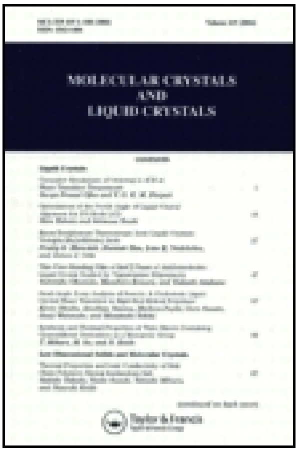

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Prospects for Electronic Processes in Organic Materials

Martin Pope [a]

[a] Chemistry Department and Radiation and Solid State Laboratory, New York University, New York City, NY

To cite this article: Martin Pope (1993): Prospects for Electronic Processes in Organic Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 228:1, 1-22

To link to this article: http://dx.doi.org/10.1080/10587259308032138

Mol. Cryst. Liq. Cryst. 1993, Vol. 228, pp. 1–22
Reprints available directly from the publisher

Printed in the United States of America

PROSPECTS FOR ELECTRONIC PROCESSES IN ORGANIC MATERIALS

Martin Pope
Chemistry Department and Radiation and Solid State Laboratory, New York University, New York City, NY

Abstract Recent progress is reported in the development of new properties and uses based on the electronic structure of organic materials, especially conjugated polymers. Examples include magnetism, superconductivity, metallic conductivity, electroluminescence, non-linear optics, 3-D optical memory, hole burning, self-assembly, biological sensors, and improved stability.

I. INTRODUCTION

I would like to thank the organizers of this conference, and, in particular, Professor Jan Kalinowski and Dr. Piergiulio Di Marco for inviting me to what promises to be a stimulating and enlightening conference. It is always a challenge for the conference chairmen to maximize the frequency of interactions among the conferees, and the choice of an island for the site of this conference represents the ultimate in design. Nevertheless, our restricted quarters are far from punitive, so we should enjoy our surroundings and relish the contact with our colleagues.

Although we represent more than twenty nations at this conference, note should be made that Italian scientists were prime movers at the birth of our field. When we use the term electron-volt, we commemorate the contributions of Volta who connected chemistry to the field of electricity. He also carried out the earliest work on the contact electrification of polymers, which in his case, was rubber. When we then consider the association of biological structures and electricity (and we will), we must refer to the pioneering work of Galvani, who, in touching a frog's leg with two different but electrically connected metals, and observing the spasmodic twitch of the leg, had the genius to conclude that electricity was a fundamental property of life. Galvani thought that the electricity came from the frog's leg, but Volta corrected him.

More close to home for us, the photoconductive properties of our favorite, anthracene, were discovered by Pocchetino in 1906(1). So our Italian colleagues should enjoy the developments that have taken place since then.

In principle, we scientists are supposed to follow our inner impulses in choosing the focus of our investigations. In practice, we are influenced by the material problems of the times, which express themselves by the availability of funds for the solution of these problems. Consider these problems: the store of free energy in the form of fossil fuel is diminishing, and is therefore becoming more inaccessible to emerging economies, and planetary environmental pollution is increasing to an alarming degree.

So, what must we do in order to make the best use of our dwindling energy supplies, to improve the economies of all the nations of the world, and to protect our environment from our presence and our needs? I know that you are all waiting eagerly for me to answer this question in the twenty minutes allotted for my talk. I am sorry to disappoint you, but I cannot give you a working solution because the most important ingredients are out of our control as scientists, and these are political systems that are intelligent, farsighted, and humane. However, we can address the major problems we have identified, with the understanding that while we may not have solutions, we will minimize our contributions to the problems. The following represents an incomplete list of some problems and how our studies can be helpful. The list is intended as a sample; you are invited to amplify wherever appropriate.

A. TO CONSERVE ENERGY

1. Use energy, particularly fossil fuels, more efficiently and wisely by:

a) Using fossil organic reservoirs (oil, coal, gas) not as fuels, but as a source of chemicals for the synthesis of renewable energy sources such as photovoltaics, fuel cells, and batteries.

b) Reducing thermal losses by using superconducting power transmission lines.

B. TO REDUCE POLLUTION AND THE GREENHOUSE EFFECT

1. Develop renewable energy sources that use solar energy.

2. Conserve our forests, which supply O_2 and store CO_2

a) by transferring and storing information electronically, instead of using paper (compact, high density information storage).

b) by reducing pollution from fossil fuel combustion; i.e. use photovoltaics and photosynthesis.

c) by reducing the dumping of lead, mercury, and cadmium from batteries; use polymer batteries.

C. TO IMPROVE THE ECONOMIES OF ALL NATIONS

1. Improve communication links that disseminate knowledge quickly, economically, and widely. This can done by developing

a) photonics, which uses light instead of electrons to transfer information, eliminating the need for expensive metal conductors.

b) small, inexpensive, powerful computers.

c) inexpensive printing equipment.

Hopefully, as economies improve, and information becomes more easily available for teaching and public health, the population of this planet will stabilize.

All of the above we can advance at this conference, because all of the above needs can be satisfied by organic materials. I am going to move swiftly over the surface of our field, pointing out some advances that in my opinion, hold promise for solving some of the problems of complex societies, and also for opening up new areas for theoretical studies. I will omit many things, not because they are unimportant, but because there will not be time enough to cover everything. In addition, I will be focusing mostly on experimental findings. In recent years, experimentalists have been able to provide theoreticians with a wealth of new phenomena to interpret. Furthermore, I will spend more time on polymers, because I feel that it will be with these materials that the greatest impact will be made on society.

II. HIGH CONDUCTIVITY MATERIALS

A. SUPERCONDUCTIVITY

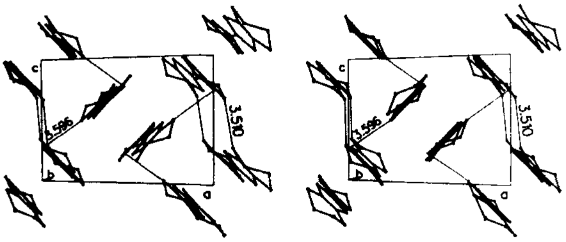

FIGURE 1 Stereo view of the ET donor molecular layer in k-$(ET)_2Cu[N(CN)_2]Br$ showing the typical arrangement of mutually perpendicular face-to-face dimers. Figure obtained from ref. 2.

The record for the ambient pressure T_c of organic superconductivity was 11.6K for the compound k-$(ET)_2Cu[N(CN)_2]Br^{(2)}$, (shown in Figs. 1, 2) which is a 1-D superconductor, until the remarkable fullerene compounds were discovered. The entry of this new form of carbon into the scientific arena has literally added another dimension to our universe. This molecule of C_{60} can be doped with metal atoms, whereupon it can become superconducting.

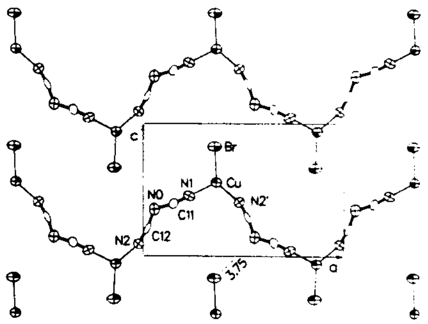

FIGURE 2 The polymeric anion layer consisting of infinite zig-zag chains of Cu-dicyanamide-Cu units; the Cu atoms complete their coordination spheres with Br. Figure obtained from ref. 2.

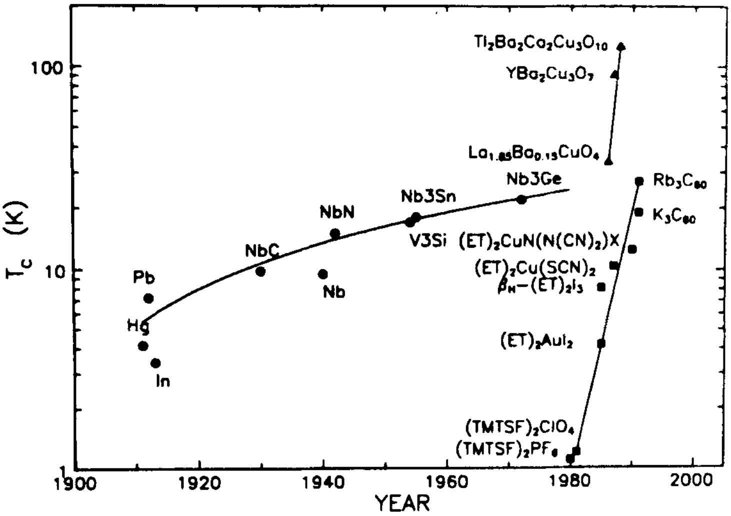

FIGURE 3 Increase in the critical temperature (T_c) for the onset of superconductivity over the century, in metallic, cuprate, and molecular superconductors. Figure obtained from ref. 5.

In rapid order, it was reported$^{(3)}$ that K_3C_{60} becomes superconducting at 18K followed by a

T_c of 28K for Rb_3C_{60}. Thus, C_{60} has become the basis for the first 3-D organic superconductor. Furthermore, there has been considerable theoretical activity directed at understanding of the mechanism of this superconductivity, which may turn out to be not entirely similar to the Bardeen-Cooper-Schrieffer model in that instead of a lattice phonon providing the source of binding for the electron pair, it is an intramolecular phonon$^{(4)}$.

The pace of discovery of high T_c materials is shown in Fig. 3$^{(5)}$. In a space of twelve years, the organic superconductors have reached a higher T_c than all but the new cuprates. This is a remarkable achievement, and is by no means the end of the story.

B. METALLIC CONDUCTIVITY

A class of materials that is attracting more attention from theorists and experimentalists, as shown in this conference, is that of conjugated polymers. In pursuing the study of these polymers, we intersect a major field of industrial research. Many of the brightest synthetic chemists in the world are involved in creating monomers and polymers with tailored physical and chemical properties. There is little doubt that as theory develops to guide synthesis, we will see an explosion of inventions in this area.

The most important polymeric conductor (as distinct from dyes mixed into polymer films, which constitute the more commercially important reprographic materials) from the technological standpoint so far is polyaniline, followed closely by poly(phenylenevinylene), polypyrrole, polyacetylene, and polyparaphenylene. The important characteristic of these polymers is that they can be doped to produce great changes in their electrical properties. Examples of all the uses that are in effect or planned for polyaniline are shown in FIG. 4$^{(6)}$.

As in the case of the organic superconductors, the pace of discovery and invention in the area has been remarkable. In just six years since the doping characteristics of polyaniline were discovered, at least twelve manufacturers are supplying products with a wide variety of functions.

As far as conductivity and physical stability are concerned, I will refer only to polyacetylene (PA), which has been extensively studied both theoretically and experimentally$^{(7)}$. So far, PA has the highest conductivity (σ), and the best mechanical properties of any of the polymeric materials. However, it still lacks chemical stability and this will certainly be an area of concentration in the future. On a weight basis, the σ of PA is better than that of Cu at room temperature, and on a weight basis, it has a tensile strength ten times greater than that of steel. The conductivity and mechanical properties improve in a correlated manner as the degree of alignment of the polymer chains is increased. Theoretically, a perfectly oriented PA shows an extrapolated value of conductivity of $2x10^5$ S/cm, and this value is defect limited (e.g. Sp^3

bonds). If the conductivity were to be limited only by phonon scattering, then at room temperature, it would be 2×10^6S/cm, which is higher than that of Cu. While these materials cannot rival metals in all cases, in the area of large-scale fabrication, they can. Thus, fabric 6 feet wide and 1000 yards long is presently being manufactured with a conductive polypyrrole covering, to be used for electromagnetic shielding. (See Fig. 4.)

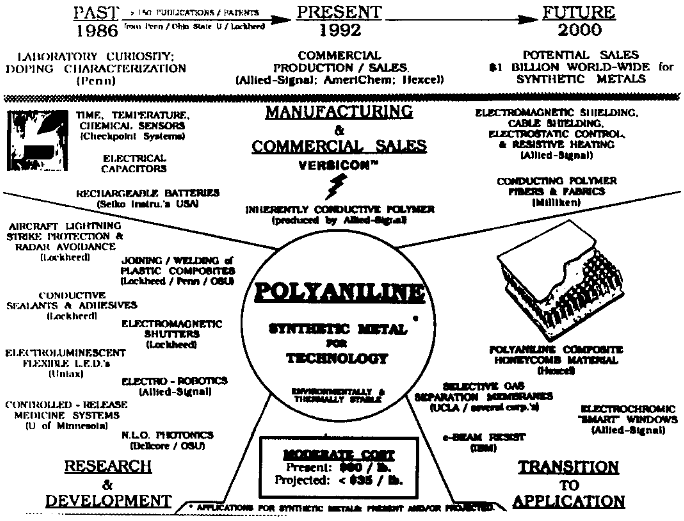

FIGURE 4 Panorama of the development of practical uses based on the electronic properties of polyaniline. Figure obtained from ref. 6.

III. BATTERIES

If electrical power production based on non-fossil-fuel consumption is to become feasible, then it would be desirable to have storage systems for electricity. In particular, intermittent systems based ultimately on sunlight, wind, tides and the like require inexpensive and convenient electricity storage systems. Batteries provide one answer to this need. Since polymers can be formed into thin films having a large surface area, batteries composed of polymers can be smaller and still deliver power levels that are competitive with those based on liquid electrolytes or molten salts, even though the polymer battery usually produces a lower current density(8).

Batteries based on a polymeric redox system are already in production. In Japan, for the past three years, it has been possible to buy a rechargeable battery based on the polyaniline-Li(9) system (see Fig. 4). In the U.S. a battery is being perfected based on a poly-p-phenylene/Li-Al alloy/cobalt oxide system that has an energy density of 70 watt-hrs/Kg. This is comparable to the performance of a Ni-Cd cell. It also has a slow self-discharge rate. (See Fig.4).

IV. LIGHT EMITTING DIODES

Another application of far-reaching significance is that of electroluminescence (EL). Not only does this provide the possibility of large-area illumination, with significant energy saving, but it makes possible compact flat video screens. EL was first reported in polymers by Burroughes, et al(10) in p-phenylene vinylene (PPV).

This thin film has a low turn on voltage (~3V), relatively high quantum efficiency (1% photons out/electron in) and shows green and orange light using different polymers. They are bright, and can easily be seen in room lighting. In addition, a LED made out of oriented polymers will emit polarized light; this opens another possibility for transferring information. Oriented photo-luminescence has already been demonstrated(7). Recent improvements in PPV involve preparing block co-polymers consisting of alternating sequences of conjugated and non-conjugated segments. This mimics the GaAs quantum well structure. By varying the degree of conjugation and co-polymerization, the colors can be varied from green-blue to orange-red; the light is also brighter(11). Finally in a private communication from Dr. C. Tang(12) at Eastman Kodak, I was informed that a brightness of 40,000 cd/m^2 was attained in an organic material; this brightness is 100 times greater than that of a TV screen. This material was not polymeric however.

I have already mentioned one of the aspects of polymers that has no parallel in inorganic materials; this is the ability to make large scale electronic structures. A second feature of conjugated polymers follows from the existence of extended-electron systems, and the accompanying ease of electronic polarizability; this leads into the ability to exhibit non-linear optical (NLO) behavior, and into the new field of photonics.

V. PHOTONICS

This field encompasses the use of the photon to accomplish many of the functions usually carried out by the electron. The material property that is a basis for this field is the NLO response to incident light. Potentially useful applications include(13)

a) frequency doubling to change the color of transmitted light; this calls for second harmonic generation (SHG).

b) switching of light from one track to another by making use of the change of refractive index by an external field, such as that produced by a controlled laser pulse (third order effect) (THG).

c) amplification of one source of light with another. Using a second-order non-linear material as a medium, a weak signal input at a frequency ω_1 can be made to interact with a high intensity beam at a higher frequency ω_3 to create a new frequency at ω_2 and an amplification of ω_1 and ω_2. This is called parametric amplification.

d) altering the transmission characteristics through a medium as a function of a light intensity change in the absorption coefficient.

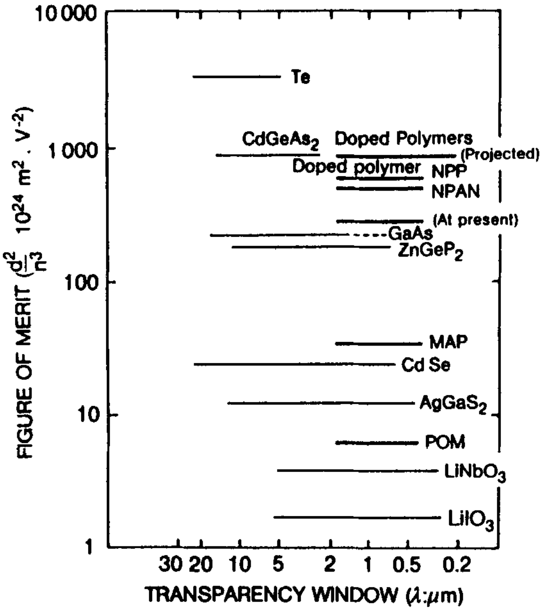

FIGURE 5 Figure of merit for non-linear materials versus wavelength. Organic materials are best in the frequency range of visible and near infrared, particularly the doped polymers. Figure obtained from ref. 16.

Already, the optical threshold of polymeric materials can be greater than 10 GW/cm^2 with a ps pulse, which is orders of magnitude greater than that of the multiple quantum well structure in GaAs.

The NLO properties of organic π-bonded materials are superior(14) in that they are non-resonant, i.e. non-absorptive of the incident or transmitted light. In inorganic system, the

NLO effects (especially THG) are resonant (absorptive) which results in a build-up of heat. Also, a non-resonant optical non-linearity has a purely electronic response, which is very rapid (femtosecond). The SHG requires a non-centrosymmetric solid, while most polymeric materials are centrosymmetric. But THG does not have this requirement, and polyacetylene shows a strong THG (although it has a serious defect due to its property of scattering light). A device that proves the feasibility of an optically activated switch operating between two waveguides using THG has already been fabricated from a polydiacetylene (15). At low light intensity, the signal travels along one waveguide. At higher light intensity, the signal switches to the other waveguide. Since the switching speed is electronic, it can be as fast as 10^{-14}s.

In Fig. 5 is shown a comparison of the various NLO materials that are in use, including conjugated polymers. As may be seen, the organic materials are approaching, and will eventually exceed, the NLO responses of inorganic materials(16).

VI. FERRI- AND FERRO-MAGNETISM

Up to this time, it was only the display of bulk ferro-magnetism that was restricted entirely to inorganic materials. However, progress is steadily being made in the synthesis of organic magnets. A. J. Epstein's group at Ohio State have recently described a compound $V(TCNE)_x y(CH_2Cl_2)$; x~2; y~1/2) which is ferrimagnetic up to its decomposition temperature of 350K. This is shown in Fig. 6. The degree of magnetization that has been achieved with this compound is comparable to that of a composite containing 6% by weight of iron at 2K, and 1.5% iron at room temperature.

As for ferromagnetism, a purely organic compound, p-nitrophenyl nitronyl nitroxide radical (p-NPNN) has been synthesized that exhibits spontaneous bulk ferromagnetism at 0.6K (Curie temperature)(18).

Finally, as another amazing characteristic of the C_{60} compounds, it has recently been found(19) that C_{60} doped with tetrakis (dimethylamine) ethylene, becomes a soft ferromagnet at 16.1 K. That is, the mixture becomes magnetized in a magnetic field, but loses its magnetization when the field is removed; the magnetization as a function of magnetic field strength shows no hysteresis, and no remanence.

VII. OPTICAL STORAGE MEMORY

While computers make calculations of profound complexity possible, there is an associated problem that accompanies this capability, the production of large quantities of information.

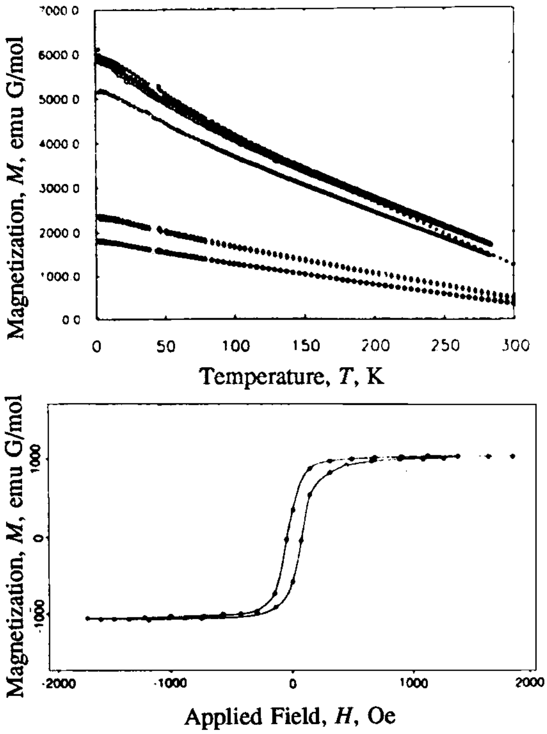

FIGURE 6 (a) Magnetization M as a function of temperature T in the presence of magnetic fields ranging from 19.5 (Top) to 0.15 (Bottom) kG for $V(TCNE)_x \bullet y(CH_2Cl_2)$. Critical temperature exceeds 350 K.
(b) Hysteresis M(H) at room temperature. The coercive field is 60 G at room temperature. The line is a guide to the eye. Figure obtained from ref. 17.

The storage and rapid retrieval of this information is a vital link to the full realization of the potential of the computer. The technique of hole-burning may provide the ultimate in information storage. In this method, a precisely tuned laser frequency is focused on a solid in order to produce a permanent, or temporary, change in the optical absorption or fluorescence at that frequency. This change in absorption or fluorescence can then be detected by a probe pulse. In a single inhomogeneously broadened absorption band, there can be as many as 10^4 homogeneous absorption profiles contained under its envelope, at liquid He temperatures. It is possible to fine-tune a laser so that all of these homogeneous lines can be addressed, and bleached, creating holes in the spectrum that can be detected (20) optically.

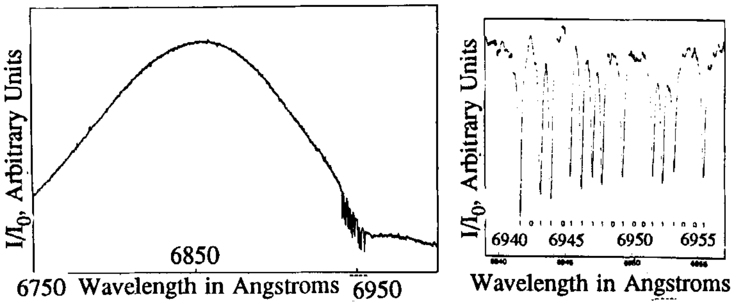

FIGURE 7 (a) Inhomogeneously broadened 0-0 absorption band of free base phthalocyanine in pmma at 4.2 K. A sequence of spectral holes has been burned near 695 nm.

(b) Enlargement of the absorption spectrum at 695 nm, showing twelve spectral holes and a possible coding of the hole pattern into binary units. Figure obtained from ref. 20.

This is shown in Fig. 7, where free-base phthalocyanine (dispersed in polymethylmethacrylate) is exposed to a series of intense, closely spaced-in-frequency laser pulses. The numerous spectral holes are clearly visible. Thus, in one geographical location, it is possible to store more than 1,000 bits of information in frequency space. Furthermore, if one were to use a material in which hole-burning could be accomplished by the interaction of two intersecting light beams, then as many as 10^{12} different geographical locations could be addressed in 1 cm^3 of material.

An example of a two-photon, 3D optical storage system(21) based on the isomerization of a spiropyran dispersed in a polymer such as polymethylmethacrylate is shown in Fig. 8. The information is stored by using two orthogonal beams of 532nm light focused on a spot in the sample, which causes an isomerization of the spiropyran to form a merocyanine. The information is read out by using two orthogonal beams of 1064nm light, which induce fluorescence of the merocyanine.

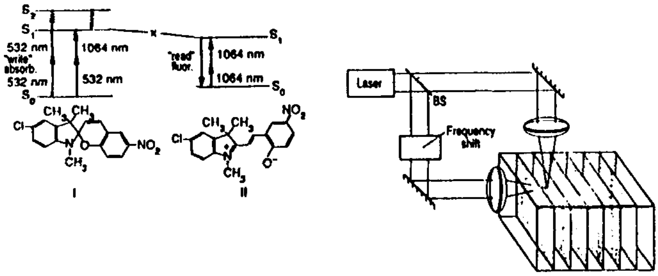

FIGURE 8 3-D optical memory. The energy level diagram with the molecular structures of the "write" and "read" forms are shown on the left. Writing requires uv excitation, which is accompanied by two-photon absorption in either of two ways as shown. Reading operates similarly to writing, except longer wavelengths are used. The schematic on the right shows a 3-D optical memory based on a two-photon process. Replacing lenses with holographic gratings allows parallel addressing. BS, beam splitter. Figure obtained from ref. 21.

VIII. MOLECULAR ELECTRONICS

As was pointed out in the Introduction, by making it possible to carry out complicated functions using electronic systems that are small in size, it becomes more feasible to place such systems in the hands of individuals in the lesser developed countries. The existence of biological systems that carry out thought processes of unmatched depth shows that small size need not limit performance. The pace of development of active electronic devices of smaller size in shown in Fig. 9(22). The new field of molecular electronics is directed towards the achievement of such small size.

In distinction with the use of molecular materials for electronics, this field of making electronics on a molecular level is in its infancy. As of now, there are serious problems in conceiving of transport over a single "molecular wire". There are problems in continuity and deductibility of current. Many parallel chains would be needed, and the closest approach to applications with single molecules involve the use of Langmuir-Blodgett (L-B) films to prepare monomolecular layers. With the L-B film technique well in hand, most of the progress being made in molecular electronics at present is in the design of the molecules that can be used to form the films.

In Fig. 10(23) is shown the structure of a typical biological membrane, consisting of a phospholipid bilayer containing islands of bilayer-penetrating proteins.

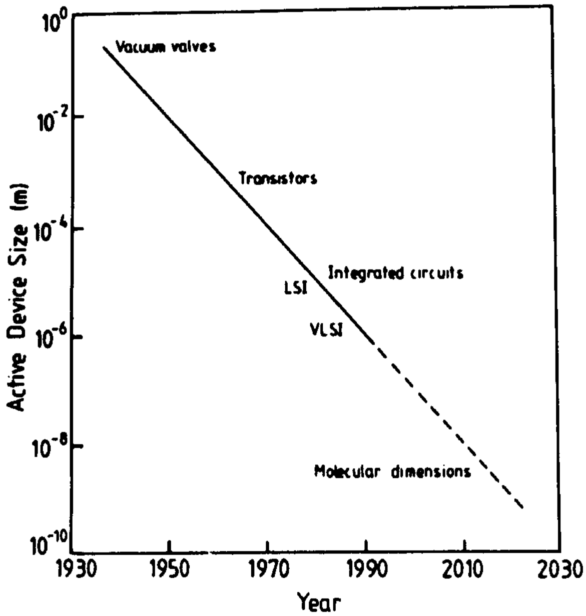

FIGURE 9 Historic and predicted device sizes over the past 60 years. The extrapolation to molecular dimensions represents the next great step. Figure obtained from ref. 22.

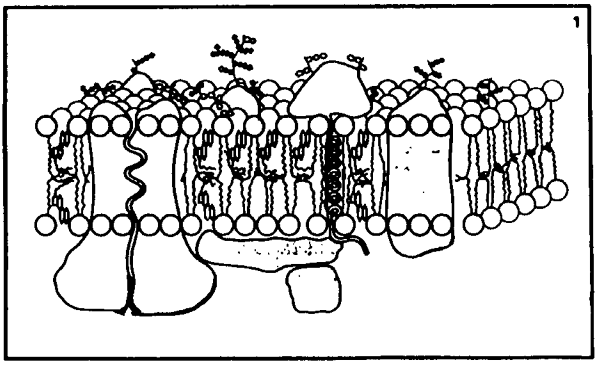

FIGURE 10 A biological membrane showing the phospholipid layer including examples of bilayer-penetrating surface-associated proteins. Figure obtained from ref. 23.

This is the model for the synthetic bilayers that are produced by means of the Langmuir-Blodgett (L-B) technique shown in Fig. 11$^{(24)}$.

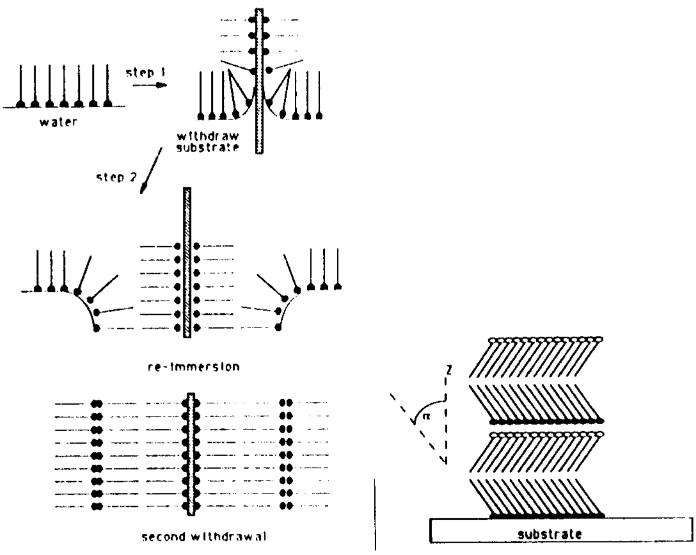

FIGURE 11 (a) Langmuir-Blodgett (L-B) film deposition process. In step 1, a hydrophylic substrate is withdrawn from the surface of the water and the hydrophylic heads of the compressed surface film adhere to the substrate. Reimmersion takes place in step 2, but with hydrophobic tail-tail deposition. Thick films can be built up. The overall structure is centrosymmetric.

(b) A L-B film made from two different surface layers, showing the tilt of the molecues. The overall structure is non-centrosysmmetric and support SHG. Figure obtained from ref. 13.

It is possible to synthesize a surface-active molecule with an electron donor at one end and an electron acceptor at the other end. In addition, one end of the molecule can be made hydrophobic (as with alkane groups) and the other end can be made hydrophylic (as with polar groups). When placed on a water surface, these compounds tend to be oriented so that the polar ends are buried in the water. When the surface film is then compressed, the molecules self-organize to form structures illustrated in Fig. 11. In order to obtain second-order nonlinear optical properties, it is necessary for the films to be non-centrosymmetric. As may be seen in Fig. 11(a), the system is centrosymmetric. However, it is possible to use alternate layers of different substances, and end up with a non-centrosymmetric system. This is shown in Fig.

11(b), and as an example, alternating layers of a merocyanine dye- and ω-tricosenoic acid produce a non-centrosymmetric system$^{(25)}$.

IX. SELF-ORGANIZATION

The ability of L-B films to self-organize can be used to organize other molecules that cannot self-organize. For example$^{(26)}$, conductive polypyrrole molecules can be dispersed throughout surface-active pyrrole molecules.

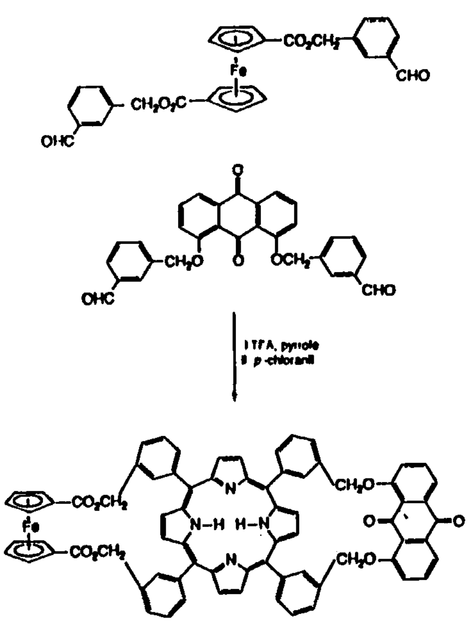

FIGURE 12 Self-assembly of a ferrocene, porphyrin, and a quinone to create a triple macrocyclic architecture. This is a rare example of the synthesis of a structure containing a donor and acceptor. The conjugated structure facilitates electron transfer across the porphyrin. Figure obtained from ref. 27.

Thus, a 3-0DOP (3-octadecanyl pyrrole) surface-active pyrrole forms a highly oriented film at a tilt angle of ~55°. A polypyrrole chain dispersed in 3-0DOP is also oriented when the surface layer is compressed. Multilayer films have a large dielectric constant (>100) at low frequency, and a large conductivity anisotropy. These are attributed to the molecular organization of the film, where the p-pyrrole is sandwiched between the ordered layers of 3-0DOP molecules. This structure resembles that of active molecules floating in a lipid cell membrane, which is essentially a L-B film. This is illustrated in Fig. 10.

More distant, but already begun, is the development of molecules that assemble themselves and self-replicate. As an example, in Fig. 12(27) is shown the self-assembly of a ferrocene, a porphyrin, and a quinone to form a triple macrocyclic structure. This is one of the few examples of the self-assembly of a donor-acceptor-electron system. Such systems are valuable for the study of electron-transfer reactions.

X. BIOLOGICAL MATERIALS

An outstanding characteristic of the biological levels of organization is the high degree to which structure is dedicated to function. Witness the placement of protein molecules in the bilipid membrane of a cell as shown in Fig. 10 and the ability of these protein molecules to effect ion transport into and out of the cell.

BACTERIORHODOPSIN

One biological material that has received considerable attention, and has shown remarkable properties is bacteriorhodopsin (BR)(28). BR is the light transducing protein in the purple membrane of Halobacterium halobium. This is shown in Fig. 13(23).

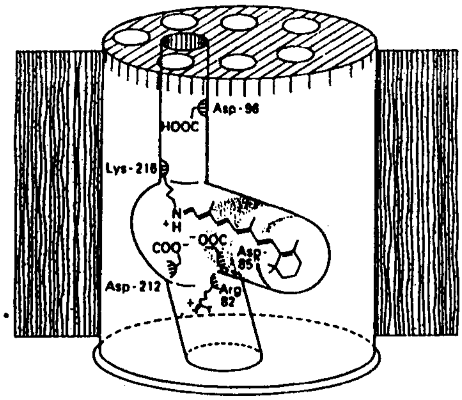

FIGURE 13 Diagram showing the conjugated retinal binding site of bacteriorhodpsin in its biological membrane , and the manner in which it spans the membrane. Figure obtained from ref. 23.

This membrane contains the BR protein in a 3:1 protein-lipid matrix. Rhodopsins are familiar since they act in our system to convert light into a nerve impulse. BR also has a photosynthetic function. BR contains a chromophore (retinyl) in a protein-binding site. Upon absorption of light, the chromophore isomerizes, producing a red-shifted product. This product converts to another relatively stable form, referred to as M, which absorbs in the blue and converts with high efficiency back to the stable BR form. Thus, BR is optically bistable, and photochromic. It can be used as an optical memory. The protein is stable, and together with the chromophore, has been selected by evolution as the best material for carrying out its function. BR has the following advantages:

a) thermal and photochemical stability.

b) ps photochemical reaction time in forward and reverse direction (45 ps).

c) high forward and reverse quantum yield, so low light levels can be used.

d) quantum yields that are independent of wavelength.

e) there is a large shift in the absorption spectrum that accompanies the photochemistry, so accurate identification of states is possible.

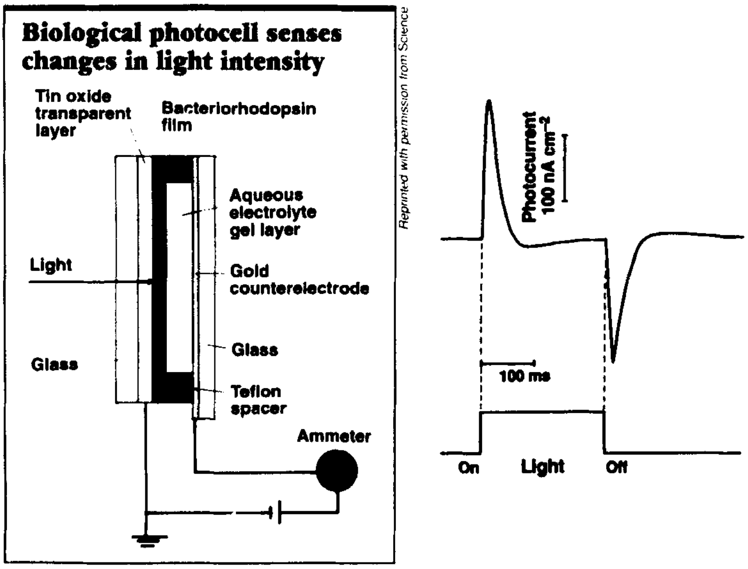

FIGURE 14 (a) Schematic of a photocell based on bacteriorhopsin.
(b) A typical profile of the photocurrent in the presence of changes in light intensity. The photocurrent responds positively (in the cathode direction) and negatively to an increase and decrease in light intensity, respectively. Figure obtained from ref. 29.

f) there is a high 2-photon cross-section, permitting activation of the I-R;

g) BR has high second order hyperpolarizability; $\beta = 2500\text{x}10^{-30}$ cm^5/esu (higher than many organic molecules), opening up NLO opportunities.

h) BR has good film forming capability, with L-B technique or polymer matrix spin-coating: it can be oriented in L-B films to better than 93%.

With these properties, devices suggest themselves, such as optical amplifiers, bi-stable and tri-stable holographic memory planes, thin film SHG, spatial light modulators, and pattern recognition assemblies. An example of the latter function is shown in Fig. 14(a)(29). Here, a thin film consisting of fragments of the BR-containing purple membrane is used in a photo cell that detects changes in light intensity as shown in Fig. 14(b).

XI. BIOSENSORS

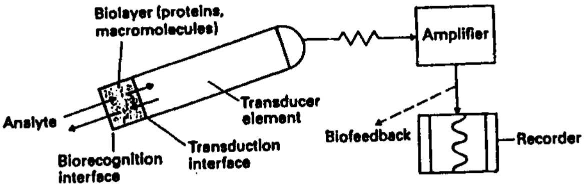

FIGURE 15 A schematic diagram of a biosensor as a dip-in probe for continuous reagentless analysis, permitting feedback and control. Figure obtained from ref. 30.

Many individuals have physiological deficiencies that require medication. As an example, diabetics lack a functioning pancreas, and so not utilize glucose properly. They must therefore use insulin, which is the pancreatic hormone, in order to correct this defect. This requires an analysis of the blood glucose level, so that the insulin dosage can be adjusted. Obviously, if the analysis and insulin dosage adjustment could be continuous, it would represent the closest and best approximation to a functioning pancreas. It would be ideal if a small device could be made that could be inserted into the human body which would carry out the sensing and dosage functions. A schematic for such a unit is shown in Fig. 15(30). The first step in the realization of such a device is to develop a micro-sensor. This was done by Heller's group(31), who attached a functioning enzyme electrically to an electrode by means of a conducting polymer wire. The enzyme is glucose oxidase. The wire is a redox macromolecule, designed to complex to the enzyme protein, and to electrically and mechanically attach the enzyme to the electrode, without deactivating the enzyme.

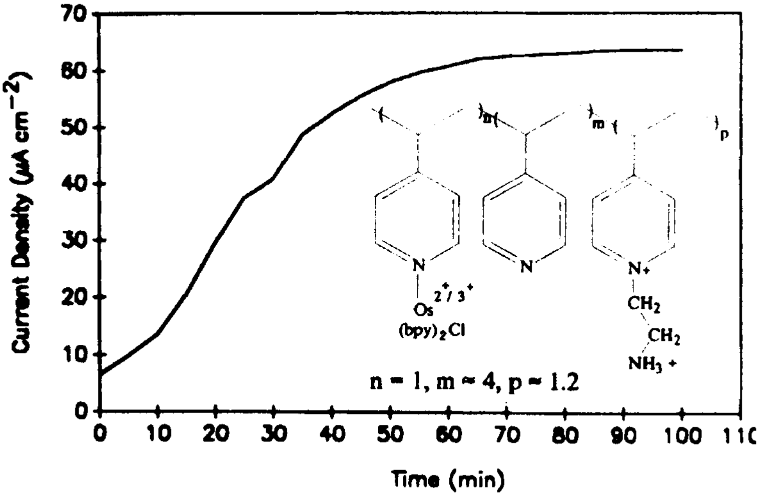

FIGURE 16 Electrically connected enzyme. The electrode-surface adsorbed redox macromolecule shown in the insert catches and irreversibly complexes glucose oxidase molecules. Glucose is present in solution, and as the enzyme molecules attach to the macromolecule, the oxidation of the glucose by the enzyme, which is now an extension of the electrode, is recorded. The time dependence of the glucose oxidation current therefore reflects the diffusional flux and binding of enzyme molecules to the macromolecules that are attached to the electrode. Figure obtained from ref. 31.

Heller used a polyelectrolyte conducting wire ($M \sim 10^5$ Dalton) consisting of 4-vinyl pyridine and 4-amino styrene with 1/7 of the pyridines complexed to $[Os(bpy)_2(py)Cl]^{+/2+}$ and with the residual uncomplexed pyridine, N-methylated to add positive charges to the chains. The electron shuttles from one-redox site to the other.

In Fig. 16, in the insert, is shown the molecular structure of the redox polymer wire. The curve shows the process of capture, and electrical connection of glucose oxidase molecules as they diffuse to a graphite electrode upon which is adsorbed the redox polymer. The solution contains glucose, and as the enzyme is caught and bound to the redox polymer, it demonstrates its viability by oxidizing the glucose molecules, and transferring electrons to the polymer, which transfers it to the graphite electrode.

XII. STABILITY

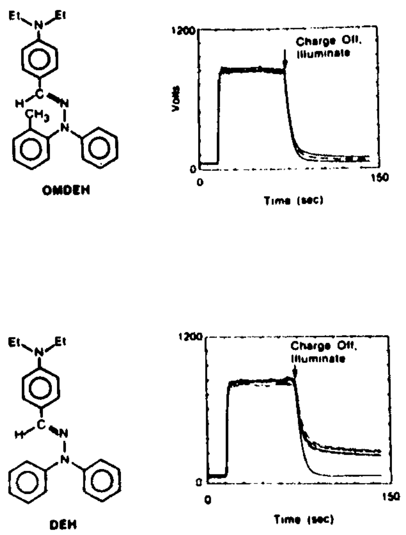

FIGURE 17 Correction of photoconductor fatigue. Comparison of photoinduced discharge curves after 4 J/cm^2 of incident light on a photoconductors formulated from DEH and OMDEH. The CH_3 blocking group on the OMDEH prevents the deleterious ring closure that produces fatigue. Figure obtained from ref.32.

For all the glamour associated with the electronic properties enumerated, and they are not exhaustive, the ability to use organic materials will depend in large part on solving the problem of poor stability in oxidizing or photochemical environments. Fortunately, here too, research can produce answers and dividends. As an example(32), in photocopying, there is a problem called photoconductor "fatigue", in which residual surface charges remain in the photoconductor upon repeated exposures. This results in lower contrast in the reproduced figure. This was traced by Pacansky to the formation of a photo-oxidation product as shown in Fig. 17.

By simple substitution of a methyl blocking group as shown in Fig. 17, the photocyclization was eliminated and the fatigue removed.

XIV. CONCLUSION

It is apparent that great strides are being made in applications, and I have not by any means mentioned all of them, for lack of time. These applications are the fruit of the close interaction of theorists and experimentalists. As the necessary quantum mechanical calculations are made to guide the efforts of experimentalists, we may expect even more rapid advances.

This work was supported by DOE Grant FGO286-ER60405. Acknowledgment is made of valuable discussions with Nicholas E. Geacintov and Charles E. Swenberg, and of the technical assistance of S.-C. Sheu and Leonard Sussman.

REFERENCES

1. A. Pocchetino, Acad. Lincei. Rendiconti, 15, 355 (1906).
2. A. M. Kini et al, Inorg. Chem., 29, 2555 (1990). Reprinted with permission. Copyright 1990, Am. Chem. Soc.
3. J.M. Williams, J.R. Ferraro, R.J. Thorn, K.D. Carlson, U. Geiser, H.H. Wang, A.M. Kini, H.-H. Whangbo, Organic Superconductors (Prentice Hall, N.J. 1992), p. 384.
4. S. Chakravarty, M.P. Gelfand, S. Kivelson, Science, 254, 970 (1991).
5. D. Jerome, Condensed Matter News, 1, 15 (1992). Copyright 1992, Gordon & Breach; with permission.
6. Private Comm., A. Macdiarmid and A.J. Epstein.
7. A. Heeger, Nobel Symposium June 13-18, 1991 Lulea, Sweden (to be published in Conjugated Polymers and Related Materials - Interconnection of Chemical and Electronic Structure (Oxford University Press, Oxford) 1992.
8. Fiona, M. Gray, Solid Polymer Electrolytes (VCH Publish ers, N.Y.), 1991, p.1.
9. op. cit., p. 6.
10. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackey, R.H. Friend, Nature, 347, 539 (1990).
11. A.B. Holmes, P.L. Burn, A. Kraft, R.H. Friend, D.D.C. Bradley, ibid 356, 47 (2992).
12. C. Tang, Private Communication.
13. P.N. Prasad, D.J. Williams, Introduction to Non-Linear Optical Effects in Molecules and Polymers, (John Wiley & Sons, Inc., New York), 1991. Copyright 1991, John Wiley & Sons, Inc.; with permission.
14. op. cit., p. 4.
15. S. Etemad, W.-S. Fann, D.D. Townsend, G.L. Baker, J. Jackel, in Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics, edited by J.L. Bredas and R.R. Chance, (Kluwer Academic Publishers, Netherlands, 1990), p. 349.
16. J.C. Dubois, op. cit., p. 321. Copyright 1990, Kluwer Academic Pub., Netherlands; with permission.
17. J.M. Manriquez, G.T. Yee, P. Scott McLean, A.J. Epstein, J.S. Miller, Science, 252, 1415

(1991). With permission.
18. M. Kinoshita, Bull. Am. Phys. Soc., 37, 46 (1992).
19. P.-M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, J.D. Thompson, Science, 253, 301 (1991).
20. W.E. Moerner, J. Mol. Electronics, 1, 55 (1985). Copyright 1985, J. Wiley & Sons, Ltd. London; with permission.
21. P.A. Parthenopoulos, P.M. Rentzepis, Science, 245, 843 (1989). With permission.
22. D. Bloor, Physics World, November 1991, p. 36. Reproduced by permission of IOP Publishing.
23. J. Findlay,, Chemistry in Britain, August 1991, p. 724. Copyright 1991, Roy. Soc. Chem. With permission.
24. See ref. 13, p. 74.
25. See ref. 13, p. 73.
26. J. Cheung, R.B. Rosner, M.F. Rubner, X.-Q. Yang, J. Chen. T.A. Skotheim, in (see ref. 11), p. 91.
27. R.W. Wagner, P.A. Brown, T.E. Johnson, J.S. Lindsay, J. Chem. Soc., Chem. Commun., 1465 (1991). Copyright 1991, Roy. Soc. Chem. With permission.
28. R.R. Birge, Ann. Rev. Phys. Chem., 41, 683 (1990).
29. T. Miyasaka, K. Koyama, I. Itoh, Science, 255, 342 (1992). With permission.
30. P. Vadgama, Chemistry in Britain, August 1991, p. 249. Copyright 1991, Roy. Soc. Chem. With permission.
31. A. Heller, J. Phys. Chem., 96, 3579 (1992). Reprinted with permission. Copyright 1992, Am. Chem. Soc.
32. J. Pacansky, IBM Res. Rept. RJ 8489, November 25, 1991. With permission.