,8], all the oxidized $(PcMF)_x$ products have strong ESR signals centered at a g value of ca. 2.00. An example of one of the ESR spectra is given in figure 3. The signals, recorded for the powders at room temperature, are symmetric and very narrow with derivative spectrum peak-peak widths of 0.35 to 2.0 G. Such narrow lines are usually associated with mobile electrons[9]. In fact, the line width found for $[(PcGaF)(BF_4)_{0.9}]_x$ is among the narrowest yet observed for organic or inorganic metals.

The number of unpaired electrons formed per introduced anion was estimated by ESR signal intensity calibration with a known standard of diphenylpicrylhydrazyl (dpph). Using this procedure, room temperature spin densities for several of the oxidized materials were evaluated.

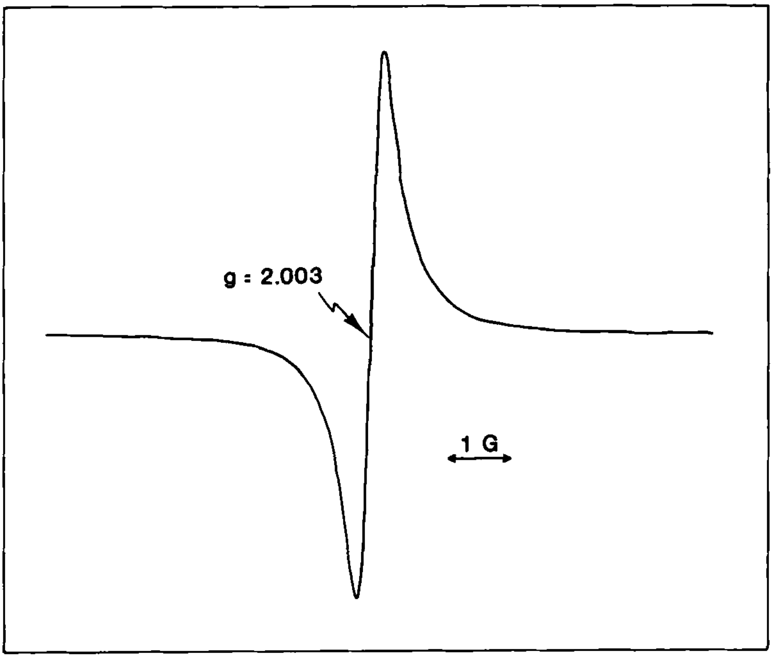

Figure 3. ESR spectrum of $[(PcGaF)(BF_4)_{0.9}]_x$ powder at room temperature.

For comparison, the spin densities in $[(PcAlF)(PF_6)_{0.38}]_x$ and $[(PcGaF)(PF_6)_{0.42}]_x$ were independently determined by magnetic suspectibility measurements using a Faraday balance. The spin densities were calculated after corrections for the diamagnetic contribution to the measured susceptibility using Pascal's constants[10]. It is found that the spin densities also calculated from ESR and magnetic susceptibility measurements for $[(PcGaF)(PF_6)_{0.42}]_x$ are in very good agreement.

The spin densities derived according to the above procedures give values of 0.03 to 0.3 unpaired electrons per introduced anion. These values show that the spins created as a result of chemical oxidation are antiferromagnetically correlated. Additionally, antiferromagnetic behavior has been observed in the temperature dependent (150°C to 295°K) ESR spectrum of $[(PcGaF)(BF_4)_{0.9}]_x$.

SUMMARY

The stacked, fluorine bridged metal phthalocyanine polymers $(PcAlF)_x$ and $(PcGaF)_x$ can be oxidized using nitrosonium salts to give materials with high conductivity. Pure products have excellent air stability and moderately good thermal stability. Incorporation of well characterized stable anions into the materials facilitates reproducibility of experiments and interpretation of physical measurements. ESR measurements demonstrate that the neutral polymers are diamagnetic while the oxidized, conducting products have a moderate number of unpaired spins with high mobilities. All results point toward antiferromagnetic interactions among unpaired electrons.

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