

Molecules to Materials

5. Molecular Material Devices

TP Radhakrishnan

TP Radhakrishnan is in the School of Chemistry, University of Hyderabad, Hyderabad 500 046.

Previous articles of this series were on:

1. Design and Fabrication of Functional Molecular Solids, Vol.3, April 1998.
2. Liquid Crystals and Molecular Conductors, Vol.3, May 1998.
3. Molecular Magnetic Materials, Vol.3, No.7, July 1998.
4. Molecular Nonlinear Optical Materials, Vol.3, No.8, August 1998.

Earlier articles in this series provided several examples to illustrate the controlled assembly of bulk structures with desired solid state properties using specifically designed molecules. The ultimate goal of these exercises is the development of devices whose building blocks are molecules. This article and the next attempt to impart the flavour of this exciting field of research and technology through brief discussions of several molecular devices. This article will focus on devices, which utilise the bulk properties of molecular materials; the examples selected are electroluminescent device, thin film transistor and an electro-optic device.

Introduction

The past few decades have witnessed the realisation of a variety of electrical, magnetic and optical properties in molecular materials. This has been described in the earlier articles in this series. The traditional view of organic solids as of no consequence to modern technology beyond the role of polymers and liquid crystals is changing fast today. Molecule-based materials with a variety of solid state properties offer great promise in a wide range of applications. A detailed discussion of this fast growing field is beyond the scope of this article; we only provide here a glimpse of some fascinating possibilities that are opening up.

In general terms there are two approaches to the utilisation of molecules in the fabrication of devices. These approaches may be distinguished based on their goals – molecular material devices and molecular scale devices. The former refers to a more conventional application of materials technology in the sense that the molecular materials are used to fabricate devices based

on their bulk physical properties. The latter concept has evolved as a new line of thinking wherein a single molecule or perhaps a collection of a handful of molecules performs the function of a device. The quest for miniaturisation appears to be heading to its logical conclusion through these developments. A wide range of devices of both kinds have been proposed and investigated. We consider some specific cases to illustrate the direction in which this area of materials science and technology is headed. In this article we discuss examples of molecular material devices – molecular electroluminiscent devices, organic thin film transistors and electro-optic devices. The next article, the last in the series, will present an overview of some molecular scale devices.

A single molecule or perhaps a collection of a handful of molecules can perform the function of a device.

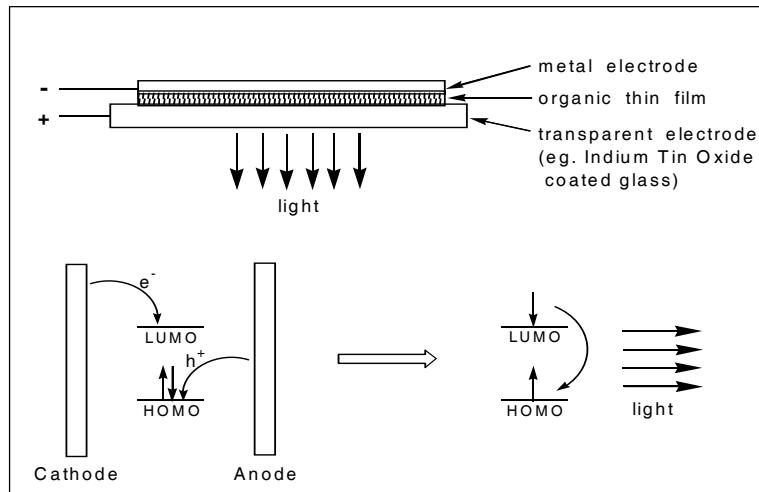
Molecular Electroluminiscent Devices

Electroluminiscence (EL) is a phenomenon with wide application in areas of illumination and display technology. This is very similar to the familiar process of photoluminescence (PL). In both cases visible light is emitted from the material, the difference being that the excitation source is ultraviolet light in the case of PL whereas it is an applied electric field in the case of EL. Though currently used EL devices (also called light emitting diodes) are based on inorganic semiconductors like gallium arsenide and zinc sulfide doped with manganese or terbium ions, it is becoming clear that greater efficiency can be achieved with fluorescent dyes and conjugated polymers. Further it is found that the voltage required to drive the luminiscence is appreciably lower with the organics, especially when used as thin films. Current EL devices run on DC voltage, but recent experiments show that certain organic polymer EL devices can be run on AC voltage as well, widening the scope of these materials for practical applications. The easier processing of organic thin film based EL devices allows large area display applications.

Electroluminiscence in semiconductor devices arises from the electron impact excitation of luminescent centres, for example



Figure 1. Schematic drawing of an organic electroluminescent device and the mechanism of light emission; HOMO and LUMO are respectively, the highest occupied and lowest unoccupied molecular orbitals of the electroluminiscent molecule.



the manganese or terbium ions doped in ZnS. On the other hand EL in organics arises from the recombination of electrons and holes injected into the material from the cathode and anode respectively. The basic phenomenon is illustrated in *Figure 1*. Depending on the energy gap between the HOMO and the LUMO, emissions of different colours can be achieved. The efficiency of the electroluminescence goes down if recombination of electrons and holes takes place too close to the electrodes. Special multilayer thin film assemblies are sometimes fabricated to ensure that the recombination takes place away from the electrodes and efficient luminiscence occurs.

Poly(phenylenevinylene) (PPV) (*Figure 2*) and its derivatives are some of the most promising conjugated polymers for EL applications. It produces an intense yellow green luminiscence of >100 candela/m² (which is about five times more luminiscent than a bright computer screen) at driving DC voltages of <10 V; for comparison, doped ZnS requires DC voltages >100 V. Another promising molecular material is a solid solution of aluminium trisoxiquinoline (AIQ) and a triphenylamine derivative (TPD) doped in a polymer matrix like polymethyl-methacrylate. A wide variety of metal complexes and π -conjugated polymers mainly based on PPV have been investigated in recent years. An interesting new family of materials being explored are based on

EL in organics arises from the recombination of electrons and holes injected into the material from the cathode and anode respectively.

Figure 2. Examples of molecules of interest in electroluminiscent devices.

spiro systems such as the spiro linked quarterphenyl (SQP in *Figure 2*) and higher analogues which show very high quantum yield (nearly 60%) blue photoluminescence. The spiro linkage apparently leads to high quality amorphous materials with high glass transition temperatures for solution processing.

The external quantum efficiency (number of photons per electron injected) of commercial inorganic light emitting diodes remains close to 1% after several decades of development, whereas in less than a decade organic EL devices have reached comparable or better efficiencies. The other advantages they offer are the low threshold voltages, possibility for large area applications and the light weight and mechanical properties of plastics. Synthetic manipulations can be used to change the extent of conjugation



in the polymers; this provides a control on the HOMO–LUMO gap and hence on the colour of electroluminiscence. The potential of molecular and polymeric EL devices for extensive commercial application is bright indeed.

Organic Thin Film Transistors

With the additional advantage in terms of easier processability that these systems possess over conventional semiconductor materials, organic materials are promising candidates for the fabrication of electronic devices such as field effect transistors.

In Part 2 of this series of articles, we have seen that molecular materials can function as semiconductors or metals or even as superconductors. Some doped polymers and oligomers show excellent semiconductor properties such as electron/hole mobility. With the additional advantage in terms of easier processability that these systems possess over conventional semiconductor materials, organic materials are promising candidates for the fabrication of electronic devices such as field effect transistors. One of the widely investigated applications of organic semiconductors is as thin film transistors (TFT's).

The basic function of a field effect transistor consists of controlling a current across two terminals called the source and the drain, in response to a voltage applied (gate voltage) at a third terminal (gate). The transistor could thus function as a switching device or as an amplifier. The utilisation of a molecular material in a TFT can be illustrated by the following example, which also highlights the crucial control of device characteristics using molecular properties. Doped polythio-phenes have been extensively studied as conducting polymers. It has been found that oligothiophenes like α -sexithienyl (α -6T in *Figure 3*) are excellent semiconductors and can be used to make thin film transistors. The schematic design of TFT's is also shown in *Figure 3*. A SiO_2 film is grown on an *n*-type silicon wafer and the oligomer film is deposited on it by vacuum deposition. Metal contacts are deposited on the organic film to serve as the source and the drain. A contact deposited on the *n*-Si wafer serves as the gate of the TFT. When a variety of oligothiophenes were studied, it was found that the field effect mobility of this transistor peaked for the α -6T oligomer. α -6T has a room temperature conductivity of $\sim 10^{-6} \text{ Scm}^{-1}$ and field effect mobility

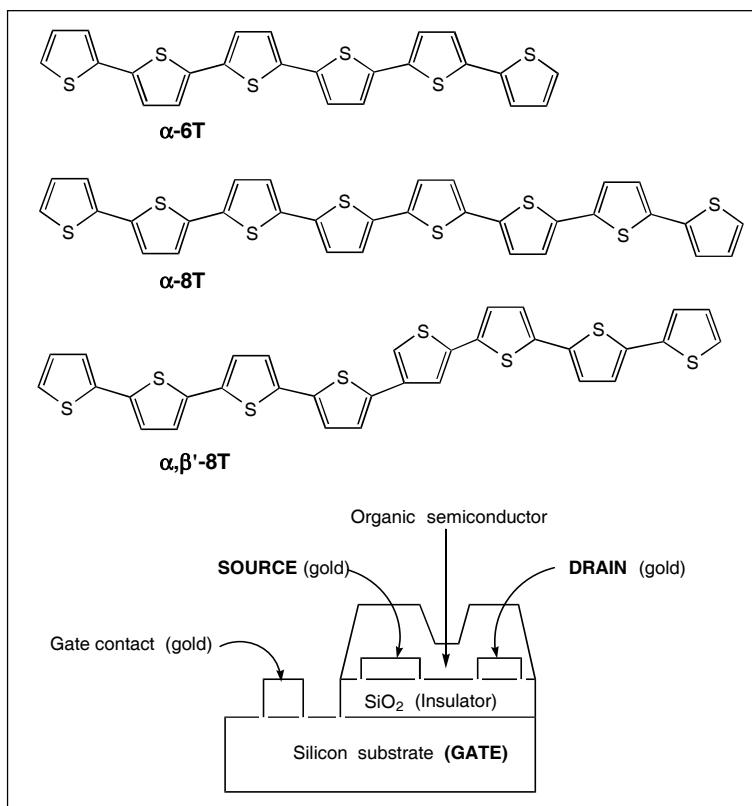


Figure 3. Oligothiophenes and the design of an organic thin film transistor.

of $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$. For shorter oligomers the limited π -conjugation leads to high resistivities typical of insulators. Interestingly, in a longer oligomer like α -8T, even though the conductivity remains comparable to that of α -6T, the field effect mobility decreases. This is attributed to the possibility of formation of larger number of disorders as the oligomer length increases. One possible source of disorder is the formation of α, β' -type linkages shown in Figure 3; the probability of formation of such disorders increases with increasing length of the oligomer. For this reason, it is argued that TFT's based on oligomeric semiconductors are superior to those based on polymeric ones. Molecular design can thus be effectively used to control the device characteristics of these thin film transistors.

Since oxidation or reduction using hole or electron doping respectively can regulate the conductivity of these organic

Molecular design can be effectively used to control the device characteristics of these thin film transistors.



It is possible to have transistors whose characteristics are controlled by the chemical medium by which they are surrounded. These can be used as sensors.

semiconductors, it is possible to devise transistors whose characteristics are controlled by the chemical medium by which they are surrounded with. This opens up possibilities for applications such as sensors.

Electro-optic Devices

In Part 4 of this series we have seen that there is currently a great surge of interest in an emerging technology based on photons as information carriers. The nonlinear optical properties of materials can be exploited in a wide variety of devices for generation, processing and transfer of information. Novel devices are required for encoding information on photonic signals by modulating their amplitude or phase, for changing their frequencies and so on. A variety of nonlinear optical (NLO) phenomena are available which can be utilised to carry out these functions. We consider below a typical example to illustrate the important role that molecular materials are likely to play in this field.

Amplitude or frequency modulation are the processes by which electromagnetic radiation such as radiowaves carry information. In photonic communication processes, laser light has to be modulated and transmitted through optical fibres. Amplitude modulation of photonic signals can be achieved using a Mach – Zehnder interferometer. The schematic diagram in *Figure 4* illustrates the principle of the interferometer. The beam is split into two paths at **A** and transmitted through a second order NLO material. When an electric field is applied to one of the paths, its refractive index changes due to the linear electro-optic effect (see Part 4 of this series). As a consequence of this, the beams passing through the two arms will develop a phase difference when they arrive at **B**, resulting in the modification of the amplitude of the output beam. When the phase difference ($\Delta\phi$) is zero there is full constructive interference between the two beams, and when it is 180° there is complete destructive interference. If the applied electric field is modulated, this modulation will be superimposed on the exiting photon signal.

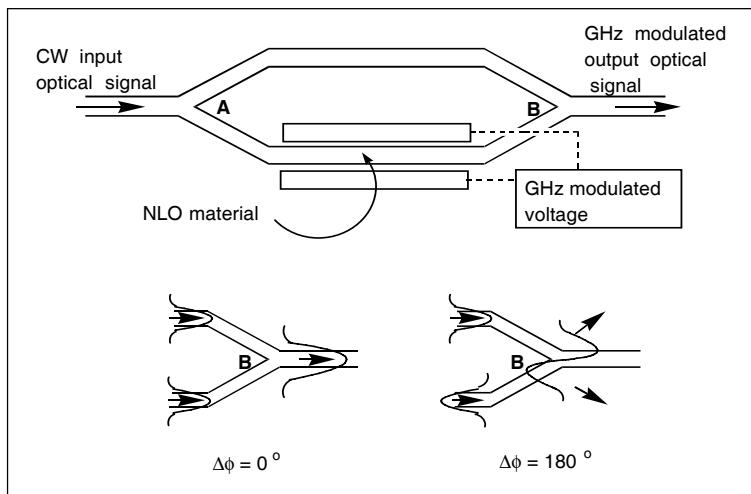


Figure 4. Amplitude modulation of photonic signals using a Mach-Zehnder interferometer.

The utility of an NLO material for such an application is decided primarily by the second order susceptibility χ^2 of the material, which determines how strongly its refractive index changes in response to changes in the applied electric field. The transparency of the material and its dielectric constant are also important parameters. Considering these factors, the appropriateness of a material for electro-optic application is quantified by what is known as a figure of merit (FOM) for such an application. Some push-pull organic compounds like substituted stilbenes possess an FOM of 1000 – 4000; this may be compared to the FOM of standard inorganic materials such as lithium niobate and gallium arsenide, which are about 7 and 1 respectively. This clearly shows that molecular materials are promising candidates in this area.

A recent example of a polymer developed for electro-optic applications is shown in *Figure 5*. A prepolymer with the ‘pendant NLO chromophores’ is first prepared. Then it is mixed with a cross-linking agent and cast into films. When electric field poling is carried out with heating, the NLO chromophore groups are oriented and then they are locked into position by the cross-linking process. Electro-optic devices fabricated from such polymeric materials have been found to have superior operating bandwidths. Conventional devices

Some push-pull organic compounds like substituted stilbenes possess an FOM of 1000 – 4000; this may be compared to the FOM of standard inorganic materials such as lithium niobate and gallium arsenide, which are about 7 and 1 respectively.



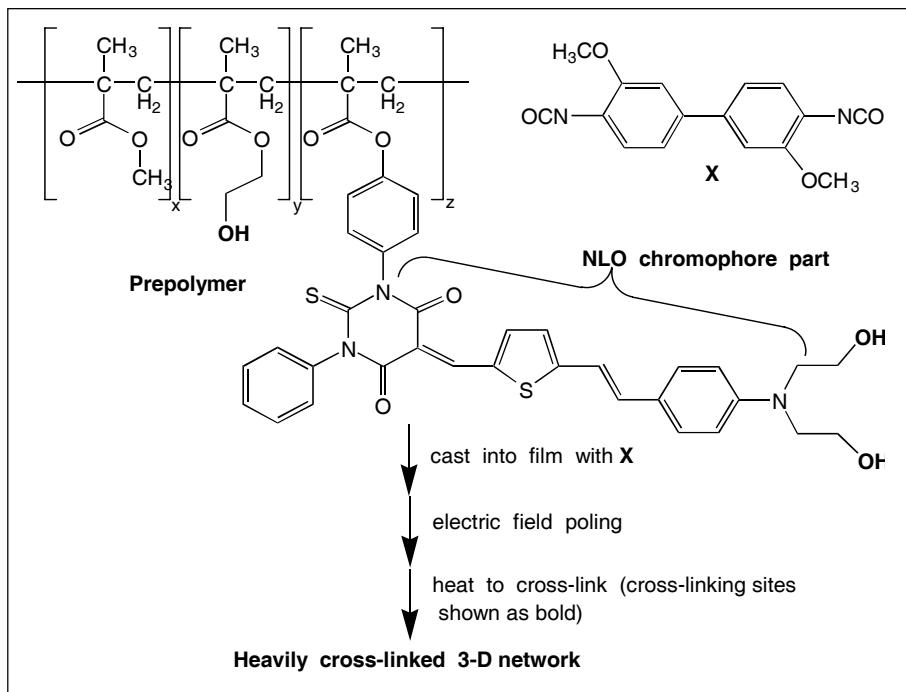


Figure 5. Fabrication of a crosslinked polymer containing an NLO chromophore for electro-optic applications.

based on inorganic materials such as lithium niobate can process electronic signals typically up to 20 GHz i.e. 20×10^9 bits of information per second. The organic polymer based devices have been shown to be capable of operating at about 60 GHz or more. This implies that these devices can handle the equivalent of about 15 million telephone conversations simultaneously.

Presently we are witnessing a steady progress from an all-electronic technology to the hybrid technology of electro-optics. Some believe that it will ultimately lead to an all-photonic technology in areas such as communication and computing. Signs of this may be found in the tremendous activity today in developing organic polymers for quadratic electro-optic applications. An interesting example of this, the 'all-photonic switch', has been discussed in Part 4 of this series.

Concluding Remarks

The discussion of solid state properties of molecular materials presented in the previous articles in this series is extended in

this article, to the description of active devices developed from such materials. The virtually limitless scope of synthetic chemistry coupled with a choice of material fabrication techniques provides for innumerable avenues of device design. The examples discussed in this article illustrate the flexibility afforded by molecular material devices in terms of fine-tuning the device characteristics using synthetic manipulations. The next article will present four examples of molecular scale devices – molecular brake, molecular photonic wire, molecular rectifier and molecular amplifier.

Acknowledgment

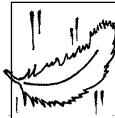
The author wishes to thank G Rajaram for a critical reading of the manuscript.

Suggested Reading

- [1] C A Mirkin and M A Ratner. Molecular electronics. *Ann. Rev. Phys. Chem.* 43. 719, 1992.
- [2] J Salbeck. Electroluminescence with Organic Compounds *Ber. Bunsenges. Phys. Chem.* 100. 1667, 1996
- [3] G Horowitz, X Peng, D Fichou and F Garnier. Organic thin film transistor using π -conjugated oligomers: influence of the chain length. *J. Mol. Electron.* 7. 85, 1991
- [4] RDagani. *Chem. Engg. News*, Improved organic transistors, light-emitting diodes developed. p.42. April 24, 1995.
- [5] C Bosshard and P Gunter. Electro-optic effects in molecular crystals and polymers. *Nonlinear Optics of Organic Molecules and Polymers*. (Eds.) HS Nalwa and S Miyata. CRC Press. Boca Raton. 391. 1997.

Address for Correspondence
 TP Radhakrishnan
 School of Chemistry
 University of Hyderabad
 Hyderabad 500 046

1948



A major article appears on a small item with big implications: "The Transistor." Three years later, in August 1951, the transistor is credited with causing "A revolution in electronics" and the demise of the bulky and fragile vacuum tube.

Scientific American
 September 1995

