

AD-A099 520

NORTHWESTERN UNIV EVANSTON IL DEPT OF CHEMISTRY
COFACIAL ASSEMBLY OF METALLOMACROCYCLES. A MOLECULAR ENGINEERING--ETC(U)
MAY 81 C W DIRK, K F SCHOCH, T J MARKS

F/G 7/4

N00014-77-C-0231

NL

UNCLASSIFIED

TR-15

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

1-1

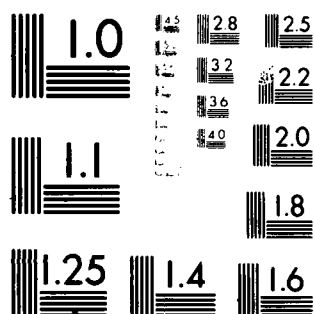
END

DATE

FILED

7-8/1

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

AD A 099 520

OFFICE OF NAVAL RESEARCH
Contract N00014-77-C-0231
Task No. NR 053-640

TECHNICAL REPORT NO. 15

Cofacial Assembly of Metallomacrocycles. A Molecular
Engineering Approach to Electrically Conductive Polymers

Carl W. Dirk, Karl F. Schoch Jr., and Tobin J. Marks

Prepared for publication in

"Electrically Conductive Polymers"

Northwestern University
Department of Chemistry
Evanston, IL 60201

May 13, 1981

SPR
JUN 1 1981
A

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*This document has been approved for public release and sale; its distribution
is unlimited.

*This statement should also appear in Item 10 of Document Control Data--
DD Form 1473. Copies of form available from cognizant contract administrator.

DTIC FILE COPY

81 6 01 132

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Interim Technical Report No. 15	2. GOVT ACCESSION NO. AD-A099520	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Cofacial Assembly of Metallomacrocycles. A Molecular Engineering Approach to Electrically Conductive Polymers	5. TYPE OF REPORT & PERIOD COVERED Interim 1981	
6. PERFORMING ORG. REPORT NUMBER		
7. AUTHOR(s) 10) Carl W. Dirk, Karl F. Schoch, Jr., and Tobin J. Marks	8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0231	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Northwestern University Department of Chemistry Evanston, IL 60201	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-053-640	
11. CONTROLLING OFFICE NAME AND ADDRESS 14, IFE-23	12. REPORT DATE May 13, 1981	
	13. NUMBER OF PAGES 18	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Phthalocyanine Conductive polymer Face-to-face polymer		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This paper discusses a strategy 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.		

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73 S/N 0102-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

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.

A

A

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

COFACIAL ASSEMBLY OF METALLOMACROCYCLES. A MOLECULAR
ENGINEERING APPROACH TO ELECTRICALLY CONDUCTIVE POLYMERS

Carl W. Dirk, Karl F. Schoch, Jr., and Tobin J. Marks

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

INTRODUCTION

In the past few years, the new condensed matter chemistry/-physics interface field of electronic materials having low-dimensional properties has undergone dramatic development.¹⁻⁶ The preparation of advanced new classes of organic, metal-organic, and inorganic substances with the properties of restricted dimensionality metals has excited theorists and experimentalists alike. This activity is stimulating important breakthroughs in chemical synthetic strategy and methodology, in spectroscopic, structural, and transport analysis, and in the fundamental theoretical descriptions of cooperative phenomena in the solid state. In terms of technology, applications as varied as rectifiers,⁷ sensors,^{8,9} solar energy conversion elements,^{10,11} fuel cell components,¹² switching devices,¹³ photoresist elements,¹⁴ chemoselective electrodes,^{15,16} electrophotographic devices,¹⁷ and durable synthetic materials to replace metals¹⁷ are being discussed. Speculation on the possibility of high temperature superconductivity remains, as always, a pervasive yet highly speculative motivation.^{18,19}

Despite the intense activity in this field, our understanding of the fundamental structural and electronic characteristics which govern charge transport is at an embarrassingly primitive level. This is equally true of the synthetic chemistry presently needed to tailor molecular assemblies for evaluating contemporary theories as well as for optimizing materials performance and processing characteristics. The central focus of our research program has been the development of rational syntheses of new low-dimensional electronic materials and physical studies of the products arising from this effort.^{20,21} The goal has been to devise controllable

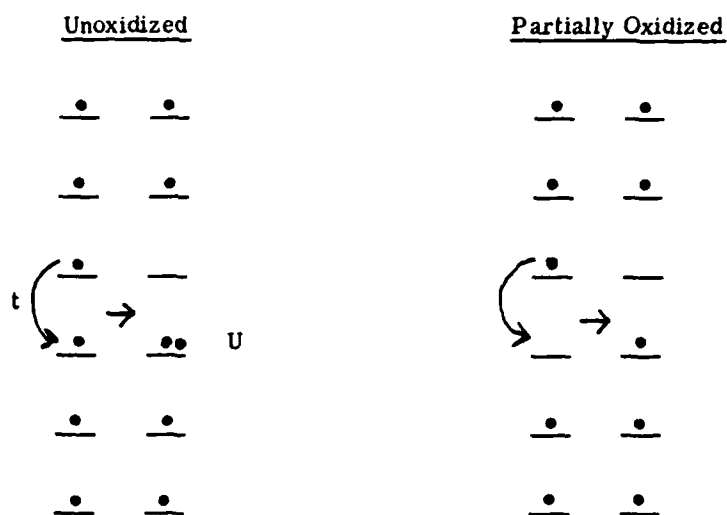
and systematic chemical approaches to such substances, so that critical characteristics can be "tuned" and collective properties correlated with changes in stoichiometry, crystal and electronic structure, etc. Our initial efforts in this direction involved materials composed of simple molecular stacks. However, as we sought greater control over lattice architecture and asked more fundamental questions about the molecular metallic state, the structural inadequacies of such materials became readily apparent.

The purpose of this article is to review a new, successful approach to the control of lattice architecture in low-dimensional materials. It involves covalently linking and bringing into the appropriate oxidation state, well-characterized and chemically flexible molecular subunits. This approach capitalizes upon a great deal of accumulated knowledge, and offers the possibility of assembling a wide variety of robust, electrically conductive polymers with well-defined and easily modified primary and secondary structures.²²⁻²⁵ We begin with a general discussion of those factors promoting the molecular metallic state. Next we show how this information and a cofacial assembly strategy lead to new types of conductive polymers. Illustrating with the phthalocyanine subunit, the chemical and physical properties of the "face-to-face" polymers are examined as a function of structure and added dopants.

REQUISITES FOR CONDUCTIVE MOLECULAR MATERIALS

Two general features now appear to be necessary for converting an unorganized collection of molecules into a conductive molecular array.^{1-6,20,21} First, the component molecules must be positioned in close spatial proximity, with sufficient intermolecular orbital overlap to provide a continuous electronic pathway for carrier delocalization, and in crystallographically similar environments. With the molecules positioned in this manner, the conduction 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"). In other words, the molecular entities to be connected in series must have fractionally occupied electronic valence shells. Within the framework of a simple one-dimensional Hubbard model, this prerequisite reflects the relatively narrow bandwidths ($4t$) and large on-site coulomb repulsions (U) in such systems.¹⁻⁶ A simplified valence bond picture of this situation is illustrated in Figure 1; partial oxidation facilitates charge mobility by creating numerous electronic vacancies. An analogous description can likewise be generated for partial reduction.

Our initial, first-generation strategy for the synthesis of mixed valent low-dimensional materials involved the cocrystallization of planar, conjugated metallomacrocyclic donor molecules (D)

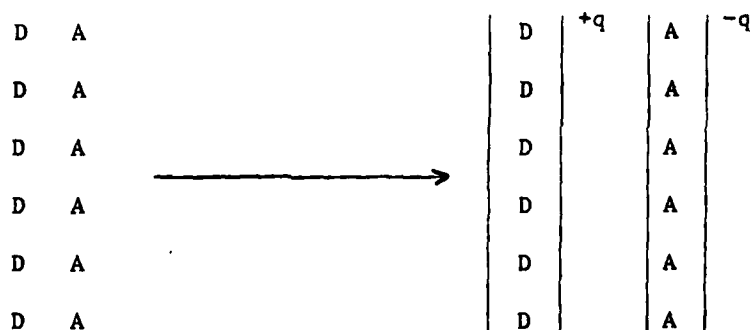


U = electron correlation energy

t = transfer integral $\approx$ bandwidth/4

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

having an MN_4 ligation sphere, with halogen acceptors (A) as shown below.^{20,21} In optimum cases, the result has been lattices composed of segregated, partially oxidized metallomacrocylic stacks and parallel arrays of halide or polyhalide counterions. An



D = donor A = acceptor

important additional feature of this approach is that the form of the halogen (even if disordered) can be determined in a straightforward manner by resonance Raman/iodine Mössbauer spectroscopic techniques.^{21,26,27} The degree of partial oxidation follows from this information and knowledge of the stoichiometry. This synthetic approach has enjoyed success for metal glyoximates,²⁸⁻³² dibenzotetraazaannulenes,^{33,34} phthalocyanines,³⁵⁻³⁷ and porphyrins.³⁸ As an illustration, nickel phthalocyanine iodide, $[\text{Ni}(\text{Pc})]\text{I}_{1.0}$, consists of stacks of staggered $\text{Ni}(\text{Pc})^{+0.33}$ units arrayed at $3.244(2) \text{ \AA}$ intervals and surrounded by parallel chains of I_3^- counterions. The 300°K conductivity of this material in the molecular stacking direction is $300\text{--}700 \Omega^{-1} \text{ cm}^{-1}$ and the temperature dependence is "metal-like" ($\rho \sim T^{1.9}$) down to 60°K .³⁷ The conductivity is predominantly a ligand-centered phenomenon, and carrier mean free paths are comparable to some of the most conductive "molecular metals."

THE COFACIAL ASSEMBLY STRATEGY

Although the above molecular macrocycle, halogen cocrystallization approach to the synthesis of mixed valent low-dimensional,

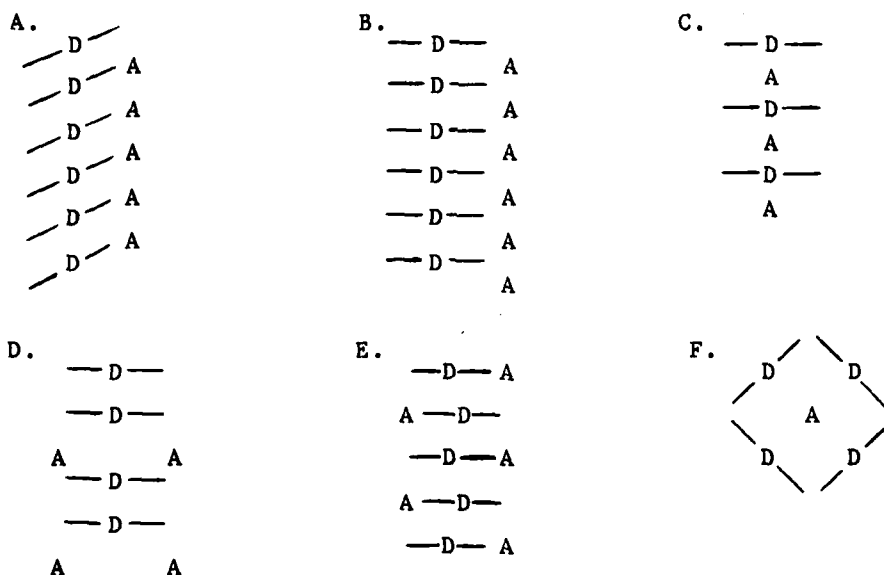
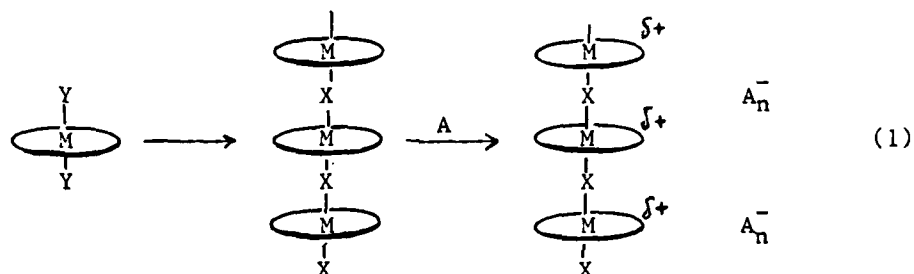


Fig. 2. Schematic illustration of some common structures for donor-acceptor complexes. A. Segregated stacking, canted donors. B. Segregated stacking, D_{nh} donor stacking. C. Integrated stacking. D. Integrated stacking, donor dimers. E. Segregated stacking, zig-zag donor stacking. F. Ion clusters without stacking.

metal-like materials is effective in many cases, it suffers, as do all strategies that rely upon molecular stacking, from a number of weaknesses. For example, in such cases the lattice architecture is dependent upon the unpredictable and largely uncontrollable forces that dictate the stacking pattern, the donor-acceptor orientations, and the stacking repeat distances. Figure 2 illustrates the complexity of the structural problem by depicting some of the types of common donor-acceptor crystallization patterns.³⁹⁻⁴⁴ A frequent pitfall in the design of new materials is that segregated stacks (Figure 2A,B) do not form and that the effort expended in donor or acceptor design is for naught. For example, our efforts to substitute various oxidizing quinones for halogens in the cocrystallization synthesis have failed because integrated stack (Figure 2C,D) insulators are apparently formed.^{45,46}

To achieve far greater control over molecular stacking we have employed the assembly process depicted in eq.(1).²²⁻²⁵ Cofacial



joining is carried out through the formation of strong covalent bonds involving the metallomacrocycle axial substituents (Y). The inherent variability of the metal, macrocycle, and bridging group offers great flexibility in terms of the structures which can be assembled, while the center-to-center mode of joining offers, in contrast to other conceivable modes of linking, superior structural control. Doping can then be carried out using either established halogenation methodology^{20,21} or, as a consequence of the enforced stacking, entirely new types of dopants (*vide infra*).

Our first studies have involved phthalocyanine systems where $M = \text{Si}, \text{Ge}, \text{Sn}$, and $X = \text{O}$. Thus, $\text{Si}(\text{Pc})(\text{OH})_2$, $\text{Ge}(\text{Pc})(\text{OH})_2$, and $\text{Sn}(\text{Pc})(\text{OH})_2$ ^{47,48} (we have developed an improved synthesis for the Si derivative) can be condensed at $300\text{--}400^\circ\text{C}/10^{-3}$ torr to form "face-to-face" polymers (Figure 3). Concurrent to doping and transport studies, we have investigated the nature of these materials as polymers. The $[\text{M}(\text{Pc})\text{O}]_n$ materials have high chemical and thermal stability; moreover, they are not significantly degraded by oxygen or moisture. We find that the polysiloxane polymer can be dissolved in concentrated sulfuric acid and recovered unchanged⁴⁹ (typical of phthalocyanines containing non-electropositive metals^{50,51}). A rough estimate of the minimum average chain length

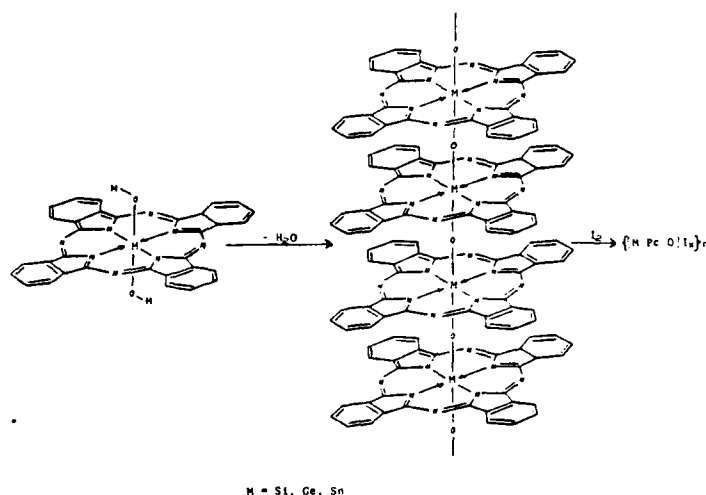


Fig. 3 Condensation reaction to produce cofacial arrays of Group IV metallophthalocyanines.

of $[\text{Si}(\text{Pc})\text{O}]_n$ produced in the condensation polymerization can be obtained by Fourier transform infrared spectrophotometric 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 sub-units or more.⁵² Preliminary light scattering molecular weight determinations in sulfuric acid solution are in agreement with this result.⁵³

Structural information on the face-to-face polymers has been derived from several lines of evidence. We have indexed the X-ray powder diffraction data in the tetragonal crystal system using iterative computer techniques.²²⁻²⁵ Data are very similar to those from the columnar crystal structures of $[\text{Ni}(\text{Pc})]\text{I}_{1.0}$ ³⁷ and $\text{Ni}(\text{dpg})_2\text{I}_{1.0}$.²⁹ The interplanar spacings in these latter tetragonal structures, determined in single crystal studies, are 3.244(2) Å and 3.27(1) Å, respectively. The corresponding spacings derived for the $[\text{M}(\text{Pc})\text{O}]_n$ materials from the powder diffraction data 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). The reliability of these metrical parameters is further supported by single crystal diffraction results on the model trimer $[(\text{CH}_3)_3\text{SiO}]_2(\text{CH}_3)\text{SiO}[\text{Si}(\text{Pc})\text{O}]_3\text{Si}(\text{CH}_3)[\text{OSi}(\text{CH}_3)_3]_2$ which contains three cofacial Si(Pc) units linked by linear Si-O-Si connections at a distance of 3.324(2) Å.⁵⁴ In addition, the $[\text{Ge}(\text{Pc})\text{O}]_n$ and $[\text{Sn}(\text{Pc})\text{O}]_n$ interplanar spacings obtained from diffraction data are in good agreement with values we estimate from ionic radii assuming linear Ge-O-Ge and Sn-O-Sn vectors, i.e., 3.58 Å for $[\text{Ge}(\text{Pc})\text{O}]_n$ and 3.90 Å for $[\text{Sn}(\text{Pc})\text{O}]_n$.²²⁻²⁵

There is ample precedent for molecules with linear Si-O-Si, Ge-O-Ge, and Sn-O-Sn linkages.⁵⁵⁻⁵⁸

7

HALOGEN DOPING OF COFACIALLY LINKED METALLOPHTHALOCYANINES

Partial oxidation of the $[M(Pc)O]_n$ materials was first carried out using iodination methodology developed in this Laboratory for simple stacked systems. Stirring the powdered polymers with solutions of iodine in aromatic solvents or exposing the powders to iodine vapor results in a substantial iodine uptake. Alternatively, the $[Si(Pc)O]_n$ polymer 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 materials characterized by elemental analysis are compiled in the lefthand column of Table 1. A survey experiment also indicated that a bromine-doped material could be prepared. X-ray powder diffraction studies demonstrate that no major structural change in the face-to-face stack occurs upon halogenation.

Table 1. Physical Data for Polycrystalline Samples of Halogen-Doped $[M(Pc)O]_n$ Polymers

Compound	$\sigma(\Omega^{-1}cm^{-1})_{300^\circ K}$	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)
$\{[Ge(Pc)O]I_{0.31}\}_n$	7×10^{-4}	0.08 ± 0.001	
$\{[Ge(Pc)O]I_{0.62}\}_n$	1×10^{-2}	0.05 ± 0.001	
$\{[Ge(Pc)O]I_{1.94}\}_n$	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 35.

That oxidation of the cofacial array has indeed occurred is confirmed by resonance Raman scattering spectroscopy in the polyiodide region (Figure 4) which reveals the characteristic totally symmetric stretching transition of I_3^- ($\nu = 108 \text{ cm}^{-1}$) and an accompanying overtone progression. For stoichiometries with $I/M < 3$, there are no more than traces of I_5^- ($\nu \approx 160 \text{ cm}^{-1}$) and no evidence of free I_2 ($\nu \approx 200 \text{ cm}^{-1}$).²¹ The nature of the doped $[M(Pc)O^{\delta+}]_n$ electronic structure was also probed 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.²⁵ A similar conclusion was reached for $[Ni(Pc)]I_{1.0}$.³⁷ ESR data for the $\{[M(Pc)O]I_x\}_n$ materials are set out in Table 2.

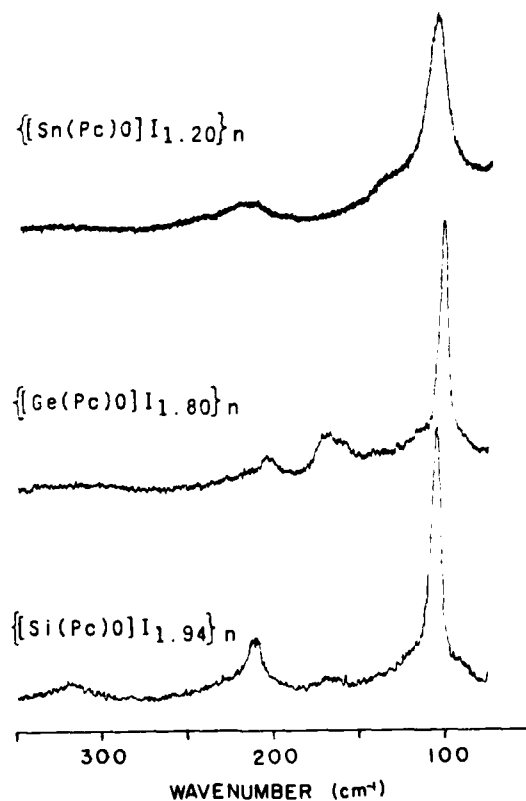


Fig. 4. Resonance Raman spectra ($\nu_0 = 5145 \text{ \AA}$) of iodine-doped phthalocyanine face-to-face polymers. From ref. 22.

Table 2. Powder ESR Data for Iodinated Phthalocyanine Face-to-Face Polymers

9

Compound	$g(300^\circ\text{K})^a$	$\Gamma(300^\circ\text{K})9G)^b$
$\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{1.40}\}_n$	2.003	5.1
$\{[\text{Ge}(\text{Pc})\text{O}]\text{I}_{0.62}\}_n$	2.002	3.2
$\{[\text{Sn}(\text{Pc})\text{O}]\text{I}_{1.20}\}_n$	2.002	6.0

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

^b Observed linewidth.

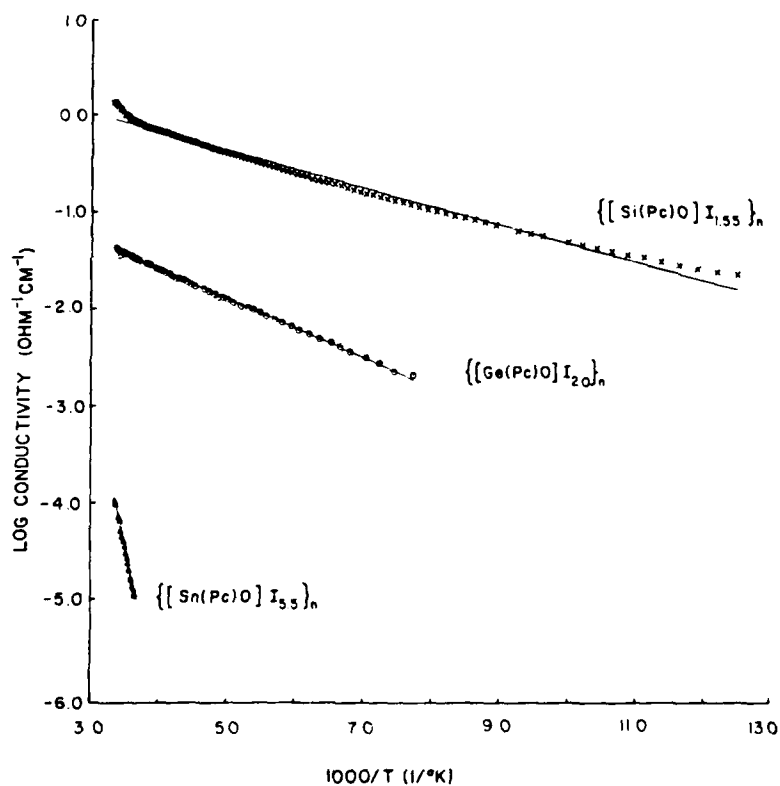


Fig. 5. Variable temperature four-probe electrical conductivity data for powders of the iodine-doped, face-to-face phthalocyanine polymers. The straight lines give least-squares fits to eq. (2). From ref. 24.

Four-probe van der Pauw^{59,60} electrical conductivity measurements on the $[M(Pc)O]_n$ powders show them to be insulators. However, iodine or bromine doping results in substantial increases in electrical conductivity (Table 1). The general trend in conductivity as a function of metal is $\sigma_{Si} \geq \sigma_{Ge} > \sigma_{Sn}$. Since it is known that the transport characteristics of iodine-oxidized metallophthalocyanines are largely ligand-dominated and relatively insensitive to the identity of the metal,³⁵⁻³⁷ the metal dependence of the conductivity observed in the face-to-face polymers is logically ascribed to structural differences such as how the interplanar separation is influenced by metal ionic radius. Indeed, the $\{[Si(Pc)O]I_x\}_n$ interplanar separation is within 0.1 Å of that in the aforementioned "molecular metal" $[Ni(Pc)]_{1.0}$ and the room temperature powder conductivities of the two materials are quite comparable (Table 1). Variable temperature studies indicate that the $\{[M(Pc)O]I_x\}_n$ powder conductivities are thermally activated (Figure 5) and least-squares fits to eq. (2) yield the activation

$$\sigma = \sigma_0 e^{-\Delta/kT} \quad (2)$$

energies shown in Table 1. Powder conductivity measurements are, of course, influenced by interparticle contact resistance and averaging over all crystallographic orientations. Thus, for low-dimensional compounds such as $[Ni(Pc)]_{1.0}$, powder conductivities are typically 10^2 - 10^3 less than single crystal conductivities in the stacking direction and exhibit the thermally activated temperature dependencies. Thus, "metal-like" temperature dependence ($d\sigma/dT < 0$) is usually masked. From the powder conductivity data on the $\{[M(Pc)O]I_x\}_n$ materials it is thus reasonable to anticipate that "metal-like" charge transport will be observed in the chain direction for the $M = Si$ and possibly $M = Ge$ materials. Further information on this question is provided by voltage shorted compaction (VSC) techniques⁶¹ which offer a qualitative means to sample stacking axis transport properties in pressed powder samples by deliberately shorting out sources of interparticle resistance. Importantly, the VSC conductivity behavior of $\{[Si(Pc)O]I_x\}_n$ samples is "metal-like."⁶² 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 minor deterioration in room temperature conductivity (apparently due to vaporization of the iodine).

Static magnetic susceptibility measurements by Faraday techniques reveal another characteristic hallmark of "molecular metals" in the $\{[Si(Pc)O]I_x\}_n$ and $\{[Ge(Pc)O]I_x\}_n$ materials. Susceptibilities are only weakly paramagnetic ($\chi_M = 300$ -500 $\times 10^{-6}$ emu after diamagnetic corrections are made) and are only

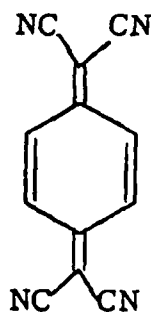
modestly dependent on temperature down to 77°K^{22,23}. Studies at lower temperature are presently in progress.

11

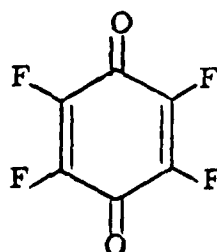
THE EFFECTIVENESS OF NONHALOGEN DOPANTS

The availability of a low-dimensional system in which the stacking variable is held constant offers an unusual opportunity, vis-à-vis those factors stabilizing the mixed valent state,⁶³⁻⁶⁶ to investigate the effects of dopants which yield integrated stack structures on reaction with molecular M(Pc) compounds. Thus, it was of interest to learn whether non-halogen oxidants with redox potentials similar to halogens could ever produce a partially oxidized, conductive metallophthalocyanine stack. This would help to define whether the marked efficacy of halogen dopants in forming mixed valent metallomacrocycles reflects, in addition to redox potential, a unique structure-forming role (small yet variable size) or whether other factors (e.g., specific Madelung, exchange, polarization, van der Waals, or core repulsion terms) might be important.

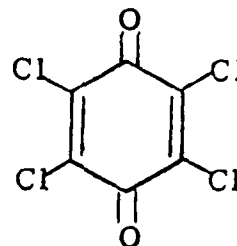
Oxidizing quinones such as those shown below form conductive, mixed valent compounds with a variety of organic donors,¹⁻⁵ but



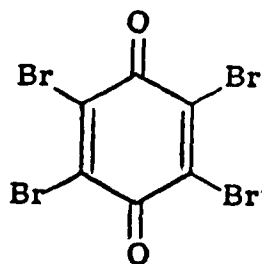
TCNQ



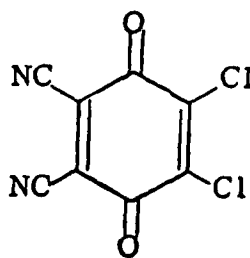
fluoranil



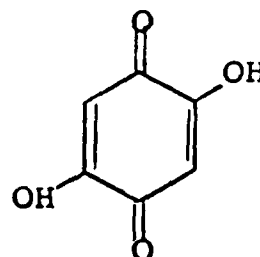
chloranil



bromanil



DDQ



DHB

all reactions with molecular metallophthalocyanines yield insulators, the structures of which no doubt consist of integrated stacks (Figure 2C).^{45,46} Doping experiments with the $[\text{Si}(\text{Pc})\text{O}]_n$ polymers were thus carried out by stirring these materials with solutions 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

12

Table 3. Electrical Conductivity Data for Polycrystalline Samples of Molecular Phthalocyanines and Cofacial Phthalocyanine Polymers with Various Dopants

<u>Dopant^a</u>	<u>Empirical Formula</u>	<u>$\sigma(\Omega^{-1} \text{ cm}^{-1})_{300^\circ\text{K}}$</u>	<u>Activation Energy(eV)</u>
none	$[\text{Si}(\text{Pc})\text{O}]_n$	3×10^{-8}	
I	$\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{1.55}\}_n$	1.4	$0.04 \pm .001$
Br	$\{[\text{Si}(\text{Pc})\text{O}]\text{Br}_{1.00}\}_n$	6×10^{-2}	
K	$\{[\text{Si}(\text{Pc})\text{O}]\text{K}_{1.0}\}_n$	2×10^{-5}	
DDQ	$\{[\text{Si}(\text{Pc})\text{O}]\text{DDQ}_{1.00}\}_n$	2.1×10^{-2}	$0.08 \pm .001$
DDQ	$\{[\text{Si}(\text{Pc})\text{O}]\text{DDQ}_{0.35}\}_n$	6.2×10^{-2}	$0.05 \pm .001$
TCNQ	$\{[\text{Si}(\text{Pc})\text{O}]\text{TCNQ}_{0.50}\}_n$	2.8×10^{-3}	$0.09 \pm .002$
ClA	$\{[\text{Si}(\text{Pc})\text{O}]\text{ClA}_{0.14}\}_n$	1.8×10^{-3}	$0.11 \pm .001$
Flr	$\{[\text{Si}(\text{Pc})\text{O}]\text{Flr}_{0.23}\}_n$	7.2×10^{-4}	$0.13 \pm .001$
Chl	$\{[\text{Si}(\text{Pc})\text{O}]\text{Chl}_{0.37}\}_n$	6.9×10^{-4}	$0.13 \pm .002$
Brl	$\{[\text{Si}(\text{Pc})\text{O}]\text{Brl}_{0.84}\}_n$	5.8×10^{-4}	$0.15 \pm .001$
DHB	$\{[\text{Si}(\text{Pc})\text{O}]\text{DHB}_{0.13}\}_n$	3.8×10^{-5}	$0.19 \pm .005$
DDQ	$\text{Ni}(\text{Pc})\text{DDQ}_{0.11}$	2.5×10^{-7}	0.43 ± 0.004
ClA	$\text{Ni}(\text{Pc})\text{ClA}_{0.91}$	8.4×10^{-7}	0.16 ± 0.002

^a

Flr = fluoranil; Chl = chloranil; Brl = bromanil; DDQ = dichlorodicyanoquinone; ClA = chloranilic acid; DHB = dihydroxybenzoquinone.

accompany the quinone doping. Indeed, the DDQ-doped materials are as conductive as most of the halogenated polymers.^{25,67} The temperature dependence of the conductivity of some representative samples is shown in Figure 6. The transport in these materials is thermally activated and least-squares fits to eq.(2) yield the activation parameters compiled in Table 3. There are some notable deviations from a linear $\ln \sigma$ vs. $1/T$ relationship (e.g., the $\{[\text{Si}(\text{Pc})\text{O}]\text{TCNQ}_{0.5}\}_n$ sample shown in the Figure) and further investigations of the reasons for this behavior are in progress. Perhaps conduction is occurring through both $\text{Pc}^{+\delta}$ and $\text{TCNQ}^{-\delta}$ stacks with different temperature dependencies. Infrared

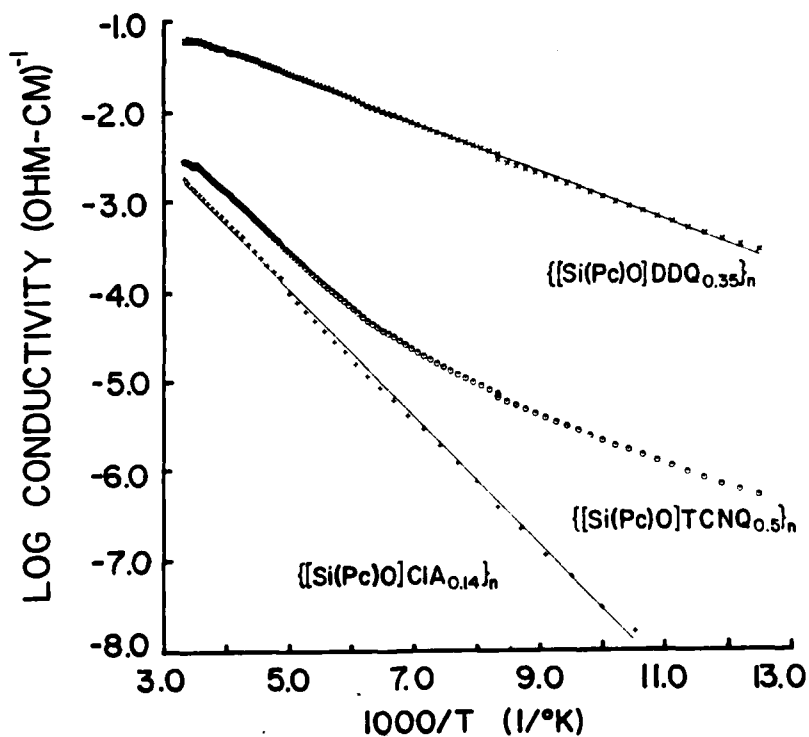


Fig. 6. Variable temperature powder conductivities of the siloxane phthalocyaninato cofacial polymer doped with high potential quinones. CIA = Chloranilic acid. From ref. 24.

spectral studies of the TCNQ-doped materials reveal a displacement of ν_{CN} to lower frequencies, consistent with electron density uptake by the quinodimethane.⁶⁸ Clearly oxidation of the $[\text{Si}(\text{Pc})\text{O}]_n$ stack by high potential quinones occurs when a segregated stack structure is enforced. Moreover, this can result in facile charge transport.

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. A number of attempts have been made in this Laboratory to partially reduce metallophthalocyanines using alkali metals.⁴⁹ In all cases, the resulting materials were insulators, and it was suspected that nonstacked materials were being produced. A preliminary experiment was conducted in which $[\text{Si}(\text{Pc})\text{O}]_n$ 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 significant increase in electrical conductivity accompanies the potassium doping. Further efforts to refine the reductive doping procedure are now in progress.

CONCLUSIONS

Cofacial metallomacrocycle assembly methodology represents what is likely the most powerful approach yet devised for controlling molecular stacking relationships in low dimensional materials. In regard to 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 metallomacrocycle identity and electronic structure, stacking distance and bandwidth, interplanar relationships and phonon dynamics, and to correlate these chemical and structural modifications with physical observables. Already, new metal ions^{69,70} and bridging functionalities^{71,72} have been successfully introduced. Future studies with new types of dopants should provide much important information on donor-acceptor relationships and on those basic factors which stabilize the mixed valent state. A wide range of magnetic, charge transport, and optical experiments remain to be carried out. These experiments should ultimately provide invaluable information on how the chemistry and lattice architecture are connected to some of the fundamental characteristics of the molecular metallic state. Finally, studies of the processing characteristics of the $[\text{M}(\text{Pc})\text{O}]_n$ materials are just beginning. Already we have learned that it is possible to produce films of $[\text{Si}(\text{Pc})\text{O}]_n$ and that halogen doping results in substantial increases in electrical

conductivity.^{72,73} Further efforts in this direction are under way.

15

ACKNOWLEDGMENTS

This research was generously supported by the Office of Naval Research and by the NSF-MRL program through the Materials Research Center of Northwestern University (grants DMR76-80847A01 and DMR79-23573). TJM is a Camille and Henry Dreyfus Teacher-Scholar. We thank our collaborators Prof. Carl R. Kannewurf, Mr. Joseph W. Lyding, and Dr. Eric A. Mintz for stimulating discussions.

REFERENCES

1. J. T. Devreese, V. E. Evrard, and V. E. Van Doren, eds., "Highly Conducting One-Dimensional Solids," Plenum Press, New York (1979).
2. W. E. Hatfield, ed., "Molecular Metals," Plenum Press, New York (1979).
3. J. B. Torrance, Accts. Chem. Res. 12:79 (1979).
4. J. S. Miller and A. J. Epstein, eds., "Synthesis and Properties of Low-Dimensional Materials," Ann. NY Acad. Sci., 313 (1978).
5. H. J. Keller, ed. "Chemistry and Physics of One-Dimensional Metals," Plenum Press, New York (1977).
6. J. S. Miller and A. Epstein, J. Prog. Inorg. Chem. 20:1 (1976).
7. A. Aviram and M. A. Ratner, Chem. Phys. Letters 29:277 (1974).
8. S. Yoshimura and M. Murakami, in reference 4, 269.
9. S. D. Senturia, C. M. Sechen, and J. A. Wishneusky, Appl. Phys. Letters 30:106 (1977).
10. C. K. Chiang, S. C. Gau, C. R. Fincher, Jr.; Y. W. Park, A. G. MacDiarmid, and A. J. Heeger, Appl. Phys. Letters 33:18 (1978).
11. M. Ozaki, D. Peebles, B. R. Weinberger, A. J. Heeger, and A. G. MacDiarmid, J. Appl. Phys. 51:4252 (1980).
12. A. G. MacDiarmid, private communication.
13. R. S. Potember, T. O. Poehler, A. Rappa, D. O. Cowan, and A. N. Bloch, J. Am. Chem. Soc. 102:3659 (1980).
14. Y. Tomkiewicz, E. M. Engler, J. D. Kuptsis, R. G. Schad, V. V. Patel, and M. Hatzakis, Extended Abstracts, Electro-Chemical Society spring Meeting, St. Louis, May, 1980, No. 63.
15. S. Yoshimura, in reference 2, 471, and references therein.
16. C. D. Jaeger and A. J. Bard, J. Am. Chem. Soc. 102:5435 (1980).

17. E. M. Engler, W. B. Fox, L. V. Interrante, J. S. Miller, F. Wudl, S. Yoshimura, A. Heeger, and R. H. Baughman, in reference 2, 541.
18. D. Davis, H. Gutfreund, and W. A. Little, Phys. Rev. B 13: 4766 (1976).
19. J. Bardeen, in reference 1, 373.
20. T. J. Marks and D. W. Kalina in: "Extended Linear Chain Compounds," J. S. Miller, ed., Plenum Publishing Corp., NY in press.
21. T. J. Marks, Ann. NY Acad. Sci. 313:594 (1978).
22. K. F. Schoch, Jr., B. R. Kundalkar, and T. J. Marks, J. Am. Chem. Soc. 101:7071 (1979).
23. T. J. Marks, K. F. Schoch, Jr., and B. R. Kundalkar, Synth. Met. 1:337 (1980).
24. C. W. Dirk, J. W. Lyding, K. F. Schoch, Jr., C. R. Kannewurf, and T. J. Marks, Organic Coatings and Plastics Chem. 43:646 (1980).
25. C. W. Dirk, E. A. Mintz, K. F. Schoch, Jr., and T. J. Marks in: "Organometallic Polymers: Perspectives," C. E. Carraher and J. E. Sheats, eds., Marcel Dekker, NY and J. Macromol. Science-Chemistry, in press.
26. R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, J. Am. Chem. Soc. 102:3322 (1980).
27. R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, J. Am. Chem. Soc. 101:7568 (1979).
28. D. W. Kalina, J. W. Lyding, M. T. Ratajack, C. R. Kannewurf, and T. J. Marks, J. Am. Chem. Soc., in press.
29. M. A. Cowie, A. Gleizes, G. W. Gryniewicz, 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.
30. L. D. Brown, D. W. Kalina, M. S. McClures, S. L. Ruby, S. Schultz, J. A. Ibers, C. R. Kannewurf, and T. J. Marks, J. Am. Chem. Soc. 101:2937 (1979).
31. T. J. Marks, D. F. Webster, S. L. Ruby, and S. Schultz, J. Chem. Soc., Chem. Commun. 444 (1976).
32. A. Gleizes, T. J. Marks, and J. A. Ibers, J. Am. Chem. Soc. 97:3545 (1975).
33. L.-S. Lin, M. S. McClure, J. W. Lyding, M. T. Ratajack, T.-C. Wang, C. R. Kannewurf, and T. J. Marks, J. Chem. Soc., Chem. Commun., in press.
34. M. S. McClure, L.-S. Lin, T.-C. Whang, M. T. Ratajack, C. R. Kannewurf, and T. J. Marks, Bull. Am. Phys. Soc. 25:315 (1980).
35. J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, J. Am. Chem. Soc. 99:286 (1977).
36. C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, Science 200:47 (1978).

37. R. P. Scaringe, C. J. Schramm, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers, and T. J. Marks, J. Am. Chem. Soc. 102:6702 (1980).
38. T. E. Phillips, R. P. Scaringe, B. M. Hoffman, and J. A. Ibers, J. Am. Chem. Soc. 102:3435 (1980).
39. T. J. Kistenmacher, in reference 4, 333.
40. S. Megtert, J.P. Pougent, and R. Comes, in reference 4, pp. 234.
41. G. D. Stucky, A. J. Schultz, and J. M. Williams, Ann. Rev. Mater. Sci. 7:301 (1977).
42. B. P. Bespalov and V. V. Titov, Russ. Chem. Rev. 44:1091 (1975).
43. D. J. Dahm, P. Horn, G. R. Johnson, M. G. Micles, and J. D. Wilson, J. Cryst. Mol. Struct. 5:27 (1975).
44. F. H. Herbstein, Perspect. Struct. Chem. IV:166 (1971).
45. K. F. Schoch, Jr. and T. J. Marks, unpublished observations.
46. L. Pace and J. A. Ibers, private communication.
47. R. J. Joyner and M. E. Kenney, Inorg. Chem. 82:5790 (1960).
48. J. B. Davison and K. J. Wynne, Macromolecules, 11:186 (1978).
49. K. F. Schoch, Jr. and T. J. Marks, unpublished results at Northwestern University.
50. F. A. Moser and A. L. Thomas, "Phthalocyanine Compounds," Reinhold, New York (1963).
51. F. A. Moser and A. L. Thomas, "Phthalocyanine Compounds," Second Edition, ACS Publications, in press.
52. C. W. Dirk, K. F. Schoch, Jr., and T. J. Marks, manuscript in preparation.
53. G. C. Berry, private communication.
54. D. R. Swift, Ph.D. Thesis, Case Western Reserve University, 1970.
55. C. Glidewell and D. C. Liles, J. Chem. Soc., Chem. Commun. 93 (1979).
56. C. Glidewell and D. C. Liles, Acta Cryst., B34:119 (1978).
57. C. Glidewell and D. C. Liles, Acta Cryst., B34:124 (1978).
58. C. Glidewell and D. C. Liles, Acta Cryst., B34:129 (1978).
59. R. C. Teitelbaum, Ph.D. Thesis, Northwestern University, August 1979.
60. K. Seeger, "Semiconductor Physics," Springer-Verlag, NY, 1973, 483.
61. L. B. Coleman, Rev. Sci. Instrum. 49:48 (1978).
62. K. F. Schoch, Jr., J. W. Lyding, C. R. Kannewurf, and T. J. Marks, manuscript in preparation.
63. A. J. Epstein, N. O. Lipari, D. J. Sandman, and P. Nielsen, Phys. Rev., B 13:1569 (1976).
64. R. M. Metzger, in reference 1d, 145.
65. J. B. Torrance and B. D. Silverman, Phys. Rev., B, 15:788 (1977).
66. R. M. Metzger and A. N. Bloch, J. Chem. Phys., 63:5098 (1975).

67. K. F. Schoch, Jr. and T. J. Marks, unpublished results; Bull. Am. Phys. Soc. 25:315 (1980).
68. 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).
69. P. M. Kuznesof, K. J. Wynne, R. S. Nohr, and M. E. Kenney, J. Chem. Soc., Chem. Commun. 121 (1980).
70. R. S. Nohr, K. J. Wynne, and M. E. Kenney, Polymer Preprints, in press. We thank these authors for a preprint.
71. C. W. Dirk and T. J. Marks, Bull. Am. Phys. Soc. 25:315 (1980).
72. C. W. Dirk, J. W. Lyding, K. F. Schoch, Jr., C. R. Kannewurf, and T. J. Marks, Abstracts, Fall Meeting of the American Chemical Society, Las Vegas, August 1980.
73. C. W. Dirk, M. S. McClure, K. F. Schoch, Jr., C. R. Kannewurf, and T. J. Marks, unpublished results at Northwestern University.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Branch Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Branch Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST. GEN

No.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 053

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. R. N. Grimes University of Virginia Department of Chemistry Charlottesville, Virginia 22901	1	Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. M. Tsutsui Texas A&M University Department of Chemistry College Station, Texas 77843	1	Dr. B. Foxman Brandeis University Department of Chemistry Waltham, Massachusetts 02154	1
Dr. M. F. Hawthorne University of California Department of Chemistry Los Angeles, California 90024	1	Dr. T. Marks Northwestern University Department of Chemistry Evanston, Illinois 60201	1
Dr. D. B. Brown University of Vermont Department of Chemistry Burlington, Vermont 05401	1	Dr. G. Geoffrey Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D.C. 20375	1	Dr. J. Zuckerman University of Oklahoma Department of Chemistry Norman, Oklahoma 73019	1
Dr. J. Adcock University of Tennessee Department of Chemistry Knoxville, Tennessee 37916	1	Professor O. T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214	1
Dr. A. Cowley University of Texas Department of Chemistry Austin, Texas 78712	1	Professor P. S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1	Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167	1
Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1	Professor R. Neilson Department of Chemistry Texas Christian University Fort Worth, Texas 76129	1
Professor H. Abrahamson University of Oklahoma Department of Chemistry Norman, Oklahoma 73019	1	Professor M. Newcomb Texas A&M University Department of Chemistry College Station, Texas 77843	1

DATE FILME

