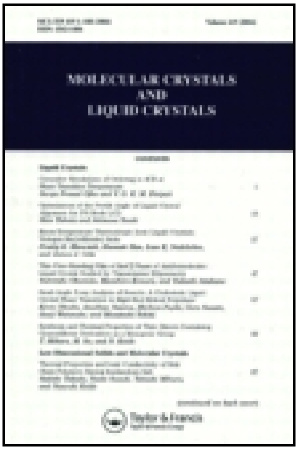

Molecular Crystals and Liquid Crystals

Enforced Segregated Stacking in Metallomacrocyclic "METALS." New Information on Phthalocyanine Donor-Acceptor Interactions

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ENFORCED SEGREGATED STACKING IN METALLOMACROCYCLIC "METALS." NEW INFORMATION ON PHTHALOCYANINE DONOR-ACCEPTOR INTERACTIONS

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Abstract The chemical, structural, optical and electrical conductivity characteristics of the cofacially joined metallophthalocyanine polymer $[Si(Pc)O]_n$ are probed in response to incremental doping by organic (dichlorodicyanoquinone) and inorganic ($NO^+BF_4^-$,$NO^+PF_6^-$) oxidants of greatly differing structural and electronic characteristics. The achievable degree of partial oxidation, the homogeneity of the doping process, and the macroscopic mechanism of charge transport appear to be remarkably similar.

INTRODUCTION

A major problem in the rational synthesis of molecular metals[1] has traditionally been control of the crystallization architecture. Failure to maintain certain essential (and delicate) spatial relationships in the mixed valent donor/acceptor crystal invariably leads to insulators. We recently showed that the cofacial assembly strategy[2] (eq. (1)) offers a unique and powerful approach to the control of

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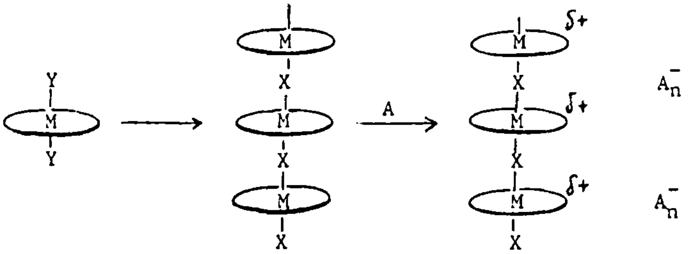
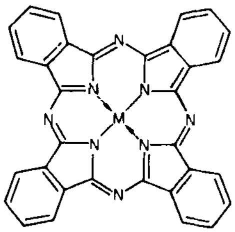


(1)

molecular stacking and crystallization architecture in low-dimensional molecular materials composed of arrayed metallomacrocycles.[3] Moreover, it offers the promise of rationally evolving an almost infinite variety of conductive macromolecules composed of well-characterized, robust, chemically versatile building blocks and possessing well-defined primary and secondary structures. For systems where the metallomacrocycle is a phthalocyanine[3] (1), M=Si,Ge, and X=O



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($[M(Pc)O]_n$, n ≈ 50–200), we have shown[2,4] via a battery of physicochemical techniques, that doping with Br_2 and I_2 results in electrically conductive, ligand-oxidized, processable[5] polymers with impressive air and thermal stability. Furthermore, the doping process is inhomogeneous, and the crystal structures of the fully doped polymers $\{[M(Pc)O]Br_{1.1}\}_n$ and $\{[M(Pc)O]I_{1.1}\}_n$ are essentially isostructural with the tetragonal "molecular metal" Ni(Pc)I[6], differing principally in the M(Pc)-M(Pc) interplanar spacing (3.244(2)Å, M=Ni; 3.30(2)Å, M=Si; 3.48(2)Å, M=Ge). This structural effect is clearly evident in the magnetic susceptibility, optical reflectivity (and the bandwidths derived therefrom), as well as in the d.c. charge transport.[4a,b] Since halogen is present largely if not exclusively as X_3^- in these materials, the degree of incomplete charge transfer, ρ, is, within experimental error, almost independent of metal and halogen dopant, i.e., $\rho \approx 0.33$, M=Ni; ≈ 0.36, M=Si; ≈ 0.36, M=Ge.

The power of the cofacial assembly strategy, however, lies beyond what can be ascertained with halogen dopants. Because segregated donor-acceptor crystallizaton is rigorously enforced by the covalent nature of the polymetallomacrocycle array, it is now possible to delve into the nature of various donor-acceptor relationships without disrupting the structure of the charge-carrying molecular spine. Thus, a whole new range of donor-acceptor combinations and experiments becomes possible. In this report we describe the type of information which can be garnered from the $[M(Pc)O]_n$ materials, using the Ni(Pc) system as a point of reference. We first illustrate the structural/oxidation state/charge transport effects of using a large, spatially-demanding organic dopant molecule. Next, we inquire whether acceptor molecules which are less spatially-demanding than Br_3^- and I_3^- might bring about a greater degree of partial oxidation in the doped $[M(Pc)O]_n$ polymers.

EXPERIMENTAL

The polymers $[Si(Pc)O]_n$ and $[Ge(Pc)O]_n$ were prepared as described elsewhere,[4a] while Ni(Pc) was freshly sublimed, and DDQ (dichlorodicyanoquinone) was recrystallized from benzene. Doping of the polymers with DDQ was carried out in benzene, while doping with $NO^{+}BF_4^{-}$ and $NO^{+}PF_6^{-}$ was carried out in dry CH_2Cl_2 using rigorously anhydrous/anaerobic Schlenk/glove box techniques. Physical measurements were performed with the instrumentation described previously.[4a,b]

ORGANIC DOPANTS

Iodine doping of Ni(Pc) produces Ni(Pc)I, the crystal structure of which consists of stacks of $Ni(Pc)^{+0.33}$ radical cations and parallel I_3^- chains.[6] Charge transport behavior in the stacking direction (Figure 1) is "metal-like" ($d\sigma/dt<0$) and reminiscent of a number of low-dimensional

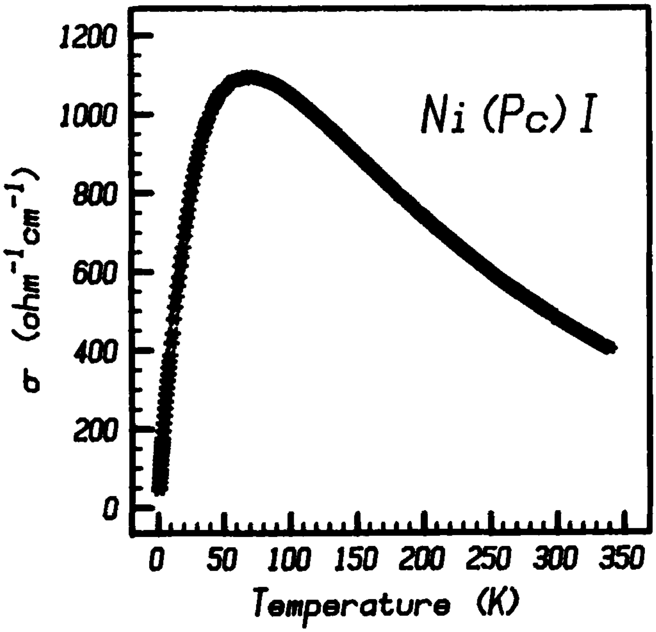

FIGURE 1. Variable temperature four-probe electrical conductivity of a typical Ni(Pc)I crystal in the needle axis (molecular stacking) direction (from reference 7).

halogen-doped organochalcogen conductors.[1,3,7] Room temperature single crystal conductivities are as high as 650 $\Omega^{-1}cm^{-1}$, while conductivities of compressed polycrystalline powders are on the order of 5 $\Omega^{-1}cm^{-1}$. In contrast, doping Ni(Pc) with organic acceptors such as DDQ, TCNQ, etc., results in insulators (σ(powder) $\approx 10^{-7}$ $\Omega^{-1}cm^{-1}$). Is this a dopant structural or electronic effect?

To answer this question, doping experiments were conducted with $[Si(Pc)O]_n$ and a variety of high potential quinoid acceptors. In all cases,[2a] large increases in $[Si(Pc)O]_n$ electrical conductivity were measured after doping. An in-depth study of the $\{[Si(Pc)O]DDQ_y\}_n$ system reveals several interesting features. As can be seen in Figure 2, the dependence of conductivity upon dopant stoi-

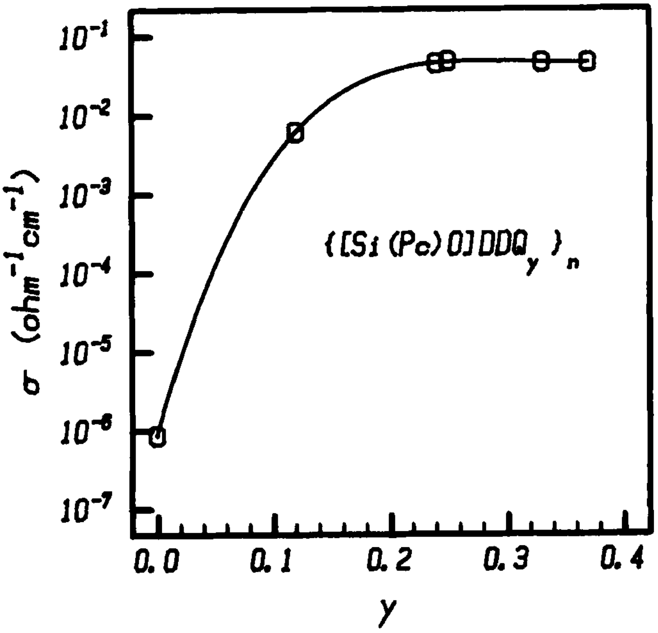

FIGURE 2. Electrical conductivity as a function of dopant level for polycrystalline $\{[Si(Pc)O]DDQ_y\}_n$ samples.

chiometry is similar to that found in halogen doping.[4b] In the latter systems, such a functional dependence could be associated with a percolation mechanism for polycrystalline charge transport,[4b,8] consistent with the inhomogeneous nature of the halogen doping process. Preliminary X-ray powder diffractometric studies of the $\{[Si(Pc)O]DDQ_y\}_n$ system indicate that the quinone doping is inhomogeneous as well. As to the stoichiometry of DDQ doping, it has so far been impossible to increase y beyond ca. 0.37, even using excess DDQ, long reaction times, high temperatures, and sonochemical doping methodology. Making the reasonable assumption[2a] that the quinone is largely present as DDQ^-, it is concluded that again $\rho \approx 0.37$ for the $[Si(Pc)O]_n$ system.

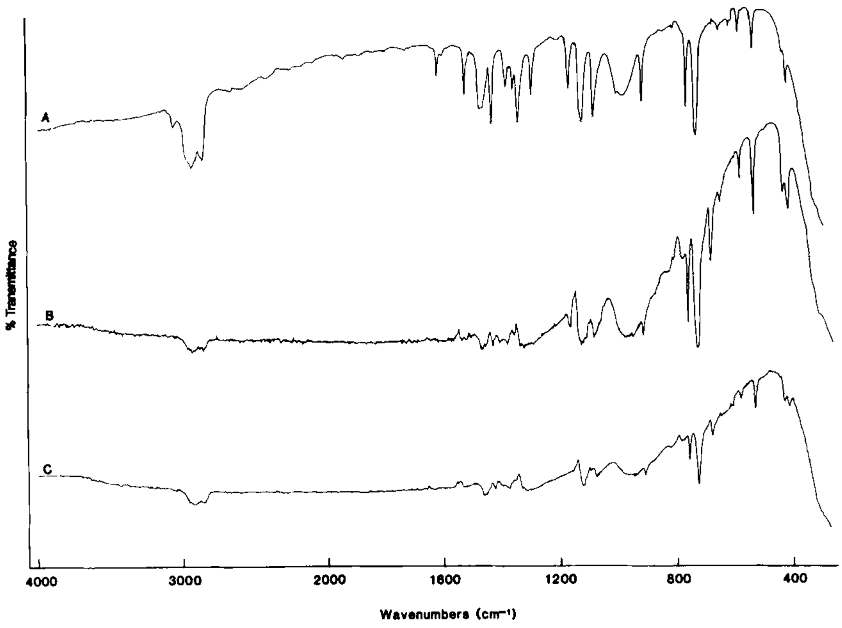

FIGURE 3. Transmission infrared spectra of $\{[Si(Pc)O]$-$DDQ_y\}_n$ materials as Nujol mulls. A. y=0.0 B. y=0.25 C. y=0.37.

Transmission infrared spectra for various $\{[Si(Pc)O]DDQ_y\}_n$ materials are illustrated in Figure 3. The characteristically broad carrier electronic absorption[4b] is clearly evident. Unfortunately, this phenomenon obscures unambiguous identification of the DDQ^- vibrational modes. Quinone radical ion spectral features have, however, been identified in less conductive quinone-doped $[Si(Pc)O]_n$ materials.[2a] In Figure 4 are shown variable

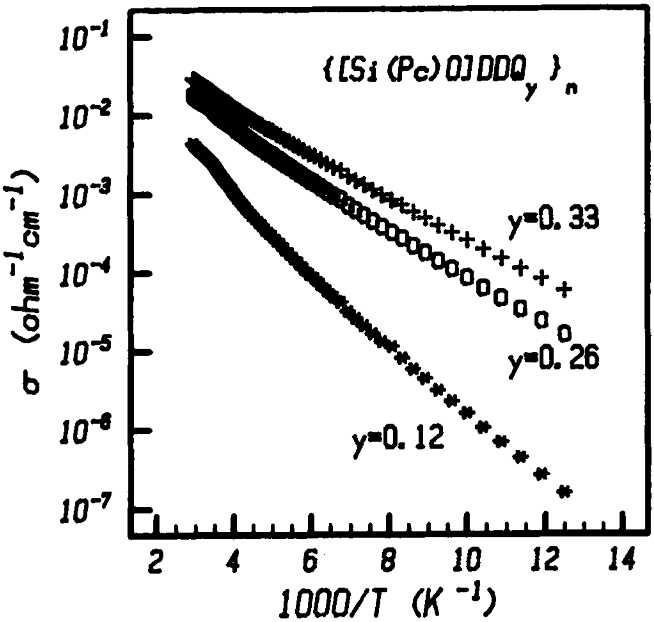

FIGURE 4. Variable temperature four-probe electrical conductivity data for several polycrystalline $\{[Si(Pc)O]DDQ_y\}_n$ samples.

temperature conductivity data for several $\{[Si(Pc)O]DDQ_y\}_n$ stoichiometries. The functional form of the σ vs. T plots and the dependence upon doping are strikingly similar to the $\{[M(Pc)O]I_y\}$ materials.[4b] In that case the temperature dependence of the transport could be fit to a fluctuationinduced carrier tunnelling mechanism in which the tunnelling is through parabolic potential barriers.[4a,9] We find that $-[\ln(\sigma/\sigma_0)]^{-1}$ vs. T plots are also linear for $\{[Si(Pc)O]DDQ_y\}_n$ materials having a broad range of y values.

TETRAFLUOROBORATE AND HEXAFLUOROPHOSPHATE COUNTERIONS

The use of nitrosyl salts (NO^+X^-) as electron transfer reagents offers a clean chemical means of oxidizing various organic substrates[10] (eq.(2)). For doping the $[M(Pc)O]_n$

$$R + nNO^+X^- \longrightarrow R^{+n}(X^-)_n + nNO_{(g)} \qquad (2)$$
$$X^- = BF_4^-,\ PF_6^-,\ \text{etc.}$$

polymers, the smaller spatial requirements of counterions such as BF_4^- and PF_6^- as opposed to those of the larger Br_3^-, I_3^-, and DDQ^- ions suggested that counterion packing requirements would be less likely to inhibit bringing the metallomacrocyclic array into a higher degree of partial oxidation. Surprisingly, however, when $[Si(Pc)O]_n$ doping is carried out under a variety of conditions, the maximum dopant levels achieved are $\{[Si(Pc)O](BF_4)_{0.36}\}_n$ and $\{[Si(Pc)O](PF_6)_{0.32}\}_n$. Again, it appears that the $\rho \approx 0.35$ oxidation state lies at the bottom of a relatively steep energetic minimum. X-ray powder diffractometry reveals that $[Si(Pc)O]_n$ doping by $NO^+BF_4^-$ and $NO^+PF_6^-$ is also inhomogeneous. Structurally, the BF_4^- and PF_6^- polymer salts appear closely related to the I_3^- and Br_3^- analogues.[4b] A preliminary analysis of the diffraction data is compatible with a tetragonal lattice where the principal departure from the halogen-doped crystal structure is in the periodicity along c, as might be expected (the BF_4^- and PF_6^- will not completely fill the available "tunnels" extending parallel to c).

In terms of electronic structure and charge transport, the σ versus y functional dependence of the $\{[Si(Pc)O](BF_4)_y\}_n$ and $\{[Si(Pc)O](PF_6)_y\}_n$ materials is similar to that for the halogen- and DDQ-doped polymers. Variable temperature conductivity data are presented in Figures 5 and 6. It can be seen that in magnitude, shape, and y dependence, the transport behavior of these materials is closely analogous to that of the $\{[Si(Pc)O]I_y\}_n$ and

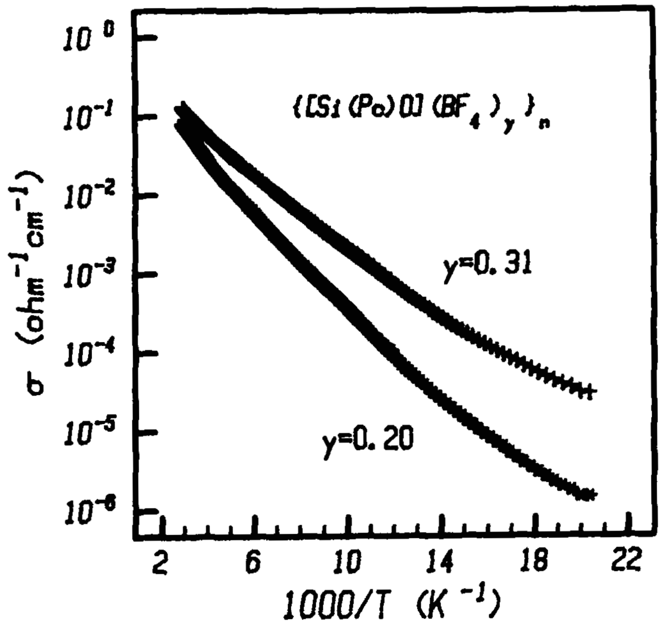

FIGURE 5. Variable temperature four-probe electrical conductivity data for two polycrystalline $\{[Si(Pc)O](BF_4)_y\}_n$ samples.

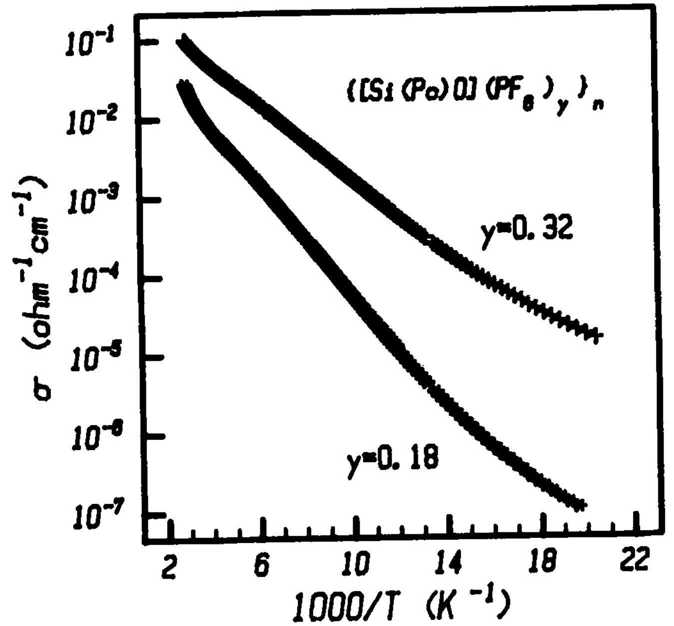

FIGURE 6· Variable temperature four-probe electrical conductivity data for two polycrystalline samples of $\{[\mathrm{Si(Pc)O}](\mathrm{PF}_6)_y\}_n$.

$\{[(\mathrm{Si(Pc)O}]\mathrm{DDQ}_y\}_n$ substances. Again, plots of $-[\ln(\sigma/\sigma_0)]^{-1}$ vs. T are linear. Not surprisingly, transmission infrared spectra of the BF_4^- and PF_6^- salts also exhibit the strong electronic features noted previously (e.g., Figure 3). Reflectivity measurements reveal a plasma-like edge in the infrared, as seen for $\{[\mathrm{Si(Pc)O}]\mathrm{I}_{1.1}\}$.[4b]

Is the rigorously enforced metallophthalocyanine stacking a requisite for producing highly conductive materials via $NO^+BF_4^-$ and $NO^+PF_6^-$ doping? The answer appears to be, surprisingly, no. Doping of Ni(Pc) with these oxidants yields materials of maximum dopant stoichiometry $Ni(Pc)(BF_4)_{0.34}$ and $Ni(Pc)(PF_6)_{0.36}$. It can be seen that the stability of the $\rho \approx 0.35$ oxidation state is not appreciably modified by the greater structural flexibility of the molecular system. In Figure 7 are shown variable

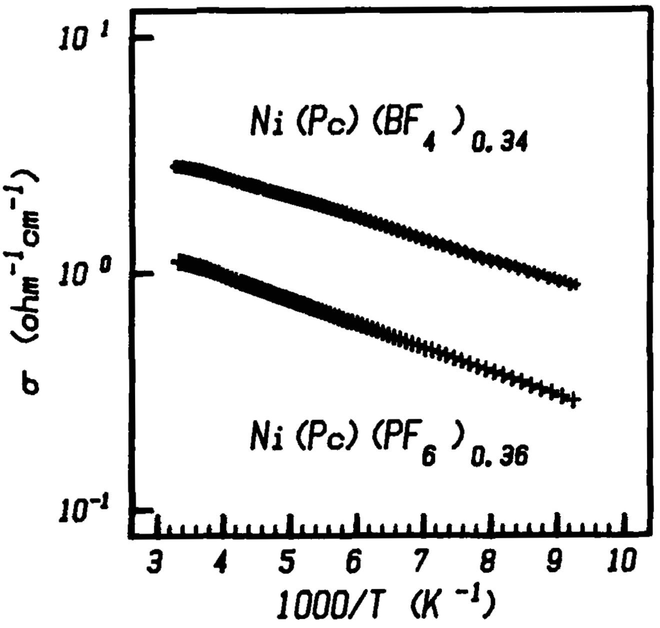

FIGURE 7. Variable temperature electrical conductivity data for polycrystalline samples of $Ni(Pc)(BF_4)_{0.34}$ and $Ni(Pc)(PF_6)_{0.36}$.

temperature conductivity data for two of the fully doped Ni(Pc) salts. The magnitude of the conductivities and their temperature dependence are similar to polycrystalline samples of Ni(Pc)I. Without more structural information, it is not possible to immediately explain the observed differences in conductivity between $Ni(Pc)(BF_4)_{0.34}$ and $Ni(Pc)(PF_6)_{0.36}$, although counterion/transport effects, well-documented in the $(TMTSF)_2X$ series,[11] appear to have a structural basis, and should not be considered unusual.[3]

CONCLUSIONS

In regard to the doped $[M(Pc)O]_n$ series as prototype electrically conductive polymers, it appears that doping inhomogeneity and the charge transport mechanism are relatively constant over a fairly wide range of acceptor dopant types. As keys to better understanding low-dimensional phthalocyanine "metals", the results for the $[M(Pc)O]_n$ series underscore the rather dopant-insensitive stability of the $\rho \approx 0.35$ partial oxidation state and the fragility of the stacking architecture, hence the molecular metallic state, in the absence of certain types of dopants and of rigorous structural control.

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