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Strategies for Control of Lattice Architecture in Low-Dimensional
Molecular Metals: Assembly of Partially Oxidized Face-to-Face
Linked Arrays of Metallomacrocycles.

C. W. Dirk, E. A. Mintz, K. F. Schoch, Jr., and T. J. Marks

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ESR, static magnetic susceptibility, and variable-temperature four-probe electrical conductivity. Evidence is presented that some of the polymers have "metal-like" conductivity in the stacking direction and that transport properties within the series can be readily manipulated by rational variation of lattice architecture (e.g., the identity of the metal, M) and acceptor characteristics. Additional information is presented on doping experiments with electron donors and on employing metallohemiporphyrazines as polymer building blocks.

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STRATEGIES FOR CONTROL OF LATTICE ARCHITECTURE IN LOW-DIMENSIONAL MOLECULAR METALS: ASSSEMBLY OF PARTIALLY OXIDIZED FACE-TO-FACE LINKED ARRAYS OF METALLOMACROCYCLES.

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ABSTRACT

This paper discusses an approach to control molecular stacking interactions in low-dimensional mixed valence materials by locking partially oxidized metallomacrocycles together in a face-to-face orientation. Thus, doping of the cofacially linked oligomers $[M(Pc)O]_n$ (M = Si, Ge, Sn; Pc = phthalocyaninato) with halogen (I_2, Br_2) or quinone (e.g., TCNQ, DDQ) electron acceptors produces robust, electrically conductive polymers with a wide range of stoichiometries and properties. The new materials have been studied by a variety of physical methods including X-ray diffraction, resonance Raman and infrared spectroscopy, ESR, static magnetic susceptibility, and variable-temperature four-probe electrical conductivity. Evidence is presented that some of the polymers have "metal-like" conductivity in the stacking direction and that transport properties within the series can be readily manipulated by rational variation of lattice architecture (e.g., the identity of the metal, M) and acceptor characteristics. Additional information is presented on doping experiments with electron donors and on employing metallohemiporphyrazines as polymer building blocks.

INTRODUCTION

The past half-dozen years have witnessed intense scientific activity in the area of low-dimensional electrically conductive materials [1-5]. Great excitement has been generated among chemists and physicists by the synthesis and properties of unusual

organic and metal-organic substances with metal-like properties. These developments can be anticipated to lead ultimately to new degrees of chemical control over collective solid state properties, to new methodology in chemical synthesis and in physical measurements, and to better theoretical models for cooperative phenomena in condensed matter. In the technological sphere, this research may lead to a new generation of electronic materials with applications as varied as sensors, rectifiers, fuel cell components, solar energy conversion elements, and electrophotographic devices. The possibility of high temperature superconductors or at least highly conductive synthetic materials which could replace metals in various applications, has contributed additional impetus to the design and study of metal-like materials.

Despite the advances that have been achieved, it is fair to say that our understanding of those molecular and electronic characteristics which control charge conduction is at a rather primitive level. That is also true of the synthetic chemical methodology required to tailor structures for testing current theories about the molecular metallic state or for optimizing materials performance and processing characteristics. A tremendous challenge exists in learning to control these factors, and the purpose of this article is to report on new developments in our Laboratory which address a number of chemical and physicochemical aspects of this problem.

STRATEGIES FOR THE DESIGN OF HIGHLY CONDUCTIVE LOW-DIMENSIONAL MATERIALS

Two features now appear to be necessary for facile charge conduction in a molecular material [6,7]. First, the component molecules must be arrayed in close spatial proximity, with sufficient

intermolecular orbital overlap to provide a continuous electronic
pathway for carrier migration, and in crystallographically similar
environments, so that the pathway has a minimum of energetic hills
and valleys. Second, the arrayed molecules must exist in formal
fractional oxidation states ("mixed valence," "incomplete charge
transfer," "partial oxidation"). That is, the molecular entities
to be connected in series must have fractionally occupied elec-
tronic valence shells. Within the framework of a simple Hubbard

MIXED VALENCE AND CHARGE TRANSPORT
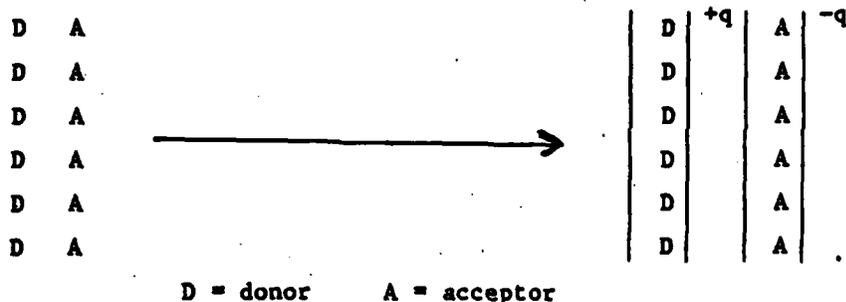
Unoxidized

Partially Oxidized
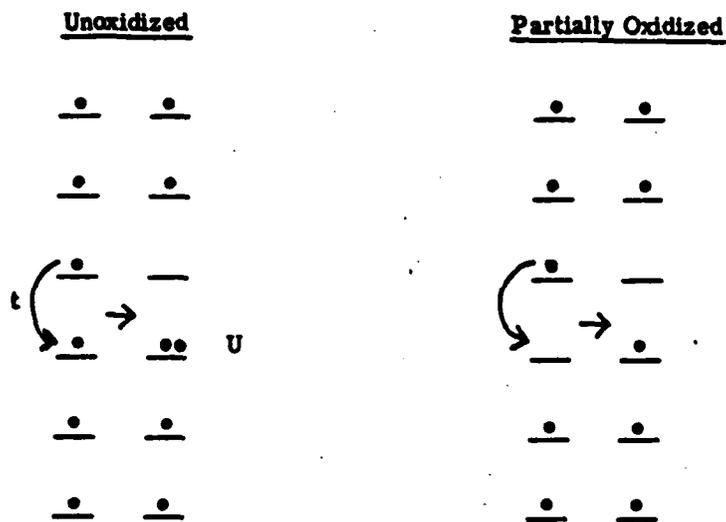
U = electron correlation energy

t = transfer integral = bandwidth/4

FIGURE 1. Schematic illustration of the effect of partial oxida-
tion on charge mobility in a low-dimensional system composed of
molecular stacks.

model [1-5], this requirement reflects the relatively narrow band-widths (4t) and large on-site Coulomb repulsions (U) in such systems. A simplified valence bond picture of this situation is illustrated in Figure 1; partial oxidation facilitates charge mobility by creating numerous electronic vacancies. A similar picture could be constructed for partial reduction.

A successful, first-generation strategy for the synthesis of mixed valent low-dimensional materials [6,7] has involved the co-crystallization of planar, conjugated metallomacrocyclic donor molecules (D) with halogen acceptors (A) as schematized below.

D	A		D $^{+q}$	A $^{-q}$
D	A		D	A
D	A	$\longrightarrow$	D	A
D	A		D	A
D	A		D	A
D	A		D	A

D = donor   A = acceptor

In optimum cases, the result has been lattices composed of segregated, partially oxidized metallomacrocyclic stacks and parallel arrays of halide or polyhalide counterions [6-8]. An important additional feature of this approach is that the form of the halogen (even if disordered) can be straightforwardly deter-mined by resonance Raman/iodine Mossbauer spectroscopic tech-niques [6-11]. The degree of partial oxidation follows from this information and knowledge of the stoichiometry. This synthetic approach has enjoyed success for metal glyoximates [8,12,13], dibenzotetraazaannulenes [14], phthalocyanines [15-17], and porphyrins [18]. The crystal structure of an example, nickel phthalocyanine iodide ([Ni(Pc)]$I_{1.0}$) [15-17], is illustrated in Figure 2. The 300°K conductivity of this material in the
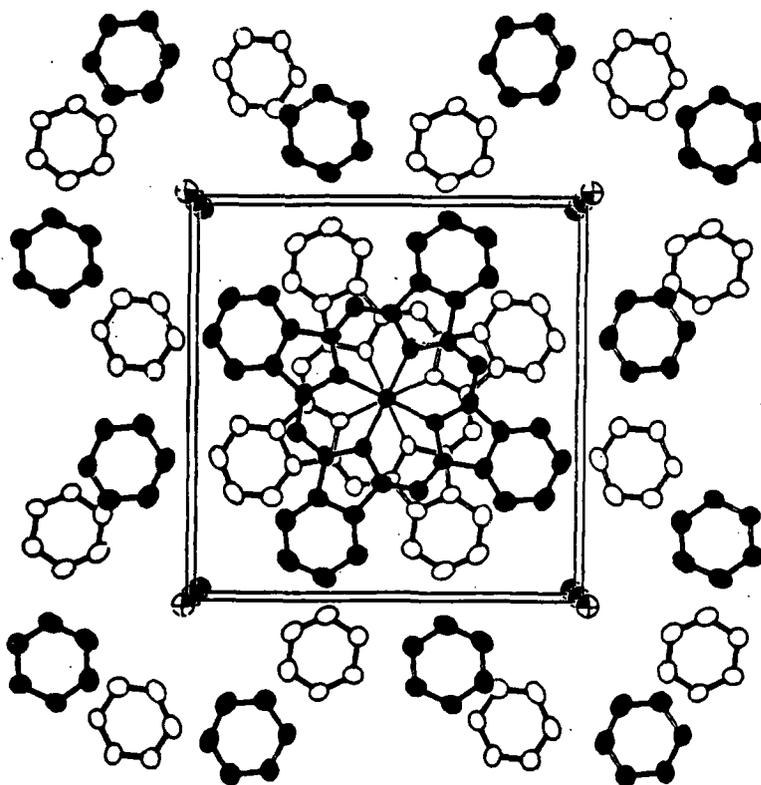
FIGURE 2. The crystal structure of nickel phthalocyanine iodide, [Ni(Pc)]I$_{1.0}$, viewed along the stacking direction. From ref. 7.

molecular stacking direction (300-700 Ω^{-1} cm^{-1}) is high (carrier mean free paths are comparable to some of the most conductive "molecular metals") and the temperature dependence is "metal-like" ($\rho \sim T^{1.9}$) down to 60°K.

Although the above strategy is frequently effective, it suffers, as do all approaches based upon simple molecular

stacking, from the weakness that the lattice architecture is totally dependent upon the unpredictable and largely uncontrollable forces that dictate the stacking pattern, the donor-acceptor orientations, and the stacking repeat distances. Figure 3 illustrates the complexity of the structural problem by depicting some of the types of crystallization patterns which have been identified. A common pitfall in the design of new materials

A.

<pre>
    D /
   / D /   A
  / D /   A
 /   D   A
    D /   A
   / D   A
  / D   A
 /   D
</pre>

B.
<pre>
—D— A
—D— A
—D— A
—D— A
—D— A
—D—
</pre>

C.
<pre>
—D—
  A
—D—
  A
—D—
  A
</pre>

D.
<pre>
   —D—
   —D—
A   A
   —D—
   —D—
A   A
</pre>

E.
<pre>
—D— A
A —D—
—D— A
A —D—
—D— A
</pre>

F.
<pre>
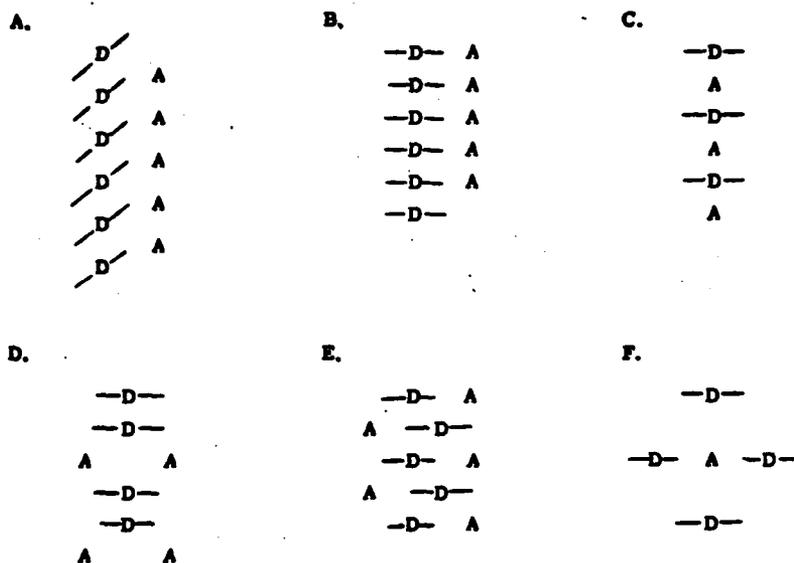   —D—
—D— A —D—
   —D—
</pre>

FIGURE 3. Schematic depiction of some common structures for donor-acceptor complexes. A. Segregated stacking, canted donors. B. Segregated stacking, D_{nh} donor stacking. C. Integrated stacking. D. Integrated stacking, donor dimers. E. Segregated stacking, zig-zag donor stacking. F. Ion clusters without stacking.

is the formation of integrated D-A stacks (3C,D), which invariably
leads to insulators [2,6,19]. As an example, attempts to substi-
tute oxidizing quinones for halogens in the aforementioned
phthalocyanine chemistry lead to integrated stack insulators [20].

A successful new approach to the control of molecular
stacking in low dimensional mixed valence materials is founded
upon the construction of macromolecules in which arrays of
metallomacrocycles are tightly locked in a "face-to-face" con-
figuration by covalent bonds [21-23]. Followed by partial
oxidation, this approach capitalizes upon a great deal of accumu-
lated chemical and physical information about the subunits, and
offers the real possibility of constructing robust new conductive
polymers with well-defined and easily manipulated primary and
secondary structures. The forces which hold the stacks together
are now covalent linkages with bond energies on the order of
80-100 kcal/mol rather than weak packing, van der Waals, and
bandwidth forces. As a result, it is now possible to both delve
into those factors which stabilize the mixed valent state without
fear of a breakdown in stacking, and to perturb systematically
bandwidth and phonon dynamics. Although we focus our discussion
primarily upon phthalocyanines (with additional remarks about
hemiporphyrazines), it should be clear that the strategy has
obvious generality.

SYNTHESIS AND PROPERTIES OF FACE-TO-FACE LINKED METALLO-PHTHALOCYANINES

The Group IVA precursor phthalocyanines $Si(Pc)Cl_2$, $Ge(Pc)Cl_2$,
and $Sn(Pc)Cl_2$ were synthesized as described elsewhere [22,24-26].
Hydrolysis in pyridine/NaOH solution converts the dichlorides to
the corresponding dihydroxides, $Si(Pc)(OH)_2$, $Ge(Pc)(OH)_2$,
$Sn(Pc)(OH)_2$ [22,24-26]. Condensation of these compounds to form

phthalocyaninato polysiloxanes, polygermyloxanes, and polystan-
nyloxanes (Figure 4) was carried out at 300-400 °C/10^{-3} torr
[22,24-26]. The resulting macromolecules have been characterized
by a broad range of chemical and physicochemical methods. These
[M(Pc)O]$_n$ materials have high chemical and thermal stability;
moreover, they are not significantly degraded by oxygen or
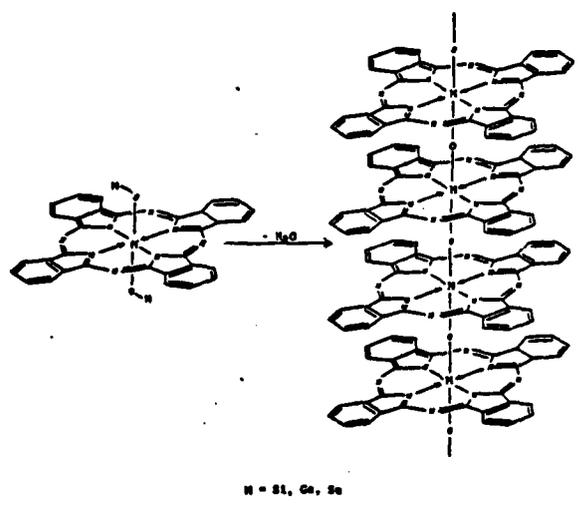moisture. The polysiloxane polymer can be dissolved in concen-

M = Si, Ge, Sn

FIGURE 4. Condensation reaction to produce cofacial arrays of
Group IV metallophthalocyanines.

trated sulfuric acid and recovered unchanged (typical of phthalo-
cyanines containing non-electropositive metals). A rough estimate
of the minimum average chain length of [Si(Pc)O]$_n$ produced in the
condensation polymerization can be obtained by infrared spectro-
photometric analysis of the Si-O stretching region. For a typical

sample, the degree of polymerization is estimated to be on the order of ca. 100 subunits or more. Structural information on the face-to-face polymers can be derived from several lines of evidence. X-ray powder diffraction patterns can be indexed in the tetragonal crystal system [21,22,24] and are very similar to the patterns exhibited by the columnar crystal structures of $[Ni(Pc)]I_{1.0}$ [17] and $Ni(dpg)_2I_{1.0}$ (dpg = diphenylglyoximato) [8]. The stacking intervals ($c/2$) in these latter tetragonal structures, determined in single crystal studies, are 3.244(2) Å and 3.271(1) Å, respectively. The stacking intervals derived for the $[M(Pc)O]_n$ materials from the powder diffraction data are found to depend upon the ionic radius of the Group IV ion and vary from 3.33(2) Å (Si-O-Si) to 3.51(2) Å (Ge-O-Ge), to 3.95(2) Å (Sn-O-Sn) [21,22,24]. These relationships are illustrated in Figure 5. The
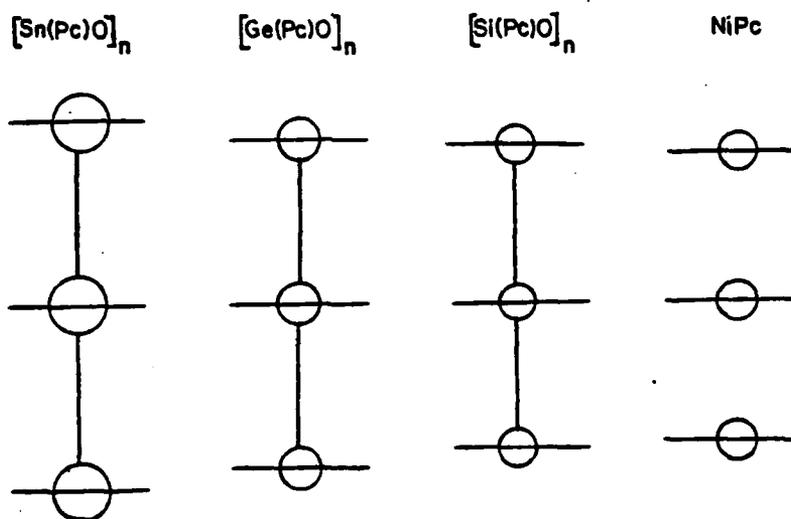

FIGURE 5. Scale drawing of the interplanar relationships in the face-to-face phthalocyanine polymers and in $[Ni(Pc)]I_{1.0}$.

reliability of these metrical parameters is further supported by single crystal diffraction results on the model trimer $[(CH_3)_3SiO]_2(CH_3)SiO[Si(Pc)O]_3Si(CH_3)[OSi(CH_3)_3]_2$ which contains three cofacial Si(Pc)O units linked by linear Si-O-Si connections at a distance of 3.324(2) Å [27]. In addition, the $[Ge(Pc)O]_n$ and $[Sn(Pc)O]_n$ interplanar spacings obtained from diffraction data are in good agreement with values estimated from ionic radii [28] assuming linear Ge-O-Ge and Sn-O-Sn vectors, i.e., 3.58 Å for $[Ge(Pc)O]_n$ and 3.90 Å for $[Sn(Pc)O]_n$ [21,22,24]. There is good precedent for molecules with linear Si-O-Si, Ge-O-Ge, and Sn-O-Sn linkages [29]. The $[M(Pc)O]_n$ polymers display vibrational and optical spectra which are characteristic of metallophthalocyanines [24].

PARTIAL OXIDATION OF COFACIALLY LINKED METALLOPHTHALOCYANINES WITH HALOGENS

Doping experiments on the $[M(Pc)O]_n$ polymers were first carried out using iodination methodology developed in this Laboratory for simple stacked systems [6,7]. Stirring the powdered polymers with solutions of iodine in organic solvents or exposing the powders to iodine vapor results in substantial iodine uptake. Alternatively, $[Si(Pc)O]_n$ can be doped by dissolving in sulfuric acid and precipitating with an aqueous I_3^- solution. The stoichiometries which can be obtained depend upon the reaction conditions; representative iodinated materials characterized by elemental analysis are compiled in the left-hand column of Table 1. A survey experiment also indicated that bromine-doped material could be prepared. That partial oxidation of the cofacial array has indeed occurred is confirmed by resonance Raman scattering spectroscopy in the polyiodide region (Figure 6). The

TABLE 1

Physical Data for Polycrystalline Samples of Halogen-Doped $[M(Pc)O]_n$ Materials

Compound	$\sigma(\Omega^{-1}cm^{-1})300°K$	Activation Energy (eV)	Interplanar Spacing (Å)
$[Si(Pc)O]_n$	3×10^{-8}		3.33(2)
$\{[Si(Pc)O]I_{0.50}\}_n$	2×10^{-2}		
$\{[Si(Pc)O]I_{1.55}\}_n$	1.4	0.04±0.001	3.33(2)
$\{[Si(Pc)O]I_{4.60}\}_n$	1×10^{-2}		
$\{[Si(Pc)O]Br_{1.00}\}_n$	6×10^{-2}		
$[Ge(Pc)O]_n$	$<10^{-8}$		3.51(2)
$\{[Ge(Pc)O]I_{1.80}\}_n$	3×10^{-2}	0.08±0.006	3.51(2)
$\{[Ge(Pc)O]I_{1.90}\}_n$	5×10^{-2}	0.06±0.003	
$\{[Ge(Pc)O]I_{1.94}\}_n$	6×10^{-2}	0.05±0.007	
$\{[Ge(Pc)O]I_{2.0}\}_n$	1×10^{-1}		
$[Sn(Pc)O]_n$	$<10^{-8}$		3.95(2)
$\{[Sn(Pc)O]I_{1.2}\}_n$	1×10^{-6}		3.95(2)
$\{[Sn(Pc)O]I_{5.5}\}_n$	2×10^{-4}	0.68±0.01	
$[Ni(Pc)]I_{1.0}$[a]	7×10^{-1}	0.036±0.001	3.244(2)

[a] Reference 15.

characteristic totally symmetric stretching frequency of
I_3^- ($\nu = 108$ cm^{-1}) [6,7,9] is observed along with an accompanying
overtone progression. For samples with I/M < 3, there are at most
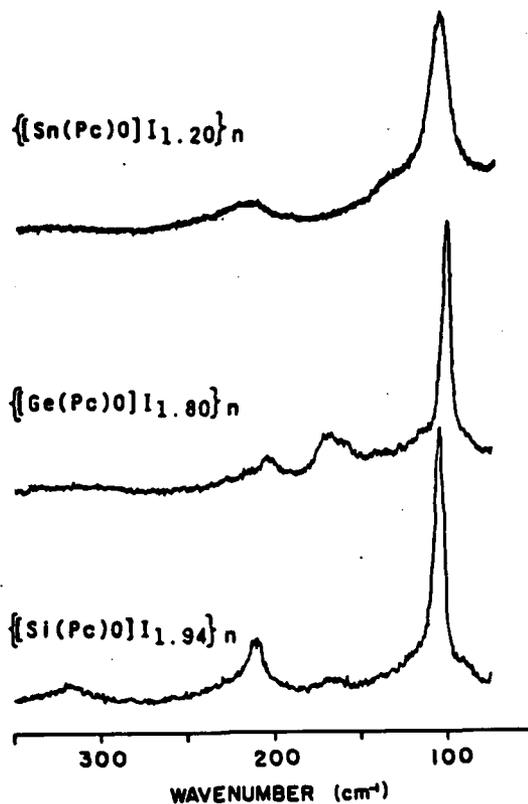only traces of I_5^- ($\nu \approx 160$ cm^{-1}) [8,10] and no indication of free

FIGURE 6. Resonance Raman spectra (ν_0 = 5145 Å)of iodine-doped phthalocyanine face-to-face polymers. From ref. 21.

$I_2(\nu \approx 200$ cm^{-1}) [8,10]. The nature of the $[M(Pc)O^{\delta+}]_n$ electronic structure was also studied by electron spin resonance (ESR). The symmetry of the lineshapes and the measured g-values are consistent with π-radical cations, i.e., the unpaired spin density is in molecular orbitals which are predominantly ligand in character [30]. A similar conclusion was reached for $[Ni(Pc)]I_{1.0}$ [17]. ESR data for the $\{[M(Pc)O]I_x\}_n$ materials are

compiled in Table 2. In regard to structural changes which might
accompany doping, X-ray powder diffraction studies indicate that
iodination does not significantly alter the interplanar separa-
tions [21,22,24].

TABLE 2

Powder ESR Data for Iodinated Phthalocyanine Face-to-Face
Polymers

Compound	$g(300°K)^a$	$\Gamma(300°K)(G)^b$
$\{[Si(Pc)O]I_{1.40}\}_n$	2.003	5.1
$\{[Ge(Pc)O]I_{0.62}\}_n$	2.002	3.2
$\{[Sn(Pc)O]I_{1.20}\}_n$	2.002	6.0

a
Average g-value; $g_\parallel$ and $g_\perp$ are not resolved.
b
Observed linewidth.

Four-probe electrical conductivity measurements on the
$[M(Pc)]_n$ powders using locally developed van der Pauw techniques
[31,32] show them to be insulators. However, iodine or bromine
doping results in large increases in electrical conductivity
(Table 1). The general trend in conductivity as a function of
metal is $\sigma_{Si} \gtrsim \sigma_{Ge} > \sigma_{Sn}$. Since the transport characteristics of
iodine-oxidized metallophthalocyanines are known to be largely
ligand-dominated and relatively insensitive to the identity of the
metal [15-17], the metal dependence of the conductivity observed in
the face-to-face polymers is logically ascribed to structural dif-
ferences such as the interplanar separation. Indeed, the

$\{[Si(Pc)O]I_x\}_n$ interplanar separation is within 0.1 Å of that in $[Ni(Pc)]I_{1.0}$ and the room temperature powder conductivities of the two materials are comparable (Table 1). The temperature dependence of the $\{[M(Pc)O]I_x\}_n$ powder conductivities is thermally activated (Figure 7), and least squares fits to Eq.(1) yield the
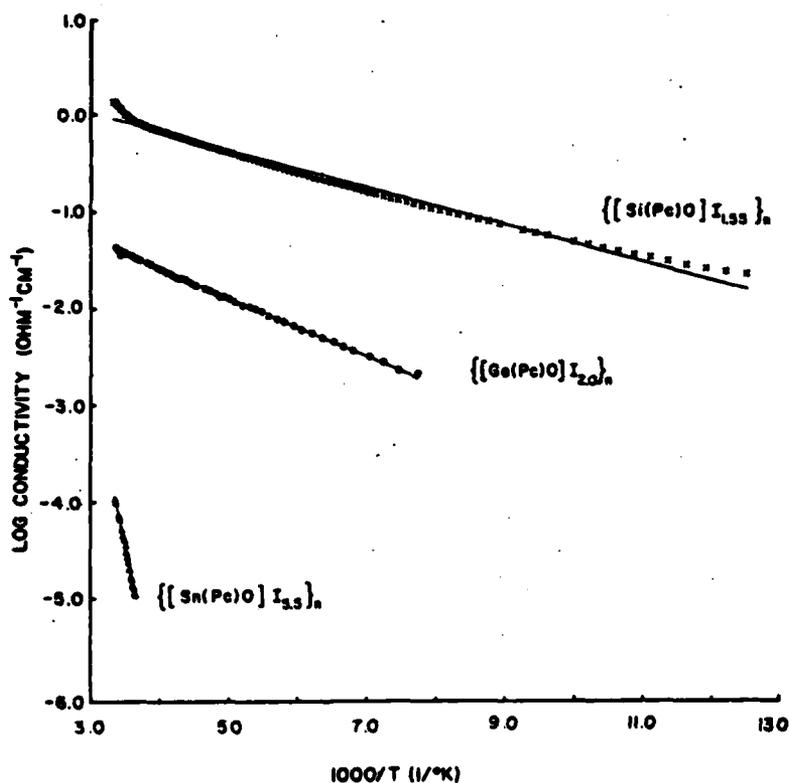

FIGURE 7. Variable temperature four-probe electrical conductivity data for powders of the iodine-doped, face-to-face phthalocyanine polymers.

$$\sigma = \sigma_0 \, e^{-\Delta/kT} \qquad (1)$$

activation parameters compiled in Table 1. Powder conductivities are, of course, affected by interparticle contact resistance and averaging over all crystallographic orientations. Thus, for low-dimensional "molecular metals" such as $[Ni(Pc)]I_{1.0}$, powder conductivities are typically 10^2-10^3 less than single crystal conductivities in the stacking direction. Thus, "metal-like" temperature dependence is usually·masked. From the powder data on the $\{[M(Pc)O]I_x\}_n$ materials it can be anticipated that high, "metal-like" conductivities will be observed in the chain direction for the M = Si and possibly M = Ge materials. Voltage shorted compaction (VSC) techniques [33] offer an effective qualitative means to sample stacking axis transport properties in pressed powder samples by deliberately shorting out sources of interparticle resistance. In the present context it is important to note that the VSC conductivity behavior of $\{[Si(Pc)O]I_x\}_n$ samples is unequivocally "metal-like" [34]. The results of the variable temperature conductivity studies also underscore the robust thermal character of the cofacially arrayed polymers. $\{[Si(Pc)O]I_x\}_n$ samples could be cycled to 300°C with only a minor decrease in room temperature conductivity (due primarily to vaporization of the iodine).

Static magnetic susceptibility by Faraday techniques reveals another characteristic signature [1-5] of "molecular metals" in the $\{[Si(Pc)O]I_x\}_n$ and $\{[Ge(Pc)O]I_x\}_n$ materials. Susceptibilities are only weakly paramagnetic (χ_M = 300-500 x 10^{-6} emu after diamagnetic corrections are made) and are only modestly dependent on temperature down to 77°K [21,22]. Studies at lower temperatures are in progress.

# RESPONSE OF THE COFACIALLY LINKED METALLOPHTHALOCYANINES TO OTHER DOPANTS

The strictly enforced molecular stacking in the $[M(Pc)O]_n$
materials offers an unprecedented opportunity to experiment with
some of the important forces [2,6,35-39] which stabilize or desta-
bilize the molecular metallic state. Thus, the electronic aspects
of the donor-acceptor interaction can be studied with far greater
control over the structural variables. It was first of interest
to learn whether non-halogen oxidants could produce a partially
oxidized, conductive metallophthalocyanine stack, or whether there
was something "magic" about iodine and bromine. High potential
quinones such as those shown below have electron affinities com-
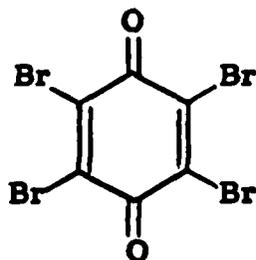parable to halogens, and produce conductive compounds with a
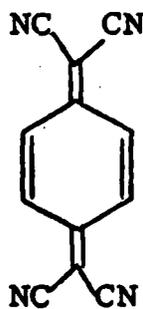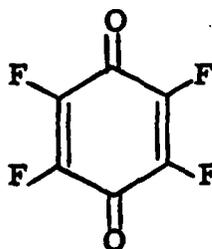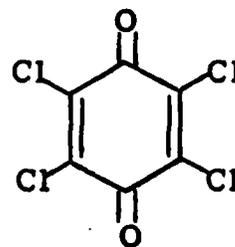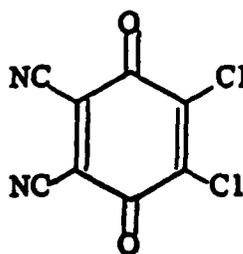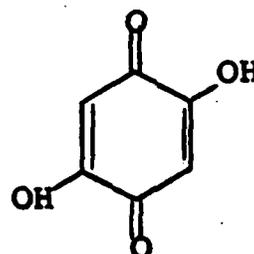
TCNQ   fluoranil   chloranil

bromanil   DDQ   DHB

number of organic donors [1-5]. With simple metallophthalo-cyanines, however, only insulators are produced [20] and con-siderable structural evidence points to an integrated stack crystal structure [40] as the reason for the low charge transport capability. It was thus of interest to determine what donor-acceptor interactions would occur in a metallophthalocyanine system which was locked into stacks. Doping experiments were conducted by stirring the $[Si(Pc)O]_n$ macromolecules with solu-tions of the above quinones. The products were characterized by elemental analysis and vibrational spectroscopy. As can be seen in Table 3, large increases in electrical conductivity accompany the quinone doping. Indeed, the DDQ-doped materials are as con-ductive as many of the halogenated polymers [23,41]. The tem-perature dependence of the conductivity of some representative samples is shown in Figure 8. The transport in these materials is thermally activated and least-squares fits to Eq.(1) yield the activation parameters compiled in Table 3. There are some notable deviations from a linear ln σ vs. 1/T relationship (e.g., $\{[Si(Pc)O]TCNQ_{0.5}\}_n$) and further investigations of the reasons for this behavior are in progress. Infrared spectral studies of the TCNQ-doped materials reveal a displacement of ν_{CN} to lower fre-quencies [41], consistent with electron density uptake by the quinone [42]. Clearly partial oxidation of the phthalocyanine stack by high potential quinones occurs when a segregated stack structure is enforced.

In principle, it should also be possible to partially reduce phthalocyanines and to create conducting materials by injecting nonintegral amounts of electron density per site [41]. A number of attempts have been made to partially reduce metallo-phthalocyanines using alkali metals [20]. In all cases, the resulting materials are insulators, and it was suspected that non-stacked materials were being produced. A preliminary experiment

TABLE 3

Electrical Conductivity Data for Polycrystalline Samples of
Cofacial Phthalocyanine Polymers with Various Dopants

Dopant[a]	Empirical Formula	$\sigma(\Omega^{-1}\,cm^{-1})300°K$	Activation Energy(eV)
none	$[Si(Pc)O]_n$	3×10^{-8}	
I	$\{[Si(Pc)O]I_{1.55}\}_n$	1.4	$0.04\pm.001$
Br	$\{[Si(Pc)O]Br_{1.00}\}_n$	6×10^{-2}	
K	$\{[Si(Pc)O]K_{1.0}\}_n$	2×10^{-5}	
TCNQ	$\{[Si(Pc)O]TCNQ_{0.50}\}_n$	2.8×10^{-3}	$0.09\pm.002$
Flr	$\{[Si(Pc)O]Flr_{0.23}\}_n$	7.2×10^{-4}	$0.13\pm.001$
Chl	$\{[Si(Pc)O]Chl_{.037}\}_n$	6.9×10^{-4}	$0.13\pm.002$
Brl	$\{[Si(Pc)O]Brl_{0.84}\}_n$	5.8×10^{-4}	$0.15\pm.001$
DDQ	$\{[Si(Pc)O]DDQ_{1.00}\}_n$	2.1×10^{-2}	$0.08\pm.001$
DDQ	$\{[Si(Pc)O]DDQ_{0.35}\}_n$	6.2×10^{-2}	$0.05\pm.001$
DHB	$\{[Si(Pc)O]DHB_{0.13}\}_n$	3.8×10^{-5}	$0.19\pm.005$
ClA	$\{[Si(Pc)O]ClA_{0.14}\}_n$	1.8×10^{-3}	$0.11\pm.001$

a
Flr = fluoranil; Chl = chloranil; Brl = bromanil; DDQ =

dichlorodicyanoquinone; ClA = chloranilic acid.

was conducted in which $[Si(Pc)O]_n$ was reacted with potassium vapor
in a sealed tube. The product was collected and handled at all
times in an inert atmosphere. As can be seen in Table 3, a signi-
ficant increase in electrical conductivity accompanies the
potassium doping. Further efforts to refine the reductive doping
procedure are now in progress.
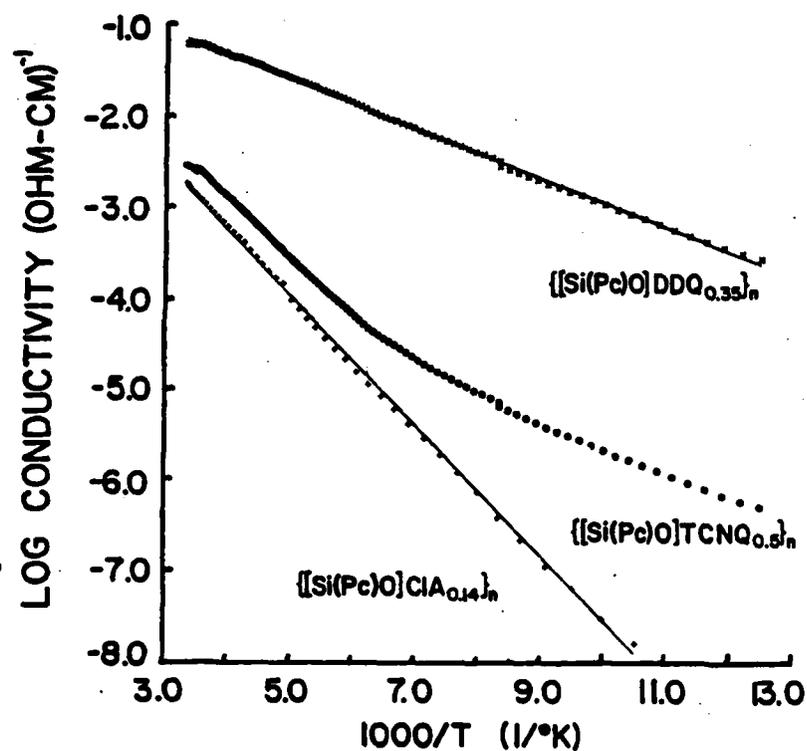
FIGURE 8. Variable temperature powder conductivities of the siloxane phthalocyaninato cofacial polymer doped with high potential quinones. ClA = chloranilic acid.

SYNTHESIS AND HALOGEN DOPING OF COFACIALLY LINKED METALLO-HEMIPORPHYRAZINES

It has also been of interest to elaborate the face-to-face conducting polymer concept to include other types of metallomacrocycles. A particularly intriguing question concerns whether such an approach could bring macrocycles which do not normally stack into a cofacial orientation and what the properties of

the resulting materials would be. Previous results in this
Laboratory indicated that metallohemiporphyrazines (M(hp), shown
below) could be oxidized with iodine when M = Ni but the products
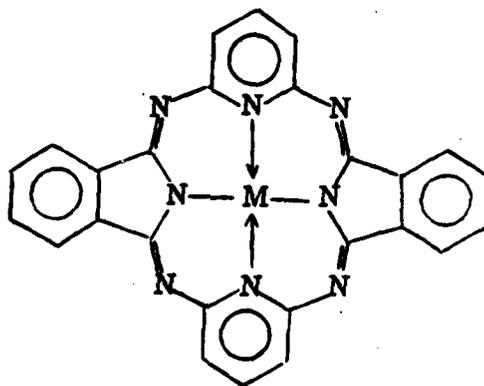
M(hp)

remained insulating [44]. Since the molecular orbital topology of
the hemiporphyrazine ligand, as probed by molecular orbital calcu-
lations at the Pariser-Parr-Pople SCF LCAO CI π-electron level
[45,46], is considerably different from phthalocyanines [45] (both
HOMO and LUMO are more localized in H_2hp [46]), it was of interest
to explore the effect of enforced molecular stacking on oxidation
state and charge transport. Face-to-face silicon and germanium
hemiporphyrazine macromolecules, [46-48] were synthesized as
depicted in Eqs.(2)-(5). The macromolecules were characterized

$$2 \underset{\text{CN}}{\overset{\text{CN}}{\bigcirc}} + \underset{\text{2}}{H_2N \overset{N}{\bigcirc} NH_2} \longrightarrow H_2hp + 4NH_3 \qquad (2)$$

$$H_2hp + MCl_4 \longrightarrow M(hp)Cl_2 \qquad (3)$$

$$M(hp)Cl_2 + 2NH_4OH \longrightarrow M(hp)(OH)_2 + 2NH_4Cl \qquad (4)$$

$$nM(hp)(OH)_2 \longrightarrow [M(hp)O]_n + n/2 \ H_2O \qquad (5)$$
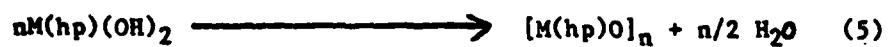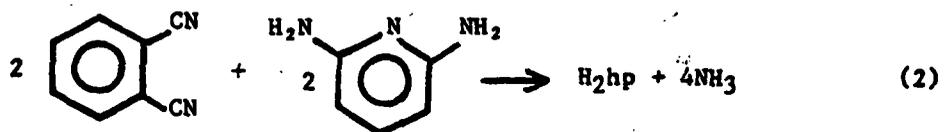
$$M = Si, \ Ge$$
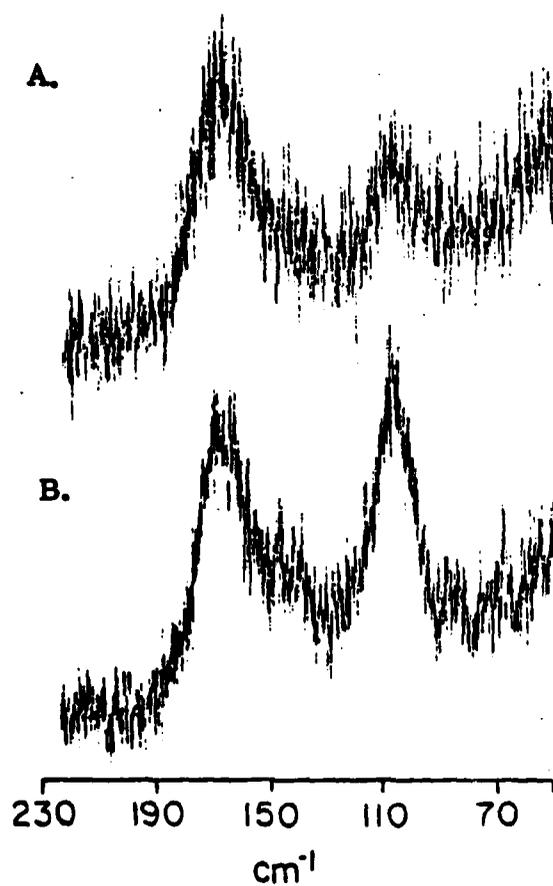
FIGURE 9. Resonance Raman spectra (ν_o = 5145 Å) of A. $\{[Si(hp)O]I_{1.51}\}_n$ B. $\{[Ge(hp)O]I_{1.48}\}_n$ as polycrystalline samples.

by elemental analysis and vibrational spectroscopy. The available structural data [47,49] indicate that $[M(hp)O]_n$ interplanar spacings should be comparable to those for the $[M(Pc)O]_n$ materials. Iodine uptake was not as facile as for the $[M(Pc)O]_n$ macromolecules, and very large excesses of iodine as well as heating of the sample were required to achieve significant dopant levels $(\{[M(hp)O]I_x\}_n$ where $x > 1$). Resonance Raman spectra (Figure 9) do indicate that oxidation has occurred in the $x \approx 1.5$ materials, yielding formally mixed valent cofacial arrays, but the degree of oxidation per added equivalent of iodine does not appear to be as great as for the phthalocyanine analogues. ESR spectra indicate the formation of π radical cations (Table 4), and the

TABLE 4

Powder ESR and Conductivity Data for Iodinated Hemiporphyrazine
Cofacial Polymers

Compound	$g(300°K)$[a]	$\Gamma(300°K)(G)$[b]	$\sigma(\Omega^{-1} \, cm^{-1})(300°K)$
$[Si(hp)O]_n$			$< 10^{-12}$
$\{[Si(hp)O]I_{1.51}\}_n$	2.003	7.8	3.0×10^{-8}
$[Ge(hp)O]_n$			2.0×10^{-16} [c]
$\{[Ge(hp)O]I_{1.48}\}_n$	2.003	6.2	6.0×10^{-9}

[a] Average g-value; $g_{\parallel}$ and $g_{\perp}$ are not resolved.

[b] Observed linewidth

[c] G. Meyer and D. Wöhrle, Makromol. Chem., 175, 714 (1974).

measured g-values are not greatly different from the aforementioned phthalocyanine polymers. Thus, oxidation involves orbitals which are predominantly ligand in composition. Room temperature pressed powder conductivity data are also given in Table 4. A significant increase in conductivity occurs upon iodination,

however charge transport values are still many orders of magnitude below those for the analogous cofacial phthalocyanines. In some respects the situation is similar to the halogenated glyoximates, which form mixed valent stacks but are only semiconducting [8,11,12]. Mixed valency and cofacial stacking are clearly a necessary but not sufficient condition to form a highly conductive macromolecule.

CONCLUSIONS AND PROSPECTS

Cofacial metallomacrocycle assembly techniques represent what is likely the most powerful approach yet developed for controlling molecular stacking architecture in low dimensional materials. In terms of fundamental understanding, we already have learned a great deal about bandwidth-conductivity and donor-acceptor relationships in conductive materials composed of molecular stacks. However, the surface has only been barely scratched in terms of the exciting research opportunities which await exploitation in this area. Further synthetic work offers the opportunity to make drastic changes in macrocycle identity and electronic structure, stacking distance and bandwidth, interplanar relationships and phonon dynamics, and to correlate these chemical modifications with physical observables. Already, efforts to introduce new metal ions [50,51] and bridging functionalities [23,52] have succeeded. Studies with new types of dopants should provide much important information on donor-acceptor relationships and on the cohesive forces which stabilize the mixed valent state. A wide variety of magnetic, charge transport, and optical experiments remain to be carried out which should ultimately provide invaluable information on how the chemistry and lattice architecture

are related to some of the fundamental characteristics of the
molecular metallic state. Finally, little is known about the pro-
cessing and fabrication properties of these new classes of
materials. Efforts in this direction are presently underway and
should provide interesting and useful information of technological
relevance.

ACKNOWLEDGMENTS

REFERENCES

[1] J. T. Devreese, V. E. Evrard, and V. E. Van Doren, Eds.,
Highly Conducting One-Dimensional Solids, Plenum Press, NY,
1979.

[2] J. B. Torrance, Acct. Chem. Res., 12, 79 (1979).

[3] J. S. Miller, and A. J. Epstein, Eds., Synthesis and Proper-
ties of Low-Dimensional Materials, Ann. NY Acad. Sci., 313
(1978).

[4] H. J. Keller, Ed., Chemistry and Physics of One-Dimensional
Metals, Plenum Press, New York, 1977.

[5] J. S. Miller and A. J. Epstein, Prog. Inorg. Chem., 20, 1,
(1976).

[6] T. J. Marks and D. W. Kalina, in Extended Linear Chain Com-
pounds, J. S. Miller, Ed., Plenum Publishing Corp., in
press.

[7] T. J. Marks, Ann. NY Acad. Sci., 313, 594 (1978).

[8] M. A. Cowie, A. Gleizes, G. W. Grynkewich, D. W. Kalina,
M. S. McClure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby,
J. A. Ibers, C. R. Kannewurf, and T. J. Marks, J. Am. Chem.
Soc., 101, 2921 (1979) and references therein.

[9] R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, J. Am. Chem. Soc., 102, 3322 (1980).

[10] R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, J. Am. Chem. Soc., 101, 7568 (1979).

[11] D. W. Kalina, J. W. Lyding, M. S. McClure, C. R. Kannewurf, and T. J. Marks, J. Am. Chem. Soc., in press.

[12] L. D. Brown, D. W. Kalina, M. S. McClure, S. L. Ruby, S. Schultz, J. A. Ibers, C. R. Kannewurf, T. J. Marks, J. Am. Chem. Soc., 101, 2937 (1979).

[13] A. Gleizes, T. J. Marks, and J. A. Ibers, J. Am. Chem. Soc., 97, 3545 (1975).

[14] L.S. Lin, T. J. Marks, C. R. Kannewurf, J. W. Lyding, M. S. McClure, M. T. Ratajack, and T.-C. Whang, submitted for publication; Bull. Am. Phys. Soc., 25, 315 (1980).

[15] J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, J. Am. Chem. Soc., 99, 286 (1977).

[16] C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, Science, 200, 47 (1978).

[17] R. P. Scaringe, C. J. Schramm, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers, and T. J. Marks, J. Am. Chem. Soc., in press.

[18] S. K. Wright, C. J. Schramm, T. E. Phillips, D. M. Scholler, and B. M. Hoffman, Synth. Met., 1, 43 (1979).

[19] R. C. Teitelbaum, T. J. Marks, and C. K. Johnson, J. Am. Chem. Soc., 102, 2986 (1980), and references therein.

[20] K. F. Schoch, Jr. and T. J. Marks, unpublished results at Northwestern University.

[21] K. F. Schoch, Jr., B. R. Kundalkar, and T. J. Marks, J. Am. Chem. Soc., 101, 7071 (1979).

[22] T.J. Marks, K. F. Schoch, Jr., and B. R. Kundalkar, Synth. Met., 1, 337 (1980).

[23] C. W. Dirk, J. W. Lyding, K. F. Schoch, Jr., C. R. Kannewurf, and T. J. Marks, Polymer Preprints, in press.

[24] C. W. Dirk, K. F. Schoch, Jr., and T. J. Marks, manuscript in preparation.

[25] R. J. Joyner and M. E. Kenney, Inorg. Chem., 82, 5790 (1960).

[26] J. B. Davison and K. J. Wynne, Macromolecules, 11, 186 (1978), and references therein.

[27] D. R. Swift, Ph.D. Thesis, Case Western Reserve University, 1970.

[28] R. D. Shannon, Acta Cryst., A32, 751 (1976).

[29] C. Glidewell and D. C. Liles, J. Organometal. Chem., 174, 275 (1979), and references therein.

[30] E. A. Mintz and T. J. Marks, unpublished results at Northwestern University.

[31] R. C. Teitelbaum, Ph.D. Thesis, Northwestern University, August 1979.

[32] K. Seeger, Semiconductor Physics, Springer-Verlag, NY, 1973, pp. 483-487.

[33] L. B. Coleman, Rev. Sci. Instrum., 49, 48 (1978).

[34] K. F. Schoch, Jr., J. W. Lyding, C. R. Kannewurf, and T. J. Marks, manuscript in preparation.

[35] J. P. Lowe, J. Am. Chem. Soc., 102, 1262 (1980).

[36] H. A. J. Groves and C. G. DeKruf, Acta Crystal., A36, 428 (1980).

[37] A. J. Epstein, N. O. Lipari, D. J. Sandman, and P. Nielsen, Phys. Rev. B, 13, 1569 (1976).

[38] R. M. Metzger, Ann. NY Acad. Sci., 313, 145 (1978) and references therein.

[39] B. D. Silverman, Phys. Rev. B, 16, 5153 (1977).

[40] L. Pace, A. Ulman, and J. A. Ibers, private communication.

[41] K. F. Schoch, Jr. and T. J. Marks, unpublished results; Bull. Am. Phys. Soc., 25, 315 (1980).

[42] R. P. Van Duyne, M. R. Suchanski, J. M. Lakovits, A. R. Siedle, K. D. Parks, and T. M. Cotton, J. Am. Chem. Soc., 101, 2832 (1979), and references therein.

[43] K. F. Schoch, Jr. and T. J. Marks, unpublished results at Northwestern University.

[44] D. W. Kalina, D. R. Stojakovic, and T. J. Marks, unpublished
results at Northwestern University.

[45] T. J. Marks and D. R. Stojakovic, _J. Am. Chem. Soc._, _100_,
1695 (1978).

[46] C. W. Dirk and T. J. Marks, unpublished results at North-
western University.

[47] J. N. Esposito, L. E. Sutton, and M. E. Kenney, _Inorg. Chem._,
_6_, 1116 (1967).

[48] R. D. Joyner and M. E. Kenney, _Inorg. Chem._, _1_, 717 (1962).

[49] E. C. Bissel, Ph.D. Thesis, Case Western Reserve University,
1970.

[50] P. M. Kuznesof, K. J. Wynn, R. S. Nohr, and M. E. Kenney,
J. Chem. Soc., _Chem. Comm._, _121_ (1980).

[51] R. S. Nohr, K. J. Wynne, and M. E. Kenney, _Polymer Preprints_,
in press. We thank these authors for a preprint.

[52] C. W. Dirk and T. J. Marks, _Bull. Am. Phys. Soc._, _25_, 315
(1980).

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