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PROSPECTS FOR MOLECULAR ELECTRONICS

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Abstract The great variety of structure and properties of molecular materials provides a basis for current and future applications in electronics and optoelectronics. The scope of molecular electronics is defined in terms of the historical development of the science and technology of molecular materials. The prospects for progress based on recent experimental, and conceptual advances is discussed.

INTRODUCTION

Any discussion of the prospects for molecular electronics must look both back as well as forward in order to see how the subject has developed up to the present. It must also define what is meant by molecular electronics. The latter is not easy since molecular electronics spans a number of disciplines and has developed along different lines in different countries. Even within a single country research scientists have disparate views on the range of topics that can be considered to constitute molecular electronics.

Historically the scientific study of electronic and opto-electronic properties of molecular materials began in the last century. The use of organic materials in devices, i.e. the use of liquid crystals in displays, was first patented over fifty years ago. However, it was really the development of the first silicon integrated circuits which prompted scientists to contemplate what the smallest entity displaying useful electronic functionality might be. Then and on numerous occasions since the progress achieved in reducing the size of active electronics components has been used as a basis

for extrapolation. These invariably suggest that devices at the molecular scale will be reached somewhen in the first half of the twenty-first century.

Such an extrapolation often obscures the dramatic changes in electronic technology which have been involved in the historical reduction in device size. The move from transistors to high density integrated circuits was almost as radical a change as the shift from vacuum tubes to transistors that preceded it. One might, therefore, anticipate that the evolution of molecular scale devices may involve a further change in device technology. Indeed if molecular scale devices are to be developed basing them on specially designed and synthesised molecules is not an unreasonable concept[1].

This idea stimulated work on organic semiconductors in the 1950s and 1960s. This was mostly premature since both the experimental and theoretical tools required to gain a firm fundamental understanding of such materials were poorly developed[2]. The discovery of intrinsically conductive polymers in the 1970s revived interest since it appeared that a molecular wire, considered an essential component for molecular electronics, was at last to hand. Interest was maintained by the series of conferences on molecular electronics organised by the late Forest Carter[3-5]. Again real progress proved difficult because there were no experimental methods available to test the ideas for molecular scale electronics that emerged.

In the 1970s liquid crystals were finally developed to the point where commercial displays were perfected. Progress has continued in this area and the technological importance of liquid crystals has increased over the last decade. Understanding of organic semiconductors and intrinsically conductive polymers has also grown steadily and interest generated in the non-linear optical and magnetic properties of molecular materials. A high level of experimental and theoretical effort centred on the macroscopic properties of molecular materials has resulted from the growth of these different topics.

In consequence we are now faced with two apparently disparate approaches to the use of molecular materials in the field of electronics. These have been termed molecular materials for electronics, and optoelectronics, (MME) and molecular scale electronics, (MSE)[6]. The former is concerned with utilisation of the macroscopic properties of molecular materials in devices. The latter attempts to answer the question whether either individual molecules or small molecular aggregates can be utilised as the elementary building blocks of electronic systems.

Many regard the quest for molecular scale devices as true molecular electronics. However, it can be argued that the distinction between MME and MSE is somewhat arbitrary and that both need to be considered as constituent parts of molecular electronics if the topic is to grow and prosper. The boundaries between the macroscopic, mesoscopic, i.e. aggregates, and molecular scales are not clearly defined. As the thicknesses of thin films used in liquid crystal devices decrease they approach the mesoscopic scale and small scale rather than macroscopic properties become important. Our understanding of macroscopic properties is generally founded on microscopic models which can also provide a basis for proposals for molecular scale electronics. We can expect that in the future studies of properties at the molecular scale will have an impact on macroscopic applications. First by providing data to help refine microscopic models of material properties and secondly by providing detailed information on the local behaviour of molecules in situations relevant to macroscopic applications, e.g. molecular alignment at surfaces.

The inclusion of both macroscopic and microscopic arenas in molecular electronics has another important aspect. Often new applications of organic materials are subject to the criticism that the materials involved lack the stability required for device manufacture and extended device lifetime. The use of liquid crystals in displays, organic semiconductors in electrophotography, etc. show that these problems can be surmounted. The existence of these current technologies ensures that there are scientists in

industrial laboratories who are willing to participate in discussions of molecular scale electronics and not simply dismiss them as too long term to be of no industrial interest.

Molecular electronics should encompass the science and technology of the use of molecular materials in key, active roles in electronic and opto-electronic devices and systems. The first European Conference on Molecular Electronics is based on this broad view of molecular electronics. It reflects the rapid advances which are being made in all aspects of the subject. It also illustrates the strong interdisciplinary character of molecular electronics and the new ideas which emerge when scientists from across the physical, biological and engineering sciences come together.

Though the progress of molecular electronics has not always been smooth the prospects for the future are good. This stems both from the scientific advances and the new ideas alluded to above. In the remainder of this brief review an attempt will be made to indicate how molecular electronics may move forward in the future.

PROSPECTS FOR MOLECULAR ELECTRONICS

Introduction

A major driving force behind research into molecular materials is the great diversity of molecular structure and function displayed by natural and synthetic materials. Nature has evolved systems of high complexity to achieve very specific functionality. The synthesis chemist has developed routes to both analogues of natural materials and totally new molecules. Once the relevant structure - property relationships are known the way is open to the targeted synthesis of molecules with properties relevant for particular end uses. While such precise targeting is not always possible there are often ground rules which mean a high likelihood that improved materials can be prepared. The end targets for the macroscopic use of molecular materials are well defined, being either current applications or those where

device demonstrators can be constructed. Thus, the cycle of synthesis, characterization, enhanced understanding of structure-property relationships and improvement of guidelines for synthesis can lead to dramatic improvements in materials.

The examples provided by natural systems encourage the belief that complex electronic systems can ultimately be realised with specially synthesised molecules. However, while living systems can provide examples of how functionality can be achieved there is little point in simply trying to duplicate what has evolved after numerous trials over long time scales. The flight of birds inspired the desire in man to fly but the methods used to achieve this are far from those adopted by nature, even though the ground rules are the same. Thus, in efforts to develop molecular scale electronics we should attempt to abstract the elements of how functionality is achieved and then embody these in simpler, manipulable molecular systems.

In the discussion that follows of molecular materials for electronics and molecular scale electronics there is no attempt to be comprehensive, an impossibility in the space available. Examples are given of recent advances which point towards future progress.

Molecular Materials for Electronics

Intrinsically conductive polymers were, as discussed in the general introduction, a factor in the revival of interest in molecular electronics in the 1970s. After the initial discovery of metallic conductivity in polyacetylene exposed to strong electron accepting and donating species numerous uses were suggested for this and the other conductive polymers discovered shortly afterwards. Despite the early enthusiasm progress has been slow because of the unstable, intractable nature of the materials to hand. Scientific progress in understanding both these intrinsically semiconducting polymers and the induced metallic phase was also hindered by the poor quality and irreproducibility of materials available. Despite this it soon became clear that the quasi-particles associated with charge carriers on the polymer chain were

different in character from those in inorganic semiconductors. The large structural deformations associated with electrons and holes produce states in the band-gap, so called solitons and polarons, and introduced new concepts into solid-state physics[7].

The development of synthetic routes via tractable precursor polymers made available purer, better characterized materials that could be manipulated into desired forms[8]. The ability to produce thin films was first used to produce field effect transistors in which the semiconductive polymer forms the gate[9]. Similar devices with oligomers as the active layers offer better high frequency performance, though not yet challenging conventional semiconductor devices[10]. The subsequent discovery of electroluminescence has created much greater interest as the prospects for large area displays on flexible polymer substrates appear encouraging[11,12].

The diversity of liquid crystalline materials and phases continues to increase, particularly those showing ferro, ferri- and antiferro-electric properties[13]. The fast switching time possessed by these materials will be of utility in a wide variety of active opto-electronic devices as well as displays.

Both single crystal and polymeric organic non-linear optical materials have been developed to the point where they are competitive with their inorganic counterparts[14]. An interesting development has been the use of the photo- and thermo-chromic properties of bacteriorhodopsin as a basis for the optical storage and logic systems[15]. This is an outstanding example of the use of a natural material in an unnatural situation to good effect. The recently announced commercial availability of this material indicates the level of interest.

Sensors, utilising enzymes are another good example of the use of natural materials to achieve a specific device goal, albeit in this case a peripheral device[16]. The specificity achieved by enzymes has not yet been matched in purely man-made sensors, though multi-element sensor utilised with neural network software to "learn" responses are getting closer. Most sensors utilise the electrochemical detection of the products of enzyme-

metabolite reactions. If direct electron transfer could be achieved this would be likely to give better sensors as well as providing insight into a molecular electronic process.

These examples are simply brief glimpses of some facets of MME, but suggest that there is tremendous scope for both the improvement of materials for existing applications and the development of new uses for molecular materials.

Molecular Scale Electronics

An example of a natural molecular electronic device that has often been cited is the bacterial photo-reaction centre[17]. These achieve close to unit quantum efficiency for the conversion of a photon into spatially separated charge. The molecular architecture with its intricate positioning of the individual active molecular units in the overall structure has been studied in detail. An analogous system has been proposed as a molecular shift register, though the complexity of the structure required has prevented practical realisation[18]. There have been many simpler proposals for 'molecular switches' on 'molecular wires', most based on the photoexcited disruption of double bonds on a polyenic chain. It is only relatively recently that these ideas have been subjected to a rigorous theoretical examination[19]. This shows that the behaviour of such structures is closer to that of metallic quantum rings, i.e. the output is dependent on the quantum mechanical interference of waves propagating along alternative paths through the structure, than the transistor switch that they were supposed to mimic. None of these early proposals have ever been subjected to experimental investigation.

Why should one be optimistic about the future of molecular scale electronics? The answer is because of the convergence at the molecular and mesoscopic scales of the branches of science shown in Figure 1. First, the development of atomic scale resolution microscopies, i.e. the scanning tunnelling microscope, the atomic force microscope and the related optical methods, provide tools for making measurements at the molecular scale[20,21].

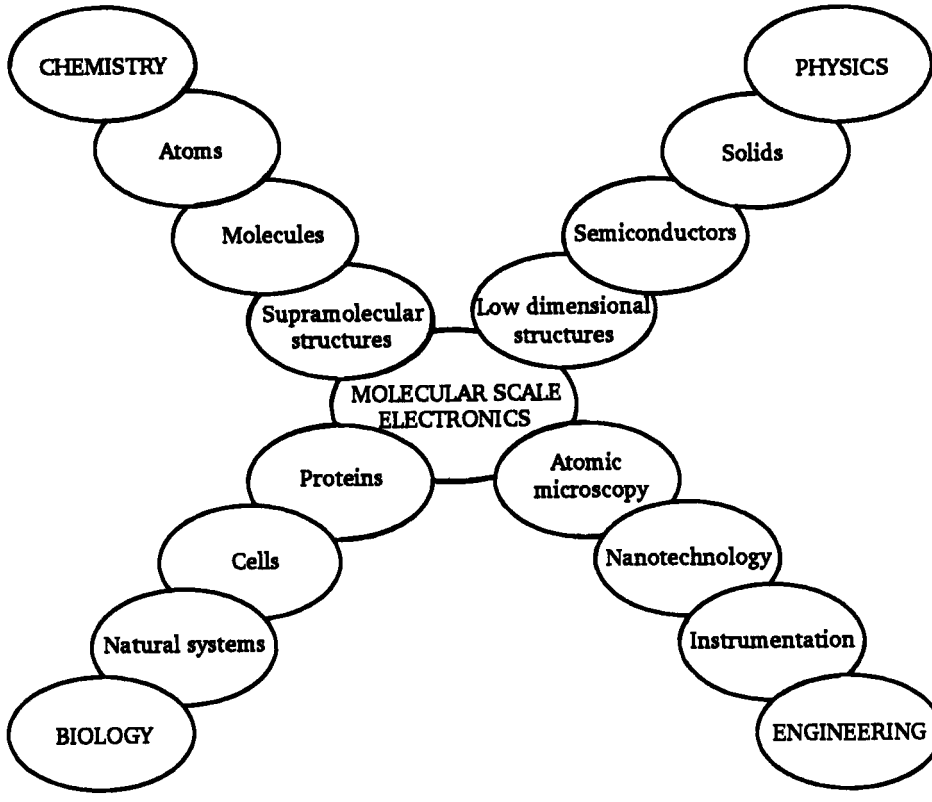

FIGURE 1 Convergence from different disciplines to the molecular scale.

These techniques are still in their infancy and the mechanisms by which organic and biological molecules give rise to contrast in the STM remain unclear. Though once again detailed theoretical studies are helping to provide insights[22]. Many of the early 'images' of organic materials have proved to be due to artifacts. However, there has been good progress in the imaging of monolayers of simple molecules on graphite and the dynamical behaviour of these systems can be observed[23]. The use of current-voltage scans can provide information about local electronic structure[24]. Early attempts to induce chemical reactions by current pulses in an STM were relatively crude. However, the fragmentation of specific molecules located

at defects has been demonstrated recently[25]. Thus, the ability to probe and manipulate individual molecules at surfaces is increasing rapidly.

While photo-chemical and photo-physical hole-burning spectroscopy in principle involves individual molecules, most studies have concerned ensembles of molecules distributed randomly in a glassy matrix. The recent observation of the repeatable switching of a single molecule and the spatial mapping of the fluorescence from single molecules are notable steps forward[26]. They demonstrate that light can be used to address objects with dimensions much smaller than an optical wavelength. The consequences of these advances for molecular electronics remain to be enunciated.

While the STM enables us to probe individual molecules and generate molecular scale structures it will probably be inappropriate as a tool for the assembly of large numbers of molecules. Chemists are turning to the question of how inter- and intra-molecular interactions can be used to direct synthesis and form both primary chemical bonds and secondary molecular structures. One approach is to use a solid surface as a substrate[27]. Much effort is being directed to the production of complex supramolecular structures in free molecules[28-29]. There are many examples in the recent literature including simple self-replicating molecules and vesicles[30,31]. They still fall short of the ability to restructure, with full biological function, shown by some biological systems but offer intriguing prospects for the future.

Advances in synthesis have thrown up molecular structures which are not directly related to natural systems. Fullerenes[32], carbon tubes[33] and the cage compounds developed by Cram[34] are all fascinating structures which could be utilised in molecular scale electronics.

Biology has progressed from the study of whole organisms to detailed investigation of the structure and function of biomacromolecules. The example of the photo-reaction centre has been quoted earlier and recent attempts to produce analogues have been successful through the synthesis of single, complex molecules which give separated charge on photo-excitation[35].

The alternative to electron based effects which nature uses to great effect, ionic motion and separation, should not be ignored. Ion-channels in membranes are the molecular switch which lies at the heart of natural neural networks[36,37]. The biologically based studies of ion-channels provide improved understanding and much simpler peptides capable of forming functioning channels have been synthesised. Thus, there are prospects for synthetic analogues of synapses, etc. which could form the basis for fluid based molecular electronic systems. Studies in this area could utilise the scanning electro-chemical microscope which, while lacking the resolution of the STM, can probe electron transfer with high spatial resolution[38].

There are examples in nature of the use of mechanical effects, e.g. the sub-cellular axonal transport of membrane-bound organelles[39]. Thus, in devising schemes for molecular scale devices mechanical and mechano-electrical effects should not be ignored. The synthesis of molecules with freely moving cyclic molecules threaded on linear chains may offer the prospect of a molecular abacus[29,40].

Finally developments in physics and engineering have resulted in semiconductor and metallic structures with dimensions on the molecular scale. The analogy of nanostructured wires and conductive molecules has been mentioned above. As the physics of low dimensional structures and other quantum devices advances are likely to emerge. The combination of such inorganic systems with molecules to provide new functionalities can be imagined but have not yet been studied in depth.

There are many ways in which molecular scale electronics could develop, perhaps too many. We are, however, still faced with the challenge of demonstrating either a molecular or a mesoscopic scale molecular switch. This requires the identification and synthesis of an appropriate molecule, its placement at a known location, verification of this emplacement and then demonstration of the switch action at the molecular or mesoscopic scale. The patch clamp technique applied to ion-channels comes close to this but does not have precision control of channel action[36,37]. The combination of synthetic

chemistry, nanotechnology and atomic resolution microscopy could in principle enable this goal to be realised. However, this would be only the first step along the road towards molecular scale electronics but is a critical step if real progress is to be made.

CONCLUSIONS

Molecular electronics is a broad subject where interdisciplinary collaboration is an essential ingredient. There is also scope for international collaboration since activities in different countries have distinct and complementary emphases and strengths. There is no question that in its widest form molecular electronics poses intellectual, scientific and technological challenges of the first order. These challenges will not be ignored so that the prospects for molecular electronics are indeed bright.

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