

21. P. J. Feibelman and D. R. Hamann, *Phys. Rev. Lett.* **52**, 61 (1984).
22. P. H. Citrin, G. K. Wertheim, Y. Bayer, *Phys. Rev. Lett.* **41**, 1425 (1978); P. Heimann, J. F. van der Veen, D. E. Eastman, *Solid State Commun.* **38**, 595 (1981); J. F. van der Veen, F. J. Himpsel, D. E. Eastman, *Phys. Rev. Lett.* **44**, 189 (1980); T. M. Duc, G. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet, J. C. Vedrina, *ibid.* **43**, 789 (1979); G. Treglia, M. C. Desjonquères, D. Spanjaard, Y. Lassailly, C. Guillot, Y. Jagnet, T. M. Duc, J. Lecante, *J. Phys. C* **14**, 3463 (1981).
23. J. A. Appelbaum and D. R. Hamann, *Solid State Commun.* **27**, 881 (1978); P. J. Feibelman and D. R. Hamann, *ibid.* **31**, 413 (1979); M. C. Desjonquères, D. Spanjaard, Y. Lassailly, C. Guillot, *ibid.* **34**, 807 (1980); A. Rosengren and B. Johansson, *Phys. Rev. B* **22**, 3706 (1980).
24. P. H. Citrin and G. K. Wertheim, *Phys. Rev. B* **27**, 3176 (1983).
25. G. Apai, R. C. Baetzold, E. Shustorovich, R. Jaeger, *Surf. Sci. Lett.* **116**, L191 (1982); R. C. Baetzold, G. Apai, E. Shustorovich, R. Jaeger, *Phys. Rev. B* **26**, 4022 (1982); G. Apai, R. C. Baetzold, P. J. Jupiter, A. J. Viescas, I. Lindau, *Surf. Sci.* **134**, 122 (1983); R. C. Baetzold, G. Apai, E. Shustorovich, *Appl. Surf. Sci.*, in press.
26. J. R. Smith, F. J. Arlinghaus, J. G. Gay, *Phys. Rev. B* **26**, 1071 (1982).
27. J. H. Rose, J. R. Smith, J. Ferrante, *ibid.* **28**, 1835 (1983); J. H. Rose, J. R. Smith, F. Guinea, J. Ferrante, *ibid.* **29**, 2963 (1984).
28. D. Spanjaard and M. C. Desjonquères, *ibid.* **30**, 4822 (1984).
29. E. Shustorovich, *J. Am. Chem. Soc.* **106**, 6479 (1984).
30. R. C. Baetzold, *Surf. Sci.*, in press.
31. E. L. Muetterties, E. Shustorovich, R. C. Baetzold, in preparation.
32. G. Ertl, M. Neumann, K. M. Streit, *Surf. Sci.* **64**, 393 (1977); P. R. Norton, J. W. Goodale, E. B. Selkirk, *ibid.* **83**, 189 (1979).
33. B. Poelsema, L. K. Verheij, G. Comsa, *Phys. Rev. Lett.* **49**, 1731 (1982).
34. E. Shustorovich, *Surf. Sci.* **150**, L115 (1985).
35. G. Ertl, S. B. Lee, M. Weiss, *ibid.* **114**, 515 (1982); J. L. Gland, B. A. Sexton, G. B. Fisher, *J. Catal.* **95**, 587 (1980); C. T. Campbell, G. Ertl, H. Kuipers, J. Segner, *Surf. Sci.* **107**, 220 (1981); J. Lee, R. J. Madix, J. E. Schlaegel, D. J. Auerbach, *ibid.* **143**, 626 (1984).
36. Most recently, we have extended our bond-order-conservation model to treat various coverage and coadsorption (promoting and positioning) effects, in good agreement with experiment (E. Shustorovich and R. C. Baetzold, in preparation).
37. R. J. Madix, personal communication.
38. We express our deep gratitude to the late Earl L. Muetterties, whose unique intuition often guided our choice of problems.

Electrically Conductive Metallomacrocyclic Assemblies

Tobin J. Marks

Until only a few years ago, the idea that a traditional organic or metal-organic substance could exhibit the electrical, optical, and magnetic properties of a metal seemed a complete contradiction in terms. Among other features, such substances lack the partially filled, spatially delocalized electronic energy levels (bands) which are an essential characteristic of a metal (1). This picture has, however, changed dramatically in the past several years, and the art of chemical synthesis has given rise to whole new classes of molecular (2-5) and polymeric (2-6) materials with properties analogous to those of metals having restricted dimensionality. The culmination is a new condensed matter field of study at the interface of chemistry, physics, and materials science that is stimulating breakthroughs in synthetic chemical strategy and methodology, in spectroscopic, structural, and transport analysis, and in the fundamental theoretical descriptions of how electrical charge is transported in the solid state of matter. Terms such as "molecular metal," "synthetic metal," "organic superconductor," "soliton conductor," and "bipolaron conductor" were unheard of only a few years ago. The application of this new knowledge to sensors, rectifiers, batteries, switching devices, photoresists, solar energy devices,

electrophotographic devices, static charge-dissipating materials, electro-magnetic shielding materials, chemoselective electrodes, and video disk coatings has also received a great deal of discussion (2-6).

Summary. The design, synthesis, and study of electrically conductive molecular and polymeric substances constitute a new scientific endeavor involving the interaction of chemists, physicists, and materials scientists. The strategies, developments, and challenges in these two closely related fields are analyzed via a class of materials that bridges both: assemblies of electrically conductive metallomacrocycles. It is seen that efforts to rationally synthesize tailored, "metal-like" molecular arrays lead logically to structure-enforced polymeric assemblies of linked molecular subunits such as metallophthalocyanines. The properties of these assemblies and fragments thereof provide information on the relationship between atomic-level local architecture, electronic structure, and macroscopic transport properties. Electrically conductive, processable polymeric materials also follow from these results.

Despite the impressive advances that have been achieved in the fields of molecular and macromolecular electrically conductive materials, it is fair to say that our current level of physical understanding of and chemical control over such systems is at a rather rudimentary level. From a synthetic chemical standpoint, the ability to tailor charge-transporting microstructures at the atomic level represents an exciting challenge and a key both to manipulating macroscopic prop-

erties and to testing theoretical predictions. A brief overview of these activities is given in this article.

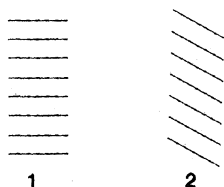
To review in detail the recent chemical progress made by the host of excellent research groups working on conductive molecular and polymeric substances is not possible in the space available here. Thus, we have chosen to be selective and to illustrate current strategies, approaches, and problems by focusing on work performed in this laboratory on a new family of materials which is at the crossroads between molecular and polymeric conductors and which embodies characteristics of each. Our long-range goal has been to develop rational, flexible syntheses of low-dimensional, metal-like molecular assemblies and, through correlated physical and theoretical in-

vestigations, to understand the properties of these assemblies as a function of architecture and electronic structure. This approach leads quite logically from rather simple systems composed of aggregated single molecules to more elaborate, structure-enforced polymeric arrays of covalently linked molecular subunits.

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A Molecular Approach and Model Systems

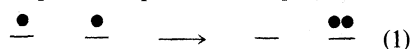
Two general features are emerging as prerequisites for converting an unorganized collection of molecules into an electrically conductive array (7, 8). First, the molecules must be arranged in close spatial proximity and in similar crystallographic and electronic environments so that an energetically flat (that is, with a minimum of "hills and valleys"), extended pathway exists for electronic charge movement. Such a situation is frequently realized when planar, conjugated molecules crystallize in a "stack" (for example, 1 or 2). The progression by



which a band structure is built up from the highest occupied molecular orbitals (HOMO's) of the molecular components of such a stack is illustrated in Fig. 1A. In a simple, Hückel-like ("tight-binding") description of the electronic structure (1), the transfer integral t (analogous to the Hückel resonance integral β) is a measure of how strongly the component molecular orbitals interact; in an extended solid, the magnitude of this interaction is expressed as the bandwidth, $4t$. An important goal in this area is to measure t accurately and, ultimately, to "tune" it.

The second requisite for the "molecular metallic" state is that the arrayed molecules must be in formal fractional oxidation states ["mixed valence," "partial oxidation (or reduction)," "in-

complete charge transfer"]. That is, the molecules must formally have fractionally occupied valence shells. Part of this requirement is analogous to the classical dictate that the highest occupied band of a metal be only partially filled (1). A valence bond depiction is presented in Fig. 1B. However, as was first noted for certain metal oxides (9), situations may arise in which the coulombic repulsion (denoted by the parameter U) of having two charge carriers on a single site (for example, as expressed in Eq. 1)

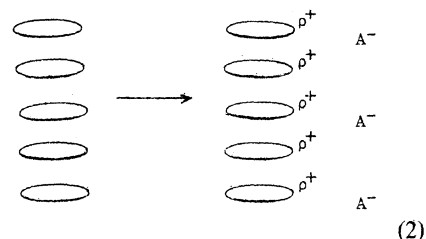


may approach or exceed the bandwidth. In the extreme case ($U \gg 4t$), a material with a formally half-filled band could actually be an insulator (10). For molecular systems, the degree to which molecular, crystal, and electronic structure influence the coulombic interactions is by no means clear, and learning to manipulate U remains an important goal.

In addition to the parameters mentioned above, the conductivity properties of molecular materials are highly sensitive to interactions between the electronic systems and various lattice vibrations (phonons). In the extreme case, a lattice distortion (a Peierls transition) accompanied by an opening of a gap in the conduction band can induce a metal-to-insulator transition at low temperatures (1). Such behavior is analogous to a Jahn-Teller instability and is predicted theoretically for an ideally unidimensional metal. However, metal-to-insulator transitions are not observed in a number of cases, and the most plausible explanation (presently qualitative) appears to be that ideal unidimensionality is not fulfilled. Other electron-phonon effects are believed to be important in

the nonclassical temperature dependence of the conductivity of many molecular metals ($\sigma \sim T^{-2}$) (11) and doubtless play a role in the properties of superconducting organic systems (2, 12). Electron-electron effects can also be important (2-5).

Synthetically, mixed valence is usually achieved by chemical or electrochemical oxidation (for example, Eq. 2) or



reduction of the components of the delocalized stack. The success of such a tactic is crucially dependent on a complex, largely uncontrollable variety of Madelung, exchange, polarization, bandwidth, van der Waals, core repulsion, crystallization kinetic, and ionization potential-electron affinity factors, which determine the lattice architecture (segregated arrays of donors and acceptors are essential) and the degree of incomplete charge transfer. Of course, such variables are not readily manipulated by conventional synthetic methodology, and serendipity has been a major ingredient in the synthesis of most molecular metals. Also, obstacles such as the growth of crystals having suitable dimensions, crystallinity, and purity for meaningful measurements are by no means trivial.

Among the donor molecules that have received the greatest attention, the tetrachalcogenafulvalenes (3) in their myriad modifications, have given rise to some of the most spectacular results. Thus, TTF

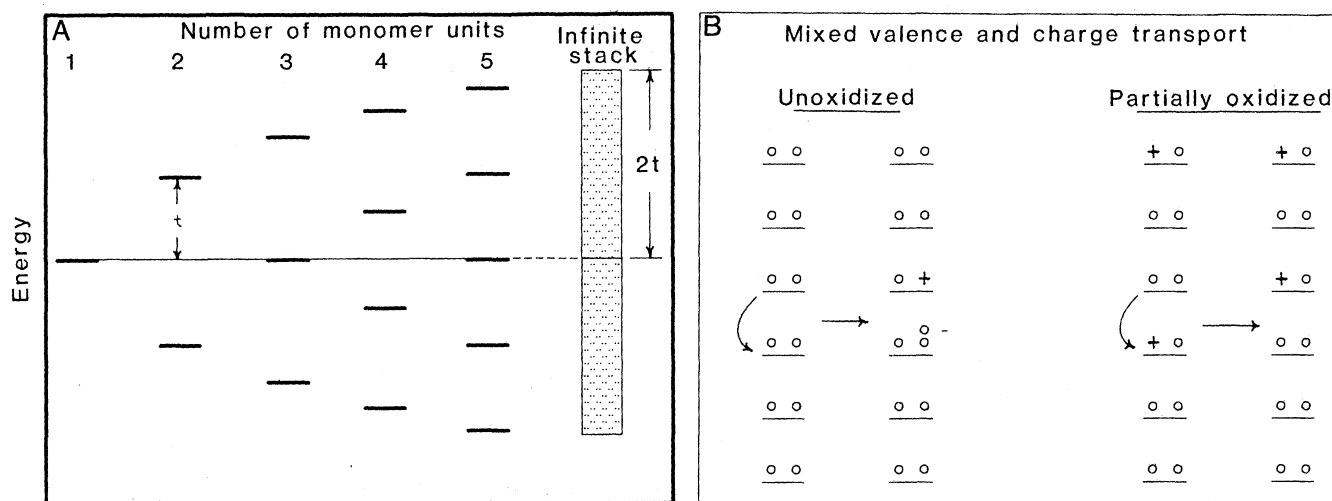
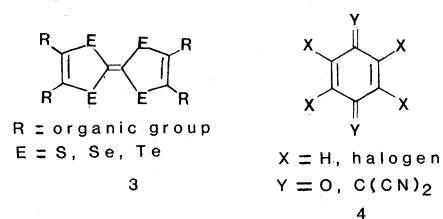
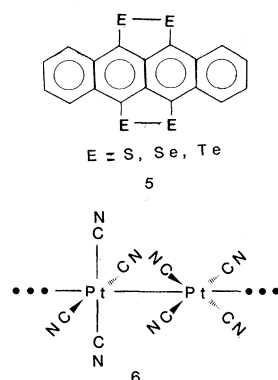


Fig. 1. (A) Schematic illustration of the energetics of arraying increasing numbers of molecular subunit HOMO's, resulting finally in band formation. The parameter t is the tight-binding transfer integral, analogous to the Hückel β integral. (B) Schematic depiction of how partial oxidation enhances charge mobility in a simple molecular stack.

(3; R = H, E = S), in combination with the electron acceptor TCNQ [4; X = H, Y = C(CN)₂], gave rise to the first true molecular metal, TTF-TCNQ (13). More recently, salts of TMTSF (3; R = CH₃, E = Se) were the first organic supercon-

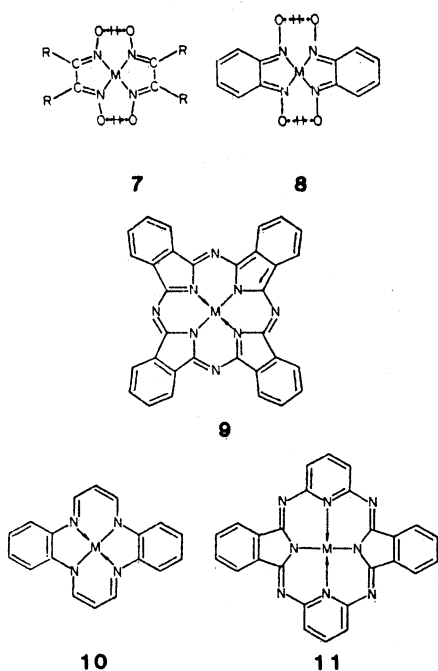


ductors (12). Other highly conductive systems are based on the tetrachalcogenatetetracene (5) (14) and tetracyanoplatinatate [6; for example, K₂Pt(CN)₄Br_{0.3}]



families. The latter material has a band structure composed primarily of partially filled platinum *d*_{z²} orbitals (1, 15).

Initial efforts in this laboratory (7) focused on synthesizing and understanding new types of stacked molecular conductors composed of glyoximate (7, 8) (7, 16), phthalocyanine [9; M(Pc)] (7, 17), dibenzotetraazaannulene (10) (7, 18), and hemiporphyrizine (11) (19) metallo-



macrocycles. As early as 1975, it was shown using resonance Raman and ¹²⁹I Mössbauer spectroscopy (to identify the form of iodine present in the crystal) that a metallomacrocyclic donor could be co-crystallized with I₂ (Eq. 2) to yield a mixed-valence, low-dimensional conductor (20). The details and import of this molecular cocrystallization-Raman analysis approach were further elaborated in 1976 (21) and 1978 (22). Extension to Br₂ as an acceptor was subsequently described (23), and this general approach has been skillfully applied to numerous other metallomacrocyclic systems (24). In optimum cases, the metallomacrocyclic-halogen cocrystallization approach

yields segregated arrays of partially oxidized donor ions and polyhalide counterions. The form of the halogen, hence the degree of incomplete charge transfer, can be readily discerned with resonance Raman and iodine Mössbauer spectroscopy (even in polycrystalline or severely disordered samples) (7, 25).

A particularly impressive example of the molecular cocrystallization approach is based on the robust, technologically important phthalocyanine (9) macrocycle (26). The material H₂(Pc)I (9; M = two hydrogen atoms) illustrates conclusively that a central metal ion is not required for high electrical conductivity and is an ideal model material for more elaborate systems (see below) (27). The diffraction-derived crystal structure of this material [tetragonal, space group *P4/mcc*, with crystallographic axes *a* = 13.979(6) and *c* = 6.502(3) Å at 25°C; *R*_F = 0.041] consists of stacks of H₂(Pc)^{+0.33} cations arrayed at 3.251(2) Å separations and parallel chains of disordered off-axis I₃⁻ counterions (Fig. 2A). The staggering angle between adjacent Pc rings is 40.0°. The electrical conductivity (σ_{||}) of a typical (0.65 by 0.07 by 0.07 mm!) H₂(Pc)I crystal in the macrocycle stacking direction (the crystallographic *c* axis) is compared to that of the somewhat less conductive nickel analog in Fig. 2B (28). At room temperature, σ_{||} for H₂(Pc)I is approximately 700 ohm⁻¹ cm⁻¹, which, adjusted for the high cross-sectional area of an H₂(Pc) stack (that is, the carrier mean free path), is among the highest reported for an organic conductor. Furthermore, the temperature dependence of σ_{||} is "metal-like" (*d*σ/*d**T* < 0) until very low temperatures and exceeds 3500 ohm⁻¹ cm⁻¹ even at 1.5 K. The first measurements of the electrical anisotropy of a metallomacrocyclic conductor underscore the pronounced unidimensionality: σ_{||}/σ_⊥ ≥ 500 for a typical H₂(Pc)I crystal.

Optical reflectivity measurements are another powerful method for studying the electronic structure of molecular metals (29). New instrumental techniques have recently yielded the first quantitative, complete far-infrared to ultraviolet polarized reflectance data for a single crystal of a metallomacrocyclic conductor (Fig. 2C) (27). The high anisotropy of this material is evident in the differences in reflectivity parallel to (R_{||}) and perpendicular to (R_⊥) the macrocycle stacking direction. The perpendicularly polarized features at 14,800 and 29,000 cm⁻¹ and the parallel-polarized feature at 18,200 cm⁻¹ are straightforwardly assigned, on the basis of our earlier work, to Pc-centered (π → π*)

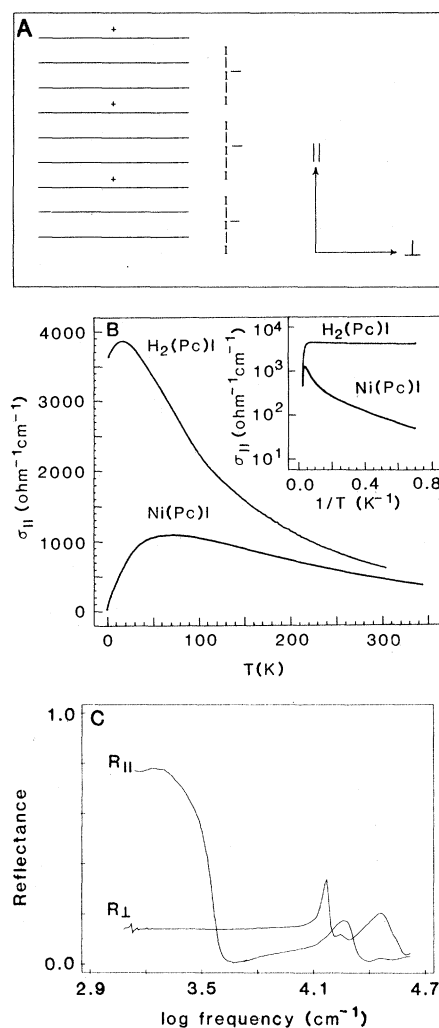


Fig. 2. (A) Schematic illustration of the H₂(Pc)I crystal structure, viewed transverse to the stacking direction (the crystallographic *c* axis). The symbols || and ⊥ denote directions parallel and perpendicular to the stacking direction, respectively. (B) Variable-temperature electrical conductivity data for typical Ni(Pc)I and H₂(Pc)I single crystals in the macrocycle stacking direction (||). The inset emphasizes the behavior at very low temperatures. (C) Reflectance spectrum of an H₂(Pc)I single crystal; R_{||} and R_⊥ denote reflectance parallel and perpendicular to the macrocycle stacking direction, respectively.

and I_3^- -centered electronic transitions, respectively (7). Most significant, however, is the parallel-polarized edgeline feature which begins at $\sim 4500\text{ cm}^{-1}$ and extends into the far-infrared. This feature is reminiscent of the classical plasma edge in the reflectance of a metal (1)—clearly the $H_2(Pc)I$ band structure is highly anisotropic. Detailed numerical analysis of the plasma edge line shape using an “electron gas” (Drude) model yields the plasma frequency (ω_p), the electron relaxation time, the effective mass of the carriers, and the tight-binding bandwidth, $4t = 1.2(1)\text{ eV}$ (27).

Although less well understood, the magnetic properties of molecular metals are also informative (30). The susceptibility of $H_2(Pc)I$ is only weakly paramagnetic ($\chi_s = 2.21(5) \times 10^{-4}\text{ emu mol}^{-1}$) and is relatively independent of temperature. This behavior is reminiscent of the Pauli susceptibility of metals (1), and a simple tight-binding analysis yields a bandwidth (unrealistically small) of $0.38(7)\text{ eV}$. The questionable reliability of susceptibility-derived bandwidths is

probably due to large on-site Coulomb repulsions (10, 31). Electron paramagnetic resonance (EPR), thermoelectric power, and solid-state nuclear magnetic resonance (NMR) measurements on $H_2(Pc)I$ all indicate that the conduction pathway is predominantly if not exclusively through the macrocyclic radical cation stacks and not through the polyiodide chains (27, 32).

Although the molecular cocrystallization method was a useful first-generation approach, attempts to significantly modify the metallomacrocyclic molecules (for example, alkylation) or the acceptor moieties (nonhalogen oxidizing agents such as TCNQ) soon revealed the limitations of such a simplistic synthetic approach. Without rigorous structural enforcement of the metallomacrocyclic stacking, it is impossible to effect controllable and informative variations in stacking architecture or in donor-acceptor spatial-electronic relationships. Clearly, the packing forces operative in most molecular conductors are rather delicate.

Cofacial Assembly Properties of Conductive Metallomacrocyclic Polymers

One attractive approach to enforce stacking architecture in metallomacrocyclic conductors is by covalently linking already proven, charge-carrying molecular subunits in a cofacial orientation. This approach is illustrated for group IVA phthalocyanines, $[M(Pc)O]_n$, in Fig. 3A, and the result is a conceptually generalizable class of extremely robust (the polymerization is carried out at 400°C ; the $M = \text{Si}$ polymer can be recovered unchanged after dissolution in strong acids) macromolecules (33, 34). Characterization studies by a variety of chemical, radiochemical, spectroscopic (infrared, Raman, optical, solid-state NMR), diffractometric, and electron microscopic techniques indicate highly regular, crystalline structures consistent with the cofacial architecture depicted in Fig. 3A and with $n = 50$ to 200. Importantly, the Pc-Pc interplanar separation increases with increasing ionic radius of M : $3.33(2)\text{ \AA}$, $M = \text{Si}$; $3.53(2)\text{ \AA}$, $M = \text{Ge}$; $3.82(2)\text{ \AA}$, $M = \text{Sn}$ (33). Furthermore, recent scanning and transmission electron microscopic studies have revealed the microscopic details of how $M(Pc)(OH)_2$ monomer crystals are topochemically transformed upon heating into $[M(Pc)O]_n$ polymer crystals (35) and have provided direct images, within the crystal lattice, of the polymer chains and the halogen doping process for $M = \text{Ge}$ (36).

The $[M(Pc)O]_n$ polymers can be converted into covalently linked, mixed-valence chain compounds by a variety of chemical and electrochemical methods (for example, Eqs. 3 to 5 for $M = \text{Si}$ and Ge). This process has been traditionally

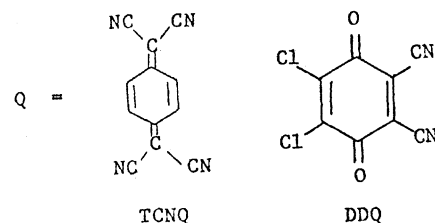
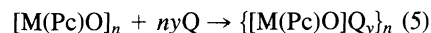
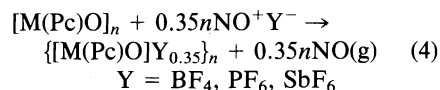
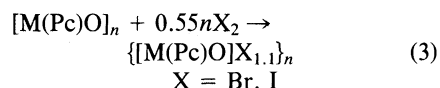
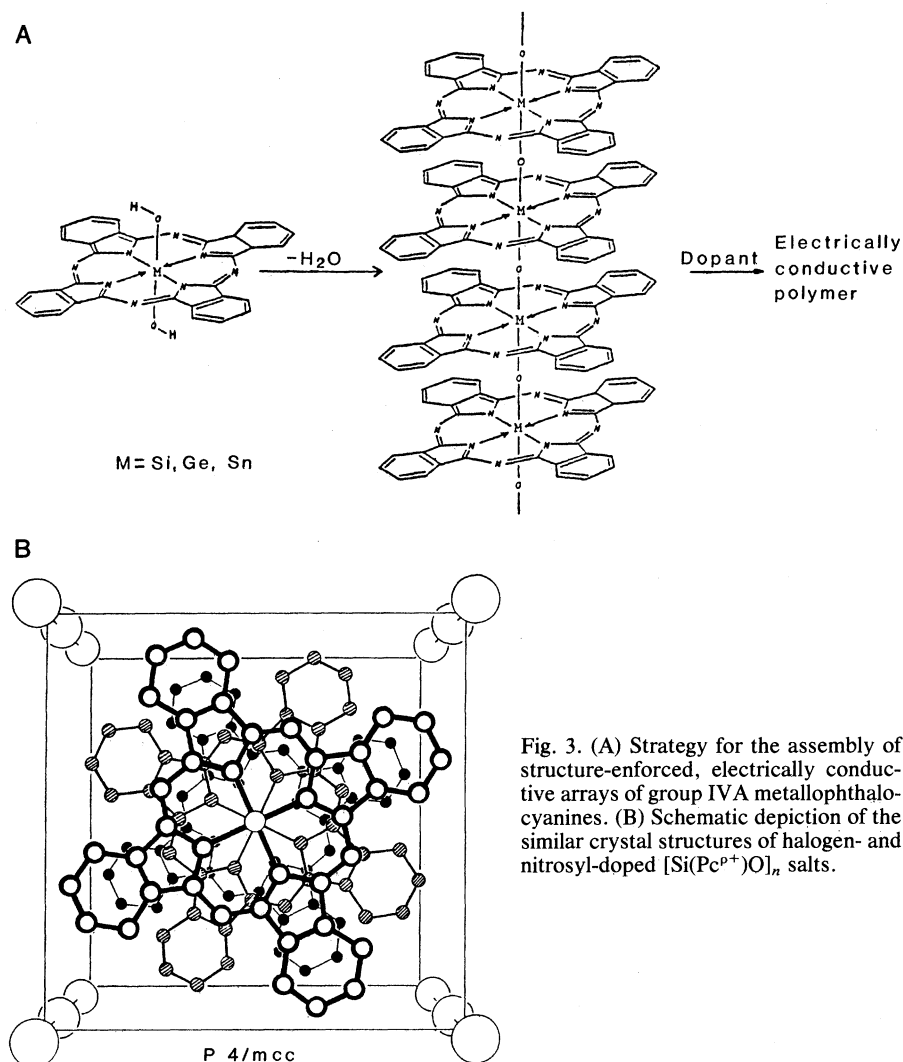


Fig. 3. (A) Strategy for the assembly of structure-enforced, electrically conductive arrays of group IVA metallophthalocyanines. (B) Schematic depiction of the similar crystal structures of halogen- and nitrosyl-doped $[\text{Si}(\text{Pc}^{p+})\text{O}]_n$ salts.



enforced, and for the first time it is possible to meaningfully probe donor-acceptor relationships for a wide range of structurally and electronically dissimilar dopants as well as to examine the effects of differing interplanar spacings on the collective properties.

The halogenated polymers were studied first since a substantial data base already existed for the molecular congeners and was available for comparisons (33). The halogen-doped materials have the important property that they appear to be stable in air for years. Diffraction studies reveal that the halogen doping process is inhomogeneous; incremental oxidation yields progressively greater amounts of a new, mixed-valence phase of discrete stoichiometry and structure, and the dopant is not distributed evenly throughout the lattice as doping progresses. The crystal structures of the halogenated polymers are illustrated in Fig. 3B. Within experimental error, the structures of Ni(Pc)I, $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{1.12}\}_n$, and $\{[\text{Ge}(\text{Pc})\text{O}]\text{I}_{1.12}\}_n$ differ only in the ring-ring interplanar spacing, namely 3.244(2), 3.30(2), and 3.48(2) Å, respectively. The form of the halogen in all of these materials is X_3^- , so the formal degree of incomplete charge transfer, $\rho = 0.33$ to 0.37, is rather insensitive to the nature of the halogen and the ring-ring interplanar separation.

The response of the $\{[\text{M}(\text{Pc})\text{O}]\text{X}_{1.1}\}_n$ collective properties to an increase in the key structural parameter of interplanar spacing is beautifully illustrated by a fall in the electrical conductivity ($\sigma_{\text{Ni}} > \sigma_{\text{Si}} > \sigma_{\text{Ge}}$), an increase in the Pauli-like magnetic susceptibility ($\chi_{\text{Ni}} < \chi_{\text{Si}} < \chi_{\text{Ge}}$), and a decrease in the optical reflectivity plasma frequency ($\omega_{\text{Ni}} > \omega_{\text{Si}} > \omega_{\text{Ge}}$), hence the tight-binding bandwidth. The latter two observables clearly indicate a structurally correlated diminution in the bandwidth with increased spacing, while the former shows the close connection to macroscopic charge transport. Relevant data are set out in Table 1. As is usually the case for conductive polymers, it has not yet proved possible to obtain sufficiently large crystals of the $\{[\text{M}(\text{Pc})\text{O}]\text{X}_{1.1}\}_n$ materials for single-crystal conductivity (or optical) studies. Hence, measurements have been on isotropic, compacted, polycrystalline samples, recognizing that for the conductivity of such materials, $\sigma_{\parallel}$ (single crystal) $\sim 100 \sigma$ (polycrystalline). Thus, in the $[\text{M}(\text{Pc}^{\rho+})\text{O}]_n$ stacking direction, $\sigma_{\parallel}$ (Si) $\sim 100 \text{ ohm}^{-1} \text{ cm}^{-1}$ and $\sigma_{\parallel}$ (Ge) $\sim 10 \text{ ohm}^{-1} \text{ cm}^{-1}$ (33). Two other observations are of interest with regard to $\{[\text{M}(\text{Pc})\text{O}]\text{X}_{1.1}\}_n$ charge transport. The

increase in the electrical conductivity as a function of doping level (a steep rise followed by a leveling off; Fig. 4A) is explicable in terms of a simple percolation model, that is, a statistical picture of how many randomly dispersed conductive particles must be introduced into a host of nonconductive particles to produce a contiguous conducting pathway (at the "percolation threshold") (33,

37). Second, the temperature dependence of the conductivity can be described by a model (fluctuation-induced tunneling) in which conduction is modulated by small, nonconducting junctions separating the larger, high-conductivity regions (38). This is indicated by a linear relation between $-1/\ln(\sigma/\sigma_0)$ and temperature (Fig. 4B), where σ_0 is a constant characteristic of the particular material.

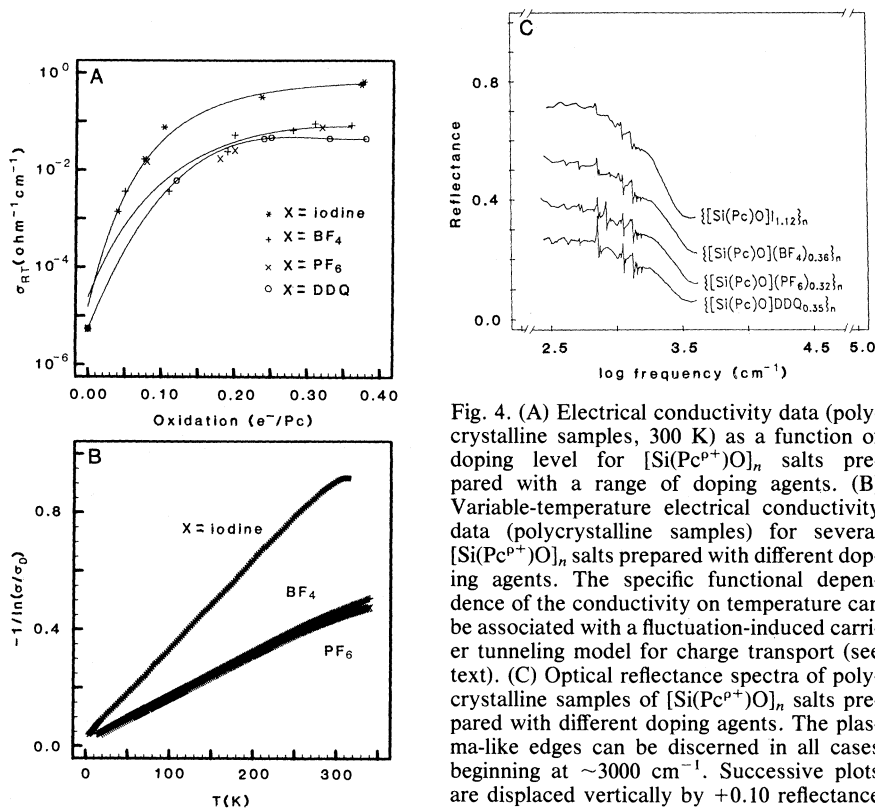


Fig. 4. (A) Electrical conductivity data (polycrystalline samples, 300 K) as a function of doping level for $[\text{Si}(\text{Pc}^{\rho+})\text{O}]_n$ salts prepared with a range of doping agents. (B) Variable-temperature electrical conductivity data (polycrystalline samples) for several $[\text{Si}(\text{Pc}^{\rho+})\text{O}]_n$ salts prepared with different doping agents. The specific functional dependence of the conductivity on temperature can be associated with a fluctuation-induced carrier tunneling model for charge transport (see text). (C) Optical reflectance spectra of polycrystalline samples of $[\text{Si}(\text{Pc}^{\rho+})\text{O}]_n$ salts prepared with different doping agents. The plasma-like edges can be discerned in all cases beginning at $\sim 3000 \text{ cm}^{-1}$. Successive plots are displaced vertically by +0.10 reflectance unit for ease of viewing and are uncorrected for the isotropic nature of the samples.

Table 1. Structural, transport, magnetic, and bandwidth parameters for electrically conductive phthalocyanine materials.

Compound	Tetragonal lattice (Å)	Charge transfer (ρ)	d-c electrical conductivity at 300 K ($\text{ohm}^{-1} \text{ cm}^{-1}$)	Pauli magnetic susceptibility ($\text{emu mol}^{-1} \times 10^4$)	Tight-binding bandwidth $4t^*$ (eV)
$\text{H}_2(\text{Pc})\text{I}$	$a = 13.979(6)$ $c = 6.502(3)$	0.33	700† 8.0‡	2.21(5)	1.2(1)† 1.1(2)‡
$\text{Ni}(\text{Pc})\text{I}$	$a = 13.936(6)$ $c = 6.488(3)$	0.33	500† 7.5‡	1.90(10)	0.99(9)‡
$\{[\text{Si}(\text{Pc})\text{O}]\text{I}_{1.12}\}_n$	$a = 13.98(5)$ $c = 6.60(4)$	0.37	0.58‡	2.35(10)	0.60(6)‡
$\{[\text{Si}(\text{Pc})\text{O}](\text{BF}_4)_{0.36}\}_n$	$a = 13.82(7)$ $c = 6.58(4)$	0.36	0.10‡	2.22(6)	0.64(6)‡
$\{[\text{Si}(\text{Pc})\text{O}](\text{PF}_6)_{0.36}\}_n$	$a = 13.99(6)$ $c = 6.58(4)$	0.36	0.10‡	2.49(7)	0.63(6)‡
$\{[\text{Si}(\text{Pc})\text{O}](\text{SbF}_6)_{0.36}\}_n$	$a = 14.31(4)$ $c = 6.58(4)$	0.36	0.15‡	2.22(3)	0.64(6)‡
$\{[\text{Ge}(\text{Pc})\text{O}]\text{I}_{1.12}\}_n$	$a = 13.96(5)$ $c = 6.96(4)$	0.37	0.11‡	2.70(10)	0.48(5)‡

*From analysis of reflectivity data.

†Single-crystal sample.

‡Polycrystalline sample.

Both of these properties are in accord with the aforementioned doping-structural model for the $\{[M(Pc)O]X_{1.1}\}_n$ materials.

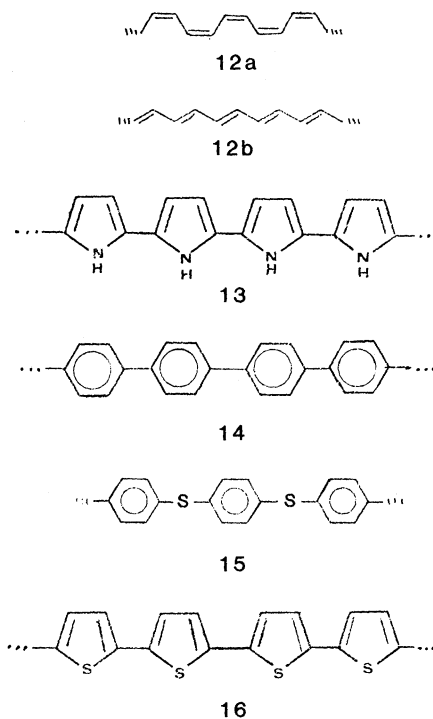
We can now ask a fascinating question. If it were possible to hold the architecture of the donor array constant, how would the halogen-related phenomenology vary as a function of dopant? The rigorously enforced stacking architecture of the $[M(Pc)O]_n$ polymers affords a unique opportunity to address this question. For example, the nitrosyl doping route of Eq. 3 involves oxidants which are different from halogens, and the resulting BF_4^- , PF_6^- , SbF_6^- counterions differ from Br_3^- and I_3^- in spatial demands, charge distributions, and polarizability (39). Nevertheless, the degree of incomplete charge transfer achieved ($\rho \sim 0.35$), the inhomogeneity of the oxidation process, and the geometries (interplanar spacings, ring-ring staggering angles) of the partially oxidized $[Si(Pc^{\rho+})O]_n$ chains (Fig. 3B and Table 1) are almost independent of dopant. As assessed by the magnetic susceptibility and optical reflectivity (Fig. 4C), the band structure does not perceptibly "feel" the counterions. It might have been expected that localization of the counterion negative charges (for instance, $I_3^- \rightarrow BF_4^-$) would have caused localization of the $[M(Pc^{\rho+})O]_n$ wave functions and band narrowing. As for the halogenated polymers, the dependence of electrical conductivity on doping level suggests percolation behavior (Fig. 4A)

and the temperature dependence of the conductivity agrees with the fluctuation-induced carrier tunneling mechanism (Fig. 4B). In addition, like the halogenated polymers, the nitrosyl-doped polymers appear to be indefinitely stable in air.

Although the crystallography is considerably more complicated and experiments are still in progress, results with DDQ (Eq. 4) as a $[Si(Pc)O]_n$ dopant are remarkably similar to those for the halogen- and nitrosyl-oxidized polymers (39, 40). Evidence for a limiting degree of incomplete charge transfer near $\rho \approx 0.40$ under normal doping conditions, percolation behavior (Fig. 4A), and a nearly invariant plasma frequency (Fig. 4C) are again observed. It is conceivable that more drastic oxidizing conditions may effect further depletion of the $[M(Pc)O]_n$ conduction band. Of particular interest would be the properties of the integral oxidation state ($\rho = +1$) material. Would it be a "Mott-Hubbard insulator" (9, 10)? Initial indications obtained with DDQ under more vigorous conditions or electrochemically doping at very high potentials suggest the exciting possibility that more highly oxidized cofacially linked arrays are indeed accessible (41).

The doped $[M(Pc)O]_n$ materials, of course, represent only one component of a rapidly growing field. The past several years have witnessed a veritable explosion in the number of other classes of electrically conductive polymers that

have been prepared and characterized. Some of the more extensively studied examples are *cis*- and *trans*-polyacetylene (12) (6, 42), polypyrrole (13) (6, 43), poly-*p*-phenylene (14) (6, 44), poly-*p*-phenylenesulfide (15) (6, 45), and polythiophene (16) (6, 46). In common with the $[M(Pc)O]_n$ polymers, all of these



materials have highly conjugated, extended structures that must be oxidized or reduced to create mobile charge carriers. However, it appears likely that completely new kinds of spinless charge carriers are involved in charge transport by oxidatively doped *trans*-polyacetylene (solitons) (42, 47) and by oxidatively doped polypyrrole (bipolarons) (48). To date, polyacetylene and polypyrrole are probably the best characterized of these conductive polymers. Nevertheless, for most of the known materials there are great uncertainties about the structures of the undoped and doped phases, polymer molecular weights, doping homogeneity, and the relative roles of intrachain versus interchain charge transport. As useful polymeric materials, which can be readily processed into films, foils, fibers, and other structures (49), most of these substances suffer in the doped state from being intractable, infusible, poorly flexible, and unstable in air. Efforts to improve the characteristics of the known conductive polymers include examples of ingenious alloying (50), doping (51), solvation (52), and functionalization (53) approaches, as well as the synthesis of completely new types of conducting polymers (54).

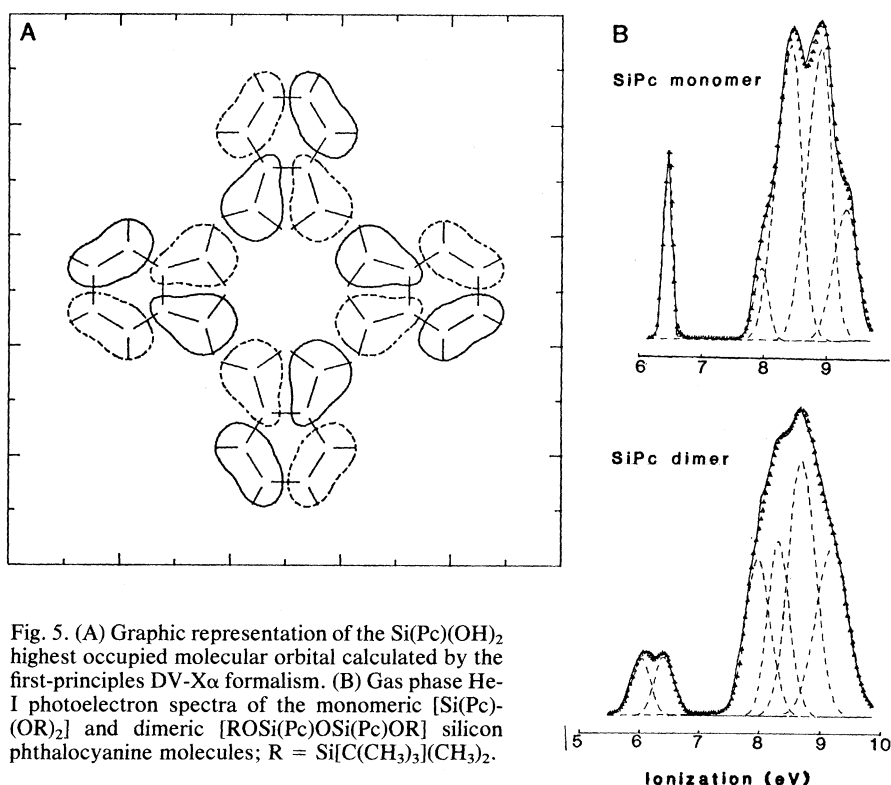
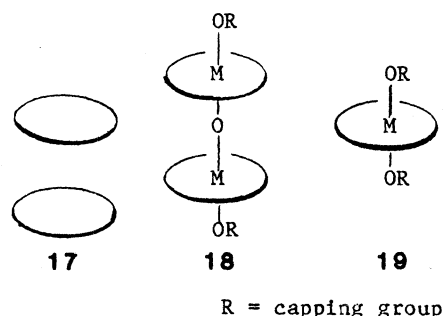


Fig. 5. (A) Graphic representation of the $Si(Pc)(OH)_2$ highest occupied molecular orbital calculated by the first-principles DV-X α formalism. (B) Gas phase He-I photoelectron spectra of the monomeric $[Si(Pc)(OR)_2]$ and dimeric $[ROSi(Pc)OSi(Pc)OR]$ silicon phthalocyanine molecules; $R = Si[C(CH_3)_3](CH_3)_2$.

Cofacial Assembly: Electronic Structure of Metallomacrocylic Polymers

Traditionally, quantum chemical approaches to understanding the electronic structures of molecular conductors have included either rigorous calculations for the individual molecular subunits together with imaginary cofacial dimers (17; see Fig. 1A) (55), or necessarily less rigorous but computationally more efficient (for instance, "crystal orbital") calculations for entire stacks (56). One very attractive feature of the $[M(Pc)O]_n$ architecture is that dimers which are actual fragments of the cofacially connected metallomacrocylic chain (18) are no longer imaginary, but can actually be synthesized, isolated, structurally characterized, and compared to the corresponding monomers (19) by a variety of



physical methods (57). The ultimate goal is to understand in depth the relationship between the collective properties of a multimolecular array and the nature of the local π - π and other electronic interactions as a function of various ground-state geometries and phonon-like excursions therefrom.

As a first step (57, 58) in probing $[M(Pc)O]_n$ electronic structure, calculations have been carried out for model phthalocyanines [for example, $Si(Pc)(OH)_2$], using the first-principles discrete variational local exchange (DV-X α) technique (59). In the case of simple arenes and cyclophanes, we have shown this method to reproduce molecular orbital energy orderings determined by photoelectron spectroscopy (which measures the energies of electrons ejected from the various molecular orbitals by an intense monochromatic light source) and details of optical spectra (60). The calculated amplitudes for the HOMO of $Si(Pc)(OH)_2$ are shown in Fig. 5A. From this result and the composition of the other molecular orbitals it can be seen that the conduction band of a partially oxidized $[Si(Pc)O]_n$ conductor will be composed principally of carbon $p\pi$ orbitals, with a great deal of the amplitude located near the macrocycle core. These results have several interesting ramifications. First,

when it is considered that each $Si(Pc)$ unit is ringed by a phalanx of hydrogen atoms, it can be seen that in the oxidized state, counterions are held at a considerable distance from the atoms and orbitals composing the conduction band structure (see Fig. 3B). This situation is considerably different from that in TMTSF (12, 61) and TTF (7, 8) salts, where chalcogen-counterion distances can be quite short and are thought to have significant effects on collective properties. The marked insensitivity of the $[Si(Pc^{p+})O]_n$ collective properties to the nature of the counterions must reflect this metrical and electronic structural situation. The DV-X α calculations also indicate little mixing of carbon π orbitals with either silicon or oxygen orbitals in the HOMO. Hence, it is unlikely that the $(-Si-O-)_n$ chains play any direct role in the conduction process.

The cofacial dimer $ROSi(Pc)OSi(Pc)OR$ {R = $Si[C(CH_3)_3](CH_3)_2$ }, which has $OSi(Pc)OSi(Pc)O$ structural parameters essentially identical to those of the corresponding $[Si(Pc^{p+})O]_n$ polymers (57), provides important new information on π - π electronic interactions. As can be seen in Fig. 1A, the HOMO-HOMO interaction energy in a dimer ($2t$) should be directly related to the tight-binding bandwidth in the corresponding polymer ($4t$).

Such a dimer "through-space" MO-MO splitting should be directly measurable by gas phase photoelectron spectroscopy. This would represent a unique, ex-situ method for assessing the bandwidth divorced from solid-state effects. Computer-analyzed, high-resolution gas phase He-I (21.2 eV) photoelectron spectra of the $Si(Pc)(OR)_2$ monomer and the corresponding dimer are shown in Fig. 5B. The lowest energy features correspond to electron ejection from the respective HOMO's, and it is clear that the dimer band is split. The splitting ($2t$) is 0.29(3) eV, which, as already explained, translates into a bandwidth of 0.58(6) eV. This result is in excellent agreement with a value (Table 1) of 0.60(6) eV obtained from a Drude analysis of the $\{[Si(Pc)O]_{1.1}\}_n$ reflectance spectrum (33). Moreover, a DV-X α calculation for the model dimer $HOSi(Pc)OSi(Pc)OH$ yields a bandwidth of 0.76 eV, which is in very good agreement with the above two experimental values (57). These conclusions, and recent successes (62) in using ab initio results to parameterize the electronic structure calculations for computational efficiency, indicate that truly meaningful connections between quantum chemical theory, chemical synthesis, and physical measurements will be possible in the future.

Processable, Conductive Polymeric Materials from Metallomacrocyces

The results discussed above provide a foundation from which to address a major problem in the area of electrically conductive polymeric materials. As already noted, many members of the current generation of substances exhibit severe limitations with regard to chemical-structural control at the molecular level, mechanical stability, air, water, and thermal stability, solubility, and processability. Most of the molecular and macromolecular phthalocyanine compounds discussed in this article have high environmental and thermal stability. Moreover, many are soluble without decomposition in strong acids; indeed, precipitation from acid solution is a common purification technique for phthalocyanines (26). These characteristics suggested a means of producing compositionally diverse, highly oriented conductive materials by a well-known processing technique: wet fiber spinning.

The tendency of rigid-rod polymers to spontaneously form oriented, liquid crystalline solids (63) suggested that $[Si(Pc)O]_n$ might be processed by extruding acid solutions into a precipitation medium. Fibers of the high-performance

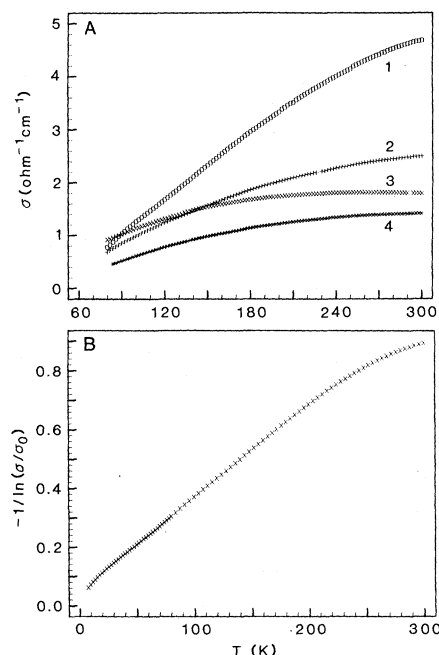
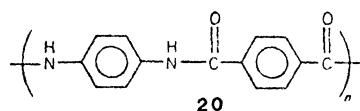


Fig. 6. (A) Variable-temperature four-probe electrical conductivity data for phthalocyanine-Kevlar hybrid fibers of composition: 1, $[Ni(Pc)(K)_{0.43}I_{1.56}]_n$; 2, $[Ni(Pc)(K)_{0.67}I_{1.07}]_n$; 3, $[Ni(Pc)(K)_{1.58}I_{1.27}]_n$; 4, $[Ni(Pc)(K)_{4.36}I_{1.66}]_n$; K = Kevlar monomer unit 20. (B) Variable-temperature four-probe electrical conductivity data for a $[Ni(Pc)(K)_{0.86}I_{1.71}]_n$ fiber plotted according to the fluctuation-induced tunneling model of charge transport.

aramid polymer Kevlar (20) are produced by just such a processing technique, and weight for weight have six times the modulus of steel (64). Indeed,



it was found that $\text{CF}_3\text{SO}_3\text{H}$ solutions of $[\text{Si}(\text{Pc})\text{O}]_n$ alone or in combination with Kevlar could be extruded to form relatively strong, oriented $[-\text{Si}-\text{O}-]_n$ and Kevlar chains are aligned along the extrusion direction] fibers. Doping can be carried out prior to or after fiber formation to yield air-stable, electrically conductive fibers (65). Even more interesting is the observation that environmentally stable, electrically conductive, molecular-macromolecular hybrid materials can be produced in an analogous fashion from molecular phthalocyanines and Kevlar (66). For $\text{Ni}(\text{Pc})$ -Kevlar- I_2 , the fibers consist of very small $\text{Ni}(\text{Pc})\text{I}$ crystalline regions dispersed in the Kevlar host. Both the $\text{Ni}(\text{Pc})\text{I}$ c axis and the Kevlar chain are preferentially oriented in the extrusion direction. Electrical conductivities are high (Fig. 6A) and variable-temperature data suggest that fluctuation-induced carrier tunneling is again operative (Fig. 6B). Studies of conductivity versus percentage $\text{Ni}(\text{Pc})\text{I}$ implicate percolation in the transport process (67), and measurements of mechanical properties evidence little degradation of the Kevlar tensile modulus at moderate $\text{Ni}(\text{Pc})\text{I}$ loadings (68). Further studies of these and related hybrid systems with other polymer hosts are in progress (69). However, it is already evident that the strategy of "marrying" the properties of well-characterized molecular metals to those of a robust, processable, orientable polymer host with complementary solubility characteristics offers an intriguing direction for the design of new electrically conductive, processable polymeric materials.

References and Notes

- For excellent introductions to condensed-matter science, see J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.* **20**, 1 (1976); H. M. Rosenberg, *The Solid State* (Clarendon, Oxford, 1975); C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, ed. 5, 1976).
- R. Comés, P. Bernier, J. J. Andre, J. Rouxel, "Proceedings of the International Conference on Low-Dimensional Conductors and Superconductors," Les Arcs-Bourg-Saint Maurice Savoie, France, 14-18 December 1982, *J. Phys. C* **3** (1983).
- J. S. Miller, Ed., *Extended Linear Chain Compounds* (Plenum, New York, 1982), vols. 1-3.
- A. J. Epstein and E. M. Conwell, Eds., "Proceedings of the International Conference on Low-Dimensional Conductors," Boulder, Colo., 9-14 August 1981, *Mol. Cryst. Liq. Cryst.*, parts A-F (1981-1982).
- L. Alcácer, Ed., *The Physics and Chemistry of Low-Dimensional Solids* (Reidel, Dordrecht, 1980).
- K. J. Wynne and G. B. Street, *Ind. Eng. Chem. Prod. Res. Dev.* **21**, 23 (1982); R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer, L. W. Shacklette, *Chem. Rev.* **82**, 209 (1982); G. Wegner, *Angew. Chem. Int. Ed. Engl.* **20**, 361 (1981); C. G. Duke and H. W. Gibson, in *Kirk-Othmer Encyclopedia of Chemical Technology* (Wiley, New York, ed. 3, 1982), vol. 18, pp. 755-793; R. B. Seymour, Ed., *Conductive Polymers* (Polymer Science and Technology Series, Plenum, New York, 1981), vol. 16.
- T. J. Marks and D. W. Kalina, in (3), vol. 1, pp. 197-331.
- J. B. Torrance, *Acc. Chem. Res.* **12**, 79 (1979); Z. G. Soos, *Ann. Rev. Phys. Chem.* **25**, 121 (1974).
- N. F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1974), chapters 1-5.
- J. B. Torrance, Y. Tomkiewicz, R. Bozio, O. Pecile, C. R. Wolfe, K. Bechgaard, *Phys. Rev. B* **26**, 2267 (1982); J. B. Torrance, J. J. Mayerle, K. Bechgaard, B. D. Silverman, Y. Tomkiewicz, *ibid.* **22**, 4960 (1980); S. Mazumdar and A. N. Bloch, *Phys. Rev. Lett.* **50**, 207 (1983); S. Mazumdar, S. N. Dixit, A. N. Bloch, *Phys. Rev. B* **30**, 4842 (1984).
- M. Weger, M. Kaveh, H. Gutfreund, *Solid State Commun.* **37**, 421 (1981); E. M. Conwell, *Phys. Rev. B* **22**, 1761 (1980).
- K. Bechgaard and D. Jérôme, *Sci. Am.* **247**, 52 (July 1982); D. Jérôme, *Adv. Phys.* **31**, 299 (1982); F. Wudl, *Acc. Chem. Res.* **17**, 227 (1984).
- A. J. Heeger, in *Highly Conducting One-Dimensional Solids*, J. T. Devreese, R. P. Evrard, V. E. van Doren, Eds. (Plenum, New York, 1979), chapter 3; A. J. Berlinsky, *Contemp. Phys.* **17**, 331 (1976).
- I. F. Schegolev and E. B. Yagubskii, in (3), vol. 2, pp. 385-434.
- J. M. Williams, A. J. Schultz, A. E. Underhill, K. Carneiro, in (3), vol. 1, pp. 73-118; T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.* **1**, 99 (1982); K. Krogmann, *Angew. Chem. Int. Ed. Engl.* **8**, 35 (1969).
- M. A. Cowie et al., *J. Am. Chem. Soc.* **101**, 2921 (1979); L. D. Brown et al., *ibid.*, p. 2937; A. S. Foust and R. Soderberg, *ibid.* **89**, 5507 (1967); H. J. Keller and K. Seibold, *ibid.* **93**, 1309 (1971).
- T. J. Marks, *J. Coatings Technol.* **48**, 53 (1976); J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, T. J. Marks, *J. Am. Chem. Soc.* **99**, 286 (1977); C. S. Schramm et al., *ibid.* **102**, 6702 (1980); J. Martinsen, R. L. Greene, S. M. Palmer, B. M. Hoffman, *ibid.* **105**, 677 (1983); D. R. Stojakovic, thesis, Northwestern University (1978).
- L.-S. Lin et al., *J. Chem. Soc. Chem. Commun.* (1980), p. 954; L.-S. Lin et al., in preparation.
- C. W. Dirk and T. J. Marks, *Inorg. Chem.* **23**, 4325 (1984).
- A. Gleizes, T. J. Marks, J. A. Ibers, *J. Am. Chem. Soc.* **97**, 3545 (1975).
- T. J. Marks, D. F. Webster, S. L. Ruby, S. Schultz, *J. Chem. Soc. Chem. Commun.* (1976), p. 444.
- T. J. Marks, *Ann. N.Y. Acad. Sci.* **313**, 594 (1978).
- D. W. Kalina, J. W. Lyding, M. T. Ratajack, C. R. Kannewurf, T. J. Marks, *J. Am. Chem. Soc.* **102**, 7854 (1980).
- H. Endres et al., *Ann. N.Y. Acad. Sci.* **313**, 633 (1978); J. S. Miller and C. H. Griffiths, *J. Am. Chem. Soc.* **99**, 749 (1977); W. E. Hatfield, in *Conductive Polymers*, R. B. Seymour, Ed. (Polymer Science and Technology Series, Plenum, New York, 1981), vol. 16, p. 57; A. J. Jircitano, M. C. Colton, K. B. Mertes, *Inorg. Chem.* **20**, 890 (1981); B. M. Hoffman and J. A. Ibers, *Acc. Chem. Res.* **16**, 15 (1983); L. W. ter Haar, W. E. Hatfield, M. Tsutsui, *Mol. Cryst. Liq. Cryst.*, in press; M. Mossayan-Deneux, D. Benlian, M. Pierrot, A. Fournel, J. B. Sorbier, *ibid.*, in press.
- R. C. Teitelbaum, S. L. Ruby, T. J. Marks, *J. Am. Chem. Soc.* **102**, 3322 (1980); *ibid.* **101**, 7568 (1979).
- F. H. Moser and A. L. Thomas, *The Phthalocyanines* (CRC Press, Boca Raton, Fla., 1983), vols. I and II.
- J. W. Lyding, T. Inabe, R. L. Burton, C. R. Kannewurf, T. J. Marks, *Bull. Am. Phys. Soc.* **29**, KH3 (1984); T. Inabe, J. W. Lyding, C. R. Kannewurf, T. J. Marks, *Mol. Cryst. Liq. Cryst.*, in press; T. Inabe et al., in preparation. Cell parameters at -100°C : $a = 13.928(5)$ and $c = 6.410(4)$ Å.
- Crystals are necessarily grown with scrupulously purified reagents in a thermostatted, vibration-free enclosure. Abrupt discontinuities in σ versus T data usually indicate poor integrity of electrical contact during measurements.
- D. B. Tanner, in (3), vol. 2, pp. 205-258; M. R. Madison, L. B. Coleman, R. B. Somoano, *Solid State Commun.* **40**, 979 (1981); B. A. Weinstein, M. L. Slade, A. J. Epstein, J. S. Miller, *ibid.* **37**, 643 (1981); J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, P. E. Seiden, *Phys. Rev. B* **19**, 730 (1979).
- H. Shiba, *Phys. Rev. B* **6**, 930 (1972); J. B. Torrance, Y. Tomkiewicz, B. D. Silverman, *ibid.* **15**, 4738 (1977).
- K. Mortensen, E. M. Conwell, J. M. Fabre, *ibid.* **28**, 5856 (1983); P. Delhaes, *Mol. Cryst. Liq. Cryst.* **96**, 229 (1983); C. Coulon et al., *J. Phys. C* **15**, 1059 (1982).
- P. J. Toscano and T. J. Marks, *Mol. Cryst. Liq. Cryst.*, in press; in preparation.
- B. N. Diel et al., *J. Am. Chem. Soc.* **105**, 1551 (1983); C. W. Dirk, K. F. Schoch, Jr., T. J. Marks, *ibid.*, p. 1539; C. W. Dirk, K. F. Schoch, Jr., T. J. Marks, in *Conductive Polymers*, R. B. Seymour, Ed. (Polymer Science and Technology Series, Plenum, New York, 1981), vol. 15, pp. 209-226; C. W. Dirk, E. A. Mintz, K. F. Schoch, Jr., T. J. Marks, *J. Macromol. Sci. Chem.* **16**, 275 (1981); T. J. Marks, K. F. Schoch, Jr., B. R. Kundalkar, *Synth. Met.* **1**, 337 (1980); K. F. Schoch, Jr., B. R. Kundalkar, T. J. Marks, *J. Am. Chem. Soc.* **101**, 7071 (1979); R. D. Joyner and M. E. Kenney, *ibid.* **82**, 5790 (1960).
- For studies of isoelectronic group IIIA $[\text{M}(\text{Pc})\text{F}]_n$ materials, see R. S. Nohr, P. M. Kuznesof, K. J. Wynne, M. E. Kenney, P. G. Siebenman, *J. Am. Chem. Soc.* **103**, 4371 (1981); for studies of $[\text{M}(\text{Pc})\text{L}]_n$ materials where L is a bridging organic ligand and M is a transition metal, see O. Schneider and M. Hanack, *Mol. Cryst. Liq. Cryst.* **81**, 273 (1982); B. N. Diel et al., *J. Am. Chem. Soc.* **106**, 3207 (1984); M. Hanack, *Chimia* **37**, 238 (1983).
- S. H. Carr, X. Zhou, T. Inabe, T. J. Marks, *Polym. Mater. Sci. Eng.* **49**, 94 (1983); X. Zhou, T. J. Marks, S. H. Carr, *ibid.* **51**, 651 (1984); *J. Polym. Sci. Polym. Phys. Ed.*, in press.
- X. Zhou, T. J. Marks, S. H. Carr, *Mol. Cryst. Liq. Cryst.*, in press; in preparation.
- S. Kirkpatrick, *Rev. Mod. Phys.* **45**, 574 (1973); C. H. Seager and G. E. Pike, *Phys. Rev. B* **10**, 1435 (1974).
- P. Sheng, *Phys. Rev. B* **21**, 2180 (1980); Y.-W. Park, A. J. Heeger, M. A. Dray, A. G. MacDiarmid, *J. Chem. Phys.* **73**, 946 (1980), and references therein.
- T. Inabe, J. W. Lyding, M. K. Moguel, C. R. Kannewurf, T. J. Marks, *Mol. Cryst. Liq. Cryst.* **93**, 355 (1983); T. Inabe, J. W. Lyding, M. K. Moguel, T. J. Marks, *J. Phys. (Paris)* **C3**, 625 (1983); T. Inabe, M. K. Moguel, T. J. Marks, R. L. Burton, J. W. Lyding, C. R. Kannewurf, *Mol. Cryst. Liq. Cryst.*, in press; T. Inabe, J. W. Lyding, M. K. Moguel, R. L. Burton, C. R. Kannewurf, T. J. Marks, in preparation.
- T. J. Marks, C. W. Dirk, K. F. Schoch, Jr., J. W. Lyding, in *Molecular Electronic Devices*, F. L. Carter, Ed. (Dekker, New York, 1982), pp. 195-210; M. K. Moguel and T. J. Marks, in preparation.
- M. K. Moguel, J. G. Gaudiello, W. J. Pietro, T. J. Marks, in preparation.
- J. C. W. Chien, *Polyacetylene* (Academic Press, New York, 1984); S. Etemad, A. J. Heeger, A. G. MacDiarmid, *Annu. Rev. Phys. Chem.* **33**, 443 (1982).
- A. F. Diaz and K. K. Kanazawa, in (3), vol. 3, pp. 417-442; G. Tourillon and F. Garnier, *J. Electroanal. Chem.* **135**, 173 (1982).
- L. W. Shacklette et al., *J. Chem. Phys.* **73**, 4098 (1980).
- J. F. Rabolt, T. C. Clark, K. K. Kanazawa, J. R. Reynolds, G. B. Street, *J. Chem. Soc. Chem. Commun.* (1980), p. 347; R. R. Chance et al., *ibid.* (1980), p. 348.
- K. Kaneto, K. Yoshino, Y. Inuishi, *Solid State Commun.* **46**, 389 (1983).
- W. P. Su, J. R. Schrieffer, A. J. Heeger, *Phys. Rev. B* **22**, 2099 (1980).
- J. C. Scott, P. Pfuger, M. T. Krounbi, G. B. Street, *ibid.* **28**, 2140 (1983).
- H. S. Kaufman and J. J. Falcetta, Eds., *Introduction to Polymer Science and Technology* (Wiley, New York, 1977).
- K. I. Lee and H. Jopson, *Makromol. Chem. Rapid Commun.* **4**, 375 (1983); M. E. Galvin and G. E. Wnek, *J. Polym. Sci. Polym. Chem. Ed.* **21**, 2727 (1983); O. Niwa and T. Tamamura, *J. Chem. Soc. Chem. Commun.* (1984), p. 817; M. A. DePaoli, R. J. Waltman, A. F. Diaz, J. Bargon, *ibid.*, p. 1015.
- W. Wernet, M. Monkenbusch, J. Wegner, *Makromol. Chem. Rapid Commun.* **5**, 157 (1984).
- M. Aldissi and R. Liepins, *J. Chem. Soc. Chem. Commun.* (1984), p. 255.
- E. T. Kang, P. Ehrlich, A. P. Bhatt, W. A. Anderson, *Appl. Phys. Lett.* **41**, 1136 (1982).
- See, for example, S. F. Wellinghoff, T. Ke-

- drowski, S. Jeneke, H. Ishida, *J. Phys. (Paris)* C3, 677 (1983); S. E. Tunney, J. Suenaga, J. K. Stille, *Macromolecules* 16, 1398 (1983).
55. P. M. Grant, *Phys. Rev. B* 27, 3934 (1983); *ibid.* 26, 6888 (1982); F. Herman, *Phys. Scr.* 16, 303 (1977); F. Herman, D. R. Salahub, R. P. Messmer, *Phys. Rev. B* 16, 2453 (1977).
56. M.-Y. Whangbo, in (3), vol. 2, pp. 127-158; C. L. Honeybourne, *J. Chem. Soc. Chem. Commun.* (1982), p. 744; M. C. Böhm, *Solid State Commun.* 45, 117 (1983); M.-H. Whangbo and K. R. Stewart, *Isr. J. Chem.* 23, 133 (1983); S. Alvarez and E. Canadell, *Solid State Commun.* 50, 141 (1984); E. Canadell and S. Alvarez, *Inorg. Chem.* 23, 573 (1984).
57. K. A. Doris, M. A. Ratner, D. E. Ellis, B. Delley, T. J. Marks, *Bull. Am. Phys. Soc.* 28, 245 (1983); E. Ciliberto *et al.*, *J. Am. Chem. Soc.* 106, 7748 (1984); N. S. Hush and A. S. Cheung, *Chem. Phys. Lett.* 47 (1977).
58. W. J. Pietro, D. E. Ellis, T. J. Marks, M. A. Ratner, *Mol. Cryst. Liq. Cryst.* 105, 273 (1984).
59. E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* 2, 41 (1973); Z. Berkovitch-Yellin, D. E. Ellis, M. A. Ratner, *ibid.* 62, 21 (1981); B. Delley and D. E. Ellis, *J. Chem. Phys.* 76, 1949 (1982); A. Rosen *et al.*, *ibid.* 65, 3269 (1975).
60. K. A. Doris, M. A. Ratner, D. E. Ellis, T. J. Marks, *J. Phys. Chem.* 88, 3157 (1984); K. A. Doris, D. E. Ellis, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* 106, 2491 (1984).
61. J. M. Williams *et al.*, *J. Am. Chem. Soc.* 105, 643 (1983).
62. W. J. Pietro, M. A. Ratner, T. J. Marks, in preparation.
63. P. J. Flory, *Proc. R. Soc. London* 234, 73 (1956); *J. Polym. Sci.* 49, 105 (1961).
64. J. R. Schaefgen *et al.*, in *Ultra-High Modulus Polymers*, A. Cifferi and I. M. Ward, Eds. (Applied Science, London, 1979), pp. 173-201; E. E. Magat and R. E. Morrison, *ChemTech* 6, 702 (1976); G. B. Carter and V. T. J. Schenk, in *Structure and Properties of Oriented Polymers*, I. M. Ward, Ed. (Wiley, New York, 1976), chapter 13; M. G. Dobb and J. D. McIntyre, *Adv. Polym. Sci.* 60-61, 61 (1984).
65. T. Inabe, J. W. Lyding, M. K. Moguel, T. J. Marks, *J. Phys. (Paris)* C3, 625 (1983); T. Inabe, J. W. Lyding, T. J. Marks, *J. Chem. Soc. Chem. Commun.* (1983), p. 1084.
66. T. Inabe, J. F. Lomax, J. W. Lyding, C. R. Kannewurf, T. J. Marks, *Synth. Met.* 9, 303 (1984); T. Inabe *et al.*, *Macromolecules* 17, 262 (1984).
67. T. Inabe and T. J. Marks, in preparation.
68. K. J. Wynne, A. E. Zachariades, T. Inabe, T. J. Marks, in preparation.
69. W.-B. Liang and T. J. Marks, unpublished results.
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Laser Probing of Chemical Reaction Dynamics

Stephen R. Leone

The advent of lasers has heralded revolutions in almost all fields of technical endeavor (1). In chemistry, much of the original excitement centered on the possibilities for laser-driven, bond-selective synthesis and isotope separation (2). While a few such schemes for laser-selective chemistry do appear promising, an even greater number of remarkable side benefits have arisen from the intense activity in this field. Tremendous progress in molecular spectroscopy has been made possible by the availability of highly developed tunable laser sources. Another area of rapid progress is in the sophisticated understanding of chemical reaction dynamics which has been obtained through laser studies of state-selective reactions. It is the latter field which is the subject of this article.

Chemical reaction dynamics is a relatively new field (3, 4). It is, in essence, a modern-day approach to the study of chemical kinetics, or the rates at which reactions proceed. Rather than merely measuring the rates of chemical reac-

tions under various conditions, chemists are now accustomed to achieving a much finer level of detail. With the availability of laser sources for selective excitation and detection, it is possible to infer many things about the dynamics, that is, the particular motions, that the molecules are likely to undergo in the chemical reaction. It is possible to interrogate, or probe, the specific forms of excitation that best lead to chemical reaction, for example, vibrational, rotational or translational motion, or electronic excitation. Thus, the study of gas-phase, state-resolved dynamics offers many answers to questions of fundamental interest in chemical reactivity.

The laser has played a central role in the development of these studies of chemical reaction dynamics. However, laser sources are not the sole means of studying chemical processes with state-selected detail. For many years, complementary techniques of spectrally resolved infrared and visible chemiluminescence and molecular beam reactive scattering have also provided exceedingly detailed results on reaction dynamics (5, 6). Lasers have, however, provided some of the most sensitive methods for detection of molecular states, as well as the means to select specific reagent

states with high resolution. Through the inherent polarization of their light, lasers can be used to study numerous chemical reactions as a function of the geometric alignment of reagents or products. With the high resolution of lasers, it is even possible to probe the differences in reactivity of closely spaced spin-orbit states. Lasers even provide the capability to probe the exceedingly short-lived transition states of simple reactions.

Data from experiments on state-selected chemical dynamics now comprise a large body of knowledge from which it is possible to infer many things about the dynamics. It is important to emphasize, though, that even a series of the most cleverly designed experiments together with appropriate theoretical interpretation (7) can only lead to powerful inferences concerning the specific motions that the molecules undergo. Nearly all experiments interrogate the system at a time that is either well before the reaction, by specific reagent state preparation, or well after the transition state of the reaction, by probing the final product states. Most of our simple pictures of the dynamical motions have been derived from this powerful combination of experimental facts, inference, and theory. Experimentalists would like to obtain even more concrete information, rather than rely so heavily on inference. This is why the possibility of more directly probing the transition states of reactions has intrigued so many investigators.

General Methods of Laser Probing

An apparatus for studying chemical reaction dynamics through either selective laser excitation of reagents or laser detection of product states can have many variations (4, 8). However, a num-

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