



Langmuir-Blodgett(LB) Film의 응용

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Introduction

The interesting effects of oil on the waves of a rough sea has been known for centuries. The first account of an experiment to investigate the phenomenon was probably that of Benjamin Franklin in 1773. He observed that only a teaspoonful amount of oil produced an instant thin oil film over a space several yards square of a pond. A quick calculation reveals that Franklin's oil film was only about 1 nm thick ($1\text{nm} = 10^{-9}\text{m}$)-about the length of an oil molecule. In 1917 Irving Langmuir studied the behaviour of certain organic compounds which spread as monomolecular films on a liquid surface. Today, such layers are referred to as Langmuir layers. He and his coworker, Blodgett, developed the technique of sequentially transferring the floating layers onto solid substrates to produce Langmuir-Blodgett(LB) films.

The concept proposed by Kuhn in the early 1960s, now known as "molecular engineering", has been arousing increasing interest amongst researchers in various fields of science and technology. It is well known that molecular engineering started by adopting the Langmuir-Blodgett(LB) technique as a tool to assemble organic molecules. This technique is based on the manipulation of monolayers formed at the air-water interface and their subsequent deposition onto a solid substrate.

To see the present and future prospects of LB film research it is helpful to consider the develop-

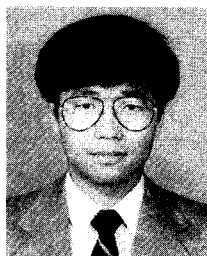
ment of biology, engineering and chemistry. With the close cooperation of physicists, chemist, biologists and electronic engineers, significant advances have now been made in perfecting the deposition technique for a range of relatively stable molecules.

This article provides a brief introduction to the preparation of multilayer films; however, the main focus is on their potential applications in the field electronics.

Deposition of Langmuir-Blodgett Films

Floating Monolayers

When spread upon the surface of a suitable sub-phase, appropriate molecules may be compressed with the aid of a barrier. Fig. 1 shows a plot of the surface pressure versus area occupied per molecule for stearic acid. The monolayer undergoes a number of phase transformations during compression. Using an isotherm of this kind it is possible to investigate the nature of the film and its degree



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No Film	Unstable Films	Stable Film with C ₁₆ Chain	C ₁₆ Chain Compounds Dissolve
Hydrocarbon	-C ₆ H ₄ OCH ₃	-CH ₂ OH	-SO ₃
	-COOCH ₃	-COOH	-OSO ₃
		-CN	-C ₆ H ₄ SO ₄
		-CONH ₂	-NR ₃ ⁺
		-CH=NOH	
		-C ₆ H ₄ OH	
		-NHCONH ₂	
		-NHCOCH ₃	

ties and unsaturated chains into the amphiphile tends to decrease the hydrocarbon chain length necessary for deposition. To produce transferred LB layers a suitable substrate, such as silicon wafer, and glass slide is normally passed vertically through the compacted monolayer. Fig. 3(a) depicts the deposition of a typical carboxylic acid. As the substrate is initially removed from the subphase, material is transferred in such a manner that the carboxylic acid head groups are attached to the oxide surface and the hydrophobic alkyl chains point away from the substrate. It is important to maintain the surface pressure within the

monolayer at a constant value during deposition so that the density of molecules is stable and a uniform LB layer is produced. A second downward passage through the air-water interface enables another layer to attach to the first and so on. In this way, it is possible sequentially to transfer the layers to produce an multilayers of LB film.

The structure that results from this mode of deposition is centrosymmetric and is termed Y-type. This means that dipolar molecules within adjacent layers are positioned so that the dipoles cancel and no net polarization results. However, some applications of LB films depend upon the presence of a polar assembly of molecules. It is possible to achieve this requirement by using materials that "prefer" to be transferred onto a substrate only on the downstroke or only on the upstroke. Such modes of deposition are referred to as X- and Z-type and the resulting structures are shown in Fig. 3 (b).

Langmuir-Blodgett Troughs

The growing interest in LB films has led to greater attention being placed on trough design and control systems to meet the stringent requirements of scientists and engineers. Therefore, mo-

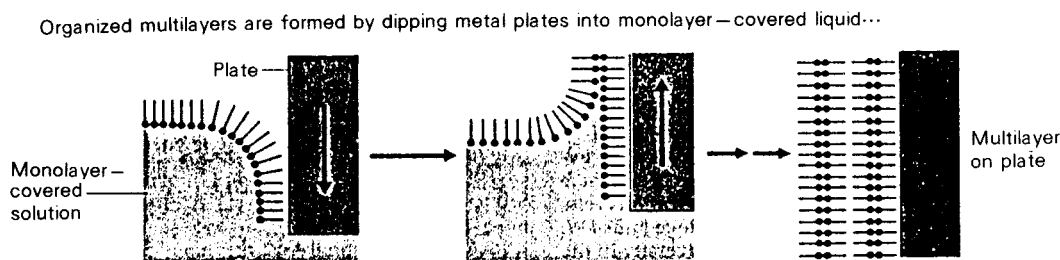


Fig. 3(a). The LB deposition process

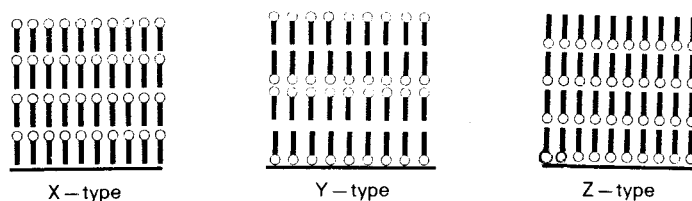


Fig. 3(b). The deposition modes for LB films

modern instruments are relatively sophisticated, and, for device-related work, need to be situated on antivibration table in clean environments. Recently it is possible to automate most features, the primary advantage from the instrument automation lies in efficient data collection and manipulation. For example, phase transitions are more apparent when the differential of the pressure-area isotherm is plotted. Also, the deposition process is programmed and monitored in a straightforward manner. Fig. 4 shows a schematic diagram of a conventional LB trough.

Analogue of Langmuir-Blodgett Films

Although the LB technique is powerful tool for

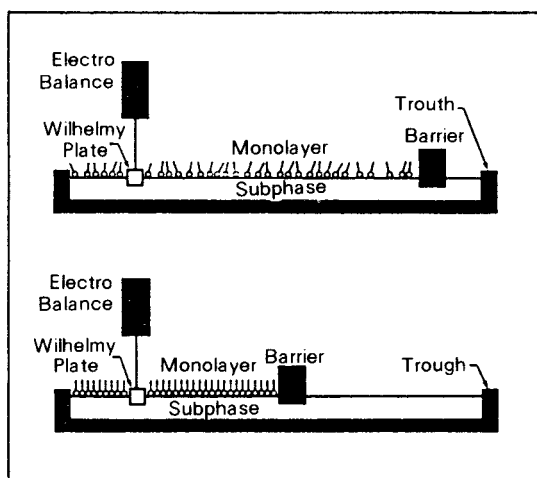


Fig. 4. Schematic diagram of a LB trough

handling molecular assemblies, this technique suffers several drawbacks, the most important being the requirement for planar substrates, a sensitivity to environment contaminants, and the large number of mechanical manipulations required to produce complex structures. Also, LB layer structures are generally held together by weak Van der Waals forces. Polymerization has been explored as a way to stabilize LB films.

In order to circumvent the short comings of the LB technique, recent efforts have been directed toward the preparation of self-assembling monolayers and multilayers. This approach is based on the spontaneous adsorption from solution of thermodynamically stable surface layers. Sagiv and co-workers and more recently Lee and co-workers have shown the new way of organizing multilayer of self-assembled structure in Fig. 5.

Lee and co-workers have found that stable, well-ordered multilayer films based on metal phosphonates can be prepared via the sequential adsorption technique. Metal phosphonates are an ideal choice for this kind of synthesis because as bulk phases their morphology resembles that of LB multilayers. The structural analogy is shown in Fig. 6. The multiple asymmetric layers of organic molecules that may be applicable to the fabrication of electrooptical switching elements and other second-order nonlinear optical devices are also reported by AT & T Bell laboratories scientists.

Building up a metal phosphonate film on a surface requires first anchoring of molecules bearing

...or by Sagiv's adsorption—synthetic method

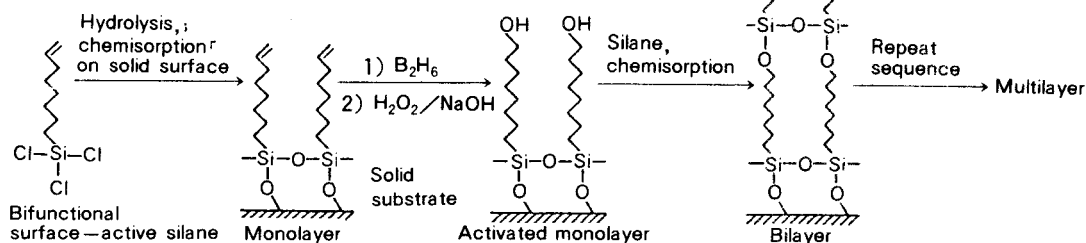


Fig. 5. Schematic representation of monolayer deposition sequence used to form multilayers

potentially quite effective for analyzing certain useful structural features at the monolayer level, are quite and difficult such as synchrotron radiation. Other useful combinations for analysis, such as infrared absorption spectroscopy(IRAS) and X-ray photoelectron spectroscopy(XPS), can be accomplished by using commercial instrumentation available in many laboratories.

XPS and IRAS are two standard spectroscopic techniques for characterizing organic films and surfaces. While XPS analysis is restricted to vacuum conditions, it has the advantage of sensing elements of molecular films in the outermost regions($\sim 5\text{nm}$) and in a variety of chemical bonding situations. On the other hand, IRAS offers the potential for analysis of molecular ordering of LB films. Continued development and application in these tools will promote efficient advances in studies of structure-property correlations in molecular LB films. An adjunct technique is single wavelength optical ellipsometry, which has been extremely useful for measuring the thickness of a LB film. Spectroscopic ellipsometry could prove quite useful in detailed structural analyses of organic films. The thickness of molecular layers are measured from reflection ellipsometry as shown in Fig. 7.

Electron diffraction has been used to study LB films for a long time, but only recently have the packing arrangements of molecules in multilayer

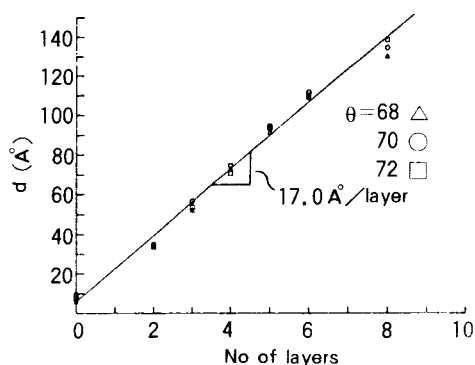


Fig. 7. Film thickness vs number of layers for metal phosphonate molecular films grown on silicon wafer

films been investigated in detail. For example, transmission electron diffraction has provided evidence that epitaxial growth occurs under certain conditions where the multilayer film assumes the structural order present in the first layer.

X-ray diffraction techniques have been used extensively to determine the monolayer thicknesses of LB films. Because the scattering of X-rays from carbon and hydrogen atoms can be assumed to be very small compared to that from heavier metal ions incorporated in a film, the lattice spacing normal to the film corresponds to the distance between adjacent planes containing metal ions. Recent experiments using synchrotron radiation indicate that diffraction studies on ordered LB layers is promising to determine molecular ordering of organic films. Fig. 8 shows the orientation models of LB monolayer of metal arachidate after synchrotron radiation experiment(NEXAFS).

Scanning tunneling microscopy(STM) is a technique capable of atomic resolution at specific sites that has received considerable attention of late since Binnig and Rohrer received the award of Nobel prize in 1986. A tunneling technique is limited to dielectric films with thickness in less than 4 nm range because anything much thicker than would prevent tunneling. Numerous reports of the use of STM to elucidate the fine micro structure of organic molecules at the molecular levels have

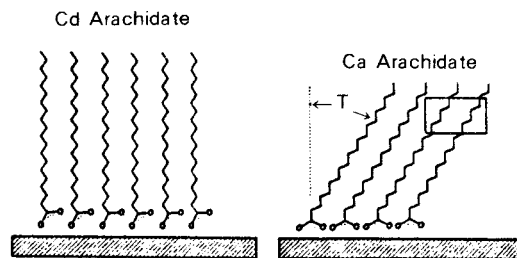


Fig. 8. Packing of hydrocarbon chains and quantum tilt model. Proposed models for the hydrocarbon chain orientation of films of cadmium and calcium arachidate. The cadmium arachidate chains are nearly normal to the surface(top), while the calcium arachidate chains are tilted by 33° .

already appeared in the scientific literatures. Among of those STM results, Fig. 9 shows the image of the surface conformations of 4-n-octy-4'-cyano-biphenyl liquid crystal. The atomic force microscope (AFM) is also an scanning probe microscope capable of resolving surface detail down to the atomic level. The potential of the AFM, which does not require a conductive sample, is shown with molecular resolution images of a nonconducting organic monolayer.

Applications of Langmuir-Blodgett Films

It is now possible to specify, design, fabricate and characterize molecular multilayer films on the basis of previous four sections. If these capabilities can be manipulated to precision while being applied to a still wider variety of materials, many applications of such materials system may become technological realities.

Electron Beam Resists

In integrated circuit technology the desire to fabricate objects with smaller feature sizes necessitates the use of lithographic tools with finer resolution than available for optical resists. The LB technique can be used to fabricate integrated circuits with minimum dimensions in the range of 0.1~0.5

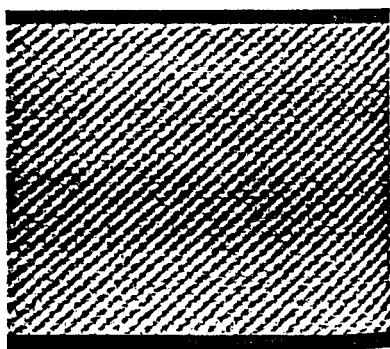


Fig. 9. Low magnification upprocessed image of 8CB on graphite obtained in the constant-current mode of imaging with a tungsten tip. Tunnel current was 0.5 nA and sample bias 1000 mV. Area of scan : 80×63 nm.

μm . Molecular films are fabricated by polymerization by electron beam irradiation. By choice of suitable amphiphilic materials, films that either degrade on exposure to the e-beam (positive resists) or those that polymerize (negative resist) can be produced.

Broers and Pomerantz have demonstrated the remarkable resolution that is better than 10nm using multilayers of fatty acid salts. Fig. 10 shows a typical example of their work.

Non-Linear Optics

The natural orientation features of monolayers and the degree of control over molecular assemblies provides good reason for utilizing non-centrosymmetric structures of LB films in applications such as pyroelectric device and optoelectronic devices.

Pyroelectric devices responded to a rate of change of temperature rather than to changes of temperature. The responsivity of a device depends approximately on the inverse of the pyroelectric film thickness, so ultrathin LB molecular film is a good candidate for the future development of high performance thermal imaging systems leading to high resolution infra-red spectrometer. Fig. 11 shows a super lattice comprising acid and amine molecules whose dipole moments are in opposite senses.

State-of-the-art guided wave optics is based on lithium niobate slab and channel wave guide stru-

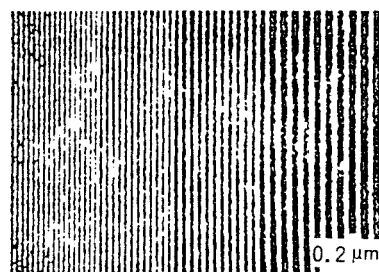


Fig. 10. Lines drawn using an electron beam incident on 138 monolayers of manganese deposited on a graphite substrate. The lines are approximately 10nm wide and, on the LHS of the photograph, as little as 20nm apart.

ctures. Inorganic material is quite difficult to be integrated with silicon and is quite expensive to produce. However, organic single crystals such as 3-methyl-4-nitroaniline, have been shown to possess exceptionally large second order electrooptic coefficients. LB films of certain organic molecules such as hemicyanine dyes have optical properties far superior to conventional crystals. Fig. 12 shows a proposed arrangement using guided waves in the film to detect a microwave electromagnetic field in a cavity.

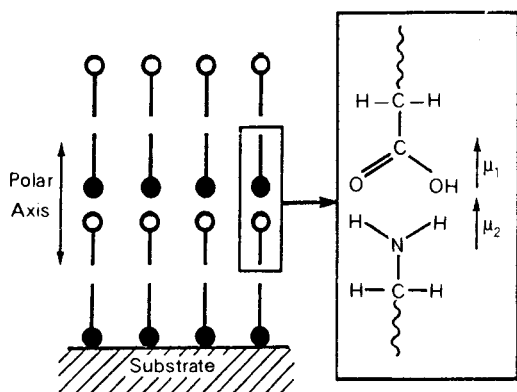


Fig. 11. Left : An organic superlattice with a unique polar axis. The two types of molecules involved could be a fatty acid and a fatty amine. The insert is designed to show that these two materials have dipole moments in opposite senses with respect to the hydrophobic chain.

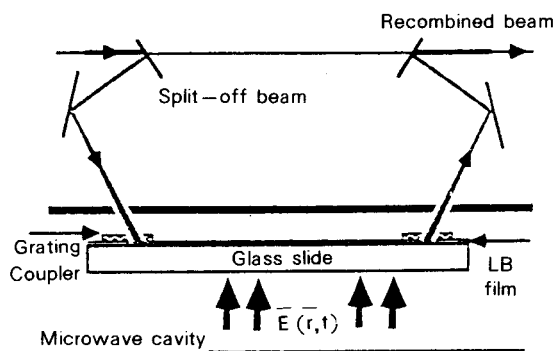


Fig. 12. Schematic diagram of a microwave detector. An alternate implementation involves a coated, coiled, optical fiber.

Biosensors

The idealized biosensor has a region in which the recognition of the molecule to be measured take place. The recognition process can then be arranged to produce or consume a simple secondary molecule, the concentration of which is monitored by a gas or ion sensor. The concept of a biosensor is shown in Fig. 13.

Recently attempts are in progress to utilize LB films for developing an optical chemical sensor for simultaneous recognition of many components in solution. The sensing principle is based on the dynamic quenching of various fluorophores embedded in an LB film. In nature, taste and olfactory cells simultaneously accept multimolecular information, which is followed by recognition of smell and taste through sophisticated information processing. Scientists are attempting to recreate this method in an artificial device, i. e., to integrate nonselective sensor elements into a single device to accomplish this multiple sensing task. Sensor consists of an optically transparent, nonfluorescent substrate and several layers of LB films, each layer containing different fluorophores. Fluorescence of an LB film may be quenched or enhanced when the film comes into contact with molecules of taste. Since each fluorophor fluores-

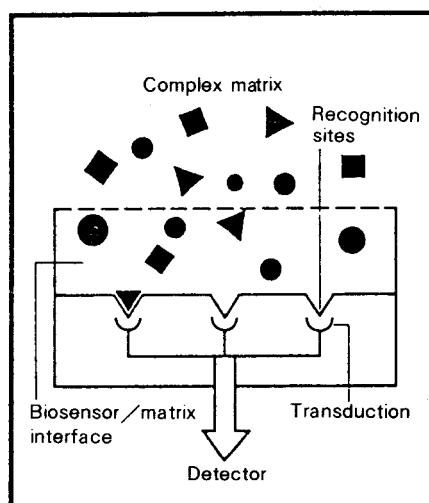


Fig. 13. The concept of a biosensor.

ces at a different characteristic wavelength, the responses of the films can be differentiated.

Optical and Electronic Devices

The good insulating properties of molecular LB films are possible to be used in field-effect devices when an organic layer is incorporated within a semiconductor structure. The integrated circuit industry is always seeking materials for thin insulating layer. As device geometries shrink, thinner and thinner layers are needed. Industry is planning on gate insulators as thin as 10~20 nm. Growing such thin films by conventional methods tends to produce pinholes and other defects without precise control of thickness. Ultrathin LB films would be prime candidates for new insulating layers in new device technologies, based on III-V compound semiconductors. Schematic diagram of a metal-insulator-semiconductor(MIS) heterojunction device is shown in Fig. 14.

Molecular Electronics

If the progress by the semiconductor industry in

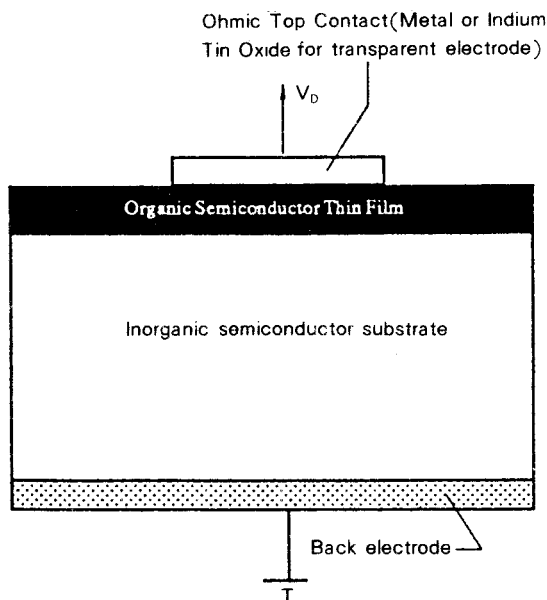


Fig. 14. Schematic cross-sectional view of an organic-on-inorganic semiconductor heterojunction device.

diminishing the size of switching elements is extrapolated from the present time by approximately 30 years, the future dimension of switch will be less than 10nm on an edge. At this size level it would appear reasonable to replace silicon as a device fabrication medium with the molecular scale medium. The idea of molecular electronics dates to the 1950s when many research projects concerned organic semiconductors, but the possibility of developing a computer based on molecular-sized electron elements was first discussed by Carter in 1979. Fig. 15 shows physical limits of integration of electronic devices on time scale.

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 metals, conducting polymers and organic conductors.

An example of supermolecular engineering is given by LB conducting films based on tetracyanoquinodimethane(TCNQ). Films of submicron thickness of classical TCNQ conducting salts or complexes are known to have poor conductivity. A promising new direction for research on charge-transfer complexes is emerging with recent reports of electroactive LB films formed from TCNQ complexes of pyridinium cations that are substituted with long hydrocarbon alkyl chains. Several families of conducting films are stable for months in room atmosphere. Some of organic

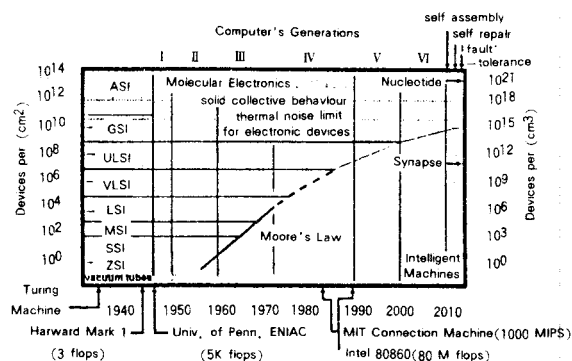


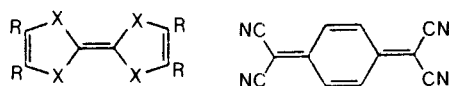
Fig. 15. Physical limits of integration of electronic devices.

conductors are shown in Fig. 16.

The primary object of this section is to show the application of three active molecular components as computing elements and to indicate a variety of elementary cellular automata. The three active molecular components include the electron tunnel switch, the soliton switch, and soliton valves. As applied to molecular electronic device technology, lithographic techniques are used to attach conducting molecular wires, the surface modification technique could be used to bond molecule wire to the designed area. In this case polysulfur nitride, $(SN)_x$ unit, and trans-polyacetylene are emphasized as molecular wires bridging microscopic leads and chargeable groups.

In 1974, Aviram and co-worker of IBM observed that several organic molecules could exist in two or more states. A hemiquinone molecule can exist in two different forms as shown in Fig. 17. However, the two forms of the molecule are actually same. When voltage is applied to the molecule it is converted from one form to another. Hemiquinones are a chemical analog for switching elements and the state of the switch can be monitored by the presence or absence of a current as shown in Fig. 17.

The prospects of a future coupling between molecular electronic devices and applied automata are quite exciting in terms of parallel processing the interpretation of visual data. This is due in part to molecular size of the molecular electronic device



- (1) X=S, R=H (TTF)
- (2) X=Se, R=Me (TMTSF)
- (3) X=Te, R=H (TTeF)

(4) TCNQ

TTF, tetrathiafulvalene ; TMTSF, tetramethyltetraselenafulvalene ; TTeF, tetratellurafulvalene ; TCNQ, 7,7,8,8-tetracyano-p-quinodimethane

Fig. 16. The structure of organic conductors.

components and to the nature of cellular automata. From concepts of cellular automata, the supermolecular information processor(SIP) may be visualized as a network of processors. In SIP based on "chemical" events, switching has a different mea-

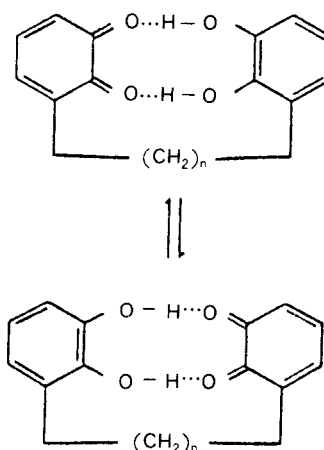


Fig. 17. The two chemical states of the hemiquinone switch(above). A circuit using hemiquinone switches with an ammeter to determine which state of the switches(below).

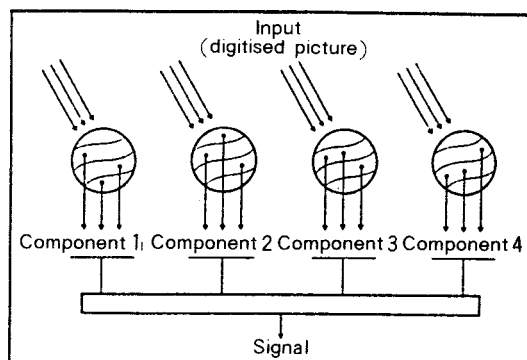
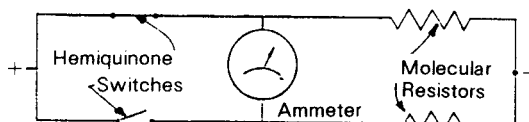


Fig. 18. A possible chemical SIP ; an array of such processors re sponding to the same input in different ways to generate a unique signal.

ning ; it relies on the recognition of one molecule by another. Within an extended set of processors a unique output signal is generated with the response to the same input in different ways in Fig. 18. This could make an exciting future for a truly molecular electronics.

Conclusions

A number of aspects are now clear concerning molecular monolayers and multilayers of organic assemblies. Their use as ordered arrays of organic materials with two dimensional characteristics become very important as we learn the relationships between the structural morphology and their macroscopic material properties.,

Organized molecular layers shows the special advantages gained from their technique for a particular application. This requires the combined efforts of interdisciplinary knowledge of chemistry, physics, biology, and electronics.

LB film research is a strong stimulus to propose ideal models and to open the pioneering future attempts in molecular engineering. The ultimate prospect of molecular layer technology is to build supramolecular machines.

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