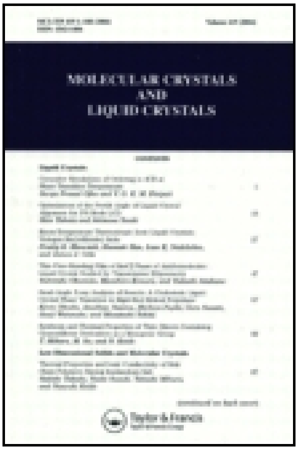

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Conducting, Partially Oxidized Fluorometal Phthalo-Cyanines

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CONDUCTING, PARTIALLY OXIDIZED FLUOROMETAL PHTHALOCYANINES*

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Phthalocyanine aluminum, gallium and chromium fluorides were prepared and doped with iodine to give $(PcMFI_x)_n$ compositions, where x = 0.012-3.4 (M=Al), 0.048-2.1 (M = Ga) and 0.12-3.3 (M = Cr). Thermogravimetric analysis proved useful for iodine analysis as complete loss of I_2 occurs below 250°C, leaving a PcMF residue. Raman and infrared spectroscopy were used to characterize the iodine-doped PcMF materials. Raman spectra (υ_o = 514.5 nm) of $(PcMFI_x)_n$ showed scattering attributable to I_3^- (106-108 cm^{-1}) and I_5^- (164-168 cm^{-1}), with the relative proportions of these bands being a function of M and sample thermal history. Iodine doping results in increases in conductivity by factors as high as 10^9, with the highest conductivity (5 ohm^{-1} cm^{-1}) being observed for $(PcAlFI_{3.4})_n$ derived from sublimed $(PcAlF)_n$. An apparent activation energy for conduction of 0.17 eV was measured for $(PcAlFI_{3.4})_n$. The crystal and molecular structure of PcGaF has been determined and will be discussed in relation to the conductivity of the doped material.

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INTRODUCTION

Organic, inorganic and organometallic materials which can be made highly conducting are of considerable interest as new candidates for optical, electronic, photoelectric and electrochemical applications. Depending on the perspective, phthalocyanines fall into one or more of the above classes of materials. Because of their thermal and hydrolytic stability, intense color, and ready availability, phthalocyanines have been the subject of study with regard to their photoconducting, semiconducting and conducting properties.[2,3] For one composition, $NiPcI_{1.0}$, detailed structural information is available and metallic behavior has been demonstrated.[4] Conductive thin films of NiPc treated with iodine at elevated temperatures have also been examined, with a view to their ultimate use as improved photosensitizers for optoelectronic devices.[5] In addition to investigations on stacked phthalocyanines, work on bridged-stacked phthalocyanines ($(MPcO)_n$, M=Si, Ge, Sn)[6] has shown that the presence of a central atom-oxygen bridge does not prevent high conductivity. Our interest in this area began with work on polymeric bridged-stacked fluorophthalocyanines, $(PcMF)_n$, M = Al, Ga, Figure 1, first

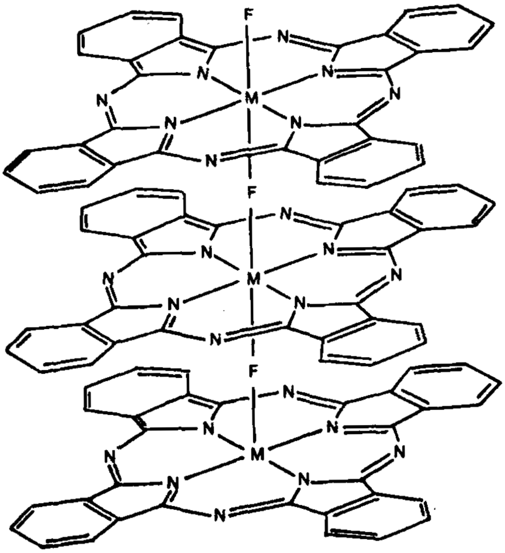

Figure 1. Proposed PcMF structure.

prepared by Kenney, et al.[7] We have shown that these materials can be doped with iodine to produce highly conducting $(PcMF\ I_x)_n$ compositions. This work is summarized below together with new results on PcCrF and the description of the crystal and molecular structure of PcGaF.

RESULTS AND DISCUSSION

The reaction of $(PcMF)_n$ (M = Al, Ga, Cr) with iodine produces highly conducting $(PcMFI_x)_n$ compositions. The rate and extent of reaction with iodine is quite dependent on PcMF purity and reaction conditions. As an example, sublimed PcAlF reacts with a saturated pentane/iodine solution to give $[PcAlFI_{3.3}]_n$ in less than 5 min., while with unsublimed PcAlF a maximum I/Al ratio of 1.5 is obtained within 24h.

$(PcMFI_x)_n$ compositions containing maximum iodine content are unstable *in vacuo* and slowly lose iodine over a period of days to weeks finally giving stable compositions. Thus, the composition $(PcAlFI_{3.4})_n$, initially obtained from a solid-vapor reaction, loses iodine to form $(PcAlFI_{2.4})_n$ after two weeks *in vacuo*. $(PcAlFI_{1.5})_n$ obtained from an iodine/heptane slurry reaction, is also unstable. This composition changes to $(PcAlFI_{1.0})_n$ after exposure to dynamic vacuum for two weeks. pumping to constant weight, most samples evolved small quantities of iodine when stored at ambient temperature and pressure, as evidenced by the discoloration of the polyethylene caps of the storage vials. Compositions prepared by heating $(PcMFI_x)_n$ were much more stable to loss of iodine. At elevated temperatures (*ca.* 250°C) under dynamic vacuum complete removal of iodine is effected leaving $(PcMF)_n$ which was identified by infrared spectroscopy, elemental analysis and TGA.

Infrared Spectra

The infrared spectra for undoped and lightly iodine-doped $(PcMF)_n$ show characteristic phthalocyanine absorptions.[3,10] As iodine doping increases, the i.r. peaks become broadened and finally obscured due to the superposition of electronic exitation absorption.[10,11] The intensity of the electronic exitation absorption increases markedly in the vicinity of 5-6% iodine content. This correlates with the rapid rise in conductivity near this iodine doping level and is consistent with a semiconductor to conductor transition.

Raman Spectra

Raman spectra (ca. 70-600 cm^{-1} for $(PcAlFI_x)_n$ compositions are shown in Figure 2, while Figure 3 shows spectra for $(PcMFI_x)_n$ and $(PcSiOI_{1.38})_n$. Phthalocyanine ring peaks in this region are insignificant compared to the resonance enhanced polyiodide modes. All $(PcMFI_x)_n$ samples exhibit intense scattering between 105 and 108 cm^{-1}. In view of previous spectroscopic studies, this band is assigned to the I_3^- symmetric stretching fundamental.[12] The moderately intense band at 164-168 cm^{-1} observed for most $(PcMFI_x)_n$ compositions is assigned to I_5^- in agreement with earlier work on iodine doped macrocycles[3,6,13]. I_2 (ν = 207 cm^{-1}) could not be detected. Iodide cannot be detected by any of the spectroscopic techniques utilized in this study, but prior work on iodine-doped phthalocyanines provides no precedent for the presence of I^-.[6,13]

It was noted above that the rate and extent of reaction of iodine with PcMF is dependent on PcMF purity and reaction conditions. The Raman spectrum is also quite sensitive to these factors. Thus $(PcAlFI_{3.3})_n$, prepared in heptane utilizing sublimed PcAlF, shows strong I_5^- scattering (Figure 1, x = 3.3). In contrast, $PcAlFI_{3.4}$,

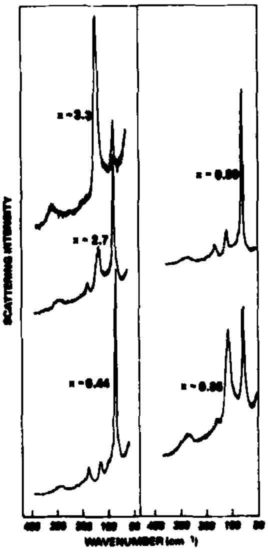

Figure 2. Raman spectra for $(PcAlFI_x)_n$. Compositions where x = 2.7, 0.90, 0.44 prepared by sequential thermolysis of x = 3.3; x = 3.3, 0.85 prepared from I_2/hexane.

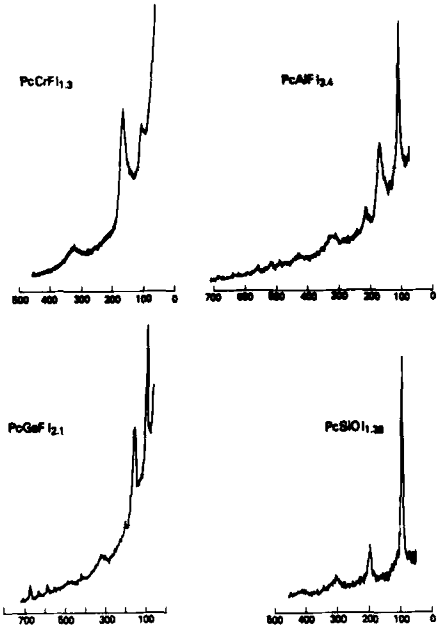

Figure 3. Raman spectra of $(PcMFI_x)_n$ compositions.

prepared _in vacuo_ from unsublimed starting material (Figure 3) shows a much stronger I_3- peak. These features are not fully understood, but the sensitivity of the anion identity to reaction conditions is clear.

The Raman spectrum of $(PcCrFI_{1.3})_n$ (Figure 3) shows that I_5- is the dominant iodine species present. When $(PcCrFI_x)_n$ compositions are heated, the I_5- and I_3- peaks attenuate at similar rates even at low iodine doping levels. This stands in contrast to the behavior of $(PcAlFI_x)_n$ compositions which (when x = 3.3, I_2/heptane) show scattering for $I_5^- > I_3^-$ (Figure 2) and rapid attenuation of I_5- scattering with a concomitant increase in I_3-scattering upon heating (Figure 2).

Thermogravimetric Analysis

TGA of $(PcAlFI_{3.3})_n$ (Figure 4) reveals two distinct iodine weight loss processes centered at 130 and 265°C, with a less distinct process at ca. 145°C. These temperatures refer to the point in the differential TGA (DTGA) mode (Figure 4, center section) where the rate of weight loss is maximum. Despite the contrasting Raman spectra for $(PcAlFI_x)_n$, where x = 3.3 and 2.7, the thermograms

(Figure 4) differ only in that a less prominent weight loss at 130°C is observed for $x = 2.7$. These results indicate that the first iodine weight loss process (130°C) is due principally to decomposition of I_5^- to I_3^-.

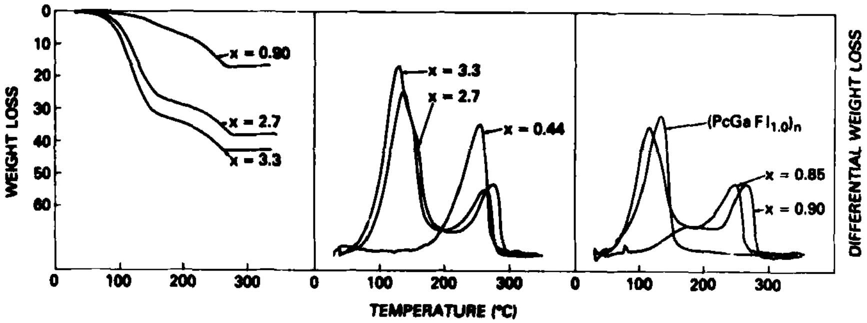

Figure 4. TGA (left) and DTGA curves for $(PcAlFI_x)_n$ and $(PcGaFI_{1.0})_n$. See Figure 2 caption for preparative methods.

Additional controlled thermolysis brings about lower iodine doping levels, $(PcAlFI_{0.9})_n$, for which a much diminished low temperature iodine weight loss is seen. Examination of the DTGA curves shows that the peak corresponding to the temperature of maximum I_2 weight loss gradually broadens and shifts to higher temperature. The shoulder at 145°C becomes obscured in the broad low temperature weight loss peak. In view of the growth of the I_3^- peak in the Raman spectrum and the continued but shifted low temperature weight loss feature in the DTGA curves, it appears that two forms of I_3^- are present in compositions such as $(PcAlFI_{0.9})_n$. The low temperature form would account for the shoulder at 145°C observed for $(PcAlFI_{3.3})_n$ and would account for the persistance of substantial low temperature iodine weight loss for compositions whose Raman spectra show weak I_5^- scattering.

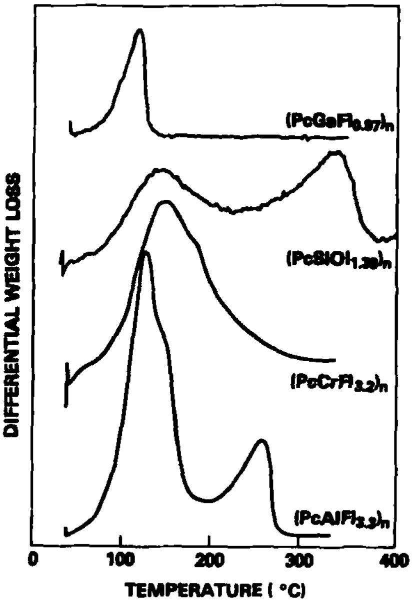

Figure 5. DTGA curves for $(PcMFI_x)_n$.

$(PcSiOI_{1.3})_n$, prepared by the reaction of $(PcSiO)_n$, with iodine in heptane, was examined by TGA so that comparisons of the thermal stability of these highly conducting materials and their Al-F and Ga-F linked analogs could be made. A low temperature (~80°C) and high temperature (300°C) loss of iodine were observed for $(PcSiOI_{1.3})_n$ (Figure 5). Raman spectroscopy confirmed earlier results[6] which showed only in the presence of I_3^-. Thus, as for certain $(PcAlFI_x)_n$ compositions, $(PcSiOI_x)_n$ compositions prepared by the solution method contain two thermally distinguishable forms of I_3^-. The "low temperature" I_3^- can be removed by thermolysis to give highly stable $(PcSiOI_x)_n$ compositions. If a comparison of thermal stability is made among the compositions with greatest thermal stability, i.e., those compositions where "low temperature weight loss" iodine has been removed, it is seen that Si-O linked systems are considerably more stable than those containing Al-F and Ga-F backbones.

Conductivity Studies

For iodine doped PcAlF and PcGaF conductivity rises rapidly with increasing iodine content until I/M equals 0.4 - 0.6, then rises more slowly with increasing iodine content. The highest iodine dopant levels give higher conductivity for Al vs. Ga. This observation correlates with the greater inter-phthalocyanine ring spacing for Ga versus Al[9] and provides evidence that the conductive pathway is through a conduction band generated by inter-ring pi-orbital overlap. The composition having the highest conductivity (5 ohm^{-1} cm^{-1}) was (PcAlFI$_{3.3}$)$_n$, prepared from sublimed PcAlF. Activation energies for conductivity were in the range of 0.02-0.05 eV for iodine doped PcAlF and PcGaF.

Iodine doped PcCrF showed similar behavior. Figure 6 shows that conductivity rises rapidly at low iodine doping levels to a maximum of about 0.5 ohm^{-1} cm^{-1} for (PcCrFI$_{0.5}$)$_n$. Much high doping levels could be achieved (to x = 3.5), but conductivity was not materially enhanced. I$_5^-$ is the principal anionic species present in the (PcCrFI$_x$)$_n$ materials (Figure 3). Upon heating, I$_5^-$ and I$_3^-$ peaks decrease in intensity monotonically and no enhancement of I$_3^-$ was observed at lower doping levels.

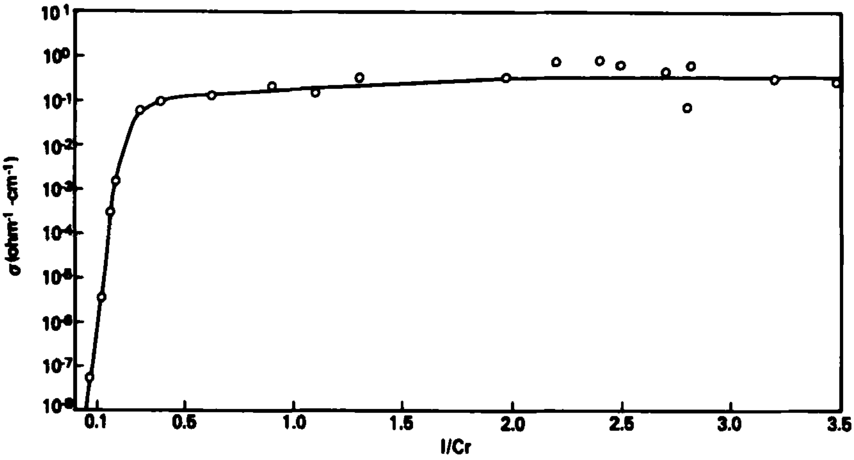

Figure 6. Conductivity versus iodine doping level for (PcCrFI$_x$)$_n$.

$(PcCrFI_x)_n$ compositions have moderate thermal stability, with all iodine being lost by about 200°C (Figure 5).

Structure of PcGaF

During the course of purifying PcGaF by vacuum sublimation, crystals suitable for an x-ray crystallographic study were obtained. In view of the paucity of structural data in this area and the unique structure proposed for PcMF compounds, we obtained a single crystal x-ray structure determination for PcGaF.[14]

The structure of PcGaF is shown in Figures 7 and 8. Gallium is octahedrally coordinated by four nitrogen and two fluorine atoms. The gallium atom is at an inversion center and thus the trans Ga-F and trans Ga-N bonds, respectively, have identical bond distances. Another consequence of the inversion center is the location of the fluorine atoms in a symmetric bridging position (Ga-F = 1.936Å). This symmetric bridging is similar to that found in $(MnPyPc)_2O$[15] and $[Me(OSiMe_3)_2SiPc$[16] and supports the symmetrically bridged structure proposed for other PcMF and PcMO compounds.

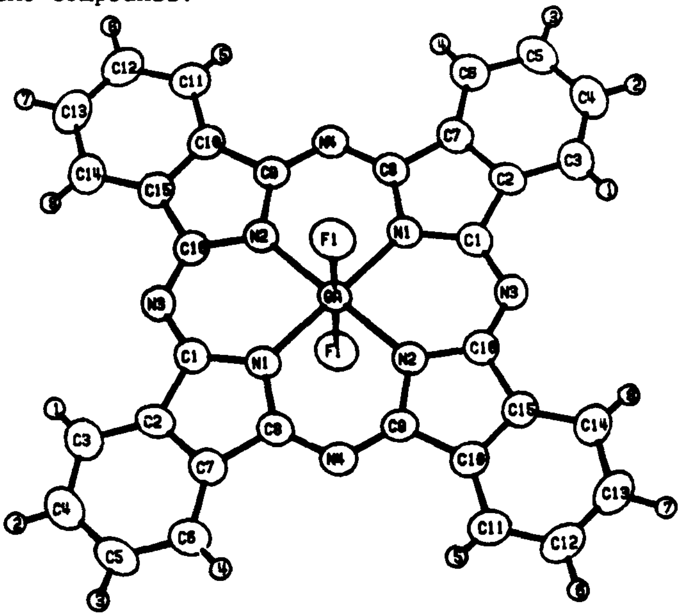

Figure 7. The structure of PcGaF. Some important distances: Ga-F(1), 1.936(1); Ga-N(1), 1.969(2); Ga-N(2) 1.970(2).

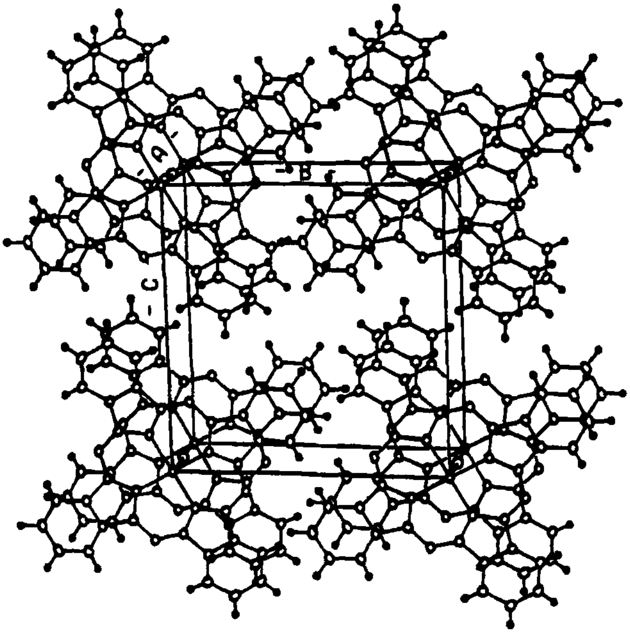

Figure 8. A view of the unit cell which shows molecular stacking.

An unusual feature of the present structure is that the Pc rings are eclipsed. In all prior structures in which Pc rings are collinearly stacked, the rings are staggered. The closest approach to a collinearly stacked eclipsed structure is found for [Me(OSiMe$_3$)$_2$SiOSiPcO]$_2$SiPc, where the central ring is rotated by 15.9° to the terminal rings.[16] Other stacked phthalocyanines are staggered at ca. 40° or more.[15,17]

Considering that conductivity occurs through a conduction band formed by the overlap of the Pc rings, it is surprising that the conductivity of iodine doped PcGaF is high (σ = 0.12 ohm^{-1}cm^{-1} (compacted pellet) for PcGaFI$_{0.93}$) in view of the relatively large ring separation observed for pristine PcGaF (3.872(2)Å).[18] The comparable compaction value for NiPcI$_{1.0}$ is 0.7 ohm^{-1}cm^{-1}, where the ring-ring separation known from a single crystal x-ray structure is 3.244(2)Å. The high conductivity for the bridge-stacked gallium materials could be explained by assuming the eclipsed ring structure for PcGaF persists in the partially oxidized material. Thus the inter-ring overlap lost due to increased inter-ring separation may be made up in large part by the eclipsed ring conformation. In contrast, $NiPcI_{1.0}$ has an inter-ring rotation of 40°, and despite a short inter-ring separation the conductivity is only modestly better than $PcGaFI_{0.93}$ due to the staggered conformation.

In summary, we have shown that iodine-doped $(PcMF)_n$ compositions are highly conducting. They have lower thermal stability with regard to loss of iodine compared to iodine doped $(PcSiO)_n$, which is exceptionally thermally stable (ca. 280°C); but because the polymer chain is linked by coordinate covalent bonds in $(PcMF)_n$, these materials can be sublimed and doped to give conducting thin films. The conductivity of $(PcMFI_x)_n$ is comparable to the SiO linked analogs despite a greater interplanar ring-ring separation for PcMF (by ca. 0.3 - 0.5 Å). This feature may be due in part to the capability of purification of $(PcMF)_n$ by sublimation vice $(PcSiO)_n$ which is less tractable, and in part to an eclipsed ring structure which seems likely at least for $(PcGaFI_x)_n$.

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