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Research News

Molecular Electronics: Silicon to Soliton and Other Trends

When the British Association for the Advancement of Science (BA) first met in Oxford some one hundred and fifty years ago, only a few scientists, apart from *Faraday*, were then engaged in the new task of assembling electrical circuits. In those days, long before the age of mass production, the diameter of conducting rods was of millimeter dimension. Nowadays, with world-wide interest in the pursuit of the ultramicro-miniature, there is intense activity in the design and construction of molecular electronic devices made up of organic semiconductors, organic metals and conducting polymers which are of either organic or inorganic provenance (such as polysulfur nitride). Into the lexicon of the molecular architect a new word has been recently introduced, a "proconductor" which is the non-conducting form of a molecular entity that can also be made conducting by loss or gain of an electron by partial oxidation or reduction. Present day studies[1] which, inter alia, seek to arrive at favored molecules for memory, logic and amplification—with a view to constructing computers based, not on silicon or gallium arsenide, but on self-assembling molecules of the kind that abound in biology—focus on such problems as whether a π-conjugated molecule, a hundred Ångstrom or so in length, can serve as a proconductor or a conductor when placed between two metallic conductors. It is conceivable that the 'electronic wiring', which, it is thought, will be a characteristic of the molecular electronic device of the future, will consist of bridges similar to those recently discussed by *Aviram* (see Fig. 1). The diameter of these 'wires' is of nanometer dimension. A diminution in diameter by a factor of 10^6 has therefore been achieved in the interval between the date of the first and most recent (September 1988 at Oxford) BA meeting.

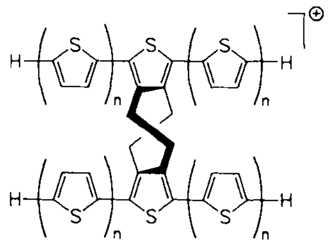
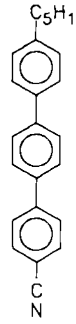


Fig. 1. A proconductor and a conductor chain connected by a σ bridge which forces the two π terminals to be at 90° to each other [1].

One of the numerous minisymposia held at Oxford focussed on some key aspects of molecular electronics. Present day microelectronic and opto-electronic industries rely mainly on inorganic materials. It has been clear for some time, however, that future requirements for more complex system designs predicate a renewed interest in the organic solid-state, the study of the electronic properties of which began in earnest forty years ago.[2,3] By the early seventies, these materials were seen to hold promise as sensors, protonic conductors and other useful devices.[4]

G. G. Roberts (University of Oxford and Thorn EMI plc) targeted his remarks largely on the wide scope and numerous advantages offered by carefully tailored Langmuir-Blodgett (LB) films. He demonstrated the advantages to be gained by capitalizing on the ultra-thinness and controlled, crystalline architecture of these monomolecular assemblies. That LB films may be used to generate dilute radioactive sources, magnetic monolayers and model biological membranes has been recognized quite early in their adoption as physico-chemical curiosities. What was not fully appreciated in the early days, however, was that considerable advantage could be taken of the comparative ease of preparing non-centrosymmetric, crystalline LB films. Materials with non-centrosymmetric structures exhibit pyroelectricity as well as strikingly non-linear optical behavior. *Roberts* referred in particular to work recently published[5,6] in which a novel organo-transition-metal complex had been synthesized specifically for use with the LB deposition procedure. Thus, by coordinating the liquid crystal compound **1** with $[Ru(PPh_3)_2Cp]$ forming **2**, the electron withdrawing nature of the parent molecule is greatly enhanced and, at the same time, multilayer formation, in the LB sense, is facilitated.[5] Optical second-harmonic generation yields a value for the hyperpolarizability much larger than that of most inorganic materials. Films of **2** have a pyroelectric coefficient (3×10^{-6} cm^{-2} K^{-1}) that is thought to be the largest yet reported. It is apparent from



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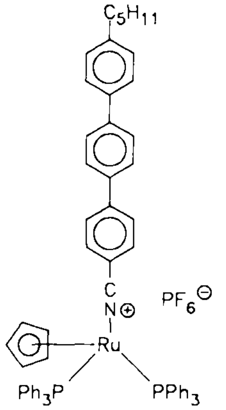

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this as well as other work by *Treadgold* et al.[7] (not presented at Oxford) that alternating LB films of polymers and merocyanine monomers (possessing large alkyl chains as quaternizing agents) are very efficient second-harmonic generators, enabling visible radiation to be generated from infrared sources. (Parenthetically, we note that it is of considerable technical and fundamental interest[8,9] that infrared–visible sum-frequency generation[10] can now be used to obtain vibrational spectra of adsorbed monolayers on metal and semiconductor surfaces).

J. White (Thorn EMI plc) dealt with the applications of liquid crystals. Although these fascinating materials have been known since the classic work in Germany in 1888, only after *G. W. Gray*'s pioneering studies at the University of Hull in the early 1970's did it become possible to produce, to order, environmentally stable liquid crystals. In the context of television displays, it is obvious that, for reasons of mass alone, the cathode ray tube cannot be a candidate for very large area (e.g. 3 m × 2 m) viewing screens. This is where it is felt that liquid crystal displays will prove advantageous, just as they have done for the currently available pocket-sized TV sets.

P. Day (Inorganic Chemistry Laboratory, Oxford and I.L.L., Grenoble) summarized the landmarks in the search for new molecular materials and superconductors. In the last few years molecular organic compounds have been discovered that not only conduct electricity like metals, but even become superconducting at low temperatures (see Fig. 2). In contrast to conventional metals, the charge-transfer salts which sometimes exhibit these properties are made from solution at room temperature by electro-crystallization. Again, in contrast to the traditional metals, the properties of 'molecular metals' are extremely sensitive to small changes in their packing arrangements. Minute alterations in the inter-molecular spacings can have profound consequences. And small chemical adjustments to the anions (e.g. the replacement of a $PF_6^{\ominus}$ for $ClO_4^{\ominus}$) in the charge-transfer salts transforms them from superconductors to normal metals or even to insulators. This is especially so for the tetrathiafulvalene derivatives. *Day* drew attention to some remarkably interesting charge-transfer complexes, prepared in his laboratory at Oxford, that changed from being semi- to superconducting on application of pressure. He also referred to the recent work of *Saito* et al. at the Institute of Solid State Physics, Tokyo, where an organic complex involving copper thiocyanate has a superconducting transition of 10.4 K (see review by *Inokuchi* in this issue). What is apparent from the behavior of such a material is that the rate of rise of the superconducting transition temperature (Fig. 2) is much steeper for molecular organic compounds than for the rare earth-alkaline-earth-copper oxides or their bismuth-based analogues.

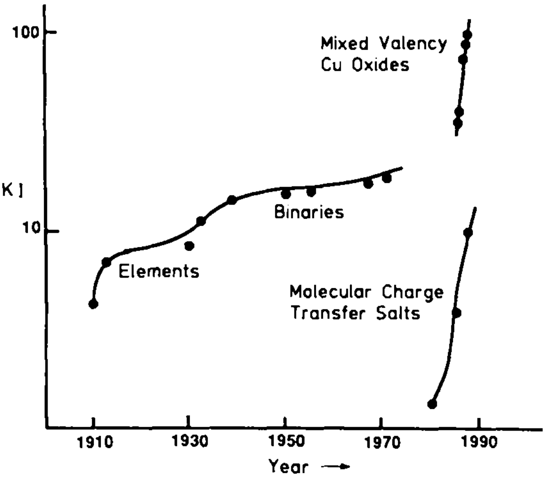

Fig. 2. The T_c history of superconductors.

H. G. Heller's presentation, based on his elegant work over the past decade at the University of Wales (first at Aberystwyth and latterly at Cardiff) was entitled 'Chameleonic chemicals'. Organic compounds that change color reversibly on exposure to light have enormous commercial potential. These thermally stable photochromic compounds can be developed for optical information storage in computers, as well as played on home video and audio equipment. By means of molecular tailoring and design, their properties can be modified so that they change color in direct sunlight and fade rapidly at room temperatures. Such compounds can be incorporated into lightweight plastic lenses which darken in sunlight and clarify under diffuse daylight. Another application lies in the security printing of banknotes, checks and other documents. By and large the chemistry of these chameleonic materials rests on the guidelines offered by the Woodward-Hoffman rules:[11] photo-stimulated, conrotatory reactions ensue freely whereas thermally-stimulated, disrotatory reactions entail overcrowding and, hence, are sluggish and unfavored.

Molecular electronics was also discussed in the Biology section of the BA meeting at Oxford, although the main emphasis was on the fundamentals of molecular recognition rather than molecular engineering. Whereas *C. R. Lowe* (Biotechnology Unit, University of Cambridge) sought to exploit the ease with which biological recognition takes place and to combine it with conventional solid-state electronics—and in so doing demonstrated how this would, inter alia, lead to effective remote sensing (especially under adverse environmental conditions) and continuous, one-line, real-time quantitative chemical or biochemical analysis—his colleague at Cambridge, *R. N. Perham* (Department of Biochemistry) ranged freely, during the course of his address, over topics such as the uncanny kinship in the architecture of the active sites in a dozen or so ostensibly quite unrelated enzymes and the role of an enzyme as an asymmetric unit. He also indicated that moving a 'recognition center' from one antibody into another was already a reality. As his was the presidential lecture of the Biology Section, he also considered other exciting areas of biochemical research: techniques are now available to enable the DNA sequence of a gene to be altered at will, thereby permitting the amino acid sequence of the encoded protein to be correspondingly changed. This testifies to the biochemists' ability directly to design protein molecules for specific, and otherwise inaccessible, purposes. *Perham* outlined how we are just beginning to acquire the ability to intervene in the elaboration of shape and form in multi-subunit, self-assembling systems.

Shortly after these minisymposia ended the 8 September issue of *Nature* appeared. In it *R. H. Friend* and his colleagues at the Cavendish Laboratory, University of Cambridge described new semiconductor devices using organic polymer diodes and transistors.[12] These devices are fashioned from polyacetylene, a conjugated polymeric semiconductor, which can readily be produced in (amorphous) thin film form, as a result of a thermally-stimulated conversion of a precursor developed at the University of Durham by *Feast* et al.[13] The devices constructed by *Friend* et al. operate in a novel way: charge is stored in localized soliton-like excitations of the polymer chain. These excitations are introduced by the presence of an adjustable surface electric charge. This is a fundamentally different method of introducing excitations from that used in devices based on silicon or gallium arsenide, where doping with controllable amounts of deliberately added impurities is the principle employed. The presence of charged solitons changes the optical properties of the hydrocarbon polymer.

The results reported by *Friend* et al. do not yet pose a threat[14] to established semiconductor technology: it must never be forgotten that the mobilities of electrons and holes in two dimensions in materials based on Si or III/V compounds, and their quantum-well variants, are phenomenally good. And, as yet, there is no organic metallic or semiconducting polymer that approaches Si in this regard. It is, therefore, arguable whether transistor devices based on organic polymers are likely to become commercial in the near future. (It is noteworthy that *Roberts* et al.[15] over a decade ago produced a p/n function based on two-dimensional LB films of anthracene. But these did not presage a growth in organic semiconductor technology). What one can reasonably expect, however, is that the elegant work of *Friend* et al. might soon lead to the development of high-performance sensors utilizing relatively cheap and easily processed organic materials.

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Conference Reports

Advanced Materials—R & D Efforts in Germany

A good three years after the German Federal Ministry for Research and Technology (Bundesministerium für Forschung und Technologie, BMFT) initiated its Materials Research Program, the first Materials Research Symposium took place in Hamm/Westphalia on September 12–14, 1988. Approximately 600 scientists and engineers discussed, in plenary lectures and review papers. the current state of knowledge and techniques in materials research. Results obtained up to now in various advanced research and development projects were presented in specialist papers and posters.

Following intensive discussions with many experts, five main themes that appeared to offer a high potential for innovation had been chosen for the Materials Research Program: ceramics, powder metallurgy, metallic materials for high temperatures and specialized applications, new polymers, and composite materials. The idea of the program is to stimulate progress by setting up joint interdisciplinary research projects involving academic research institutes and industrial laboratories, with well-matched complementary work plans carefully drawn up and agreed in advance. The industrial partners contribute with about 50% of the cost of such R & D projects. Federal funding up to a total of DM 1.1 billion is to be made available over the ten-year program. The Materials Research program is being supervised on behalf of the BMFT by the Materials Research Project Group of the KFA (Nuclear Research Center), Jülich.

The DM 940 million that has been committed to the Materials Research Program up to the time of this interim review in Hamm is divided between 265 collaborative projects involving 637 research laboratories; Table 1 summarizes the distribution between topics. Of the funding provided by the BMFT, 34% has gone to academic research institutes and 66% to industrial laboratories.

Table 1. Distribution of presently committed research funds between the five main themes of the Materials Research Program (million DM).

	Ceramics	Powder metallurgy	High temperature metals	Polymers	Composites
Total budget	251	94	176	200	220
BMFT contribution	124	58	99	103	116

Ceramics

This part of the program is aimed mainly at research and development on monolithic ceramics, and also includes ceramic films. It is strongly focussed on high performance structural ceramics (engineering ceramics). At present there are very few applications for which the reliability of complex shaped ceramic engineering components under dynamic load is adequate. It should be possible to greatly improve the reliability of ceramic components by quality control during manufacture, or by structural reinforcement, helped by the expected development of more reliable non-destructive testing methods. The powders used as starting materials for the manufacture of ceramic engineering components can be synthesized by reactions in the solid state, by production from melts, or by precipitation from solutions or from gaseous phases. An example of the