

MOLECULAR ELECTRONICS

This paper provides an overview of research in the field of molecular electronics and of the molecular electronics research program at APL. In the past 20 years, organic molecular crystals have been developed that span the range from electrical insulators to room-temperature metals to superconductors. Conducting organic polymers have been prepared in a variety of forms in which electrical conductivity can be systematically controlled over a range of 10 orders of magnitude. Several novel technical applications are described.

INTRODUCTION

Molecular and polymeric materials are an essential part of present-day electronics and computers. It is estimated that over 2.4 billion pounds of organic and polymeric materials are used annually by the U.S. electronics industry. Their main application is as insulating and structural support materials.¹ Another important application is for lithographic resists for integrated circuit fabrication in both large-scale integration and very-large-scale integration applications.² However, the active elements of almost all electronic devices and computers, namely conductors and semiconductors, are fabricated from metals or inorganic materials because of their versatility, speed, stability, reproducibility, and the familiarity of the electronics industry with their manufacturing processes and electronic characteristics.

WHAT IS MOLECULAR ELECTRONICS?

The rapid development of the semiconductor industry has been marked by the increasing density and complexity of semiconductor chip circuitry. Considerable attention has been given to the inherent problems associated with increasing the density of integrated circuits. In the future, fundamental physical considerations will set limits on the size and properties of such circuits that can be manufactured by conventional techniques. Some of the limitations arise from processing considerations, materials properties, and operational constraints.

Although semiconductor technology has not yet reached its full potential, future generations of computers may require revolutionary technologies based on totally different types of materials to increase memory and processing capabilities. One possible class of materials that may find applications in information processing and storage is carbon-based (organic) semiconductors and conductors.

The replacement of inorganic semiconductors and metals by organic macromolecular, polymeric, or even biological materials that control or modify electrical and/or optical signals has recently been termed mole-

cular electronics. This new interdisciplinary field, combining organic chemistry, solid-state physics, and microelectronic engineering, may revolutionize electronic and computer speed and capacity by making devices from complex molecular structures.

Organic compounds and polymers are a viable alternative to the traditional inorganics because of their extremely small size, abundance, diversity, ease of fabrication, and potential low cost. For example, the typical dimensions of organic molecular structures (10 to 100 angstroms) are two to three orders of magnitude smaller than existing and proposed devices developed by current state-of-the-art lithographic techniques. Organic semiconductors offer an additional feature in that it is possible to control the electronic and optical properties of an organic device by altering or tailoring the organic molecular structure before fabricating the device. In molecular electronic devices, the electronic and/or optical properties are locked into the molecular structure instead of being fabricated by the processing technique. This feature, called molecular architecture or molecular engineering, may greatly simplify future manufacturing processes by reducing the number of fabrication steps, hence increasing production yield.

Current research in molecular electronics centers on designing and fabricating new synthetic molecular materials, evaluating them, and using them in novel technical applications. Research is currently divided into two areas: molecular crystals, including monomeric compounds and organic charge-transfer complexes; electroactive polymers, sometimes called plastic metals or synmetals (synthetic metals), including materials such as doped polyacetylene, polypyrrole, and poly(p-phenylene).

MOLECULAR CRYSTALS: AN OVERVIEW

Typically, crystalline molecular materials are made by combining two very different classes of compounds called donors and acceptors. One, if not both, of these is usually a flat ringlike structure having a carbon backbone; it may contain elements such as sulfur, selenium, tellurium, nitrogen, and hydrogen in its

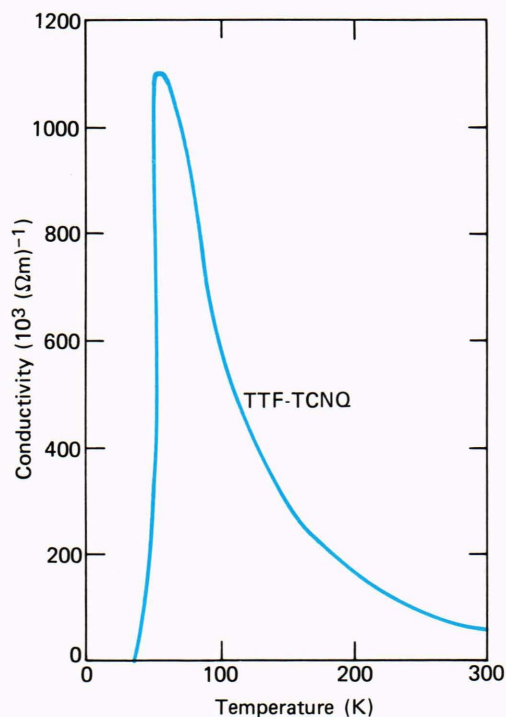


Figure 3—Electrical conductivity of TTF-TCNQ as a function of temperature.

ductivity in TTF-TCNQ, many new synthetic metals were prepared, and an extensive theoretical interpretation of the relationship between molecular structure and the organic metallic state was developed.

Soon after metallic conductivity was achieved in organic solids, speculation arose that organic materials might also exhibit superconductivity. That search was successful in 1979 when organic superconductivity was observed in a charge-transfer complex containing TMTSF.⁶ TMTSF, the chemical acronym for tetramethyltetraselenafulvalene, is a structural analog of TTF (Fig. 2). When TMTSF was complexed with the anion hexafluorophosphate (PF_6^-), a new organic salt was produced that superconducts at a critical temperature (T_c) of 0.9 K and an applied pressure of 12 kilobars. Not long after, a similar complex, $(\text{TMTSF})_2\text{ClO}_4$, was found to undergo a transition to a superconducting state at a T_c of 1.2 K; this salt exhibits superconductivity at ambient pressure.⁷ The onset of superconductivity in these organic materials is believed to be associated not with carbon p - π interactions but rather with the two-dimensional overlap of selenium atomic orbitals. X-ray crystallographic analysis reveals that there are several close selenium interstacking and intrastacking distances.

Superconductivity at higher critical temperatures and lower applied pressures has since been reported by several research groups. In 1984, β -(BEDT-TTF)₂I₃ (Fig. 2), a complex salt with two-dimensional sulfur-sulfur orbital interactions, was found to undergo a superconducting transition with a T_c of 1.4 K at ambient pressure. Its critical temperature can be raised to about 8 K when the pressure is increased to

12 kilobars.⁸ By comparison, the inorganic superconductor with the highest known critical temperature (24 K) is an alloy of germanium and niobium; superconductivity was first reported in inorganic materials 68 years before the first report in organics.

Although the discovery of superconductivity in organic solids is still too new to have led to commercial applications, these findings clearly demonstrate that organic materials can span a range of electrical conductivity from insulating to superconducting.

CONDUCTING ORGANIC POLYMERS: AN OVERVIEW

The study of electronic transport in organic polymers is more than 30 years old. The first organic polymers prepared were electrically insulating with conductivities as low as 10^{-14} (ohm-centimeter)⁻¹. The insulating properties result because all electrons in the polymer are localized in the hybrid-atom molecular orbital bonds, i.e., the saturated carbon framework of the polymer. The insulators, which include polymers such as poly(*n*-vinylcarbazole) or polyethylene, have extremely large band gaps; energies as high as 10 electronvolts are required to excite electrons from the valence to the conduction band (Fig. 4). Electrical applications of such organic polymers are limited to insulating or supporting materials where low density and excellent processing and mechanical properties are desirable.

Semiconducting organic polymers, sometimes called electroactive polymers, exhibit conductivities from 10^{-9} to 10^2 (ohm-centimeters)⁻¹ (Fig. 4). They can be classified into three groups on the basis of their chemical structure: (a) composite polymers that combine graphite-like structures with metal particles (the concentration of metal particles may often reach 85 percent by weight); (b) polymeric charge-transfer complexes in which a cationic species, often a metal ion, or an anionic species, such as the triiodide ion (I_3^-), or an organic anion, such as TCNQ^- or TNF^- (trinitrofluorene), interacts with the polymer chain; and (c) conjugated polymers that show semiconducting properties because the π -orbital overlap along the unsaturated polymer chain allows electronic conduction.

High electrical conductivity has been observed in several conjugated polymer or polyene systems (Fig. 4). The first and simplest organic polymer to show high conductivity was doped polyacetylene. In the doped form, its conductivity is greater than 200 (ohm-centimeters)⁻¹.⁹ Although polyacetylene was first prepared some time ago, it was not until 1977 that this polyene was modified by combining the carbon chain with iodine and other molecular acceptors to produce a material with metallic conductivity.

Polyacetylene consists of a linear chain of carbon atoms with alternating single and double bonds. It has one hydrogen atom attached to each carbon atom (Fig. 5), and each carbon atom has four valence electrons surrounding the nucleus. Three of the electrons are

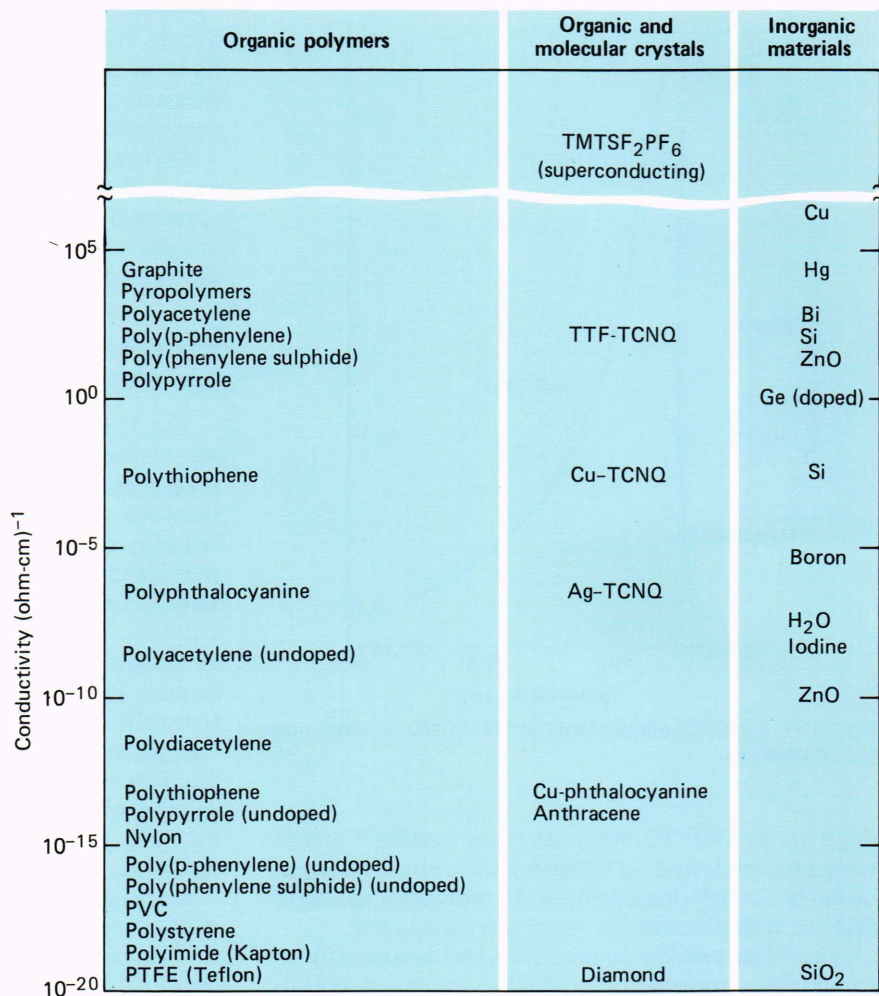


Figure 4—Compilation of electrical conductivities.

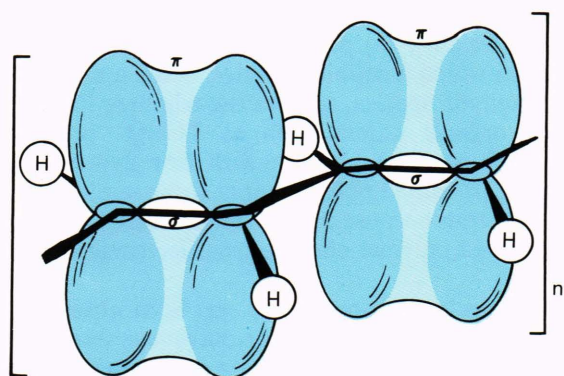


Figure 5—Hybrid molecular orbitals in polymer chains.

used to form σ bonds to hydrogen and adjacent carbon atoms. The electrons reside in sp^2 -type hybrid orbitals. The fourth electron, however, is in a p_z bonding orbital and is not directly involved in σ bonding. These p_z atomic orbitals protrude from each carbon atom approximately normal to the carbon chain and form π -type bonds with neighboring carbon atoms to yield an extended molecule orbital. The π -bonded molecular orbitals form a conduction band as is found

in traditional semiconductors and metals. In fact, the band gap for pristine polyacetylene is reported to be in the range of 1.4 to 1.9 electronvolts.¹⁰

Polyacetylene is prepared in a one-step synthesis from its monomer, gaseous acetylene. The product forms as a thin film, has a silver-gray metallic luster like aluminum foil, and can exist in either of two isomeric forms (cis or trans). If the reaction temperature is below 250 K, the film is entirely in the cis form (see Fig. 6); if the temperature is above 375 K, a trans isomer is produced. When the temperature of the cis isomer is elevated, a cis-trans isomerization occurs, converting all of the polymer to the more stable trans product. Examination of the polyacetylene films reveals that they are microcrystalline and that the structure is composed of a network of randomly oriented fibrils. The highly anisotropic electrical conductivity of crystalline polyacetylene before doping ranges from 10^{-5} to 10^{-8} (ohm-centimeter)⁻¹.¹¹

The doping of polyacetylene is not performed in the conventional manner, as, for example, silicon might be doped with minute amounts of arsenic or phosphorus. Rather, in the context of the conducting polymer field, doping refers to the chemical or electrochemical introduction of large amounts of acceptor or do-

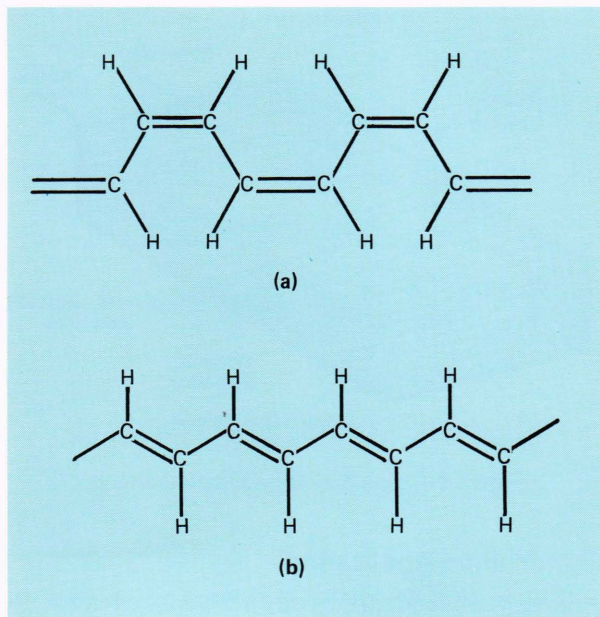


Figure 6—Polyacetylene. (a) Cis form and (b) trans form.

nor species into the polymer chain to produce carbonium ions or carbon ions, respectively. For example, when polyacetylene is exposed to strong electron acceptors such as iodine, bromine, or arsenic pentafluoride (AsF_5), the conductivity rises more than 12 orders of magnitude, and the product exhibits a p-type conductivity (Fig. 7).¹⁰ If the polymer is combined with metal ions such as sodium, lithium, potassium, or silver, an n-type conductivity is observed.

The actual nature of the electrical conductivity in doped and undoped polyacetylene is still highly speculative. Several possible theories have been developed to explain the properties of these polymers. In an ideal infinite chain length of polyacetylene, the π electrons would be expected to form a half-filled conduction band leading to one-dimensional metallic behavior. In reality, however, an infinite length of $(\text{CH})_x$ units would be an intrinsic semiconductor with an electron band gap of approximately 2 electronvolts because the alternating double-bond/single-bond structure has two units per unit cell instead of one; hence, a semiconductor band gap is formed through a Peierls metal-to-semiconductor transition.

An interesting theory invoked to explain the properties in undoped and doped polyacetylene involves soliton waves.¹² If two segments of the undoped polymer chain, both in the lowest energy or ground state, are out of phase by one carbon unit, a bond defect or soliton exists at the kink in the chain where the two segments meet; i.e., a shift in bond direction occurs. This neutral soliton can migrate along the polymer chain, thus displacing the electronic configuration of the π electrons as it moves. A soliton distortion can be spread over as many as 15 carbon atoms. In heavily doped polyacetylenes, the chemical dopant (acceptor or donor) produces an ionized soliton at the point in the chain where charge transfer takes place. This

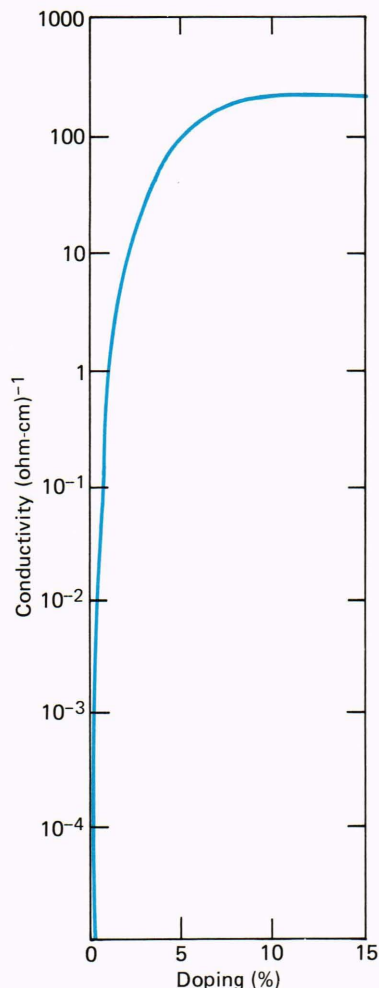


Figure 7—Electrical conductivity of trans-polyacetylene film as a function of doping concentration.

charged soliton, like the neutral soliton, can also displace the electronic configuration as it moves down the polymer chain.

In the 10 years since the discovery of the first highly conductive organic polymer, work on numerous other conductive polyene systems (Fig. 4), including poly(p-phenylene) (PPP), poly(p-phenylene sulfide) (PPS), polypyrrole (PP), and poly(p-phenylene vinylene) (PPV), has proved that, as a class of materials, the unsaturated conjugated organic polymers can be in an electrically conducting form and still maintain the low density, processibility, and elasticity that make polymers unique materials.

One of the most scientifically and technologically studied of the new organic polymers is polypyrrole. It can be prepared electrochemically on metal electrodes in solution from its planar aromatic monomer pyrrole and an electrolyte such as Et_4NClO_4 (tetraethylammonium perchlorate) or Et_4NBF_4 (tetraethylammonium tetrafluoroborate) (Fig. 8). The highly stable, flexible films of polypyrrole produced by the one-step electro-oxidation have room temperature p-

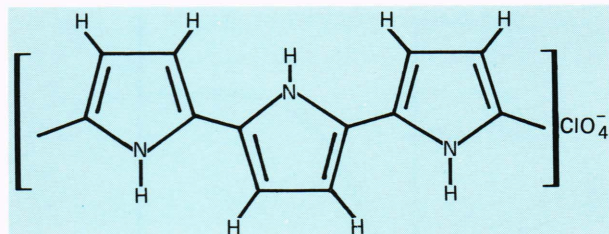


Figure 8—Chemical structure of conductive polypyrrole.

type conductivities ranging from 10 to 100 (ohm-centimeters)⁻¹.¹³

Electron micrographs show that the polymer is densely packed with no evidence of a fibrillar structure. The proposed structure of polypyrrole is shown in Fig. 8. The polymer is believed to be formed by linking pyrrole rings at the α -carbon positions. Each ring contains four carbon atoms, three hydrogen atoms, and one nitrogen atom, and the rings appear to carry a partial positive charge with a ratio of pyrrole to counter anions of about 4:1.

In addition to showing high electrical conductivity, polypyrrole films can be electrochemically driven or “switched” repeatedly between a black, highly conductive, 100 (ohm-centimeter)⁻¹ oxidized form and a yellow, nonconducting neutral form. The switching rate for thin films is approximately one cycle per second.¹⁴

APPLICATIONS OF MOLECULAR ELECTRONIC MATERIALS

Molecular electronic materials show great promise in a wide range of applications. Many of these uses will be in direct competition with existing inorganic materials, while the novel properties reported in many molecular crystals and polymers ensure that entirely new applications and technologies will emerge from the field.

A partial list of applications currently under development includes capacitors, transistors, batteries, memory devices, chemical sensors, transducers, and plastic wiring. A complete description of each application and material is lengthy; however, three novel areas of application are described briefly below to illustrate the role these materials may play in future technologies.

Lightweight Rechargeable Batteries

Highly conductive organic polymers are being evaluated as electrode materials in both disposable and rechargeable batteries. When two sheets of polyacetylene or poly(*p*-phenylene) are separated by an insulating film of polycarbonate saturated with electrolyte (lithium perchlorate) and are completely encapsulated in a plastic casing, a “plastic” battery can be made (Fig. 9).¹⁵ The two sheets of polyacetylene or poly(*p*-phenylene) act as the anode and cathode for the battery. These novel polymeric batteries have several notable features: they are rechargeable, are one-tenth the weight of a conventional lead-acid battery, and are flexible enough to fit into a variety of configurations.

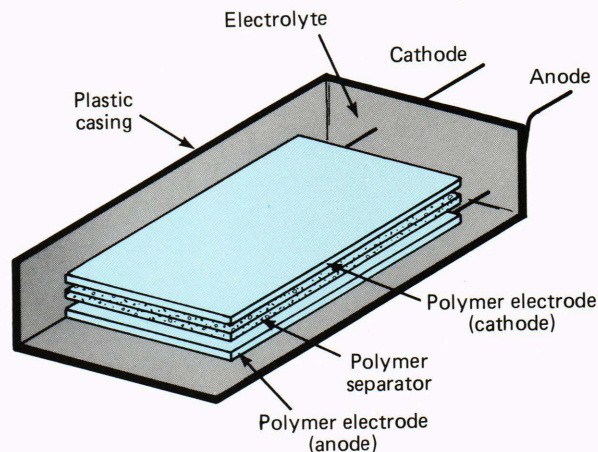


Figure 9—Schematic of a plastic battery.

Photovoltaic Applications

Several conductive polymers are being tested for use as coatings on photovoltaic and photoelectroactive semiconductors in solar energy conversion. As an example, a film of conductive polypyrrole used as an overcoat on the activated semiconductor cadmium sulfide can enhance the evolution of oxygen at the electrode/electrolyte surface and thereby increase the lifetime of the cell a million times.¹⁶

In another example, a photoelectrochemical cell has been fabricated using polyacetylene as the active photoelectrode. In a Schottky barrier configuration, this solar cell can deliver an open-circuit voltage of 0.3 volt and a short-circuit current of 40 microamperes per square centimeter under an illumination equivalent to one sun.¹⁷ Polyacetylene may be an attractive material for solar cells because studies suggest it is a direct band-gap semiconductor with an optical band gap matching the solar spectrum.

Electrochromic Polymer Displays

An electrochromic display is a thin solid-state device that changes color reversibly when subjected to a small electrical potential. This new display technology has several advantages over liquid crystal displays currently in use: low power consumption, good optical contrast, a wide viewing angle, and an all-solid-state construction.

In a unique application of charge-transfer organic materials, electrochromism has been reported in a thin-film system consisting of a polymer, polymethacrylonitrile (PMCN), and organic redox materials such as TTF or pyrazoline.¹⁸ An electrochromic display cell structure using these materials is shown in Fig. 10a. It consists of a transparent glass electrode, the electrochromic polymer system, and a thin gold semitransparent counterelectrode.

When the structure is electrically biased (1.0 to 3.5 volts), the optical density of the film changes (i.e., the color changes) because the organic complex undergoes a reversible electron transfer reaction from a neutral form to an oxidized form (Fig. 10b). Using a TTF re-

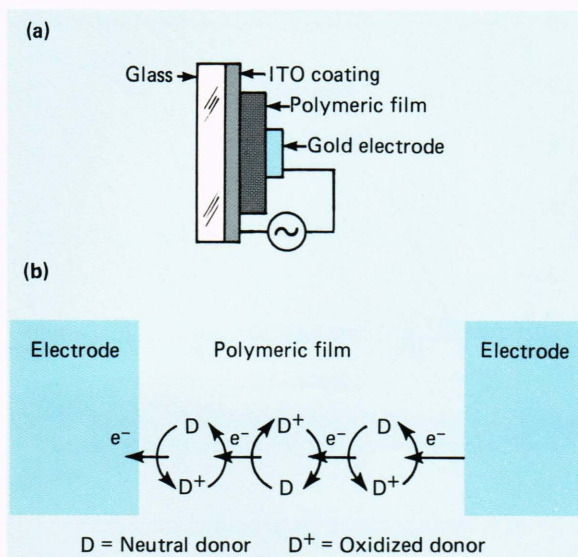


Figure 10—(a) Cell structure of an electrochromic display. (b) Electrochromic mechanism in polymeric film.

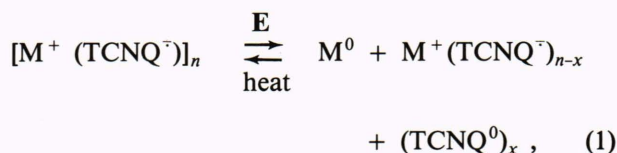
dox compound, the color of the display changes from yellow to bright red, while pyrazoline changes from transparent to yellow. Multicolor displays are also being studied that use combinations of organic compounds that exhibit multiple coloration at different applied potentials.

MOLECULAR ELECTRONICS AT APL

Realizing the great potential of molecular electronics, research at APL has focused on synthesizing and evaluating a wide range of organic and polymeric materials with useful electronic, optical, or magnetic properties. Many of the more promising materials have been further investigated in a variety of conventional and novel device configurations. It is anticipated that, as a result,³ it will be possible to develop materials, techniques, engineering, and necessary basic scientific principles for future technological development in the area of molecular electronics.

Our current explorations have centered on the design, synthesis, and fabrication of bistable switching materials that can be used to store and process information. The switching materials are used in devices that rely on very fast, reversible, electron transfer reactions to change the solid-state properties of thin-film structures. The logic or memory operation is performed within the confines of the organic molecular structure of the device. Three distinct classes of bistable devices have been demonstrated using organic materials based on charge-transfer complexes of the TCNQ type: optical, electrical, and optoelectronic switches.¹⁹⁻²⁵ All are activated by electric fields induced by applied potentials, optical beams, or various combinations of the two.

It has been postulated that the effect of the applied electric field on an organometallic charge-transfer salt (e.g., copper-TCNQ) is to induce a phase transition to a nonstoichiometric complex salt, to neutral acceptor molecules (TCNQ⁰), and to metal atoms:



where M can be silver, copper, sodium, potassium, or lithium.

The reaction shown in Eq. 1 is reversible, and the thermodynamically favored initial phase (left side of the equation) can be readily reformed by heating the complex phase (right side of the equation) of the salt. The observed changes in the electrical and/or optical properties of devices fabricated from these organic materials are direct consequences of the electric-field-induced reaction shown in Eq. 1.

Various diagnostic techniques including infrared, Auger, X-ray, photoelectron, and Raman spectroscopy have been applied to specimens from the copper-TCNQ (CuTCNQ) family to validate the mechanism shown in Eq. 1.²¹ Raman spectroscopy is a useful method for determining changes in oxidation state because it can monitor changes in the vibration energies (frequency) of molecules. The frequency changes are measured in wave numbers, centimeter⁻¹, a unit proportional to the energy of a vibrational mode. For example, the strong Raman bands observed in the switched and unswitched CuTCNQ films can be used to differentiate the two species (see Fig. 11). The TCNQ ν_4 (C=C stretching) Raman bands are strongly affected by the π -electronic structure of TCNQ. The fully charged charge-transfer species has a maximum at 1451 centimeter⁻¹, whereas in the neutral TCNQ species, the band is shifted to 1375 centimeter⁻¹. Using this technique,²⁶ it is easy to distinguish the switched from the unswitched complex.²⁶⁻³¹

Photochromic Properties

Spectroscopic techniques reveal that two types of reversible switching effects in the organometallic materials are induced by external electric fields at optical frequencies. The type of effect observed depends on the irradiance (expressed in watts per square centimeter) of the incident optical beam. At low irradiance levels, optoelectronic switching from a high to a low electrical impedance state can be induced, while at increased irradiance levels, high optical contrast patterns can be generated directly on the thin-film material. In the first case, small amounts of neutral donor and acceptor molecules are produced during the irradiation. They remain locked in the crystal structure of the thin-film material and readily recombine when heated to form the original charge-transfer salt. In the second case, the higher irradiance levels produce macroscopic amounts of neutral donors and acceptors that are visible to the unaided eye. Under these high irradiance levels, the original crystal structure is often distorted, and increased heating is required to reform the original donor-acceptor complex.

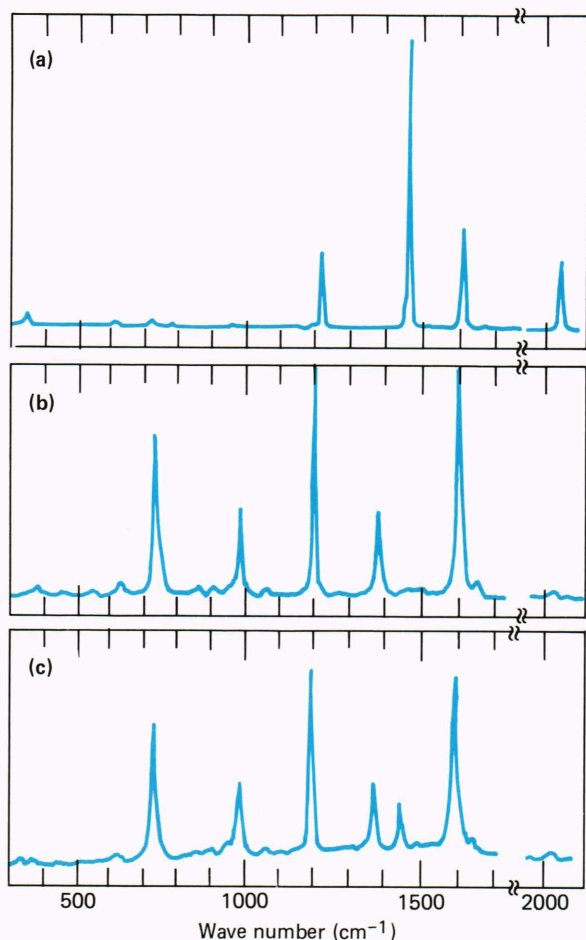


Figure 11—Raman spectra. (a) Neutral TCNQ; (b) CuTCNQ film; (c) CuTCNQ film after exposure to an argon-ion laser.

An area of significant interest is the change in the macroscopic optical properties of these organometallic materials in an electromagnetic field. The potential for large changes in transmission and reflection in CuTCNQ and other members of the family makes these compounds prime candidates for high-speed photochromic filters.³² The films undergo a change from their blue and violet colors to a rather pale yellow that is characteristic of neutral TCNQ. As is shown in Fig. 12, a typical CuTCNQ film formed by solid-state diffusion is rather poorly transmitting from the mid-visible to the near-infrared region in the vicinity of 1100 nanometers, and there is a substantial increase in transmission extending into the infrared. Upon irradiating the CuTCNQ film with an Nd:YAG laser at 532 nanometers, one observes a significant increase in transmission throughout the spectrum ranging from the mid-visible to the infrared. Dramatic increases are observed in the red end of the spectrum and in the near infrared, regions that are of particular interest with respect to many of the principal laser sources.

The transmission properties of silver-TCNQ (AgTCNQ) film are shown in Fig. 13. In contrast to the changes observed in CuTCNQ, the switched and unswitched films are quite similar in the infrared por-

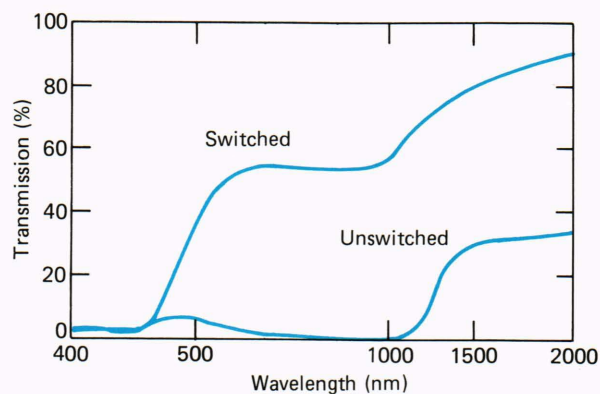


Figure 12—Typical CuTCNQ transmission switch: 30-millijoule pulse from a frequency-doubled Nd:YAG laser.

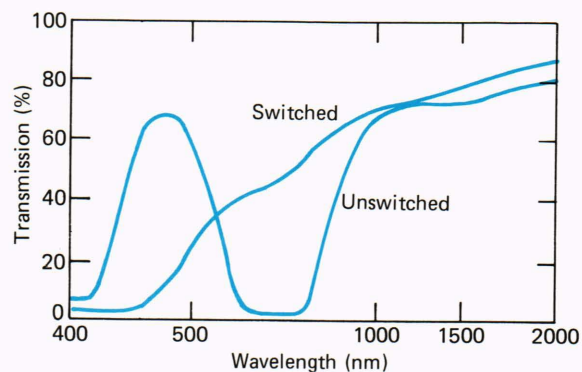


Figure 13—Typical AgTCNQ transmission switch: 45-millijoule pulse from a frequency-doubled Nd:YAG laser.

tion of the spectrum. Large changes in transmission are noted in the visible part of the spectrum between 400 and 600 nanometers. The switched AgTCNQ becomes strongly transmitting in a band centered at 500 nanometers, while the unswitched film is poorly transmitting in the same region.

An Erasable Compact Disk

The interaction of laser radiation with matter in optical storage systems has received considerable attention. Different media, including photographic films, photoresists, photosensitive polymers, photochromics, thin amorphous films, and electro-optic materials, have been proposed as optical storage systems.³³ The mechanism of optical storage by means of interaction with laser light varies considerably. In all of these systems, however, the process of optical storage relies on changes in the optical density, surface morphology, magnetism, or refractive index of the photosensitive material. Present optical storage systems have been applied in the fields of document storage, audio and video reproduction, and direct data collection. Optical storage systems have not seen widespread application in computer technology because most optical media are not erasable.

We have recently developed an erasable optical recording medium using the electric-field-induced switch-

ing effect in films of copper or silver complexed with the electron acceptors tetracyanoethylene (TCNE), tetracyanonaphthoquinodimethane (TNAP), TCNQ, and derivatives of TCNQ (Fig. 2). The switching in these materials is reversible and fast, with switching times of less than 10 nanoseconds in static switching experiments.

Figure 14 shows a cross section of a typical erasable optical disk medium using one of the TCNQ family of organometallic materials. An approximately 2000-angstrom-thick organic charge-transfer salt is deposited on an aluminum, glass, or polycarbonate supporting base using a solid-state diffusion process. The solid-state diffusion deposition guarantees that the organic film will be uniform over a wide area and that the size of the individual crystallites (less than 1 micrometer) will be minimized. The disk is complete when a thin protective polymer overcoat is cast over the organometallic layer.

The disk can be placed in an optical recording, playback, and erasure system. Figure 15 is a diagram of a typical laser diode optical recording system. Information on the spinning disk is recorded, read, and erased by modulating the intensity of the laser. The laser is focused to a diameter of less than 1 micrometer on the disk by means of a series of collimating and objective optics, providing information storage of 10^8 to 10^9 bits per inch. To record information, the intensity of the modulated laser is increased above the power threshold of the particular organic charge-transfer complex, thus producing a series of high-contrast spots on the surface of the rotating recording medium. The precise sequence of spots (bits) on the medium stores information in a binary code of 0s and 1s. The stored information is read by illuminating each bit with a continuous reduced-power beam (below the write threshold) and by monitoring the reflected intensity with a suitable photodetector. The information can subsequently be erased by adjusting the laser power level and pulse duration to cause localized heating of the medium.

Figure 16 is an example of optical information storage using this organometallic medium. It shows the magnified surface of an AgTCNQ optical disk. Note

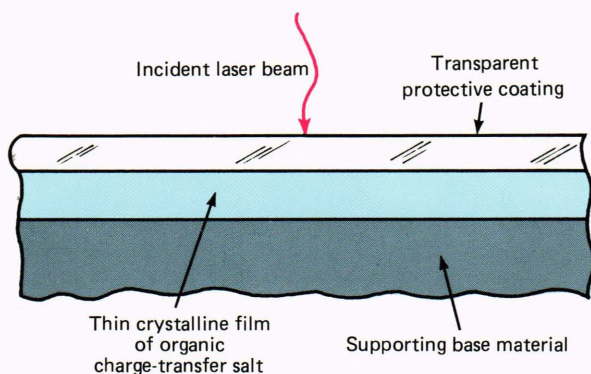


Figure 14—Schematic of an optical storage disk using an organic charge-transfer complex.

the high contrast between the optically switched regions (spots) and the background. The spots were made with the 532-nanometer line from a pulsed Nd:YAG laser; the laser energy was about 5 microjoules per pulse. The spot size was approximately 20 micrometers.

We have irradiated a number of other CuTCNQ and AgTCNQ type charge-transfer complexes with lines from an argon-ion laser, an Nd:YAG laser, an HeNe laser, a GaAlAs laser, and a CO₂ laser. In the majority of materials studied, the write-threshold power is relatively independent of wavelength throughout the visible and infrared region of the spectrum. The threshold writing power varies between 3 and 150 milliwatts depending on the specific choice of metal-acceptor complex. Those power levels are well within the capabilities of most moderately powered commercial laser systems.

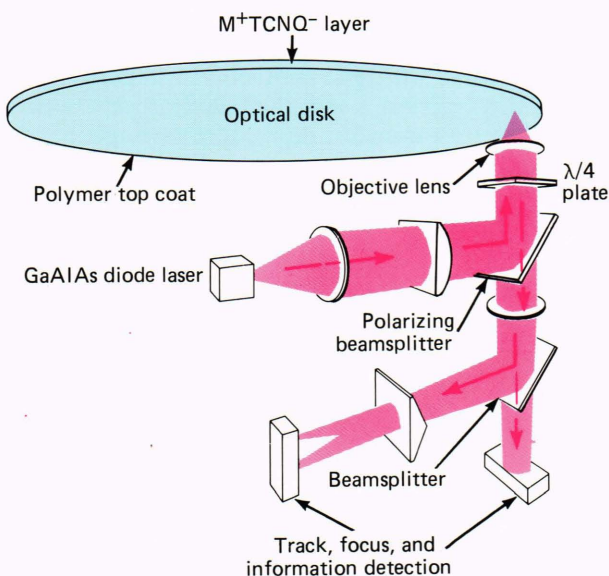


Figure 15—A typical optical recording system.

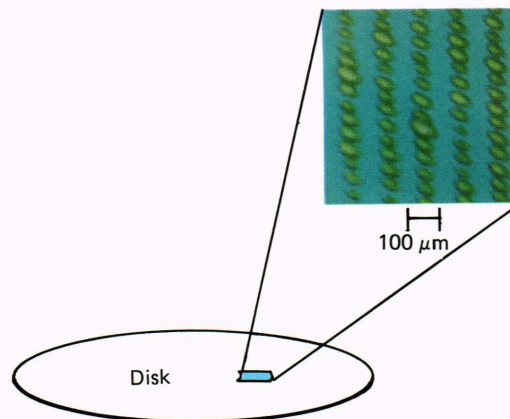


Figure 16—Magnified surface of an AgTCNQ optical disk showing the high contrast between optically switched and unswitched regions.

A Novel Multiple-State Optical Recording System

Existing optical storage media retain information by switching between two states. We have shown that organic charge-transfer complexes can be used to devise multistate optical recording systems. These media (unlike existing binary media that store information by switching between two states, 0 and 1) can store two or more bits of information in the same area that normally stores only one.³⁴

To understand how organic molecules can be used to make such a switch, one must first understand the general principles of two-stage electron transfer reactions. Examples of such reactions exist in reversible radical ion systems. The formation of quinhydrone, produced from the radical ion semiquinone, which is itself formed initially from the reduction of quinone, is a reversible two-stage electron-transfer reaction. This reversible redox system with a transfer of two electrons in two separate steps is shown in Fig. 17. The chemical structures have large delocalized systems in both the reduced and semireduced oxidized states. The stages differ only by two charges; otherwise, they are iso- π -electronic with one another. An important aspect of this reaction is that the redox process occurs only as electron transfer; no rupture of single bonds takes place in the reversible process. Each radical partner in the system has high thermal stability, which is important for possible applications in optical processing and storage.

It has been our intent to take this general principle of organic chemistry and apply it to the metal-TCNQ class of organometallic semiconducting materials. By combining the multistage redox aspect found in many organic amphoteric compounds with the interesting chemical and optical properties associated with the switching effect observed in CuTCNQ- and AgTCNQ-type complexes, we can make a totally new multistate switching material for optical recording applications.

Thin films containing two different radical ions mixed in a nearly 1:1 ratio have demonstrated multiple optical switching effects. In one experiment, neutral TCNQ(O-*ipr*)₂⁰ is added to a CH₃CN (acetonitrile) solution containing copper metal foil and allowed to form the CuTCNQ(O-*ipr*)₂ complex. The film of

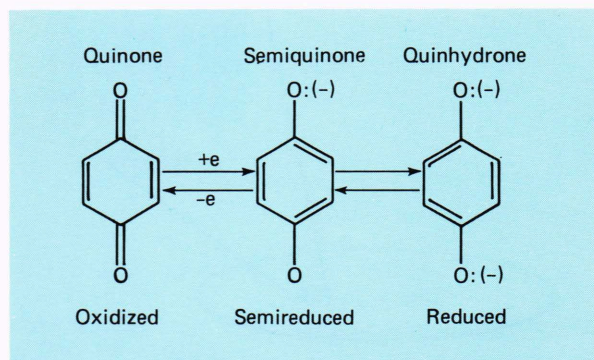


Figure 17—Reversible two-stage, electron-transfer reaction of quinone.

CuTCNQ(O-*ipr*)₂ is then reacted again in a solution of TCNQ⁰ in CH₃CN, which displaces some of the TCNQ(O-*ipr*)₂⁰ in the film. The result is a mixed complex of the formula Cu(TCNQ⁻)_x(TCNQ(O-*ipr*)₂)_{1-x}. The resulting thin polycrystalline film is then irradiated with increasing power density using an argon-ion laser source. Changes in the composition of the film are monitored using Raman spectroscopy. We have shown in an earlier experiment (Table 1) that the electric field strength required to cause the switching transition depends on the reduction potential of the acceptor molecule. We were able to make use of this field-strength dependence to switch each copper salt sequentially from the charge-transferred complex to a new solid phase containing some neutral acceptor molecules.

In the multistate optical recording medium, a single laser source is used to record sequentially and access multiple bits of information at one location on the surface of the film. One method of accessing information is by measuring shifts in the Raman bands between fully charge-transferred species and neutral molecules formed by the stepwise increase in laser writing power.

The results of a typical experiment are outlined in Fig. 18. The unrecorded medium is first accessed using an argon-ion laser operating at low power level in a Raman spectrometer. Strong ν_4 (C=C stretching) Raman bands are observed for both CuTCNQ and CuTCNQ(O-*ipr*)₂ in the unswitched film shown in Fig. 18. The two compounds can easily be distinguished from one another because the CuTCNQ(O-*ipr*)₂ stretching frequency at 1390 centimeter⁻¹ is shifted approximately 15 centimeter⁻¹ from that of CuTCNQ at 1375 centimeter⁻¹.

To record a bit of information at a particular location, the power of the argon ion laser is briefly increased to 20 milliwatts. At that power level, the CuTCNQ(O-*ipr*)₂ switches to produce neutral species, but the field strength is not great enough to switch the TCNQ. In Fig. 18, we see that the result of this 20-milliwatt exposure is to produce a new band at 1467 centimeter⁻¹ corresponding to neutral TCNQ(O-*ipr*)₂⁰.

To record a second bit of information at the same spot, the power of the argon ion laser is momentarily increased to 40 milliwatts. In Fig. 18, the result of this

Table 1—Relationship between reduction potential of the acceptor and field strength at switching threshold.

Polycrystalline charge-transfer complexes	Reduction potential of the acceptor (V)	Approximate field at switching threshold (V/cm)
CuTCNQ(OMe) ₂	- 0.01	2.4 × 10 ³
CuTCNQ	+ 0.17	5.7 × 10 ³
CuTNAP	+ 0.20	8.2 × 10 ³
CuTCNQF ₄	+ 0.53	1.3 × 10 ⁴

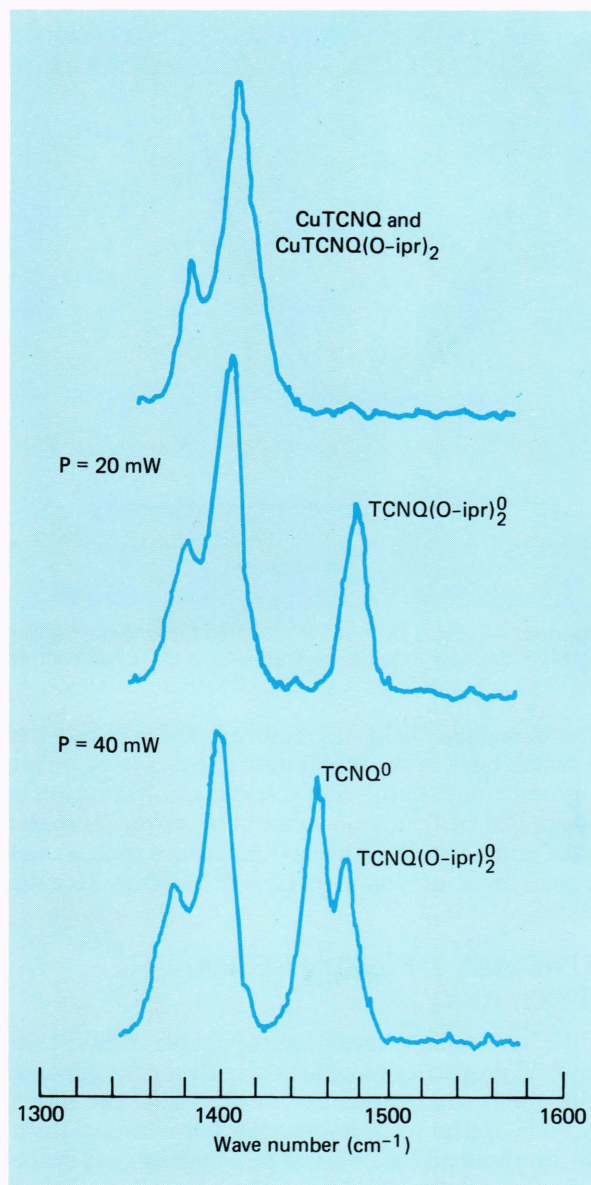


Figure 18—Raman spectra of multistate optical switching medium.

increased laser exposure (which exceeds the optical switching threshold for both CuTCNQ and CuTCNQ(O-iper)₂) is to produce a new Raman band at 1451 centimeter⁻¹. This strong band is evidence of the formation of neutral TCNQ species in the film. The two separate reactions producing neutral acceptor molecules can then be reversed using heat to reform their original charge-transfer complexes.

This experiment demonstrates the possibility of a multistate information system using semiconducting organometallic films from the TCNQ family. It is expected that multiswitching can be observed in a wide variety of other related radical-ion acceptor salts by mixing different molecules together or by changing the donor metal. A film composed of CuTCNQ and AgTCNQ will switch at different applied electric fields in a manner similar to the metal TCNQ-TCNQ(O-iper)₂ system.

At present, we are chemically linking the various acceptor molecules through σ - and π -bonding systems. We are also synthesizing and studying new molecules that combine the multistate or amphoteric properties of molecules such as hydroquinone in a single, strongly delocalized, acceptor molecule.

Two Terminal Organometallic Logic Elements for Novel Computer Architecture Applications

Recent interest in the field of computer hardware design has centered on the possibility of constructing a delocalized content-addressable memory using parallel processing. An associative memory processor differs from a serial processor in that data are stored and addressed by content rather than by specific address location.^{35,36} A computer model simulation developed by J. J. Hopfield has shown that content-addressable memory is feasible and may offer significant benefits in processing speed, familiarity recognition, error correction, simplified software, and insensitivity to individual logic element failure.³⁷

An associative memory is a device that stores and processes information in a number of cells. The individual cells are recorded on and accessed by their content. Therefore, each logic element must be able to process as well as store data. The cells are interconnected in a large matrix or array. In an associative memory, the storage capacity increases asymptotically in relation to the number of storage elements, making high-density arrays essential to the basic architecture. To fabricate such dense circuitry, simply constructed logic elements are advantageous. A basic logic element that might meet these requirements for associated memory processing is a two-terminal bistable electronic switch.

We are currently evaluating the possibility of building an associative memory using organometallic molecular materials. Earlier work demonstrated two-terminal bistable electrical switching and memory phenomena observed in polycrystalline films of either copper or silver complexed with the electron acceptors TCNE, TNAP, TCNQ, and various TCNQ derivatives.²⁰⁻²⁶

The basic device consists of a thin polycrystalline film of a copper or a silver charge-transfer complex sandwiched between two metal electrodes to which an electrical connection can be made. We have developed an all-solid-state method, compatible with microelectronic techniques, to make the two-terminal switching devices for possible use in large arrays. A magnified two-terminal bistable switching element prepared by this technique is shown in Fig. 19.

Using the solid-state processing technique, we have prepared a 4 × 4 matrix of 1-bit, two-terminal, bistable storage elements. A magnified photograph of the matrix, before electrical contact was made to the eight metal pads, is shown in Fig. 20. The substrate is glass, the first metal deposited is copper, the acceptor molecule is TCNQ, and the top metal pad is aluminum.

Threshold and memory behavior are observed in each of these logic elements by examining current as

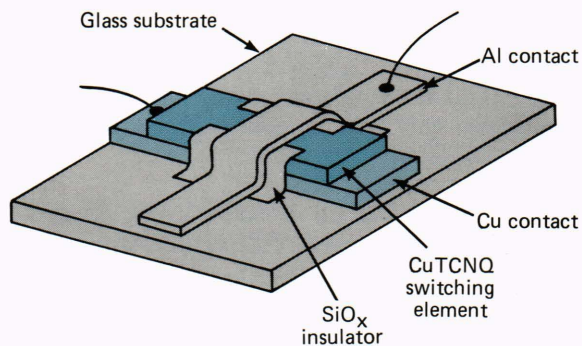


Figure 19—Schematic of a CuTCNQ bistable switching element.

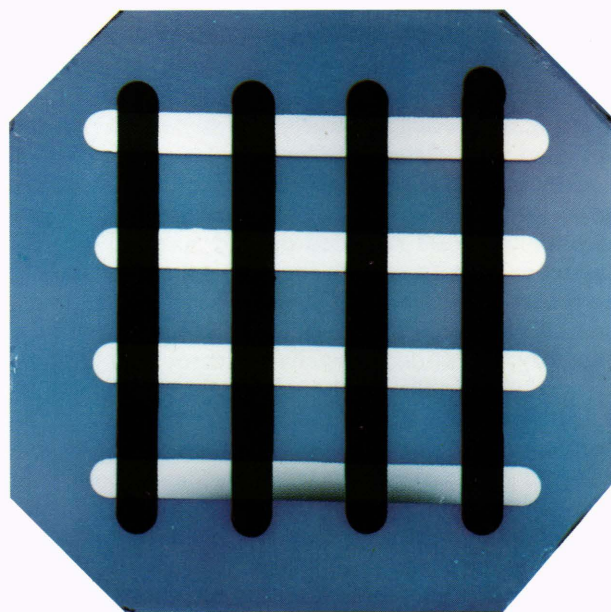


Figure 20—Photomicrograph of a 4 × 4 matrix of organic switching elements.

a function of voltage across the two-terminal structure. Figure 21 shows a typical DC current-voltage curve for a 5-micrometer thick Cu/CuTCNQ/Al system. There are two stable nonohmic resistive states in the material. Switching occurs when an applied potential across the sample surpasses a threshold value (V_{th}) of 2.6 volts, corresponding to a field strength of approximately 8.1×10^3 volts per centimeter. At this field strength, the initial high impedance of 1×10^4 ohms drops to a low impedance value of 200 ohms. A rise in current to 4 milliamperes and a decrease in the voltage to approximately 1.2 volts along the load line (dotted line) are observed in the CuTCNQ system. These results are representative of the switching effects observed in all of the metal charge-transfer salts examined and are characteristic of two-terminal S-shaped or current-controlled negative-resistance switches.

It has also been observed that once the film is in the conducting state, it will remain in that state as long as an external field is applied. In each case, the film eventually returned to its initial high-impedance state

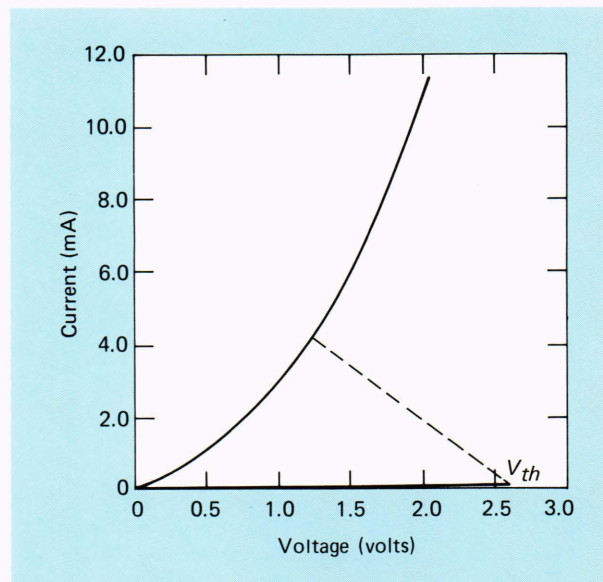


Figure 21—Typical DC current-voltage characteristic showing high- and low-impedance states for a CuTCNQ sample.

after the applied field was removed. The time required to switch back to the initial state appears to be directly proportional to the film thickness, the duration of the applied field, and the amount of power dissipated in the sample while in the low-impedance state, as well as the choice of donor metal and electron acceptor species.

SUMMARY OF APL'S RESEARCH PROGRAM

We have demonstrated that the unique chemical and physical properties of a particular class of organometallic solids can be used as fast photochromic filters, erasable optical recording media, two-terminal bistable threshold and memory logic elements, and optoelectronic switches. These materials may find application in both conventional and novel information processing and storage. Two novel applications of these organometallics are in optical recording media and in high-density memories. Organometallic charge-transfer salts provide an avenue to extend the present limits of recording density imposed by conventional laser and optics systems by recording and accessing multiple bits of information at a single spatial location. In this system, the information is stored in and read from specific molecular energy levels in various organic radical-anion species. In the two-terminal bistable switches, the rapid resistance changes that accompany the field-induced phase transition may be used in logic elements for associative memories.

In the various devices and applications, the concept of molecular architecture is used, i.e., the chemical structure dictates the specific physical properties observed in each device. This research has established a foundation of materials and fundamental scientific principles amenable to the design of new molecular electronic devices.

In 1985, a limited license was granted to the W. R. Grace Company to develop an erasable optical recording system based on organic molecular complexes.

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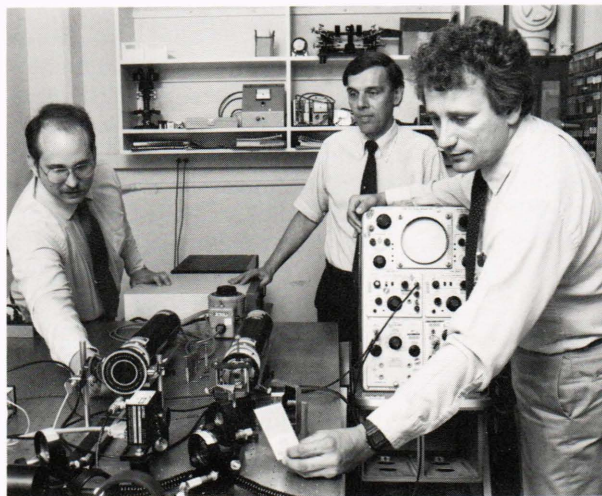
RICHARD S. POTEEMER (right) was born in Milton, Mass., in 1953. He was educated at Merrimack College, where he obtained a B.S. in 1975, and at The Johns Hopkins University, where he obtained an M.A. in chemistry in 1978, a Ph.D. in chemistry in 1979, and an M.S. in technical management in 1986. During 1979-80, he was a JHU/APL Postdoctoral Fellow. In 1981, he was employed in APL's Milton S. Eisenhower Research Center as a senior chemist in the Quantum Electronics Group. In 1986, he was appointed program supervisor of the Materials Science Group. Dr. Potember is a visiting professor in the JHU Department of Chemistry (1984-85 and 1986-87) and an instructor in the JHU G.W.C. Whiting School of Engineering, Department of Materials Science, since 1985. His research interests include organic chemistry, physical-organic chemistry, polymer chemistry, photochemistry, and the electrical and optical properties of organic solids.

ROBERT C. HOFFMAN (left) was born in Bethesda, Md., in 1959 and received his B.S. degree in chemistry from Loyola College in Baltimore in 1982. He is currently a doctoral candidate in the Department of Materials Science and Engineering, G.W.C. Whiting School of Engineering, The Johns Hopkins University. He is also a JHU/APL Graduate Student Fellow and is conducting his dissertation research at the Milton S. Eisenhower Research Center in the area of organic semiconductors. His work at APL has included research on novel optical storage materials and the optical properties of organic solids.

THEODORE O. POEHLER (center) was born in Baltimore in 1935. He received his Ph.D. in electrical engineering from The Johns Hopkins University in 1961 and joined APL in 1963. He is present-

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ly director of the Milton S. Eisenhower Research Center. Dr. Poehler previously served as supervisor of the Quantum Electronics Group; director of the APL Evening College Center; and director, Part-Time Graduate Programs, G.W.C. Whiting School of Engineering, The Johns Hopkins University. Dr. Poehler is an ex officio member and secretary of the APL Advisory Board. He is a specialist in solid-state physics, semiconductors, thin films, and optical lasers. He currently holds a joint appointment as professor in the Departments of Electrical Engineering and Materials Science and Engineering at Johns Hopkins.