

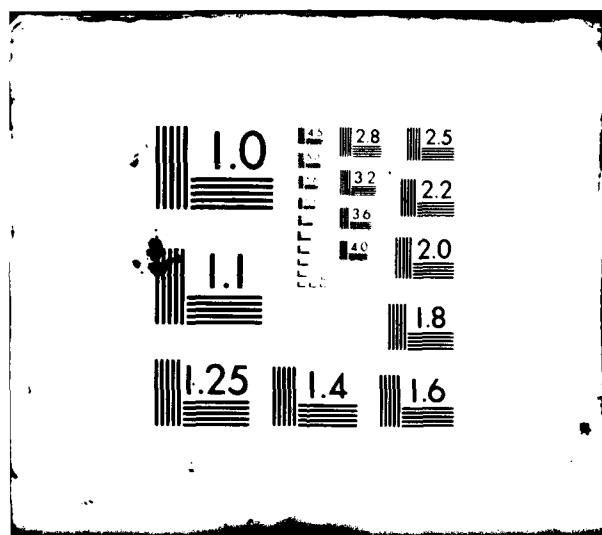
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Rational Control of Electronic Structure and Lattice
Architecture in Electrically Conducting Molecular/
Macromolecular Assemblies

by

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

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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, variable-temperature four-probe d.c., electrical conductivity, and voltage-short-circuit techniques. Evidence is presented that some of the macromolecules 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. Insight into those acceptor properties which stabilize the mixed valent state is provided.



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RATIONAL CONTROL OF ELECTRONIC STRUCTURE AND LATTICE ARCHITECTURE IN ELECTRICALLY CONDUCTING MOLECULAR/MACROMOLECULAR ASSEMBLIES

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INTRODUCTION

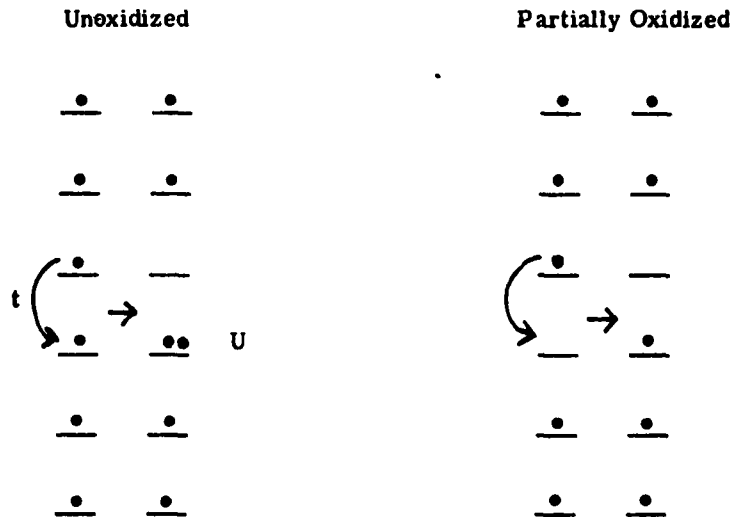
The past several years have witnessed the advent of advanced new types of organic, metal-organic, and inorganic materials with unusual, highly anisotropic, and potentially tailorable electrical, optical, and magnetic properties (1-5). Such materials have stimulated much activity in the chemistry and physics communities. As a result, there have been advances in chemical synthetic strategy and methodology, in spectroscopic and charge transport measurement techniques, and in condensed matter theory. Furthermore, applications of this new knowledge to sensors (6), rectifiers (7), switching devices (8), photoresists (9), fuel cells (10), chemoselective electrodes (11), solar energy conversion elements (12), and electrophotographic devices (13) have been the subject of much discussion. Of course, to develop such technology there must be an intimate understanding at the molecular level of those structural and electronic variables which govern collective properties. A refined synthetic chemistry for constructing desired molecular assemblies and optimizing performance characteristics is also required. Despite the advances which have been achieved, our understanding of and our ability to exert chemical control over the above factors is at a primitive level, thus representing a major barrier to progress.

Research in this Laboratory has focused on the evolution of rational, flexible syntheses of new low-dimensional electronic materials and on understanding the physical properties of the products which result (14,15). In this article we review our recent work on constructing molecular arrays composed of cofacially linked, partially oxidized metallomacrocycles. By beginning with chemically-versatile and well-characterized molecular precursors, this strategy capitalizes upon a great deal of accumulated chemical and physical information about the component subunits. Our strategy offers the possibility of constructing robust new conductive assemblies with well-defined

and easily-manipulated microstructures. The covalent bonds which hold such arrays together are far stronger than packing, van der Waals, and band formation forces. As a result, it has been possible to delve into those factors which stabilize the metallic state without fear of a breakdown in stacking, to control lattice microstructure, and to deliberately perturb bandwidth and phonon dynamics.

REQUIREMENTS FOR HIGHLY CONDUCTIVE MOLECULAR SOLIDS

Two features are now generally recognized as necessary for transforming an unorganized collection of molecules into an electrically conductive molecular array. First, the component molecules must be positioned in close spatial proximity, and in crystallographically similar environments, with sufficient intermolecular orbital overlap to provide a continuous electronic pathway for carrier delocalization. With the molecules positioned in this manner, the conduction pathway has a minimum of energetic "hills" and "valleys." Second, the arrayed molecules must be in formal fractional oxidation states ("mixed valence," "partial oxidation," "incomplete charge transfer"). That is, 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 (16). A simplified, valence bond picture of this situation is depicted in Figure 1;



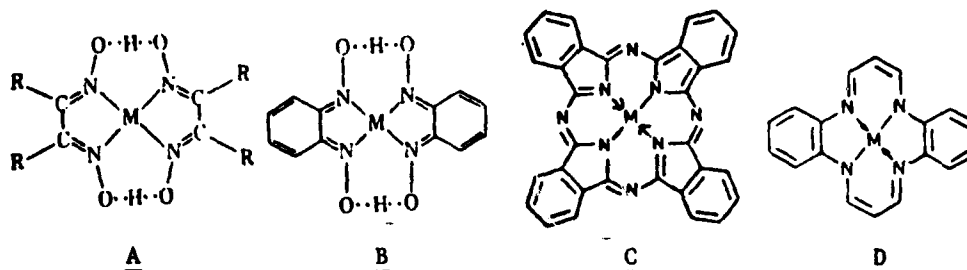
U = electron correlation energy

t = transfer integral = bandwidth/4

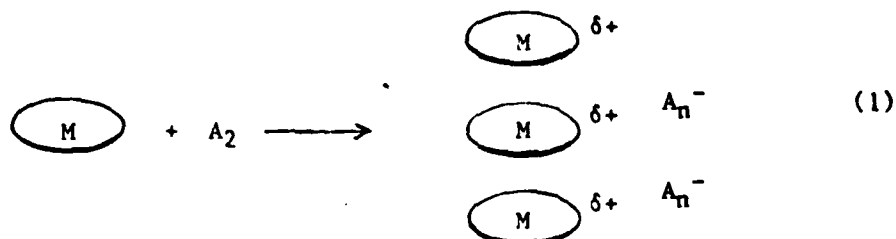
Fig. 1. Schematic diagram of how partial oxidation enhances charge transport in a simple molecular stack.

partial oxidation enhances charge mobility by creating numerous electronic vacancies. An analogous description can be generated for partial reduction.

Our initial approach to synthesizing low-dimensional mixed-valent arrays was to cocrystallize planar, conjugated metallomacrocylic donor molecules such as glyoximates (A,B) (17-19), phthalocyanines (C) (20,21), and tetraazaporphyrins (D) (22) having an MN_4 core structure, with bromine or iodine ox-



dants (A), as shown in eq. (1). When successful, the result is a crystal composed of segregated (i.e., donors and acceptors in separate columns), partially oxidized metallomacrocylic stacks and parallel arrays of halide or



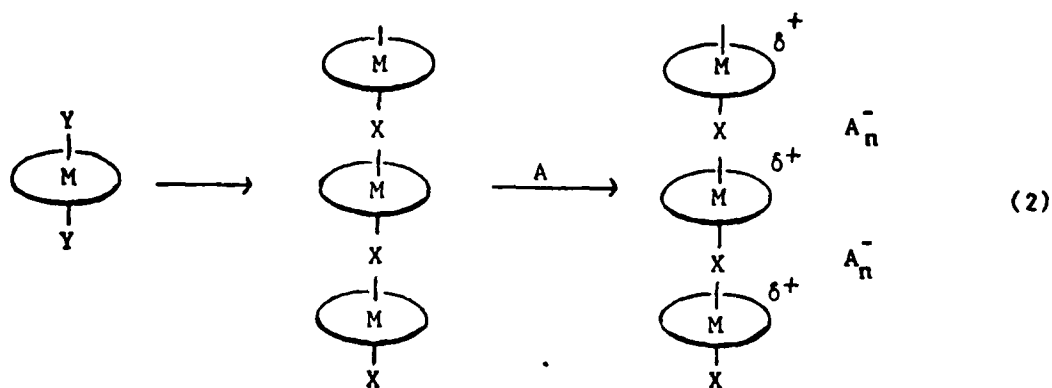
polyhalide counterions. We also demonstrated that the form of the halogen (even if disordered) could be determined in a straightforward fashion by resonance Raman and iodine Mössbauer spectroscopic techniques (15,19,23,24). The degree of partial oxidation ($\delta+$) follows from this information and the stoichiometry. As an example, nickel phthalocyanine iodide, $[\text{Ni}(\text{Pc})]\text{I}_{1.0}$, crystallizes in stacks of staggered $\text{Ni}(\text{Pc})^{+0.33}$ units arrayed at 3.244(2) Å intervals and surrounded by parallel chains of I_3^- counterions. The 300°K conductivity of this material in the molecular stacking direction is 300-700 $\Omega^{-1} \text{ cm}^{-1}$ and the temperature dependence is "metal-like" ($\rho \sim T^{1.9}$) down to 60°K (21). The conductivity is predominantly a ligand-centered phenomenon, and carrier mean free paths are comparable to some of the most conductive "molecular metals."

The molecule/halogen cocrystallization approach to the synthesis of mixed valent, low-dimensional, metal-like materials is often effective. Nevertheless, all strategies that rely upon molecular stacking suffer 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. There are numerous conceivable donor-acceptor crystallization patterns which do not involve segregated stacking of the components (25-28). Indeed, a common pitfall in the design of new materials is that segregated stacks do not form, and that the elegant effort expended in donor or acceptor design is for naught. This problem severely limits the ability to design and tailor microstructures which lead reliably to electroactive molecular assemblies.

THE COFACIAL ASSEMBLY APPROACH

Our approach to controlling molecular stacking involves the assembly of macromolecules in which arrays of metallomacrocycles are rigidly locked into a "face-to-face" configuration by strong, covalent bonds (eq.(2)) (29-31). The



architecture of the stack can be varied by suitable modification of the macrocycle, the metal (M), and the connecting linkage (X). Our first studies have capitalized on pioneering chemistry of Kenney (32) and involve 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 $\text{Sn}(\text{Pc})(\text{OH})_2$ can be condensed at $300\text{--}400^\circ\text{C}/10^{-3}$ torr to form "face-to-face" phthalocyanine polymers (Figure 2). As a prelude to doping and transport measurements, we first investigated the properties of these compounds 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 recovered unchanged from concentrated sulfuric acid (typical of phthalocyanines containing non-electropositive metals (33)). A rough estimate of the minimum average chain length 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 subunits or more (31). This result is in agreement with preliminary light scattering data from sulfuric acid solutions (34) and measurements of the amount of water evolved during polymerization (35). Infrared analyses of the germanium and tin analogues (considerably more difficult measurements) yield minimum average chain lengths on the order of 30 or more subunits (36).

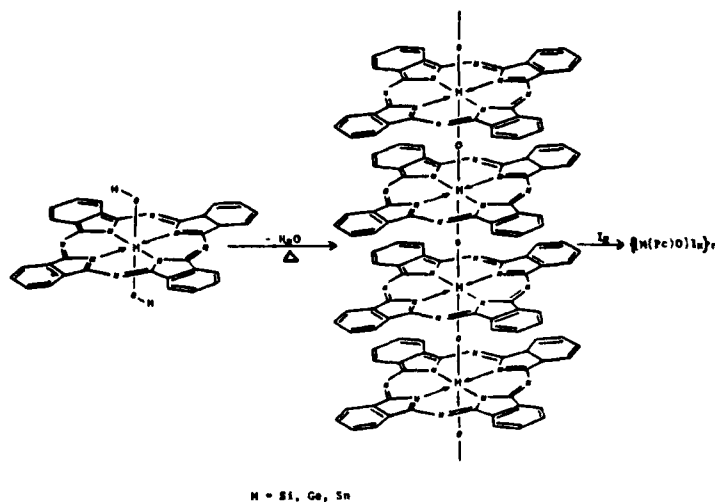


Fig. 2. Polymerization reaction to produce cofacial arrays of Group IVA metallophthalocyanines.

Structural information on the face-to-face polymers has been derived from several lines of evidence. X-ray powder diffraction data can be indexed in the tetragonal crystal system using iterative computer techniques. Data are very similar to those from the columnar crystal structures of $[\text{Ni}(\text{Pc})]\text{I}_{1.0}$ (21) and $\text{Ni}(\text{dpg})_2\text{I}_{1.0}$ (17). The interplanar spacings ($c/2$) in these latter tetragonal structures, determined in single crystal studies, are 3.244(2) Å and 3.271(1) Å, respectively. The corresponding separations derived for the $[\text{M}(\text{Pc})\text{O}]_n$ materials from the powder diffraction data are a function of the metal ionic radius and vary from 3.32(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 $[(\text{CH}_3)_3\text{SiO}]_2(\text{CH}_3)_2\text{SiO}[\text{Si}(\text{Pc})\text{O}]_3\text{Si}(\text{CH}_3)[\text{OSi}(\text{CH}_3)_3]_2$ which contains three cofacial $\text{Si}(\text{Pc})\text{O}$ units linked by linear Si-O-Si connections at a distance of 3.324(2) Å (37). Furthermore, the $[\text{Ge}(\text{Pc})\text{O}]_n$ and $[\text{Sn}(\text{Pc})\text{O}]_n$ interplanar spacings obtained from diffraction data agree with values estimated from standard ionic radii (38) 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 $[\text{Sn}(\text{Pc})\text{O}]_n$. There is good precedent for molecules with linear Si-O-Si, Ge-O-Ge, and Sn-O-Sn linkages (39). Importantly, then, we have achieved a means to manipulate the interplanar spacings of electrically conductive subunits in a metallomacrocyclic system where the transport properties are relatively insensitive to the identity of the metal ion.

PARTIAL OXIDATION WITH HALOGENS

Following assembly of the metallophthalocyanines into cofacial arrays, doping experiments were conducted using the halogenation procedure (14,15) developed in this Laboratory for simple, stacked metallomacrocyclic systems. Stirring the powdered polymers with solutions of iodine in organic solvents

or exposing the powders to iodine vapor results in substantial iodine uptake. Alternatively, $[\text{Si}(\text{Pc})\text{O}]_n$ 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; examples of these materials are listed in Table 1. A survey experiment also indicated that bromine-doped materials could be prepared. That oxidation of the cofacial array has indeed occurred was confirmed by resonance Raman scattering spectroscopy in the polyiodide region. Powder ESR data confirm that the oxidation is ligand centered, producing arrays of π cation radicals ($g = 2.002$) (31).

Table 1. Physical Properties of Polycrystalline Samples of Halogen-Doped $[\text{M}(\text{Pc})\text{O}]_n$ Polymers and $[\text{Ni}(\text{Pc})]\text{I}_{1.0}$.

Compound	$\sigma(\Omega^{-1}\text{cm}^{-1})_{300^\circ\text{K}}$	Activation Energy (eV)	Interplanar Spacing (Å)
$[\text{Si}(\text{Pc})\text{O}]_n$	3×10^{-8}		3.33(2)
$\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{0.50}\}_n$	2×10^{-2}		
$\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{1.55}\}_n$	1.4	0.04 ± 0.001	3.33(2)
$\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{4.60}\}_n$	1×10^{-2}		
$\{[\text{Si}(\text{Pc})\text{O}]\text{Br}_{1.00}\}_n$	6×10^{-2}		
$[\text{Ge}(\text{Pc})\text{O}]_n$	$< 10^{-8}$		3.51(2)
$\{[\text{Ge}(\text{Pc})\text{O}]\text{I}_{0.31}\}_n$	7×10^{-4}	0.08 ± 0.001	
$\{[\text{Ge}(\text{Pc})\text{O}]\text{I}_{0.62}\}_n$	1×10^{-2}	0.05 ± 0.001	
$\{[\text{Ge}(\text{Pc})\text{O}]\text{I}_{1.94}\}_n$	6×10^{-2}	0.05 ± 0.007	
$\{[\text{Ge}(\text{Pc})\text{O}]\text{I}_{2.0}\}_n$	1×10^{-1}		
$[\text{Sn}(\text{Pc})\text{O}]_n$	$< 10^{-8}$		3.95(2)
$\{[\text{Sn}(\text{Pc})\text{O}]\text{I}_{1.2}\}_n$	1×10^{-6}		3.95(2)
$\{[\text{Sn}(\text{Pc})\text{O}]\text{I}_{5.5}\}_n$	2×10^{-4}	0.68 ± 0.01	
$[\text{Ni}(\text{Pc})]\text{I}_{1.0}^a$	7×10^{-1}	0.036 ± 0.001	3.244(2)

^a

Reference 20.

Four-probe van der Pauw (40) electrical conductivity measurements on compacted $[M(Pc)O]_n$ 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 $\sigma_{Si} > \sigma_{Ge} > \sigma_{Sn}$. 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 (20,21), the metal dependence of the conductivity observed in the face-to-face polymers is logically ascribed to microstructural 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 3) and least-squares fits to eq.(3) yield the activation energies compiled in Table 1. Powder conductivity measurements are, of course, influenced

$$\sigma = \sigma_0 \exp (-\Delta/kT) \quad (3)$$

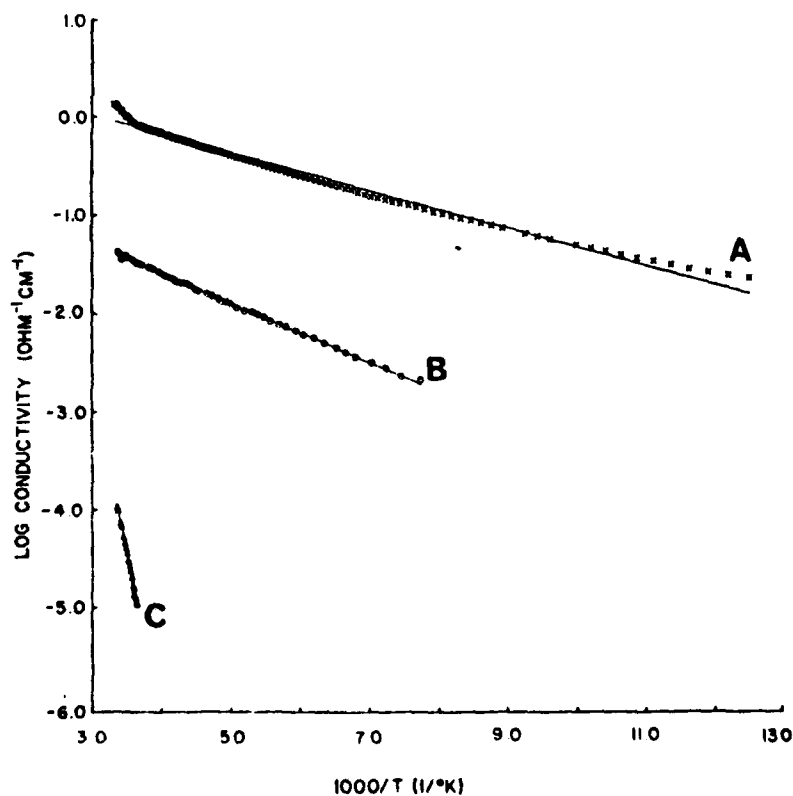


Fig. 3. Variable temperature, four-probe electrical conductivity data for compacted powders of A. $\{[Si(Pc)O]I_{1.55}\}_n$ B. $\{[Ge(Pc)O]I_{2.0}\}_n$ C. $\{[Sn(Pc)O]I_{5.5}\}_n$. The straight lines indicate least-squares fits to eq.(3).

by interparticle contact resistance and random crystallographic orientations. For low-dimensional compounds such as $[\text{Ni}(\text{Pc})]\text{I}_{1.0}$, powder conductivities are typically 10^2 – 10^3 less than single crystal conductivities in the stacking direction and exhibit thermally activated temperature dependences. Thus, "metal-like" temperature dependence ($d\sigma/dT < 0$) is usually masked. However, from the magnitudes of the powder conductivities of the $\{[\text{M}(\text{Pc})\text{O}]\text{I}_x\}_n$ materials it is possible to anticipate that "metal-like" charge transport will be observed in the chain direction for the $\text{M} = \text{Si}$ and perhaps $\text{M} = \text{Ge}$ materials. Further information on this question is provided by voltage shorted compaction (VSC) measurements (41). This technique offers a qualitative means to ascertain anisotropic transport properties in pressed powder samples by deliberately shorting out sources of interparticle resistance. As can be seen in Figure 4, this measurement (42) reveals metal-like ($d\sigma/dT < 0$) behavior at higher temperatures, a relatively broad maximum, and a transition to a less conducting state at low temperatures. The results of the variable temperature conductivity measurements also underscore the robust thermal character of the cofacially arrayed polymers. $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_x\}_n$ samples could be cycled to 300°C with only minor deterioration in room temperature conductivity (apparently due to vaporization of the iodine).

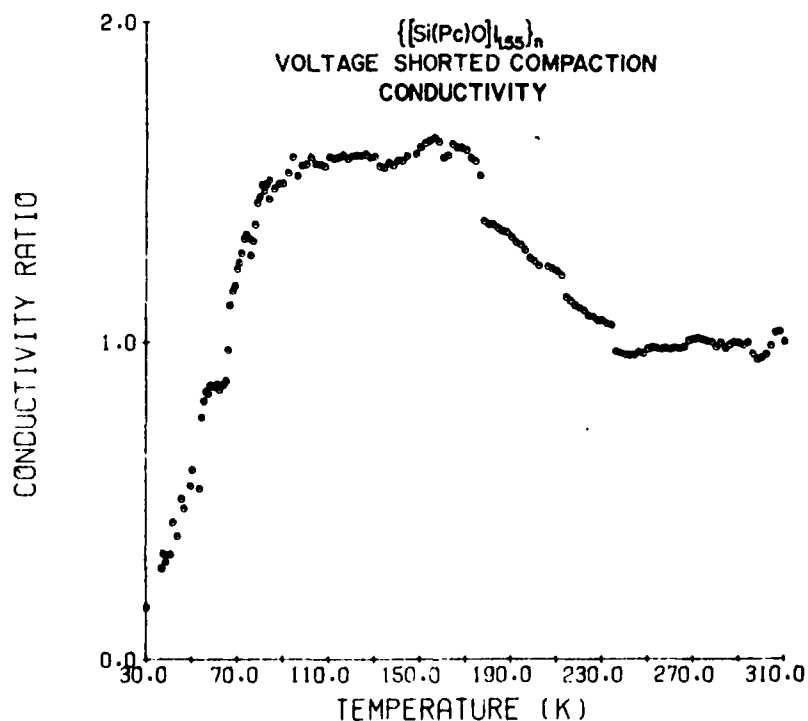


Fig. 4. Voltage shorted compaction conductivity measurement on $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{1.55}\}_n$.

Weak, relatively temperature independent paramagnetism is another characteristic of highly conductive materials with appreciable bandwidths (1-5). Static susceptibility measurements on the $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_x\}_n$ and $\{[\text{Ge}(\text{Pc})\text{O}]\text{I}_x\}_n$ materials by the Faraday method reveal weak ($\chi_m = 300-500 \times 10^{-6}$ emu after corrections for diamagnetism) paramagnetism which varies only modestly with temperature from 300-77°K. Again, there is evidence for a "metal-like" material.

WHAT CONSTITUTES AN EFFECTIVE DOPANT?

Halogens are known to be especially effective acceptors for stabilizing low-dimensional mixed valent arrays of a great many organic and metal-organic donors (15), with the present systems being only a small subset. In attempting to understand why halogens are so effective at partially oxidizing metallomacrocycles, it is first instructive to consider those factors which stabilize a donor-acceptor lattice. For a charge-transferred material, the crystal binding energy (E_C^D) can be expressed approximately as in eq.(4),

$$E_C \approx \rho(I-A) + \rho^2 E_M + \rho^2 E_{ex} + \rho^2 E_{pol} + E_B^D + E_{vdW}^D + E_{CR}^D \quad (4)$$

where ρ is the degree of incomplete charge transfer, I is the gas-phase ionization potential of the neutral donor molecule, A is the gas phase electron affinity of the neutral acceptor, E_M is the Madelung energy, E_{ex} is the exchange energy, E_{pol} is the polarization energy gained by interaction with dipoles induced on neighboring sites, E_B^D is the energy gained by band formation, E_{vdW}^D is the van der Waals energy, and E_{CR}^D is the core repulsion energy (43). Although such a relationship at first appears intractable for predicting which systems will form low-dimensional mixed valent lattices, holding the acceptor constant leads to an interesting empirical result. In Table 2 are collected gas phase ionization potentials (44) of molecular

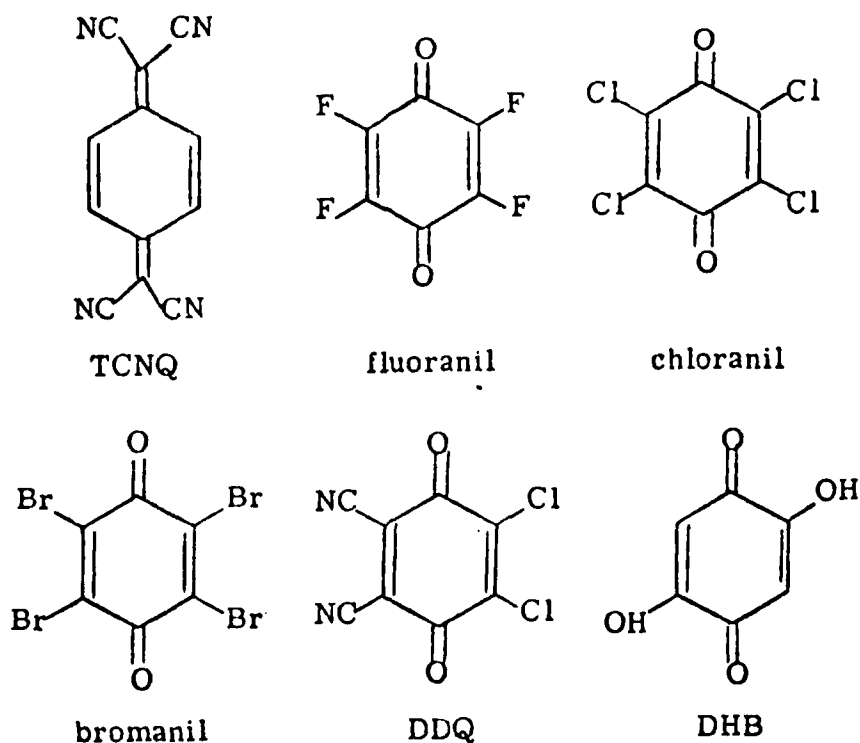
Table 2. Gas Phase Ionization Potentials of Molecular Donors Forming Mixed Valent Salts with Iodine.^a

<u>Donor</u>	<u>Ionization Potential (eV)</u>
Perylene	6.97
TMPD	6.84
TTF	6.83
TMTTF	6.40
TTT	6.50
M(Pc)	6.36-6.41
M(OEP)	6.31-6.39

^aTMPD = N,N,N',N'-tetramethylphenylenediamine; TTF = tetrathiafulvalene; TMTTF = tetramethyltetrathiafulvalene; TTT = tetrathiatetracene; M(OEP) = 2,3,7,8,12,13,17,18-octaethylporphyrin.

donor systems known to form low-dimensional mixed valent solids with iodine. The surprising observation is that for a wide spectrum of donors, including phthalocyanines and porphyrins, the ionization potentials fall within a narrow range (especially when the perylene complex, which is marginally stable, is excluded). Conjugated donors with higher or lower ionization potentials generally appear not to form mixed valent salts (15). These observations suggest that the I-A term in eq.(4) plays a dominant role, and that the other terms remain nearly constant for the classes of donors presently under consideration.

Halogens are not the only acceptors that form mixed valent materials with organic donors. Organic oxidants such as the high potential quinones shown below form a wide range of partially oxidized conductive salts (1-5). For



this reason, it was of interest to explore the response of molecular metallo-macrocycles (e.g., metallocphthalocyanines) to quinone oxidants. In all cases investigated to date, and in striking contrast to halogen dopants, only poorly conductive materials were produced (42). This result raises the interesting question of whether, in addition to electron affinity (I-A in eq.(4)), halogens may play some other role, e.g., structure-forming, in stabilizing the mixed valent lattice. There is some evidence that quinones may promote the formation of integrated stack crystal structures (28).

The availability of the face-to-face polymer system with enforced metallomacrocycle stacking suggests an intriguing experiment to begin to differentiate the redox and structure-forming properties of the dopants. Would conductive, mixed valent metallomacroscopic arrays be produced by quinone oxidants if segregated stacking were inviolably guaranteed? 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. That reduction of the quinone occurs, with concurrent oxidation of the metallomacroscopic array, is demonstrated by infrared spectroscopy. As exemplified by Figure 5, the reduced quinone anions (45) (along with neutral quinone) can be readily detected. As can be seen in Table 3, large increases in electrical conductivity accompany quinone doping of the face-to-face phthalocyanine polymers (but not the molecular phthalocyanine) (42). Indeed, the DDQ-doped materials are nearly as conductive as those doped with halogens. Variable temperature transport data are shown in Figure 6 for several samples. The temperature dependences are thermally activated and activation energies derived from least-squares fits to eq.(3) are compiled in Table 3. Clearly, if the stacked donor microstructure

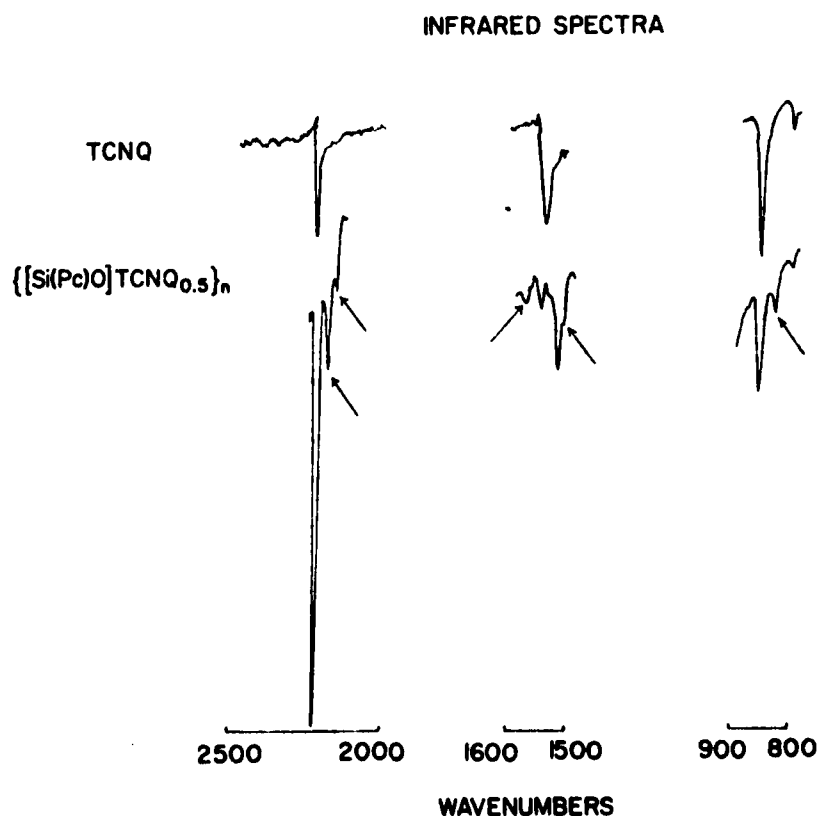


Fig. 5. Solid state infrared spectra of TCNQ and $[\text{Si}(\text{Pc})\text{O}]_n$ doped with TCNQ. The arrows indicate normal modes assignable to TCNQ^- .

Table 3. Charge Transport for Polycrystalline Samples of Molecular Phthalocyanines and Cofacial Phthalocyanine Polymers with Various Dopants

Dopant ^a	Empirical Formula	$G(\Omega^{-1} \text{ cm}^{-1})_{300^\circ\text{K}}$	Activation Energy(eV)
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}	
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}	
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	$\{[\text{Si}(\text{Pc})\text{O}]\text{Chl}_{0.037}\}_n$	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.

can be preserved, mixed valent conductive assemblies can in fact be produced with quinone or probably many other oxidants. This adds a new dimension to the types of conductive materials which can be fabricated and the range of properties which can be incorporated.

It would also seem possible to produce conductive materials by donor rather than acceptor doping. A number of attempts have been made in this Laboratory to partially reduce metallophthalocyanines using alkali metals (36). In all cases, the resulting materials were insulators, and it was conjectured that nonstacked materials were being produced. A preliminary

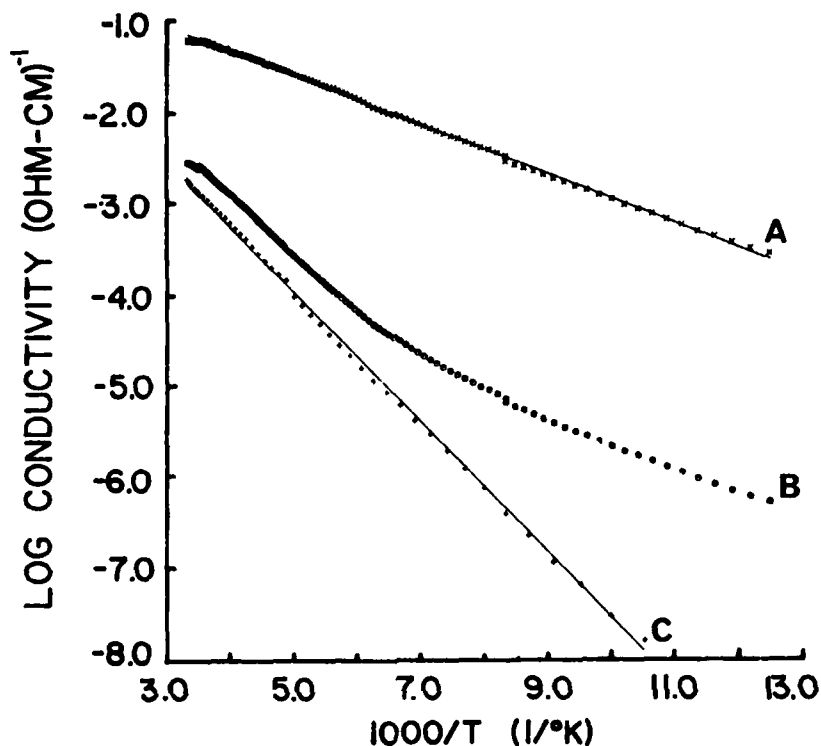


Fig. 6. Variable temperature powder conductivity data for A. $\{[\text{Si}(\text{Pc})\text{O}]\text{DDQ}_{0.35}\}_n$ B. $\{[\text{Si}(\text{Pc})\text{O}]\text{TCNQ}_{0.50}\}_n$ C. $\{[\text{Si}(\text{Pc})\text{O}]\text{ClA}_{0.14}\}_n$.

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 under 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 in progress.

CONCLUSIONS

The cofacial metallomacrocycle assembly strategy represents what is likely the most powerful approach yet devised for controlling molecular microstructure in low dimensional, electroactive 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 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 macrocycles (46), metal ions (47,48) and bridging functionalities (49) have been introduced. We have also 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 (50).

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