



HAL
open science

CONDUCTING PARTIALLY OXIDIZED GROUP IIIA HALO-PHTHALOCYANINES

D. Weber, P. Brant, R. Nohr, S. Haupt, K. Wynne

► **To cite this version:**

D. Weber, P. Brant, R. Nohr, S. Haupt, K. Wynne. CONDUCTING PARTIALLY OXIDIZED GROUP IIIA HALO-PHTHALOCYANINES. *Journal de Physique Colloques*, 1983, 44 (C3), pp.C3-639-C3-644. 10.1051/jphyscol:19833126 . jpa-00222637

HAL Id: jpa-00222637

<https://hal.science/jpa-00222637>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

CONDUCTING PARTIALLY OXIDIZED GROUP IIIA HALO-PHTHALOCYANINES

D.C. Weber, P. Brant, R.S. Nohr, S.G. Haupt and K.J. Wynne

Naval Research Laboratory, Washington, DC 20375, U.S.A.

Résumé - Nous décrivons les résultats du dopage des fluorures et chlorures de phthalocyanines du groupe IIIA avec les sels nitrosiles de BF_4^- et PF_6^- . Un résultat intéressant est que, bien que non polymérique le chlorure présente des propriétés semblables à celles observées sur le fluorure qui est polymérique.

Abstract - We report results of doping Group IIIA phthalocyanine fluorides and chlorides with nitrosonium salts of BF_4^- and PF_6^- . Although the chloride system is not polymeric it exhibits properties similar to the polymeric fluoride system.

Because of their thermal, photo, and hydrolytic stabilities, phthalocyanines (Pc's) have received considerable attention in the quest for new electroactive materials. Previously we reported that the iodine doping of PcMF ($M=\text{Al, Ga, Cr}$) gave highly conducting $(\text{PcMFIx})_n$ compositions (12). Based on x-ray powder pattern studies, we assumed that the bridged-stacked structure had a ring-ring separation of 3.66Å and 3.86Å for PcAlF and PcGaF respectively. In continuing the investigation of these phthalocyanines polymers, we used BF_4^- and PF_6^- as dopants and found that the resulting products had very good thermal and oxidative stabilities. In addition, the corresponding PcMCl systems were prepared and studied. We present the results of that study.

Experimental

The precursor phthalocyanines, PcMCl , were prepared from the reaction of phthalonitrile with the appropriate metal chloride. The PcMCl was converted to the fluoride PcMF , by base hydrolysis followed by treatment with HF. Nitrosonium salts of PF_6^- and BF_4^- were purchased from Alfa Inorganics and stored at -10°C until used. Weighed portions of the PcMX and the appropriate nitrosonium salt were transferred in a dry box to a reaction vessel containing a stirring bar. The reaction vessel was then attached to a vacuum line and dry, degassed nitromethane was condensed into the vessel. When the mixture warmed to room temperature, a gas evolved from the solution for approximately one half hour. After standing for an additional half hour, the reaction vessel was opened to air and the reaction product filtered. The product was washed with portions of nitromethane and dried in vacuo. Due to the extremely small particle size some of the PcMX was lost and typical yields were ~85-90%. Elemental analysis (Galbraith Analytical Labs, Knoxville, TN) were obtained and are summarized in Table I. Products were further characterized by a number of different physical methods. A Perkin-Elmer 58B Spectrometer was used to record infrared spectra of the products as Nujol mulls supported between KBr plates. Thermogravimetric analysis (TGA) were recorded using a Dupont 951 Controller coupled with a 2990 Thermal Analyzer. Electron spin resonance spectra of the

powders were recorded at X-band with a Braker ER-200D Spectrometer. Conductivities of pressed pellets were determined by the 4 point van de Paaw method.(3) Single crystal x-ray structures were performed by Molecular Structure Corporation.

Table I
Elemental Analysis for [(PcMF)(Y)x]n

		C	H	N	Al or Ga	F	P or B
(PcAlF)(PF ₆) _{0.28}	calc.	64.1	2.67	18.7	4.82	8.49	1.45
	found	64.4	2.87	18.7	4.54	7.55	1.26
(PcAlF)(PF) _{0.59}	calc.	59.7	2.49	17.4	4.19	13.4	2.84
	found	59.6	2.75	17.2	3.57	11.5	2.43
(PcAlF)(BF ₄) _{0.44}	calc.				4.52	8.66	
	found				4.54	8.78	
(PcGaF)(PF ₆) _{0.31}	calc.	59.4	2.48	17.3	10.8	8.4	1.49
	found	59.5	2.68	17.3	10.9	7.45	1.54
(PcGaF)(BF ₄) _{1.25}	calc.	54.1	2.25		9.82	16.07	
	found	53.9	2.78		10.3	8.1	

Results and Discussion

The reaction of PcMF with NOBF₄ and NOPF₆ to yield [PcMF(Y)x]n occurs rapidly in dry nitromethane or methylene chloride. These compositions have good thermal stability as evidenced by the relatively high temperature (125°C) required to cause a weight loss during TGA analyses. (Figure 1) Mass spectroscopic studies indicate that the weight loss in the temperature range 125-175°C is predominately due to loss of organic fragments assigned to C₆H₄(CN)(CNF)⁺, M/e=147; (C₆H₄)CNH⁺, M/e=104; and (C₆H₄)⁺, M/e=76. This is contrasted to weight loss (TGA) or fragmentation (MS) studies performed on the pure unoxidized PcMF, which does not show decomposition below 400°C. The initial decomposition process is believed to result from reaction of the dopant anion and the oxidized Pc ring. Further support for the argument is give by mass spectroscopic studies₄ at higher temperatures that show dopant ion fragmentation peaks (eg PF_n⁻ n=1,4); conspicuously absent from these spectra are

the molecular ion peaks, i.e., BF_3^+ or PF_5^+ .

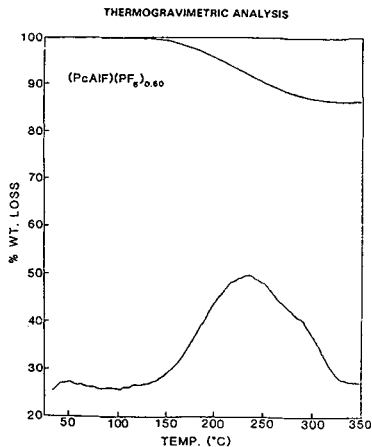


Figure 1 Thermogravimetric analysis of $(\text{PcAlF})(\text{PF}_6)_{0.59}$

The IR spectra for pure and oxidized PcAlF are compared in Figure 2 and show major differences. A broad envelope of absorption that is centered at ca. 1800cm^{-1} increases in intensity as the dopant concentration is increased. This low lying electronic absorption is superimposed on, and eventually obscures, all but the strongest IR peaks. In PF_6^- doped samples the sharp absorption characteristic of PF_6^- is observed at 845cm^{-1} . The BF_4^- peaks of appropriately doped samples are not observed due to the Pc peaks.

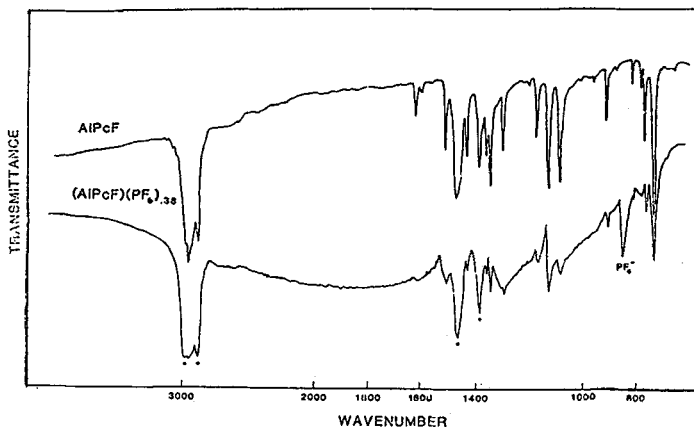


Figure 2 Infrared spectra of pure and doped PcAlF. Lines denoted with (*) are due to mineral oil.

Compressed pellet conductivity measurements give high conductivities for the BF_4 and PF_6 doped materials. For $(\text{PcAlF}(\text{PF}_6)_{0.59})_n$, $\sigma_{\text{RT}} = 0.3 \text{ ohm}^{-1} \text{ cm}^{-1}$ and for $(\text{PcAlF}(\text{BF}_4)_{0.9})_n$, $\sigma_{\text{RT}} = 1 \text{ ohm}^{-1} \text{ cm}^{-1}$. The analogous Ga samples give $\sigma_{\text{RT}} = 2 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ for a 66% PF_6 doped composition, and $\sigma_{\text{RT}} = 2 \text{ ohm}^{-1} \text{ cm}^{-1}$ for a 90% BF_4 doped sample. Conductivities reported are for the highest obtainable doping levels; lower doping levels give lower conducting samples. Temperature dependent conductivity measurements reveal low activation energies for $\text{PcAlF}(\text{PF}_6)_{0.7}$ (0.051 eV) and (0.068 eV) for $\text{PcGaF}(\text{PF}_6)_{0.7}$.

The ESR spectrum of the pure, unoxidized polymer does not indicate the presence of unpaired electrons, but the $(\text{PcMF}(\text{Y})_x)_n$ materials exhibit ESR spectra having a single, narrow, nearly symmetrical absorption with a g value very close to the free electron value (2.0015–2.0022). (Figure 3) The line widths are between 0.3 and 2.5G and the line shapes are strongly Lorentzian. The temperature dependent ESR measurements from -150°C to RT exhibit Curie behavior. The number of unpaired spins formed per dopant molecule was determined independently by ESR and magnetic susceptibility measurements and found to be between .003 and 0.3. These results are consistent with the existence of hole-species produced by partial oxidation of an electron band formed from the extended Pc rings. The combination of the free electron g values and the narrow line which indicates that the unpaired electrons are delocalized on the Pc rings.

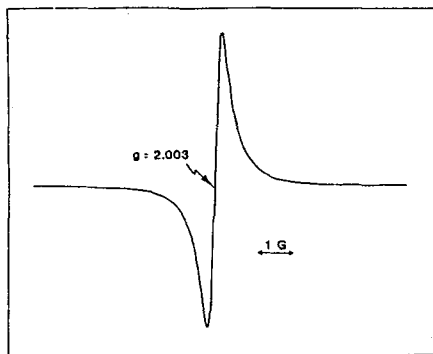


Figure 3 Room temperature x-band ESR spectrum of $\text{PcAlF}(\text{PF}_6)_{0.59}$. Frequency modulation 100kHz and modulation amplitude 0.8G.

Single crystal x-ray diffraction studies of PcGaF have confirmed that the structure of these compounds is identical to the model based on earlier powder pattern studies. The Pc rings are stacked in an eclipsed fashion, and bridged by fluorines with a ring-ring spacing in the Ga system of 3.87Å.

The remarkable feature of these materials is the stability of the conductivity after exposing the samples to ambient air. The conductivity of a sample of $[\text{PcAlF}(\text{BF}_4)_{0.44}]_n$ stored in ambient air remained at $3 \times 10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$ for more than one year. The stability of $[\text{PcMF}(\text{Y})_x]_n$ to thermal stress and air oxidation is contrasted to the behavior of the iodine doped PcMF (2) and many other conducting polymers. (6–8)

Because the PcMCl derivatives are the precursors to the corresponding PcMF analogs, a considerable amount of time and effort could be saved if the chlorides underwent similar doping. Although the PcMCl derivatives are not believed to be polymeric, the similarities between the PcMCl and PcMF systems were sufficient to warrant attempts at doping the PcMCl materials with the

nitrosonium salts of BF_4^- and PF_6^- . The PcMCl derivatives behaved analogously and gave products with similar properties.

The thermal stabilities were the same as noted with the fluorides, i.e., the samples decomposed at $\sim 125^\circ\text{C}$ liberating mostly organic fractions containing fluorine. The IR spectra are similar but the underlying electronic band appears to be centered at $\sim 2200\text{ cm}^{-1}$ rather than 1800 cm^{-1} . This band also shows the same growth in intensity with increased doping concentration. Also, in the PcMCl derivatives we observe the PF_6^- stretches that were obscured in the PcMF system.

The pressed pellet room temperature conductivities are $3.7 \times 10^{-3}\text{ ohm}^{-1}\text{ cm}^{-1}$ for $\text{PcAlCl}(\text{PF}_6)_{0.07}$, $1.3 \times 10^{-2}\text{ ohm}^{-1}\text{ cm}^{-1}$ for $\text{PcAlCl}(\text{BF}_4)_{0.5}$, $1.4\text{ ohm}^{-1}\text{ cm}^{-1}$ for $\text{PcGaCl}(\text{PF}_6)_{0.7}$, and $3.2\text{ ohm}^{-1}\text{ cm}^{-1}$ for $\text{PcGaCl}(\text{BF}_4)_{0.7}$. The temperature dependent measurements give activation energies of 0.09 eV and 0.019 eV for the 70% doped PcAlCl and PcGaCl respectively. ESR experiments again give the sharp, narrow, free electron g values for the doped chloride as was observed for the fluorides.

A single crystal x-ray structure has been obtained for PcGaCl and proves conclusively that the structure is not polymeric. The PcGaCl units are arranged in a skewed stack along the b-axis of the triclinic unit cell (Figure 4). The interplanar spacing is 6.9 \AA and is too large to allow the π interactions to give rise to the electronic properties observed. A closer look at the crystal structure reveals that the adjacent stack is arranged so that the chlorine atoms point down and the Pc planes interleave with the original stack. This gives a Pc-Pc planar spacing of 3.4 \AA ; a value that is consistent with the observed electrical properties.

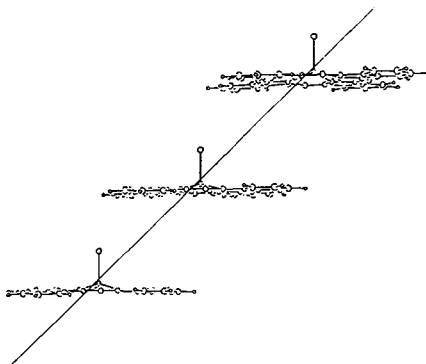


Figure 4 View along b axis of PcGaCl crystal (Note Cl sitting above the Pc plane).

In summary, we have prepared new, stable compositions whose conductivity is variable by 7-9 orders of magnitude. This is particularly significant in view of the processability of the parent diamagnetic materials, which can be sublimed to form thin films. We have also demonstrated that the parent material need not be polymeric to give rise to the good electrical properties.

References

1. P. M. Kuznesof, K. J. Wynne, R. S. Nohr, and M. E. Kenney, *J. Chem. Soc. Chem Commun.*, **1980**, 121.

2. R. S. Nohr, P. M. Kuznesof, K. J. Wynne, M. E. Kenney and P. G. Siebenman, J. Amer. Chem. Soc., 1981, 103, 4371.
3. K. J. Wynne and R. S. Nohr, J. Chem. Soc. Chem. Commun., 1981, 1210.
4. E. Konig, Magnetic Properties of Coordination and Organometallic Compounds of the Transition Elements, Springer-Verlag, Berlin, 1965.
5. L. J. Van der Pauw, Philips Res. Rep. 1958, 13, 1.
6. F. E. Saalfeld, J. J. DeCorpo, J. R. Holtzclaw, J. Wyatt, P. Brant, and D. C. Weber, Intl. J. Mass Spectrometry and Ion Physics 1981, 40, 101.
7. C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, J. Amer. Chem. Soc. 1978, 100, 1013
8. J. M. Pochan, D. F. Pochan, and H. W. Gibson, Polymer 1980, 21, 250.