ELECTRICALLY CONDUCTIVE MACROMOLECULES VIA COFACIAL ASSEMBLY TECHNIQUE (U)

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# Electrically Conductive Macromolecules Via Cofacial Assembly Techniques

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## Keywords
- Phthalocyanine
- Conductive polymer
- Face-to-face polymer

## Abstract
The properties of low-dimensional mixed valence material consisting of molecular stacks are critically dependent on the rather capricious and unpredictable intermolecular forces that dictate whether stacks form, whether the stacks are segregated, the orientation of donor with respect to acceptor, the relative orientation of units within a stack, and the stacking repeat distance. Discussed in this lecture are rational approaches to overcome such problems.
by combining polymer chemistry with recently developed methodology for synthesizing stacked, partially oxidized metallomacrocycles and for measuring the degree of incomplete charge transfer. New results on the chemical, structural, and electronic properties of highly conductive macromolecules prepared by covalently linking metallomacrocycles in a rigid, face-to-face configuration as shown below, followed by doping, are presented. We examine in detail the response of the solid state properties to systematic variation of $M$, $X$, and dopant.
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INTRODUCTION

There is currently great interest among chemists and physicists in the
design and properties of synthetic molecular materials with the character-
istics of metals (1). Recognized prerequisites for high electrical conduc-
tivity in organic and metal-organic solids include certain essential spacial
and electronic relationships between component molecules. In particular, at
least one set of the molecular constituents must be arrayed in close proximity
and in crystallographically similar environments. In addition, this spe-
cies must be in a formal fractional oxidation state, commonly referred to as
"mixed valence," "incomplete" charge transfer," or "partial oxidation." The
combination of these features provides both a structural pathway for charge
conduction and an electronic environment that reduces bandwidth, band-filling,
and coulombic impediments to carrier mobility. A successful, first-genera-
tion synthetic strategy for the construction of such mixed valent lattices
has involved the cocrystallization of planar, conjugated metallomacrocyclic
donor molecules with halogen electron acceptors (2). In optimum cases, the
result has been crystal structures composed of segregated, partially oxidized
donor stacks and off-axis arrays of halide or polyhalide counterions. Fur-
thermore, the degree of partial oxidation can be readily determined from the
stoichiometry and resonance Raman/iodine Mössbauer characterization of the
form(s) of the halogen present (2,3).

Although straightforward and sometimes successful, the cocrystalliza-
tion strategy provides minimal flexibility in terms of acceptor selection and
offers little control over stacking architecture. Both donor-donor and donor-
acceptor interactions are completely at the mercy of largely unpredictable
and uncontrollable intermolecular forces. We recently reported a new, suc-
cessful approach to control of molecular stacking and lattice architecture in
low-dimensional mixed valence materials (4). It involves the assembly of
well-characterized metallomacrocyclic subunits into cofacial arrays, followed
by partial oxidation using techniques we have previously developed (2,3).
The general approach is schematized below. Such structures offer the exci-
The possibility of assembling a wide variety of new conductive polymers with stringent control over primary and secondary structure as well as over performance and processing characteristics. Furthermore, such macromolecules offer a unique opportunity to experiment with bandwidth, acceptor identity, cohesive forces, and lattice dynamics in a low-dimensional material. In this contribution we elaborate upon our initial results involving Group IV phthalocyanines (Pc) (M = Si, Ge, Sn; X = O; A = I) and begin to examine the aforementioned parameters by introducing a variety of new dopants (A) and bridging functionalities (X).

EXPERIMENTAL

The precursor compounds M(Pc)Cl₂, M = Si, Ge, Sn, were prepared as described elsewhere (4). These were converted into the corresponding [M(Pc)O]ₙ polymers by hydrolysis and then dehydration at 400°C/10⁻³ mm (4,5). The [M(Pc)OR]ₙ polymers were prepared by reaction of the MPCl₂ compounds with HOROR diols in pyridine (6). Doping was carried out by reacting the powdered polymers with solutions of the appropriate dopant (4,7). Potassium was introduced by heating the polymer with potassium metal in a sealed, evacuated Pyrex tube. This material was handled under inert atmosphere at all times. Stoichiometries of the doped polymers were established by elemental analysis.

Electrical conductivity measurements were performed on compressed polycrystalline samples using four-probe ac or dc van der Pauw techniques. Data were acquired with a computer-controlled transport analysis system (8). X-ray powder diffraction studies were carried out with a Picker 6147 diffractometer using CrKα radiation. Resonance Raman spectra were acquired on spinning solid samples using Ar⁺(5145A) excitation. Magnetic susceptibility studies were carried out with a Faraday balance.

RESULTS AND DISCUSSION

Condensation of dihydroxy silicon, germanium, and tin phthalocyanines yields polymers in which the phthalocyanine macrocycles are rigidly held in a face-to-face orientation (eq.(1)). Doping with iodine produces, as indicated by resonance Raman spectroscopy (Figure 1), materials of formal stoichiometry [M(Pc)ₓOₓIₓ]ₙ for x > 1. Oxidation is accompanied by large increases in electrical conductivity (Table 1) with the general trend for the doped materials being σₜₙ > σ₉ > σₓ, i.e., correlating inversely with Pc-Pc

TABLE 1. ELECTRICAL CONDUCTIVITY DATA FOR POLYCRYSTALLINE SAMPLES OF HALOGEN-DOPED [M(Pc)O]ₙ MATERIALS.

<table>
<thead>
<tr>
<th>Compound</th>
<th>σ(A⁻¹ cm⁻¹)</th>
<th>Activation Energy (eV)</th>
<th>Interplanar Spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Si(Pc)O]ₙ</td>
<td>3 x 10⁻²</td>
<td>0.04 ± 0.001</td>
<td>3.33 (2)</td>
</tr>
<tr>
<td>[Si(Pc)O]₁₂₃</td>
<td>2 x 10⁻²</td>
<td>0.04 ± 0.001</td>
<td>3.33 (2)</td>
</tr>
<tr>
<td>[Si(Pc)O]₁₄₅</td>
<td>1 x 10⁻²</td>
<td>0.06 ± 0.003</td>
<td>3.51 (2)</td>
</tr>
<tr>
<td>[Si(Pc)O]Br₂</td>
<td>6 x 10⁻²</td>
<td>0.06 ± 0.003</td>
<td>3.51 (2)</td>
</tr>
<tr>
<td>[Ge(Pc)O]₁₂₃</td>
<td>&lt; 10⁻⁸</td>
<td>0.05 ± 0.007</td>
<td>3.95 (2)</td>
</tr>
<tr>
<td>[Ge(Pc)O]₁₄₅</td>
<td>1 x 10⁻⁵</td>
<td>0.06 ± 0.003</td>
<td>3.95 (2)</td>
</tr>
<tr>
<td>[Ge(Pc)O]Br₂</td>
<td>6 x 10⁻³</td>
<td>0.06 ± 0.003</td>
<td>3.95 (2)</td>
</tr>
<tr>
<td>[Sn(Pc)O]₁₂₃</td>
<td>&lt; 10⁻³</td>
<td>0.06 ± 0.003</td>
<td>3.95 (2)</td>
</tr>
<tr>
<td>[Sn(Pc)O]₁₄₅</td>
<td>1 x 10⁻⁴</td>
<td>0.06 ± 0.003</td>
<td>3.95 (2)</td>
</tr>
</tbody>
</table>
interplanar spacings determined from X-ray powder diffraction and structures of model compounds (9). The temperature dependence of the conductivity (Figure 2) can be fit approximately to a thermally activated model (eq. (2))

$$\sigma = \sigma_0 e^{-\Delta E/kT}$$

(2)

with the activation energies (Table I) following the general trend $\Delta S_1 << \Delta S_2 << \Delta S_3$. The conductivity parameters for the $[\text{Si(Pc)O}]_{10}$ polymers are comparable to those for pressed pellets of the "molecular metal" Ni(Pc)I (10), suggesting that the partially oxidized siloxane and possibly germoxane polymers are also "metal-like" in the chain direction. Further support for this contention is derived from static susceptibility measurements on the doped polymers, which reveal weak, nearly temperature independent paramagnetism.

The cofacially connected macromolecules provide an informative environment for testing the characteristics of various dopants, since the uncertainty as to whether or not stacking occurs has been virtually eliminated. Oxidizing quinones form conductive solids with a variety of organic donors, but curiously not with metallophthalocyanines (11). Since there is reason to believe that the latter donors form integrated stack structures (DADADA) with these large, planar acceptors, doping experiments were carried out with the locked-stack cofacial polymers; the result is a broad new class of conductive macromolecules (Table II, Figures 3 and 4). The preliminary conductivity

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Empirical Formula</th>
<th>$\sigma$ (0$^{-1}$cm$^{-1}$) 300 K</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>$[\text{Si(Pc)O}]_n$</td>
<td>$3 \times 10^{-3}$</td>
<td>0.04 ± 0.001</td>
</tr>
<tr>
<td>I</td>
<td>$[\text{Si(Pc)O}]_{1.53}I_n$</td>
<td>1.4</td>
<td>0.13 ± 0.001</td>
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<tr>
<td>Br</td>
<td>$[\text{Si(Pc)O}]Br_{1.53}J_n$</td>
<td>$6 \times 10^{-2}$</td>
<td>0.15 ± 0.001</td>
</tr>
<tr>
<td>K</td>
<td>$[\text{Si(Pc)O}]K_{1.53}M_n$</td>
<td>$2 \times 10^{-3}$</td>
<td>0.19 ± 0.005</td>
</tr>
<tr>
<td>Flr</td>
<td>$[\text{Si(Pc)O}]Fl_{1.53}J_n$</td>
<td>$7.2 \times 10^{-4}$</td>
<td>0.14 ± 0.001</td>
</tr>
<tr>
<td>Chl</td>
<td>$[\text{Si(Pc)O}]Ch_{1.53}J_n$</td>
<td>$6.9 \times 10^{-4}$</td>
<td>0.06 ± 0.001</td>
</tr>
<tr>
<td>Brl</td>
<td>$[\text{Si(Pc)O}]Br_{1.53}J_n$</td>
<td>$5.8 \times 10^{-4}$</td>
<td>0.08 ± 0.001</td>
</tr>
<tr>
<td>DDQ</td>
<td>$[\text{Si(Pc)O}]DDQ_{1.53}J_n$</td>
<td>$2.1 \times 10^{-2}$</td>
<td>0.14 ± 0.001</td>
</tr>
<tr>
<td>DHB</td>
<td>$[\text{Si(Pc)O}]DHB_{1.53}J_n$</td>
<td>$3.8 \times 10^{-3}$</td>
<td>0.06 ± 0.001</td>
</tr>
<tr>
<td>CIA</td>
<td>$[\text{Si(Pc)O}]CIA_{1.53}J_n$</td>
<td>$1.8 \times 10^{-3}$</td>
<td>0.14 ± 0.001</td>
</tr>
</tbody>
</table>

Fir = fluoranil; Chl = choromil; Brl = bromanil; DDQ = dichlorodicyanquinone; CIA = chloranilic acid.

data roughly parallel the oxidizing strengths of the organic acceptors. In principle, doping with electron donors could also lead to high conductivity, and although alkali metal doping of metallophthalocyanines yields insulators (11), the first result with $[\text{Si(Pc)O}]_n$ and potassium indicates a significant increase in conductivity upon doping (Table II).

In an effort to modify the stacking architecture and bandwidth, polymers were prepared with organic bridging groups (eq. (3)). These functionalities

$$n\text{Si(Pc)Cl}_2 + n/2 \text{HOROH} \rightarrow [\text{Si(Pc)ORO}]_n + 2n\text{HCl}$$

(3)

R = -CH$_2$CH$_2$ - , $E$-C$_6$H$_4$, -(CH$_2$)$_1$, -(CH$_2$)C(CH$_3$)$_2$CH$_2$-

increase the interplanar spacing while still maintaining a continuous molecular array. In all cases the polymers can be doped with iodine, and Raman
spectroscopy indicates that oxidation occurs (Figure 1). In most cases, $I_3^-$ is the predominant polyiodide present. As can be seen in Table III, the electrical conductivity roughly parallels the inverse of the interplanar spacing. The temperature dependence of the charge transport for the $-OCH_2CH_2O-$ bridged material is illustrated in Figure 2.

These preliminary results and recent data on isoelectronic $[M(Pc)F]_m$ Group IIIA analogues (12) underscore the potential of the cofacially assembled metallomacrocycle polymers for delving into the factors which stabilize and accentuate the molecular metallic state. They also suggest ways to tailor new materials for optimum performance and processing characteristics.

**ACKNOWLEDGMENTS**

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**REFERENCES**


2. T.J. Marks, in reference 1b, p. 594.


**IODINE RESONANCE RAMAN SPECTRA**

\[
\text{[(Si(Pc)O)_{1.55}]_n} \\
\text{[(Si(Pc)OCH_2CH_2O)_{1.46}]_n}
\]

230 190 150 110 70 cm\(^{-1}\)

*Figure 1. Resonance Raman spectra \((\nu_0 = 5145\text{Å})\) of iodine doped polymers.*
Figure 2. Variable temperature conductivity data for iodine doped polymers.

Figure 3. Variable temperature conductivity data for quinone doped polymers. Abbreviations are explained in Table II.

Figure 4. Variable temperature conductivity data for quinone doped polymers. Abbreviations are explained in Table II.
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