Effect of Iodine Incorporation on the Electrical Conductivity of Films of Nickel Phthalocyanine

W. A. Orr[†] **and S. C. Dahlberg***

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974.

Received November 27, 1978

Abstract: Films of phthalocyanine dyes are increasingly being utilized to photosensitize a variety of optoelectronic devices. One practical limitation to further application is the insulating nature of these films. In this paper, we demonstrate how permanently conductive ($2\ \Omega^{-1}\ \mathrm{cm}^{-1}$) films of NiPc films can be prepared by heating in an iodine ambient at temperatures ranging from 140 to 200 °C. (Heating in iodine at lower temperatures results in NiPc films which were only transiently conductive.) These changes in conductivity are accompanied by changes in the optical absorption, morphology, and X-ray diffraction. Before treatment in iodine, the NiPc films are blue and have a sharp absorption edge at 750 nm. In contrast, the iodized NiPc films are green and have a less pronounced absorption edge at 700 nm with an additional absorption peak at 978 nm. The iodine treatment also resulted in some cracking in the NiPc film. Although the blue and green NiPc films are both tetragonal, there are pronounced shifts in the X-ray diffraction peaks, and the green films are preferentially oriented along the (200) direction.

Introduction

Deposition of films of semiconducting dyes such as phthalocyanine can modify the optoelectronic properties of a variety of materials.[1-7] For example, photoinduced charge injection from metal-free phthalocyanine has been used to photosensitize amorphous selenium in xerographic applications.[1,2] Metal-free phthalocyanine has also been utilized to photosensitize SiO_2 in the fabrication of spectrally sensitive photo-MOS transistors.[3,4] An increase in the optically modulated transmission of electrons, which is related to surface photovoltaic effects, has been noted for copper phthalocyanine films on silicon.[5] The conversion efficiency of solar cells can be greatly increased by the deposition of films of either porphyrin or the closely related phthalocyanine dyes.[6] Schottky barriers fabricated from magnesium phthalocyanine have a photovoltaic efficiency of 0.01%, which is the one of the highest ever observed for a solar cell made of organic material.[7]

As a result of these recent applications, there is interest in further exploitation of the optoelectronic properties of these dyes. One characteristic of these dye films which at present limits their use is their low intrinsic conductivity. In this paper, we have doped iodine into films of nickel phthalocyanine (NiPc) and this has markedly increased the conductivity of the resulting films. This is in agreement with other workers who have reported similar increases in phthalocyanine conductivity due to iodine incorporation.[8-11] This increase in conductivity has been attributed to the partial oxidation of the NiPc and the presence of chains of polyiodide counterions.[8-10] A variety of chemical preparations have been used to prepare iodized NiPc in the literature.[8-11] In this paper, iodine is sublimed and the vapor is allowed to diffuse into films of NiPc. This chemical treatment leads to pronounced changes in the crystallographic structure, film morphology, optical absorption, and electrical conductivity.

Sample Preparation

Films of NiPc were deposited by sublimation onto unheated glass slides at a base pressure of 10^{-5} Torr.[12,13] The NiPc powder was obtained from Eastman Kodak and was used without further purification. Film thickness was approximately 2000 Å as determined by Talysurf measurements. Some of these films were heated in an iodine atmosphere, which was maintained by the sublimation of solid iodine in a loosely stoppered Pyrex beaker through which nitrogen was continuously flushed. This Pyrex beaker was heated by immersion in hot silicon oil. The glass slides with the sample film were inserted in a Teflon boat so that the NiPc was prevented from directly contacting the solid iodine, since such contact destroyed the films.

Iodine treatments were performed at a range of temperatures. For temperatures between 100 and 140 °C, the NiPc films turned from their initial blue color to black and had a conductivity which was initially quite high. This conductivity rapidly decreased and after 48 h the films returned to the insulating behavior characteristic of the films before the iodine treatment. Although these films were no longer conductive, they retained their characteristic black color. In contrast to these black films, treatment at temperatures above 140 °C produced films which were a lustrous green and had a high, stable conductivity ($\sim 2\ \Omega^{-1}\ \mathrm{cm}^{-1}$). The iodine treatment used to produce the green iodized NiPc films which are examined in this paper was at 160 °C for 2 h.

Results and Discussion

The NiPc films before and after the iodine treatment differ in a number of ways. Table I shows the location and intensity of the X-ray diffraction peaks for the blue insulating and green conducting NiPc films. (No diffraction peaks were observed for the black films.) Both films have a diffraction pattern which is consistent with a tetragonal structure. Because of the limited number of peaks, an estimate of lattice parameters has not been attempted. The diffraction peaks are consistent with the literature: the blue films have the same pattern as that reported for the α form of NiPc,[14] while the diffraction peaks for the green films resemble those reported for iodized NiPc.[8] The X-ray results insulted that the green films were preferentially oriented along the (200) direction.

Figure 1 shows the morphology of the green NiPc film under magnification. The iodine treatment has caused the initially continuous blue NiPc to exhibit some cracking and pinhole formation. This cracking became severe when the films were heated in iodine at temperatures exceeding 210 °C, and the resulting films did not adhere to the glass substrate. The black NiPc films which are prepared at lower temperatures did not exhibit this cracking, but globule formation did occur.

Figure 2 shows the optical absorption curves for the NiPc films before and after iodine treatment. Before iodine treatment, the blue NiPc film is characterized by a sharp absorption edge at 750 nm, which is in approximate agreement with the lowest absorption band (671 nm) reported for NiPc in solution.[15] There is a slight amount of structure on the optical absorption curves, which is indicated in Figure 2 with arrows. The absorption edge for the green NiPc film after iodine treatment is approximately at 700 nm and is much less sharp. The incorporation of the iodine is also associated with a pronounced absorption maxima (978 nm) below the absorption

---

[†] Participant in Bell Laboratories Graduate Research Program for Women.

0002-7863/79/1501-2875$01.00/0

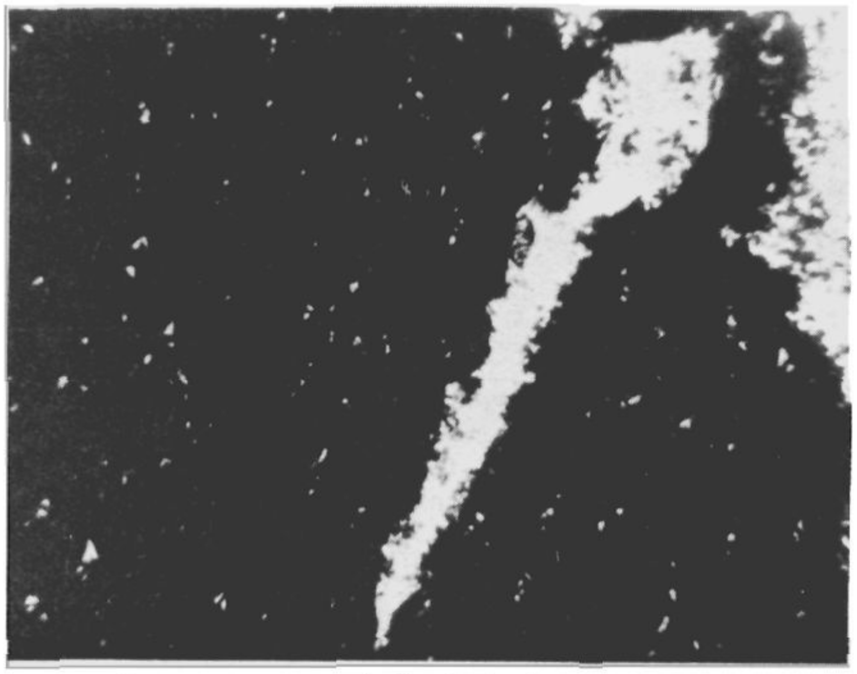

Figure 1. Photograph of green iodized NiPc film (× 400).

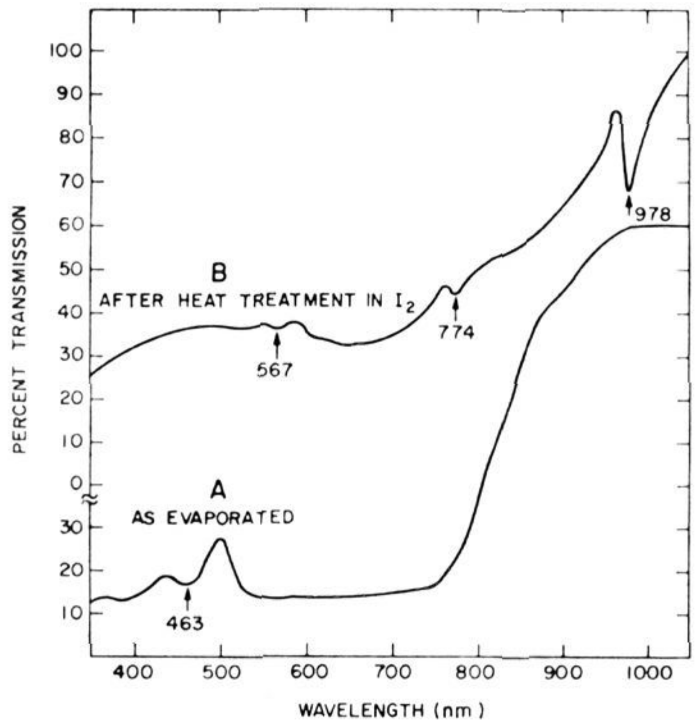

Figure 2. Optical absorption of NiPc films before and after iodine incorporation.

edge. The near-IR optical absorption measured for these iodized NiPc films is consistent with the reported increase in near-IR photoconductivity for iodized H_2Pc (i.e., metal-free phthalocyanine).[11] The absorption spectrum of the black film has an absorption edge which is initially at 623 nm which shifted to 655 nm as the film became insulating. Because of this transient behavior, the absorption spectra of the black film is not shown in Figure 2. The absorption maxima at 978 nm which is associated with the permanently conductive green NiPc film is not observed for the transiently conductive black NiPc film.

Figure 3 shows the conductivity of the green NiPc film as a function of sample temperature. This data has been normalized to the room temperature conductivity, which was approximately 2 Ω^{-1}-cm^{-1}. The measurements in Figure 3 were made using the standard four point probe technique. The probes were constructed from gold wires and provided ohmic contact to the films over the entire temperature range. The sample temperature, which was monitored by a chromel-alumel thermocouple, was varied by placing it in a glass container which was immersed either in heated silicone oil or a dry ice/methanol mixture. In addition to the data shown in Figure 3, it was also determined that the green NiPc films were insulating at liquid nitrogen temperature.

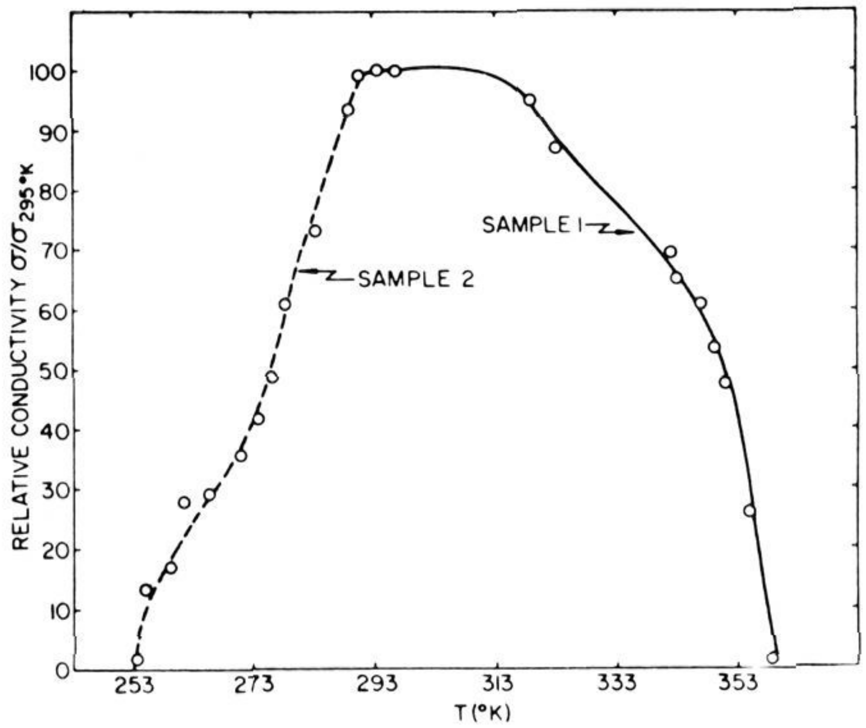

Figure 3. Temperature dependence of the conductivity of green iodized NiPc films, normalized to room temperature. For discussion of hysteresis, see text.

Table I. Location of X-ray Diffraction Peaks (Cu Kα Radiation)

sample	d, Å	I/I_1
blue NiPc, as evaporated	12.96	100
	3.65	96
	3.58	95
	3.32	95
	3.23	80
green NiPc, after iodine treatment	14.11	87
	9.94	100
	7.03	36
	6.28	34
	4.42	41
	3.67	33

The data points in Figure 3 were obtained by changing the temperature and waiting until the conductivity reached an apparent equilibrium before measurement. Pronounced hysteresis in the conductivity was noted as the temperature was changed. After either heating or cooling, the green NiPc films did not return to their original high conductivity, but instead became more insulating. For this reason the two samples illustrated in Figure 3 had not been previously subjected to any temperature changes. Understanding this loss of conductivity when the iodized NiPc films are heated is relatively straightforward since the heated films closely resemble the blue insulating NiPc films before iodine treatment. Apparently the iodine diffused out of the NiPc at these elevated temperatures. The reversibility of the iodine incorporation has been reported in the literature.[8] The reason for the loss of conductivity when the iodized NiPc films are cooled is less clear, since the films retain their characteristic green color. This result, which has been repeated for a number of films and is quite reproducible, differs from the conductivity temperature dependence obtained in the literature, where the conductivity of the iodized NiPc increased with decreasing temperature until a sudden return to insulting behavior was observed at approximately 100 K.[9] The reason for this discrepancy is not yet clear, although it should be noted that the methods used to prepare the iodized NiPc differ and the iodized NiPc films in ref 9 were more conductive than our own.

Conclusion

Conductive thin films of nickel phthalocyanine can be readily fabricated by heating in iodine vapor and these films have been characterized by their X-ray diffraction, optical absorption, and morphological features.

Acknowledgments. The authors would like to acknowledge both discussions and assistance from E. A. Chandross, R. Hartless, C. Miller, G. L. Miller, J. Mock, M. Musser, F. Padden, M. Robbins, D. Rode, G. Taylor, and F. Wudl. One of the authors (W.A.O.) would also like to thank the Bell Laboratories Graduate Research Program for Women for financial support.

References and Notes

(1) P. J. Regensburger and N. L. Petruzzella, *J. Non-Cryst. Solids*, **6**, 13 (1971).
(2) P. J. Regensburger, U.S. Patent 3 928 034 (no. 14 282) (Feb 26, 1970).
(3) B. W. Flynn, A. E. Owen, and J. Mavor, *J. Phys. C*, **10**, 4051 (1977).
(4) A. E. Owen and J. Mavor, British Patent 24081/72 (1972).
(5) S. C. Dahlberg, to be published.
(6) A. D. Adler, U.S. Patent 3 935 031 (Jan 17, 1976).
(7) A. D. Ghosh, D. L. Morel, T. Feng, R. F. Shaw, and C. A. Rowe Jr., *J. Appl. Phys.*, **1**, 230 (1974).
(8) A. Gleizes, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 3545 (1975).
(9) C. J. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks. *Science*, **200**, 45 (1978).
(10) J. L. Peterson, C. J. Schramm, B. M. Hoffman, and T. J. Marks, *J. Am. Chem. Soc.*, **99**, 286 (1977).
(11) Y. Aoyagi, K. Masuda, and S. Namba, *J. Phys. Soc. Jpn.*, **31**, 524 (1971).
(12) P. E. Fielding and F. Gutman, *J. Chem. Phys.*, **26**, 414 (1957).
(13) H. Tackikawa and L. R. Faulkner, *J. Am. Chem. Soc.*, **100**, 4379 (1978).
(14) A. A. Ebert Jr. and H. B. Gottheb, *J. Am. Chem. Soc.*, **74**, 2806 (1952).
(15) M. Whalley, *J. Chem. Soc.*, 866 (1961).

Adsorptive and Catalytic Properties of Isolated Units of $[Fe_4S_4(SR)_4]^{2-}$

Robert G. Bowman and Robert L. Burwell, Jr.*

Contribution from the Ipatieff Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received September 19, 1978*

Abstract: Reaction of 3-mercaptopropyltrimethoxysilane with wide pore silica gel produced a gel with surface $\equiv SiCH_2CH_2CH_2SH$ groups. Exchange between RS- groups occurred when this material was exposed to $[Fe_4S_4(S\text{-}t\text{-}Bu)_4][(n\text{-}Bu)_4N]_2$ in acetonitrile, to produce a silica gel containing the Fe_4S_4 unit bound to the surface with accompanying $n\text{-}Bu_4N^+$ counterions. Since the $n\text{-}Bu_4N^+$ ion decomposed at about 110 °C, a gel in which this ion had been replaced by Ca^{2+} was also prepared. These Fe_4S_4-attached gels exhibited no catalytic activity for the hydrogenation of carbon monoxide, ethylene, propylene, 1,3-butadiene, or acetylene at 25–250 °C nor for the oxidation of hydrogen, carbon monoxide, ethylene, or 1,3-butadiene at 25–100 °C. Significant adsorption of carbon monoxide and hydrogen appeared only at subzero temperatures and it was not clear whether such adsorption should be characterized as strong physisorption or very weak chemisorption.

Although the primary biochemical function of the complex $[Fe_4S_4(SR)_4]^{2-}$ appears to be electron transfer, the question inevitably arises as to whether these units have separate catalytic activity.[1] Holm has suggested that "it is entirely probable that dihydrogen activation and heterolytic cleavage, evidenced by H/D exchange, occurs at a 4-Fe site", and he noted that hydrogenase is an iron-sulfur enzyme which contains no other metals or prosthetic groups.[1] The only clear case of catalysis by a molecular Fe_4S_4 complex is that reported by Schwartz and van Tamelen[2] in which $[Fe_4S_4(SC_2H_5)_4]^{n-}$ catalyzes the α,α addition of thiols to isocyanides. The reduced unit with $n = 4$ was somewhat more active than the unit with $n = 2$. Averill and Orme-Johnson[3] have reported a study of the interaction of hydrogen and carbon monoxide with $[Fe_4S_4(SPh)_4]^{n-}$ in *N,N*-dimethylacetamide. Exposure to carbon monoxide for $n = 3$ results in the appearance of an EPR signal which decreases upon removal of the carbon monoxide. Exposure to hydrogen does not generate an EPR signal. The authors suggest that hydrogen is heterolytically dissociated in hydrogenase with a hydride ion becoming attached to an iron atom and a proton to some basic group attached to the imbedding protein.

The work of the present paper was undertaken on the view that it would be useful to know how the Fe_4S_4 unit behaved when it was in the most inert environment possible. To this end, we have avoided the presence of solvents and have exposed the Fe_4S_4 unit directly to gas-phase adsorptives and reactants. Silica gels have been prepared which contain $\equiv SiCH_2CH_2CH_2SH$ groups at the surface and Fe_4S_4 units have been attached to this thiol-modified gel by RS exchange with $[Fe_4S_4(S\text{-}t\text{-}Bu)_4][(n\text{-}Bu_4N)_2]$. A similar procedure has been used to attach Fe_4S_4 units to the surface of a tin oxide electrode.[4] Our objective was to assess the degree to which the isolated Fe_4S_4 unit behaves as a coordinatively unsaturated species to carbon monoxide and hydrogen and to ascertain whether it possesses any catalytic activity in hydrogenation and oxidation reactions.

Experimental Section

Thiol-Modified Silica Gel. Davison grade 62 silica gel (70–80 mesh, nominal pore diameter 14 nm, specific pore volume 1.1 $cm^3\ g^{-1}$, specific area 285 $m^2\ g^{-1}$) was washed successively with 0.1 M nitric acid and water to a pH of 7. It was then dried in flowing helium at 160 °C. The modification was effected as previously described[5] by refluxing 10 g of gel and 6 g of redistilled 3-mercaptopropyltrimethoxysilane in 100 cm^3 of *m*-xylene for 24 h under flowing nitrogen. The gel was washed successively with *m*-xylene and acetonitrile until silver nitrate in acetonitrile gave a negative test for mercaptan. The gel was dried in vacuo at 100 °C for 1 h. Microanalysis for C, N, and S led to calculated coverages for various preparations which ranged between 1.35 and 1.67 molecules of silane attached per nm^2 (0.578–0.709 mmol g^{-1}). During preparation, some of the thiol groups appeared to have become converted to disulfide groups, since use of Ellman's reagent[6] gave surface concentrations of sulfhydryl groups between 0.77 and 0.84 per nm^2.[7] This number was not affected by exposure of the gel to air.

Preparation of (Fe_4S_4)-Attached Gel. The iron-sulfur complex $[Fe_4S_4(S\text{-}t\text{-}Bu)_4][(n\text{-}Bu_4N)_2]$ was prepared by the method of Holm[8] and recrystallized from acetonitrile–methanol. It exhibited the correct melting point and visible spectrum and satisfactory analyses for C, H, N, S, and Fe. This compound was reacted with the thiol-modified silica gel in Schlenck-type glassware by bubbling nitrogen through