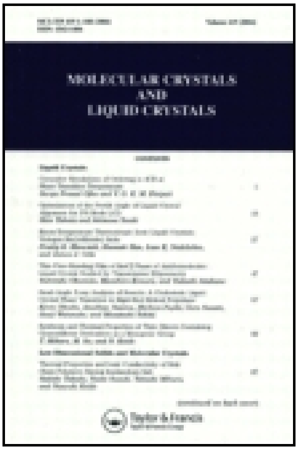

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Electronic Properties of The Conductive Polymers $[Si(Pc)O]x_y)_N$ With Different Doping Agents

T. Inabe [a], M. K. Moguel [a], T. J. Marks [a], R. Burton [b], J. W. Lyding [b] & C. R. Kannewurf [b]

[a] Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois, 60201

[b] Department of Electrical Engineering and the Materials Research Center, Northwestern University, Evanston, Illinois, 60201

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ELECTRONIC PROPERTIES OF THE CONDUCTIVE POLYMERS $\{[Si(Pc)O]X_y\}_n$ WITH DIFFERENT DOPING AGENTS

T. INABE, M. K. MOGUEL AND T. J. MARKS
Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201

R. BURTON, J. W. LYDING AND C. R. KANNEWURF
Department of Electrical Engineering and the Materials Research Center, Northwestern University, Evanston, Illinois 60201

Abstract Electrically conductive polymers have been prepared from the cofacially joined metallophthalocyanine polymer $[Si(Pc)O]_n$. Optical and electrical properties are investigated as a function of the type and degree of the incremental doping added to form the $\{[Si(Pc)O]X_y\}_n$ systems. The dopants are: X = BF_4, PF_6, SbF_6 and I. In spite of the variation in structural and electronic characteristics of the doping agents, there is a considerable similarity in the behavior of the electronic transport.

A successful effort has been under way in preparing new electrically conductive polymers based on the metallophthalocyanine system $[Si(Pc)O]_n$[1,2]. This paper specifically compares transport parameters for employing nitrosyl salts (NO^+X^-) as doping agents to prepare conductive polymers through the reaction:

$$[Si(Pc)O]_n + nyNOX \rightarrow \{[Si(Pc)O]X_y\}_n + nyNO$$

where X^- is SbF_6^-, PF_6^- or BF_4^-. Regardless of the conditions employed for the doping process, the same degree of maximum partial oxidation is achieved in each case. X-ray diffraction data indicate that the doping is inhomogeneous and that the crystal structure is tetragonal for all X. These results are analogous to those previously reported for the halogen-doped systems.[1]

Since single crystal samples are not yet available for these systems, pressed powder compactions were prepared for both optical reflectance and electrical conductivity studies. Optical reflectance data were obtained over the frequency range of 50 to

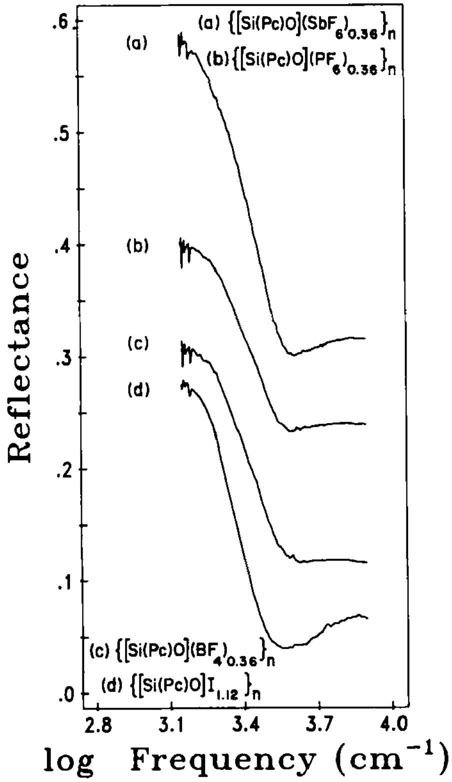

FIGURE 1 Optical reflectance at 300°K versus frequency. Each curve is displaced +0.1 reflectance units vertically from the origin of the curve immediately below.

50,000cm^{-1}; the measurement systems have been described elsewhere.[1] Figure 1 shows that portion of the spectra where the significant rise in the reflectance data has been identified as the plasma edge. There is a notable similarity in this feature for the nitrosyl salts and halogen doped polymers.

The data of Figure 1 were analyzed using the Drude model for the dielectric function:

TABLE I Transport Parameters.

Conducting polymers	Tetragonal lattice parameters (Å)	Charge transfer ρ	Plasma frequency ω_p (cm^{-1})	Background dielectric constant ϵ_∞	Electronic relaxation time τ (sec) x 10^{-15}	Optical conductivity[a] $(\Omega\cdot cm)^{-1}$	DC Electrical conductivity at 300°K $(\Omega\cdot cm)^{-1}$	Bandwidth 4t (eV)	Effective mass ratio m^*/m_0
$\{[Si(Pc)O](SbF_6)_{0.36}\}_n$	a = 14.31 c = 6.58	0.36	4548	2.21	9.18	597	0.15	0.64	2.3
$\{[Si(Pc)O](PF_6)_{0.36}\}_n$	a = 13.99 c = 6.58	0.36	4596	2.16	4.09	271	7.7×10^{-2}	0.63	2.4
$\{[Si(Pc)O](BF_4)_{0.36}\}_n$	a = 13.82 c = 6.58	0.36	4706	2.29	5.10	355	8.6×10^{-2}	0.64	2.3
$\{[Si(Pc)O]I_{1.12}\}_n$	a = 13.98 c = 6.60	0.37	4557	2.78	6.10	398	0.58	0.60	2.5

[a] Calculated from: $\sigma_{opt} = \omega_p^2\tau/4\pi$.

$$\varepsilon(\omega) = \varepsilon_\infty - (\omega_p^2)/(\omega^2 + i\omega/\tau). \quad (1)$$

In Table I the parameters from the fit are tabulated and compared to those for the iodine doped system. Based on the simple tight-binding model for one-dimensional systems, the plasma frequency may be used to calculate the bandwidth, 4t, where t is the transfer integral, and also the ratio of the effective mass of the carriers to the free-electron mass.[3] To within experimental error and the selection of the best reliability index for the computer fit of the data to Eq. (1), the bandwidths for the nitrosyl dopants are identical and essentially the same as that obtained for the halogen dopants.

The electrical conductivity values in Table I were obtained from variable temperature four-probe measurements.[2] The conductivity values extracted from the optical data suggest that the conductivity for electronic transport along the stacking axis (the c axis) should be on the order of 10^2 to 10^3 $(\Omega \cdot cm)^{-1}$ at 300^0K. The comparison of transport properties for the phthalocyanine polymers indicates a considerable similarity in the conduction mechanism when different doping agents are added to the system.

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