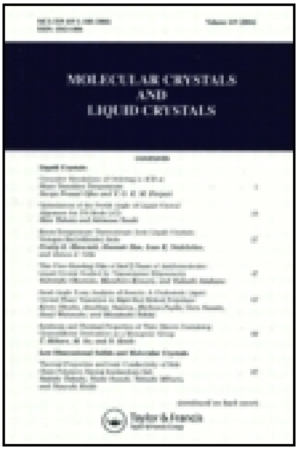

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Metallophthalocyanine Based Low-Dimensional Polymers and Related Molecular Compounds. Charge Transport and Electronic Structure Studies of A Metal-Free "Molecular Metal"

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METALLOPHTHALOCYANINE BASED LOW-DIMENSIONAL POLYMERS AND RELATED MOLECULAR COMPOUNDS. CHARGE TRANSPORT AND ELECTRONIC STRUCTURE STUDIES OF A METAL-FREE "MOLECULAR METAL"

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Abstract Single crystals of $H_2(Pc)I$ behave as a "molecular metal" with $\sigma_{RT} \approx 700\ \Omega^{-1}cm^{-1}$ ($\sigma_{\parallel}/\sigma_{\perp} \approx 500$) and $\sigma_{max} \approx 4000\ \Omega^{-1}cm^{-1}$. The static magnetic susceptibility is Pauli-like, and a Drude analysis of the optical reflectivity yields a tight-binding bandwidth of 0.77(7) eV.

INTRODUCTION

Regardless of whether structural control derives from strong covalent bonds or less rigorous packing forces, it is now known that cofacially arrayed, partially oxidized assemblies of metallophthalocyanine molecules can display high electrical conductivity in the stacking direction.[1] Nevertheless, the role of the metal atom (if any), the anisotropy of the conductivity, and the magnitude of the π-π interactions as expressed by tight-binding bandwidths are crucial issues which remain incompletely resolved. Important information on a number of these questions is provided by the present single crystal study of a "metal-free" metallophthalocyanine conductor, $H_2(Pc)I$ ($H_2(Pc)^{+0.33}(I_3^-)_{0.33}$).

EXPERIMENTAL

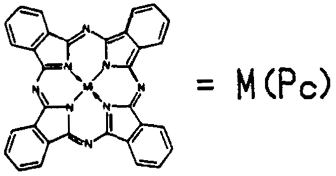
Single crystals of $H_2(Pc)I$ were grown in a vibration-free enclosure by diffusion techniques, using rigorously purified

$H_2(Pc)$, I_2, and 1-chloronaphthalene. Four-probe electrical conductivity measurements were performed with the automated apparatus described elsewhere.[1] Abrupt discontinuities in the σ vs. T relationship were found to be largely an artifact of poor contact integrity and/or thermal shock. Specular reflectance and magnetic susceptibility data were acquired and analyzed as described previously.[1]

RESULTS AND DISCUSSION

Crystals of $H_2(Pc)I$ are structurally similar to those of Ni(Pc)I (tetragonal), with $\underline{a}$ = 13.928(5) and $\underline{c}$ = 6.410(4) Å (-100°C); the iodine is present predominantly as I_3^- by resonance Raman spectroscopy. Variable-temperature four-probe conductivity measurements were made on over 50 samples, and typical stacking axis ($\sigma_{\parallel}$) data are shown in Figure 1. Room temperature conductivities are invariably higher than for Ni(Pc)I. In the first anisotropy measurements for such materials, we find that $\sigma_{\parallel}/\sigma_{\perp} \approx 700$ at room temperature by Montgomery techniques. In general, $H_2(Pc)I$ samples display a progressively higher σ_{max} at a progressively lower T_{max} as the purity of the starting materials is increased.

Variable temperature magnetic susceptibility studies of $H_2(Pc)I$ powders and single crystals reveal, after subtraction of small "Curie tails", largely Pauli-like behavior with $\chi_s = 2.21(5) \times 10^{-4}$ emu mol^{-1}. These results are rather similar to those for Ni(Pc)I, where $\chi_s = 1.90(8) \times 10^{-4}$ emu mol^{-1}.[1] Attempts to calculate a tight-binding bandwidth for $H_2(Pc)I$ from the susceptibility data yield an <u>unrealistically small</u>[1,2] value of 0.38(7) eV, possibly a consequence of large on-site Coulomb repulsions. Specular reflectance data on pressed pellets of $H_2(Pc)I$ (Figure 2) reveal a pronounced plasma-like edge and a reflectance minimum at ca. 4400 cm^{-1} (in good agreement with polarized single crystal measurements[3]). Analysis using a Drude model yields the following



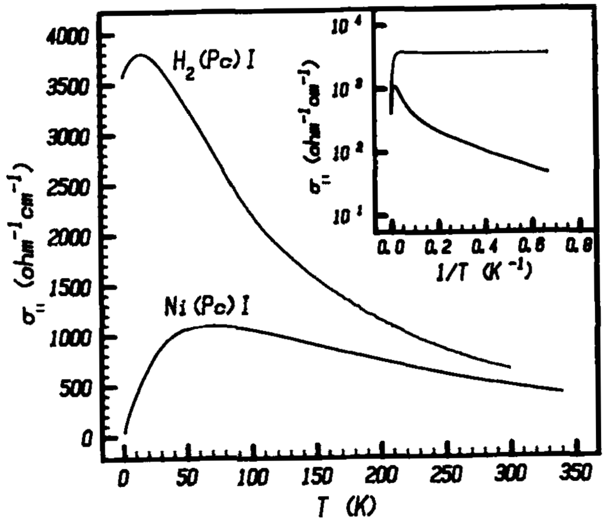


FIGURE 1 Variable temperature conductivity data for representative Ni(Pc)I and $H_2(Pc)I$ crystals. The inset shows the data in a ln σ vs 1/T format.

parameters: ω_p = 4850(50) cm^{-1}, ε_∞ = 2.48(5), τ = 2.7(1) x 10^{-15} sec, and σ_{opt} = 203 $\Omega^{-1}cm^{-1}$. Making the usual tight-binding assumptions, the bandwith is determined to be 0.77(7) eV with the carrier effective mass ratio m^*/m_0 = 2.02.

Clearly a partially oxidized phthalocyanine can exhibit all the characteristic signatures of a "molecular metal" with only protons occupying the macrocyclic core. Further work on this fascinating system is in progress.

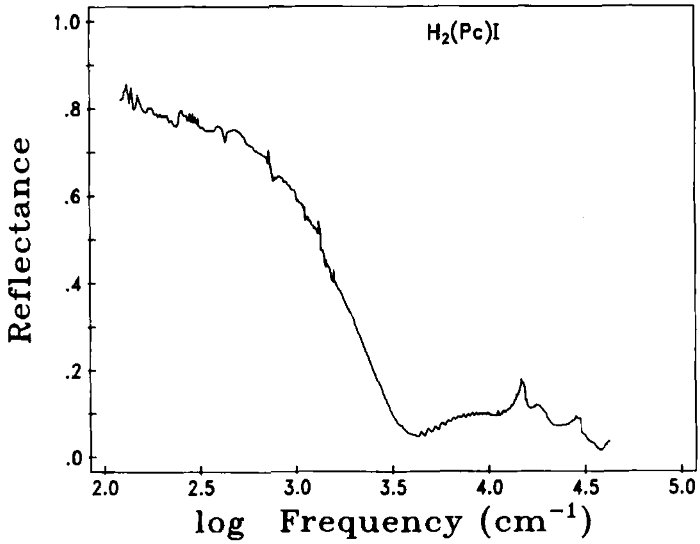


FIGURE 2 Specular reflectance spectrum of a compressed polycrystalline $H_2(Pc)I$ sample.

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