Conducting organics and polymers for electronic and optical devices

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In the past 20 years, organic molecular crystals and organic polymers have been prepared in a variety of forms such that electrical conductivity can be systematically controlled over a range of 10 orders of magnitude. Recently, a number of potential applications have emerged from this research. This paper provides a brief overview of current research into the possibility of using organic polymers and charge-transfer complexes to fabricate electronic and optical devices.

(Keywords: conducting polymers; electronic devices; optical devices; charge-transfer complexes)

INTRODUCTION

The rapid development in the semiconductor industry has been marked by the increasing density and complexity of semiconductor chip circuitry. Considerable attention has been paid to the inherent problems associated with increasing the density of integrated circuitry. In the future, fundamental physical considerations will set limits on the size and properties of integrated 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 new technologies based on totally different types of materials to increase memory and processing capabilities. One possible class of materials that may find applications in the electronics industry is carbon-based (organic) semiconductors and conductors.

The replacement of inorganic semiconductors and metals by organic macromolecular, polymeric or even biological materials has recently been termed 'Molecular Electronics'. This new interdisciplinary field, combining organic chemistry, solid-state physics and microelectronic engineering offers the potential of revolutionizing electronic and computer speed and capacity by making devices from complex molecular structures.

Organic compounds and polymers offer viable alternatives to the traditional inorganics in many applications because of their extremely small size, abundance, diversity, ease of fabrication and potential low cost. For example, the typical dimensions of organic molecular structures (10–100 Å) 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 it. In molecular electronic devices the electronic and/or optical properties are locked into the molecular structure instead of produced 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 density, speed and production yield.

Current research in molecular electronics centres on the design and fabrication of new synthetic molecular materials, evaluating these materials and then using them for novel technical applications. Research in this field is currently divided into two areas: (1) electroactive polymers, sometimes called plastic metals or synmetals (synthetic metals); (2) molecular crystals that include monomeric compounds and organic charge-transfer complexes. *Figure 1* shows the structural formulae of several common electroactive polymers and monomeric compounds discussed in this paper.

CONDUCTING ORGANIC POLYMERS: AN OVERVIEW

The study of electronic transport in organic polymers is more than thirty years old. The first organic polymers prepared were electrically insulating with conductivities as low as 10^{-14} $(\Omega\,\mathrm{cm})^{-1}$. The insulating properties are the result of all of the electrons in the polymer being localized in the hybrid-atom molecular orbital bonds, i.e. the saturated carbon framework of the polymer. These insulators, which include polymers such as poly(n-vinylcarbazole), or polyethylene, have extremely large band gaps with energy as high as 10 eV required to excite electrons from the valence to the conduction band. Electrical applications of insulating organic polymers are limited to insulating or supporting materials where low weight and excellent processing and mechanical properties are desirable.

Semiconducting organic polymers, sometimes called electroactive polymers, exhibit conductivities from 10^{-9} to 100 $(\Omega\,\mathrm{cm})^{-1}$. These polymers can be classified into

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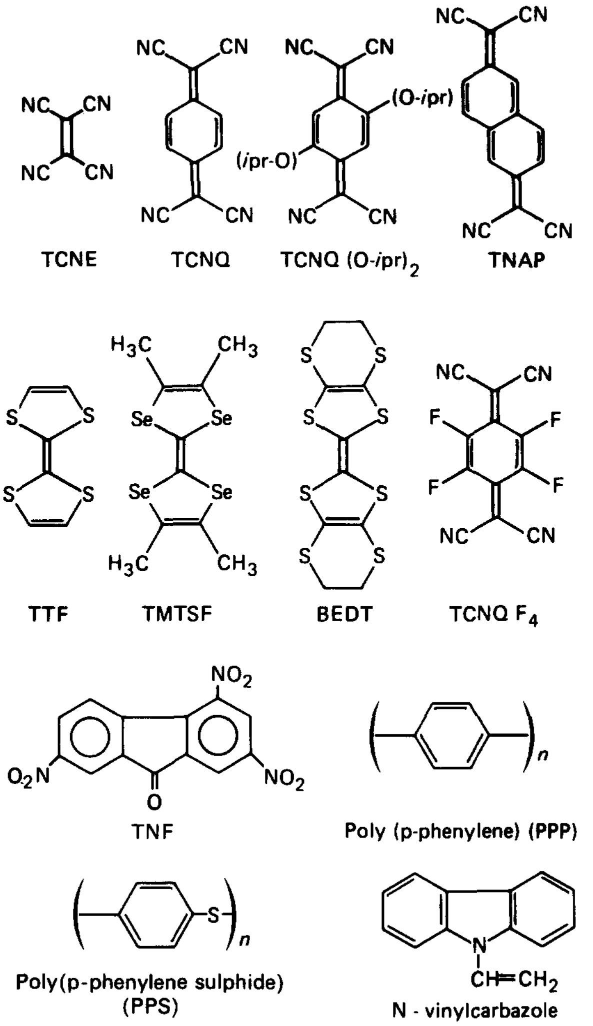

Figure 1 Structural formulae of organic donor and acceptor molecules

three groups based on their chemical structure: (1) composite polymers that combine graphite-like structures with metal particles (the concentration of metal particles may often reach 85 wt% in composite polymers); (2) polymeric charge-transfer complexes in which a cationic species, often a metal ion or an anionic species such as the iodide ion $(I_3)^-$ or an organic acceptor such as TCNQ or TNF (trinitrofluorenone) interacts with the polymer main chain by altering the molecular orbital arrangement through electron interactions; (3) conjugated polymers that show semiconducting properties because the π-orbital overlap along the unsaturated polymer chain allows the conduction electron to interact with neighbouring π-orbitals on adjacent carbon atoms.

High electrical conductivity has been observed in several conjugated polymer or polyene systems (*Figure 2*). The first and simplest organic polymer to show high conductivity was 'doped' polyacetylene (*Figure 3*)[1]. In the 'doped' form its conductivity is in excess of 200 $(\Omega\ \mathrm{cm})^{-1}$. 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[2].

The actual nature of the electrical conductivity in doped and undoped polyacetylene is still a matter for speculation. However, several possible explanations 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 energy band leading to one-dimensional metallic behaviour. In reality, however, a finite length of $(CH)_x$ chains would be an intrinsic semiconductor with an electron band gap of approximately 2 eV because the alternating double-bond–single-bond structure has two atoms per unit cell instead of one; hence a semiconductor band gap is formed through a Peierls metal–semiconductor transition.

In the ten years since the discovery of the first highly conductive organic polymer, work on numerous other conductive polyene systems (*Figure 1*), including poly(*p*-phenylene) PPP, poly(*p*-phenylene sulphide) PPS, polypyrrole PP, and poly(*p*-phenylene vinylene) PPV has proved that, as a class of materials, the unsaturated

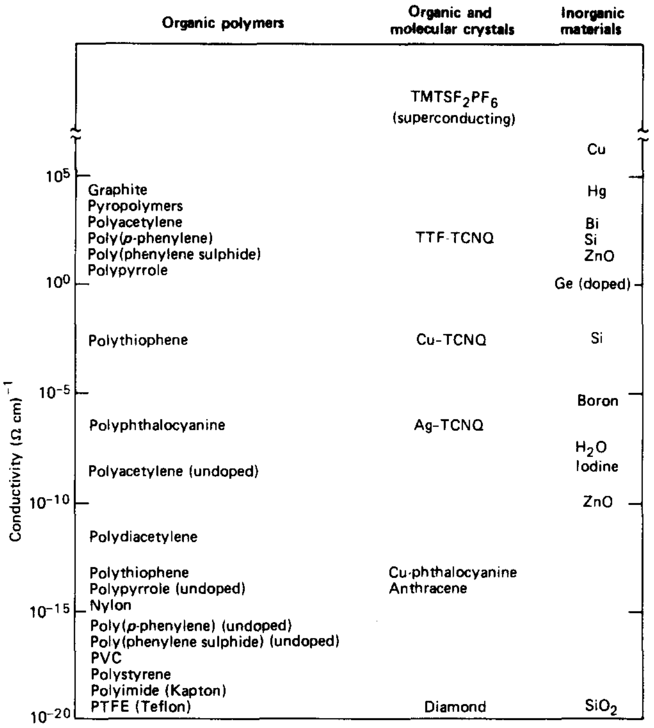

Figure 2 Compilation of electrical conductivities of organic polymers

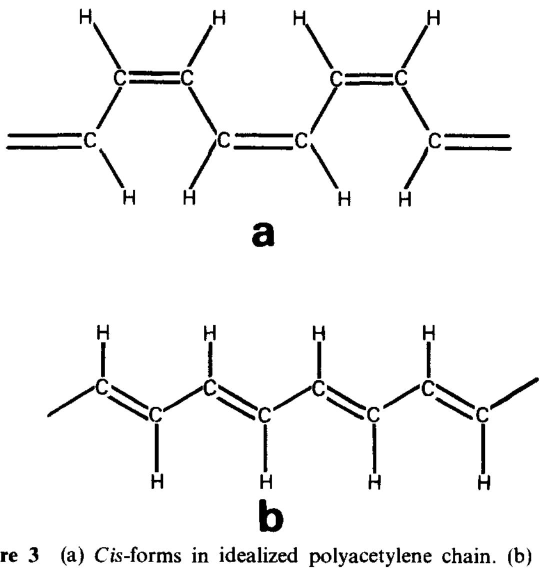

Figure 3 (a) *Cis*-forms in idealized polyacetylene chain. (b) *Trans*-forms in idealized polyacetylene chain

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 new conductive organic polymers is polypyrrole (*Figure 4*). The highly stable, flexible films of polypyrrole produced by a one-step electrooxidation have room-temperature p-type conductivities ranging from 10 to 100 $(\Omega\,\mathrm{cm})^{-1}$. No additional dopants are required to produce electrical conductivity[3].

In addition to showing high electrical conductivity, polypyrrole films can be repeatedly electrochemically driven or 'switched' between a black highly conductive 100 $(\Omega\,\mathrm{cm})^{-1}$ oxidized form and a yellow non-conducting neutral form. The switching rate for thin films is approximately once per second[4].

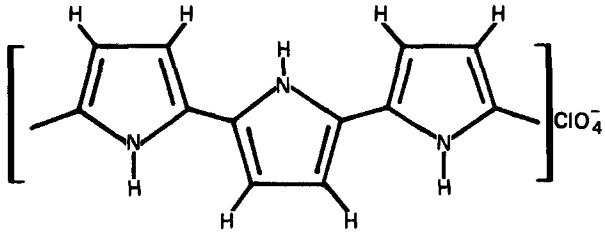

Figure 4 Chemical structure of conductive polypyrrole

APPLICATIONS FOR MOLECULAR ELECTRONIC MATERIALS

Molecular electronic materials show great promise in a wide range of applications. Many of the possible 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.

A partial list of applications and materials currently being investigated is shown in *Tables 1* and *2*. *Table 1* summarizes applications related to electronic devices while *Table 2* is devoted to optical and electro-optic applications.

Field-effect transitor utilizing poly(N-methylpyrrole)

Chemically prepared semiconducting poly(*N*-methylpyrrole) has been used in a p-type silicon wafer solid-state field-effect transistor[5]. The π-conjugated polymer, made electrically conducting by doping with aqueous $FeCl_3$, is deposited as a thin film over source, drain and (SiO_2) gate electrodes of the FET (see *Figure 5*). The electrical conductivity of the polymer, measured in an Au/PNPy/Au sandwich-type cell, is $2\times10^{-5}\,\mathrm{S\,cm^{-1}}$. The polymer was also fabricated into a Schottky type diode to confirm that the polymer was a p-type semiconductor.

When no gate voltage is applied, the *I–V* characteristics of the device show a linear response as

Table 1 Applications of molecular electronic materials

Application	Materials	Significance
Rechargeable Battery	Perchlorate doped polyacetylene-lithium system	High energy capacity: 341 w-hr-kg^{-1}; lightweight rechargeable system.
	Electrochemically doped poly(n-vinyl carbazole)	Voltage remains constant during discharge; rechargeable lightweight system.
	Poly(vinyl pyridine) – I_2	Comprises cathode in LiI battery.
Chemical Sensors	Cu Phthalocyanine	Langmuir-Blodgett film of asymmetrically substituted Cu-phthalocyanine detects NO_2.
	Poly(ethylene maleate) cyclopentadiene	Detects acetone, methylene chloride, benzene, MeOH, pentane; Surface Acoustic Wave (SAW) device.
	Triethanolamine on Si	Detects 70 ppb SO_2 (SAW device)
Microphone and Speaker (transducers)	Polyvinylidine	Versatile organic piezoelectric material used in sonar hydrophones, microphones, and medical imaging.
Wiring, coatings & shielding	Poly(vinyl acetals) doped with $Et_3NH^+(TCNQ)_2^-$	10^4 Ω·cm resistivity, easily produced and fabricated.
	Polypyrrole, electrochemically doped Doped polyacetylene (AsF_5, I_2Li, K) Doped polyphenylene (AsF_5,Li^2,K), and polyphenylene sulfide (AsF_5) Polythiophene, electrochemically doped	Conductivity cap be varied by selectively doping material (from 1 to 2000 $(\Omega\cdot\mathrm{cm})^{-1}$).
Transparent conductive thin films	Polypyrrole polymer complexes	Antistatic packaging for semiconductor and electronics industries; high optical transmission and electrical conductivity.
Electronic Devices (diodes, transistors, capacitors)	Poly(N,N′-dibenzyl-4,4′-bipyridium)	Demonstration of molecule-based rectifier; threshold voltage varied by altering molecular materials used.
	Na^+ implanted polyacetylene	Stable in O_2 atmosphere.
	3,4,9,10-perylene tetracarboxylic dianhydride on on n-Si or p-Si	High reverse breakdown voltage.
	Polypyrrole on Si	Used to make organic transistor.
	Quinolinium-TCNQ N-methyl acridinium-TCNQ.	Used as electrolytes in solid electrolytic capacitor.
Memory Devices	Ag and Cu salts of TCNQ, TNAP and derivatives	Exhibits reversible memory switching; threshold switching voltage can be altered by changing donor or acceptor.

Table 2 Applications of molecular optical materials

Application	Materials	Significance
Optical Display Devices	Conducting polythiophene complexes	Produces colored displays with fast switching times and better viewing geometry (no polarizing elements) than LCD devices.
	Tetrathiafulvalene or pyrazoline in polymethacrylonitrile doped with $LiClO_4$	
	Poly(3-bromo-N-vinylcarbazole) N,N′-di(n-heptyl)-4,4′-bypyridinium dibromide	Very fast (<200 msec) photochromic changes observed. High speed, reversible, and exhibits memory effects.
Electrophotography	Poly(vinyl carbazole)-trinitrofluorenone CuTCNQ + poly(N-vinyl carbazole)-trinitrofluorenone Polycarbonate-triphenylalanine N,N′-diphenyl-N,N′-bis(3-methyl phenyl)-[1,1′-biphenyl]-4,4′-diamine in polycarbonate	High quantum efficiency. Charged by halogen lamp, multiduplication up to 50 copies.
Optical Information Storage (optical recording)	Metal-TCNQ complexes	Erasable, high contrast media.
	Photochromic dyes	High sensitivity, stable and erasable.
	Liquid crystalline polymers	Liquid crystal polymers provide high contrast and high resolution with high sensitivity.
	1,4-dihydroxyanthraquinone	Used in amorphous SiO_2 matrix as frequency domain storage media; requires cryogenic temperatures.
Photovoltaics	Polyacetylene/n-ZnS	Used in Schottky barrier configuration; polyacetylene bandgap matches solar spectrum well.
	Electrochemically doped Poly(N-vinyl carbazole) merocyanine dyes	Conversion efficiencies 0.015 to 2.00%.
Optoelectronic Devices	Metal-TCNQ complexes	Electrical switching behavior occurs in conjunction with applied optical field.
Photonic Devices (Solid state optical switching elements)	Electrochemically doped polythiophenes	Optoelectronic switching accompanied by optically induced doping; subsequent undoping occurs electrochemically.
	Urea	Used in optical parametric oscillator; conversion efficiencies approach 20%; tunable through visible and IR.
	Methylnitroaniline	Used as frequency doubling material.
	1:1 copolymer of methylmethacrylate and glycidilmethylmethacrylate polyphenylsyloxane polydiacetylene	Used as optical waveguide in integrated optics.
	Liquid crystalline polymers	Used as light valve in optical logic networks.

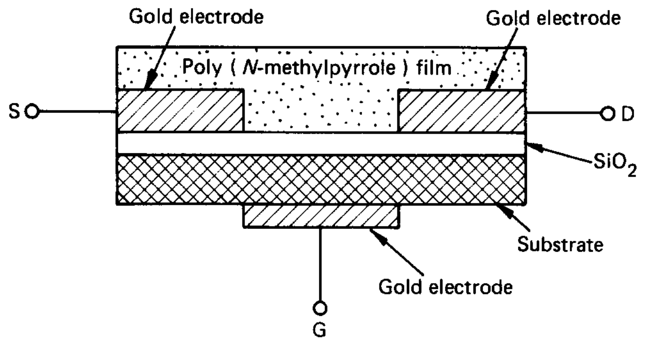

Figure 5 Schematic view showing cross-sectional view of poly(*N*-methylpyrrole) FET device

current is passed between the source and drain electrodes. However, when the gate voltage is increased to approximately -0.30 V, the source current exhibits a nonlinear increase and tends to saturate. The mobility of the field effect was measured at 10^{-2} cm^2 V^{-1} s^{-1} for a constant drain voltage. The phenomenon occurs reversibly and is similar to the operating characteristics of conventional inorganic semiconductor devices.

The mechanism of the increase in conductivity is believed to be due to the accumulation of holes in the polymer at the junction of the polymer thin film and the SiO_2 gate insulator when a negative bias is applied to the gate electrode. This work suggests that the excellent physical properties of conducting polymers may be useful in preparing a variety of other FET devices.

Lightweight rechargeable batteries

Highly conductive organic polymers are being evaluated for 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 in an electrolyte (lithium perchlorate) and completely encapsulated in a plastic casing, a 'plastic battery' can be made[6] (*Figure 6*). The two sheets of polyacetylene or poly(*p*-phenylene) act as both anode and cathode for the battery.

These novel polymeric batteries have several notable features. They are rechargeable, ten times lighter than a conventional lead–acid battery, and flexible enough to fit into a variety of design configurations.

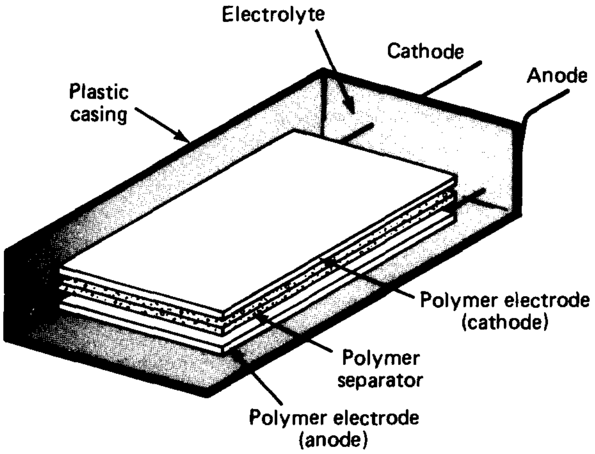

Figure 6 Schematic of 'plastic' battery

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 sulphide, can enhance the evolution of oxygen at the electrode–electrolyte surface and increase the lifetime of the cell by a factor of a million[7].

In another example, a photovoltaic cell has been fabricated using polyacetylene as the actual active photoelectrode. In a Schottky barrier configuration, this solar cell delivered an open circuit voltage of 0.3 V and a short-circuit current of 40 μA cm^{-2} under an illumination equivalent to 'one sun' (1353 W m^{-2})[8]. Polyacetylene may be an attractive solar-cell material because studies suggest it is a direct band-gap semiconductor with an optical band gap matching the solar spectrum. The electronic structure is analogous to traditional inorganic semiconductors in that the strong π-electron overlap along the polymer chain leads to large energy bandwidths.

Electrochromic polymer displays

An electrochromic display is a thin solid-state device that changes colour reversibly when subjected to a small electrical potential. This new display technology has several advantages over liquid-crystal displays currently in use. Electrochromic displays have 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[9]. An electrochromic display-cell structure made by using these materials is shown in *Figure 7a.* It consists of a transparent glass electrode, the electrochromic polymer system and a thin gold semitransparent counter-electrode.

When the structure is electrically biased (1.0–3.5 V), the optical density of the film changes, i.e. the colour changes, because the organic complex undergoes a reversible electron-transfer reaction from a neutral form to an oxidized form (*Figure 7b*). By using a TTF redox compound, the colour of the display changes from yellow to a bright red, while pyrazoline switches from transparent to yellow. Multicolour displays are also being studied, which use combinations of organic compounds that exhibit multiple colouration at different applied potentials.

An erasable compact disk

The interaction of laser radiation with matter for use in optical storage systems has received considerable attention. A variety of different media, including photographic films, photoresists, photosensitive polymers, photochromics, thin amorphous films and electro-optic materials have been proposed as optical storage systems. Present optical storage systems have been applied for document storage, audio and video reproduction and direct data collection. However, 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 by using the electric-field-induced optical switching effect in films of either copper or silver complexed with the electron acceptors tetracyanoethylene (TCNE), tetracyanonapthoquinodimethane (TNAP), tetracyanoquinodimethane (TCNQ) or other derivatives of TCNQ (*Figure* 1)[10–16]. The optical change in these materials is reversible and fast, with switching times of less than 10 ns observed in static switching experiments.

The observed changes in the optical properties of films fabricated from these organic materials is a direct consequence of the laser-induced reaction

$$n[M^+(TCNQ^{\bar{\cdot}})] \underset{heat}{\overset{E}{\leftrightarrows}} xM^0 + (n-x)[M^+(TCNQ^{\bar{\cdot}})] + x(TCNQ^0)$$

where M can be silver, copper, sodium, potassium or lithium. The reaction shown here is reversible and the thermodynamically favoured initial phase can be readily reformed by heating the complex phase (right side of equation) of the salt.

Various diagnostic techniques including infra-red, Auger, X-ray photoelectron and Raman spectroscopy have been applied to help understand this reaction. These

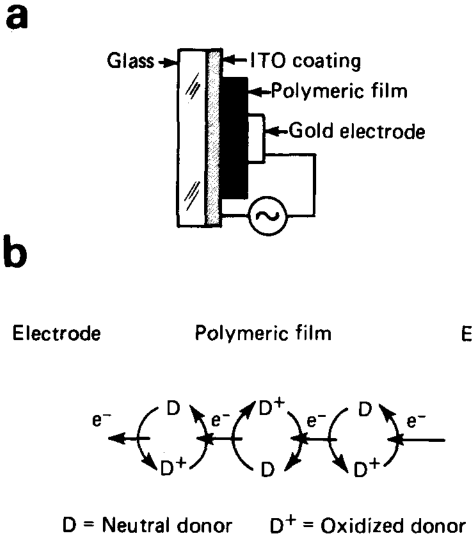

Figure 7 (a) Cell structure of electrochromic display. (b) Colouring electrochromic mechanism in polymeric film

experiments suggest that the effect of the applied electric field (laser) on an organometallic charge-transfer salt (for example, copper TCNQ) is to induce a phase transition to a non-stoichiometric complex salt containing neutral acceptor molecules (TCNQ$^{\circ}$).

Figure 8 shows a cross section of a typical erasable optical disk medium made by using the TCNQ family of organometallic materials. An approximately 2000 Å thick organic charge-transfer salt is deposited on aluminium, glass or polycarbonate-supporting base by using a solid-state diffusion process. This 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 μm) will be minimized. The disk is completed when a thin protective polymer overcoat is cast over the photoactive organic layer.

The disk can then be placed in an optical recording, playback and erasure system. A block diagram of a typical laser-diode optical recording system is shown in *Figure 9*. Information is recorded, read and erased on the spinning disk by modulating the intensity of the laser. 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 reading of stored information is accomplished by illuminating each bit location with a continuous reduced power beam (below write threshold) and monitoring the reflected intensity with a suitable photodetector, which converts the light into electrical impulses. The information can subsequently be erased by adjusting the power level and pulse duration to cause localized heating on the medium.

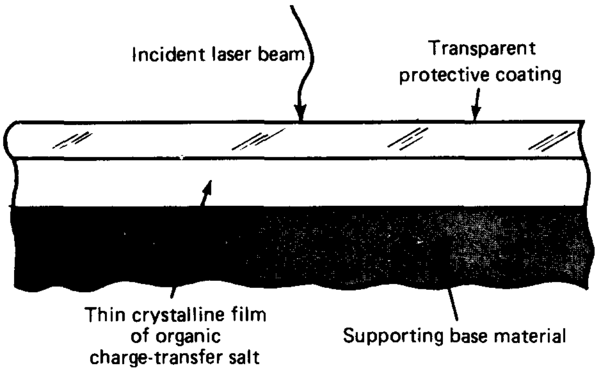

Figure 8 Schematic of optical storage disk using organic charge-transfer complexes

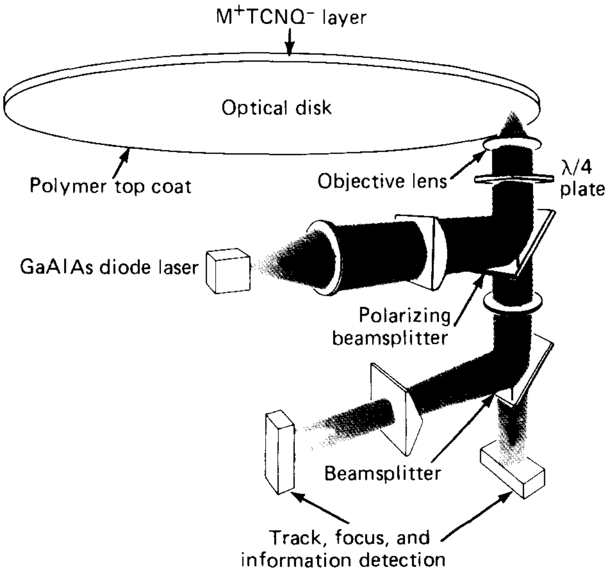

Figure 9 Block diagram of typical optical recording system

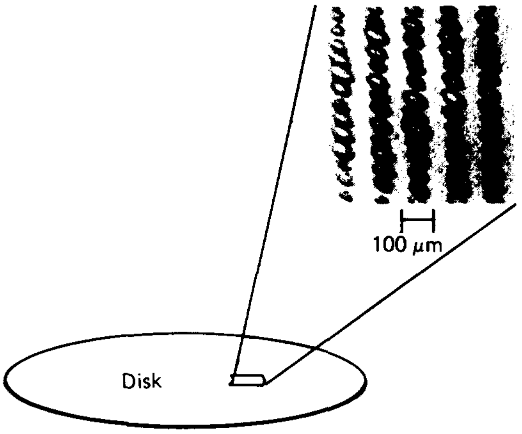

Figure 10 Magnified surface of AgTCNQ optical disk showing high contrast between optically switched and unswitched regions for various laser intensities

An example of optical information storage using this organic medium is shown in *Figure 10*. The figure shows the magnified surface of a AgTCNQ optical disk. Note the high contrast between the optically switched regions (spots) and the background. The spots were made with the 532 nm line from a pulsed Nd:YAG laser; laser energy was about 5 MJ per pulse. Spot size was approximately 20 μm.

We have irradiated a number of other copper and silver TCNQ-type charge-transfer complexes with the 458, 488 and 514 nm lines from an argon-ion laser, the 532 and 1064 nm lines from a Nd:YAG laser, the 633 nm line from a He:Ne laser, the 780 nm line from a GaAlAs laser and the 10600 nm line from a carbon dioxide laser. In the majority of materials studied, the write threshold power is relatively independent of wavelength throughout the visible and infra-red region of the spectrum. The threshold writing power varies between 3 and 150 mW depending upon the specific choice of metal and acceptor complex. These power levels are well within the capabilities of most moderately powered commercial laser systems.

Photochromic properties of metal–organic charge-transfer complexes

An area of technological 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 this family make these compounds strong candidates as high-speed photochromic filters.[15,17] We have observed that these films undergo a change from their respective blue and violet colours to a rather pale yellow colour characteristic of neutral TCNQ. As shown in *Figure 11a*, a typical CuTCNQ film formed by solid-state diffusion is rather poorly transmitting from the mid-visible into the near infra-red close to 1100 nm, and there is a substantial increase in transmission extending into the infra-red. Upon irradiating the CuTCNQ film with a Nd:YAG laser at 532 nm, one observes a significant increase in transmission

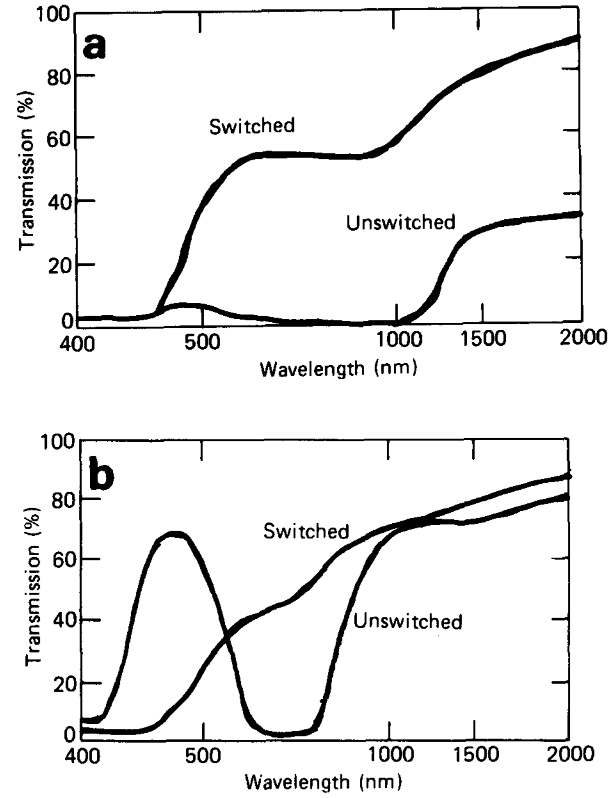

Figure 11 (a) Typical CuTCNQ transmission switch: 30 mJ pulses from frequency-doubled Nd:YAG laser (532 nm). (b) Typical AgTCNQ transmission switch: 45 mJ pulses from frequency-doubled Nd:YAG laser (532 nm)

throughout the spectrum, ranging from the mid-visible to the infra-red. Dramatic increases are observed at the red end of the spectrum and in the near infra-red, those regions that are of particular interest with respect to many of the principal laser sources.

The transmission properties of an AgTCNQ film are shown in *Figure 11b*. In contrast to the changes observed in CuTCNQ, the switched and unswitched films are quite similar in the infra-red portion of the spectrum. Large changes in transmission are noted in the visible part of the spectrum between 400 and 600 nm. The switched AgTCNQ becomes strongly transmitting in a band centred at 500 nm, while the unswitched film is poorly transmitting in the same region.

CONCLUDING REMARKS

It may be premature to evaluate the technological significance of this new field of science to the electronics industry. However, this paper provides firm examples of organic macromolecules and polymers with specific chemical and physical properties useful in device applications such as lightweight rechargeable batteries, photovoltaic solar cells, junction and electro-optic devices, photochromic filters and information-storage and processing media.

In each of the various devices and applications discussed in this paper, the novel concept of molecular architecture is demonstrated, i.e. the precise design and synthesis of chemical structure controls the specific physical properties observed in a particular device application. Current research in this field has also established a foundation of materials and fundamental scientific principles amenable to the design of new molecular electronic devices.

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