

# Molecules to Materials

## 6. Molecular Scale Devices

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Previous articles of this series were on:

1. Design and Fabrication of Functional Molecular Solids, Vol.3, No.4, April 1998.
2. Liquid Crystals and Molecular Conductors, Vol.3, No.5, May 1998.
3. Molecular Magnetic Materials, Vol.3, No.7, July 1998.
4. Molecular Nonlinear Optical Materials, Vol.3, No.8, August 1998.
5. Molecular Material Devices, Vol.3, No.10, October 1998.

**The concept of individual molecules functioning as active devices has been around for a few decades. The active device size has continuously decreased during this century, starting with meter-sized vacuum valve tubes of the early 1930's and 40's, through millimeter-sized transistors in the 1960's to micrometer-sized integrated circuits in the 1970's and 80's. Thus the molecular scale devices represent the logical evolution to nanoscale devices expected towards the end of this century and the beginning of the next. This article presents some examples to provide a glimpse of the activity in this area.**

### Introduction

The first four articles in this series highlighted several examples to illustrate the controlled assembly of bulk structures with the desired electrical, magnetic and nonlinear optical properties using specifically designed molecules. The fifth article discussed the design of devices such as electroluminescent device, thin film transistor and electro-optic device with molecules as the building blocks. Exploitation of the bulk properties of the molecular materials was illustrated with these examples. In this article we look at the so-called molecular scale devices wherein individual molecules themselves act as active devices.

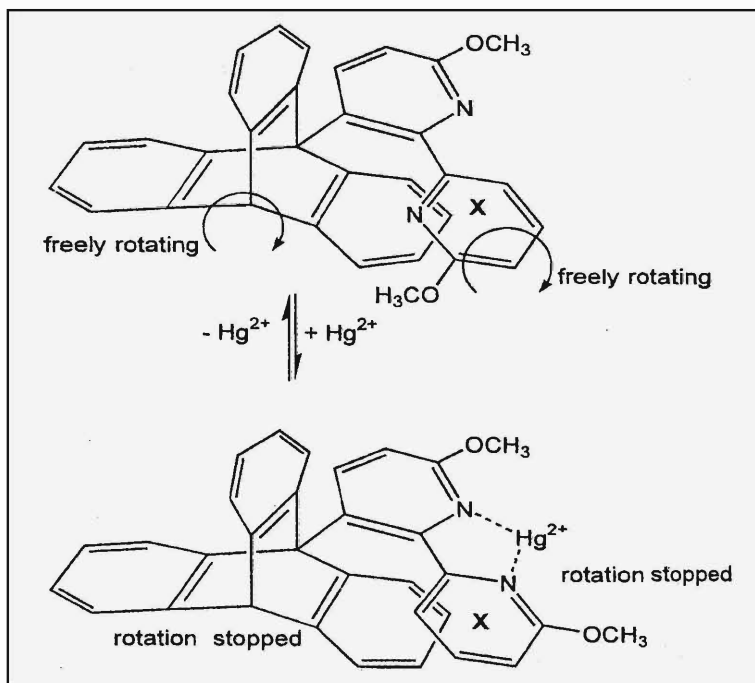
Current scientific literature has numerous reports of single molecules carrying out a wide variety of electrical, magnetic, optical and mechanical functions. Molecules functioning as electronic components, switches, gates, wires, shuttles, brakes, motors and several more devices have been demonstrated. Molecules in solution, in the adsorbed state on surfaces or in the solid state such as crystals and thin films, could function as

molecular scale devices. Thus these devices go beyond the purview of molecular materials that we have discussed so far. We present in this article examples which illustrate mechanical, optical and electronic functions carried out by molecular scale devices. The specific devices considered are the molecular brake, molecular photonic wire, molecular rectifier and molecular amplifier.

## Molecular Brake

A triptycene based molecule has been shown to function as a remarkable 'molecular brake' that can be engaged and disengaged by metal complexation and release respectively. The molecule in solution with no complexed metal ion (*Figure 1*) shows free rotation of the triptycene moiety as verified by its nuclear magnetic resonance (nmr) spectrum. Cooling even to  $-70^{\circ}\text{C}$  only slows down this rotation, but does not stop it altogether. However, when  $\text{Hg}^{2+}$  ions are added, the cation gets coordinated by the two pyridine moieties enforcing a fixed orientation of the ring marked X. Immobilisation of ring X as

Molecular brake functions as a nanoscale device in which the molecular mechanical action can be controlled effectively using chemical activation and deactivation.



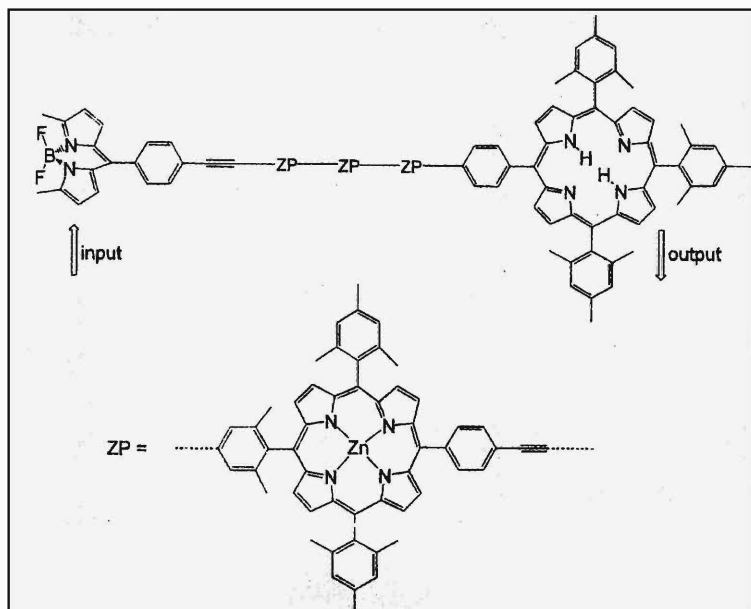
*Figure 1. Mechanism of action of a molecular brake; the brake may be engaged/disengaged by the addition/removal of  $\text{Hg}^{2+}$  ions.*

A high yield of energy transfer with negligible electron transfer and no modification of the molecular electronic structure of the pathway, are necessary conditions for making a molecule qualify as a molecular photonic wire.

shown in *Figure 1* obstructs the rotation of triptycene and stops it effectively at low temperatures. This was clearly demonstrated by recording the nmr spectrum. The brake can be disengaged easily by taking the metal ions away, using for example, a good complexing agent such as EDTA. Thus this molecular brake functions as a nanoscale device in which the molecular mechanical action can be controlled effectively using chemical activation and deactivation.

### Molecular Photonic Wire

Just as electrons flow through an electrically conducting wire, photons can be made to flow through what may be termed a 'photonic wire'. Optical fibers serve such a function. Now imagine a single molecule carrying a light signal from one end to the other – this would be a molecular photonic wire. The long molecule consisting of a boron-dipyrromethene dye, three zinc porphyrins and a free base porphyrin shown in *Figure 2* has been found to be one such. It was observed that the excitation at one end using light of wavelength 485 nm resulted in nearly 76% transmission of the energy to the other end. This was detected



*Figure 2. Molecular photonic wire consisting of a boron-dipyrromethene dye, three zinc porphyrins (ZP) and a free base porphyrin; the input (excitation) and output (emission) sites are indicated.*

by the emission of light (649 nm) by the free base porphyrin moiety. Though energy transfer in molecules is nothing new, the high yield of energy transfer with negligible electron transfer and no modification of the molecular electronic structure of the pathway, makes this molecule qualify as a molecular photonic wire.

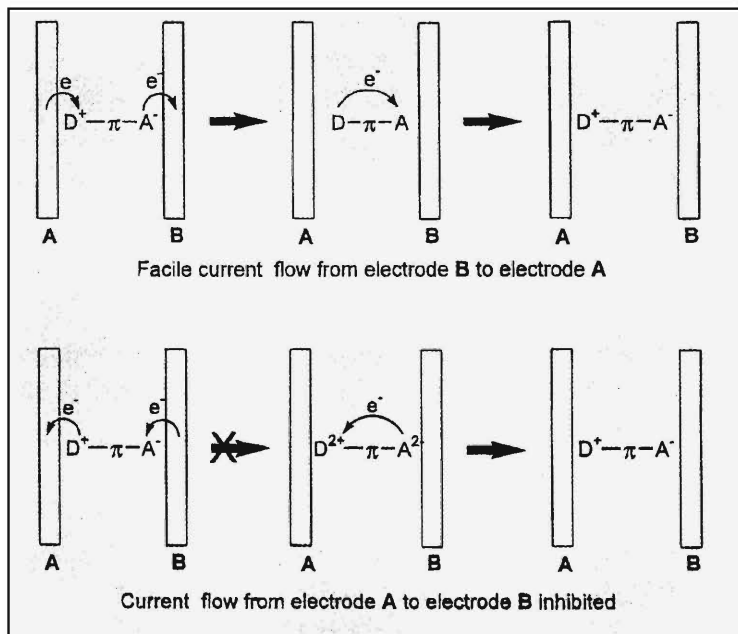
A push-pull molecule could act as a molecular rectifier.

## Molecular Rectifier

Nearly 25 years ago it was proposed that molecules having an asymmetric distribution of charge could act as rectifiers and lead to vectorial transport of electricity. The idea could be pictured as follows. Imagine a molecule  $D-\pi-A$  in which an electron donating group, D and an electron withdrawing group, A are connected by a  $\pi$ -electron conjugated path (this could also be a  $\sigma$ -electron nonconjugated path). As mentioned in the discussion on molecular NLO materials (Part 4 of this series), such molecules are sometimes referred to as push-pull molecules. In these molecules there will be an inherent charge polarisation resulting in a 'zwitterionic' structure  $D^+-\pi-A^-$ . In addition to the  $D^+-\pi-A^-$  state, the  $D-\pi-A$  state would also be energetically accessible and if designed appropriately, states such as  $D^{2+}-\pi-A^{2-}$  would be very high in energy and hence inaccessible. If one were to attempt to send an electrical signal through this molecule, the flow of electron from the  $D^+$  end to the  $A^-$  end *i.e.* from electrode A to electrode B (*Figure 3*) would be facile. In other words, an electric current can flow from electrode B to electrode A freely. However the reverse flow of charge from B to A would be very difficult since that would involve the generation of the high energy species  $D^{2+}-\pi-A^{2-}$ . Thus a push-pull molecule could act as a molecular rectifier.

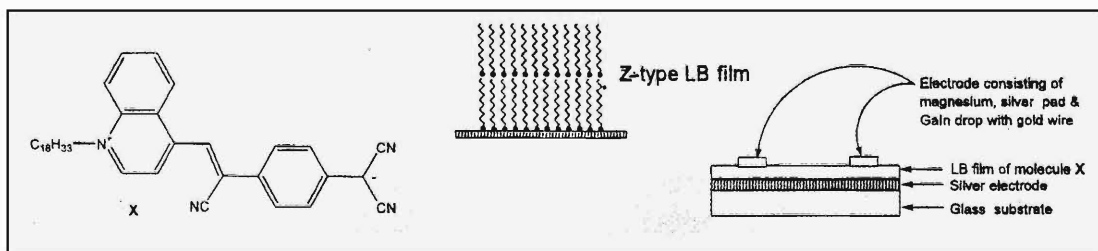
Initial efforts towards realising such an idea were based on depositing two layers of molecules X and Y on a substrate such that electron transport from X to Y is facile whereas that from Y to X is not. The experimental efforts were complicated by the difficulty of making good electrical contacts between metal electrodes and organic molecular materials, these contacts

Figure 3. Mechanism of action of a molecular rectifier; A and B are the electrodes and D- $\pi$ -A represents the 'push-pull molecule'.



themselves often producing an electrical rectification effect. A successful demonstration of a truly 'molecular rectifier' was finally achieved a few years ago. The zwitterionic molecule used and a simplified schematic picture of the experimental setup is shown in Figure 4. The amphiphilic molecule with the D<sup>+</sup>- $\pi$ -A<sup>-</sup> system was deposited as a multilayer Langmuir-Blodgett film on a silver-coated glass substrate. The film was grown in such a way that in each layer the zwitterionic groups were oriented towards the substrate and the alkyl chains away (known as a Z-type LB film). Electrical contacts were made on top of the LB film surface and the current-voltage characteristics were recorded by applying small voltages across the LB film. Typical rectification behaviour was demonstrated *i.e.* currents were high

Figure 4. Molecular rectifier – the amphiphilic push-pull molecule used, schematic drawing of a Z-type LB film and the setup for the demonstration of molecular rectification.



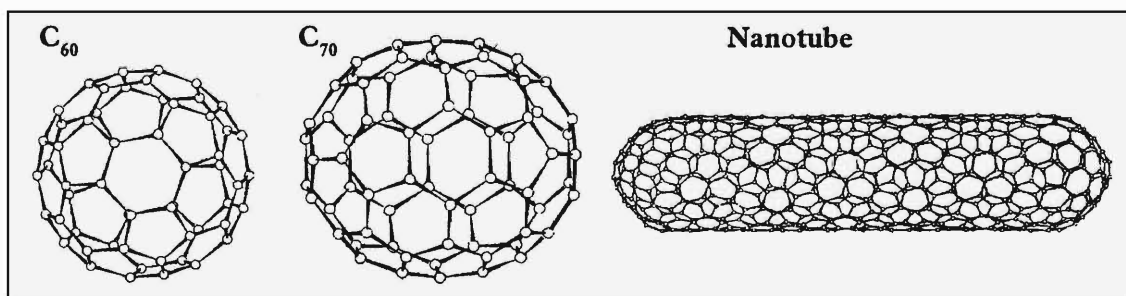
for forward bias and markedly lower for the reverse bias. The important question of whether the electrode-molecule interaction was causing the rectifier action was also addressed in this investigation. This was done by depositing additional layers of  $\omega$ -tricosenoic acid (a long chain acid with no zwitterionic component in it) as a passive layer between the active molecule and the electrode and still observing the rectification action. This particular experiment has convincingly demonstrated that single molecules with asymmetric charge distribution can function as a rectifier.

### Molecular Amplifier

Fabrication of thin film transistors from oligomeric organic molecules has been discussed in the previous article (Part 5) where the semiconducting property of bulk thin films was utilised for achieving transistor action. There has been considerable excitement of late, over the possibility of using single molecules as transistors to perform switching or amplification of electrical signals. Discovery of the pure carbon cage structures such as fullerenes and carbon nanotubes (*Figure 5*) and the subsequent hectic research activity in this area has unraveled a plethora of physical properties of these materials and possible technological applications. The carbon nanotubes, tubular carbon frameworks with typical diameters of several nm and lengths of several  $\mu\text{m}$ , are proposed to be ideal one-dimensional conductors. It was found that the Peierls' instability commonly found in one-dimensional metals (see Part 2 of this series) is absent in these nanotubes, so that they remain highly conducting

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*Figure 5.  $C_{60}$ ,  $C_{70}$  and a carbon nanotube.*



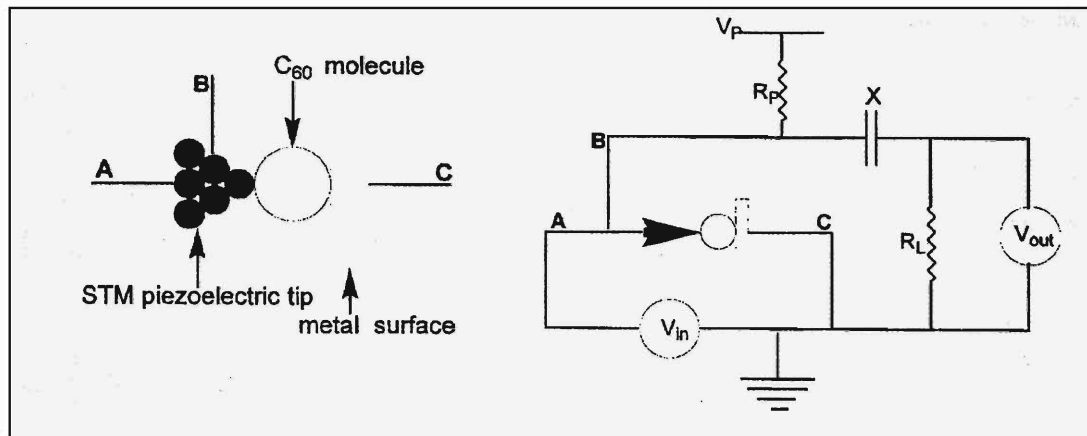
Single-molecule transistors based on carbon nanotubes have been demonstrated.

down to very low temperatures. Using high resolution microscopy techniques electrical leads have been attached to these nanosized molecular conductors so that they can be used as devices. These pure carbon systems open up new possibilities in molecular scale electronic devices; for example, single molecule transistors based on carbon nanotubes have been demonstrated.

Recently a fascinating application of  $C_{60}$  as a single molecule electromechanical amplifier was also demonstrated. The conductivity of  $C_{60}$  can be changed continuously and reversibly by nearly two orders of magnitude by the application of force in the nN (nano Newton) range. This results from the shift of the molecular orbitals of  $C_{60}$  induced by the small but finite changes in the molecular dimensions. This delicate property of  $C_{60}$  is utilised in the electromechanical amplifier. A  $C_{60}$  molecule adsorbed on a metal surface was addressed by the piezoelectric tip of a scanning tunneling microscope (STM). In piezoelectric materials, application of a stress produces an electric polarisation. Conversely, the application of an electric field produces a strain in such materials which can induce minute size changes. Application of a few millivolts to the piezoelectric element in the STM causes sub-nanometer variation of the tip altitude. This in turn causes small variations of the dimension and hence the conductivity of the  $C_{60}$  molecule and the current conducted changes by an order of nA (nano Amperes). Schematic pictures of the amplifier and the circuit used to demonstrate its action are provided in *Figure 6*. The terminals A, B and C provide the connections to the amplifier and the capacitor X serves to isolate the external part of the circuit from the bias voltage. With a suitable choice of the bias voltage  $V_p$ , polarisation resistance  $R_p$  and load resistance  $R_L$ , it was observed that an input voltage of  $\sim 20$  mV across the terminals A and C was amplified by the system to  $\sim 100$  mV output across terminals B and C. It was shown that this molecular amplifier response was continuous and reliable and devoid of problems such as hysteresis encountered in conventional electromechanical relays. It is believed

It is believed that replacement of the piezoelectric tip by polymer piezoelectrics would lead to further miniaturisation of the device, leading to overall mm scale dimensions.





**Figure 6.** Molecular amplifier using a single  $C_{60}$  molecule and the circuit used to demonstrate the amplifier action.  $V_{in}$ ,  $V_{out}$ : input and output voltages;  $V_p$ : bias voltage;  $R_p$ : polarisation resistance;  $R_L$ : load resistance;  $X$ : capacitor.

that replacement of the piezoelectric tip by polymer piezoelectrics (poly (vinylidene fluoride) is a well-studied piezoelectric organic material) would lead to further miniaturisation of the device, leading to overall mm scale dimensions.

## Concluding Remarks

We have traced in this series of articles the development of a fascinating area at the confluence of fundamental research in chemistry, physics and material science, which at the same time holds immense promise for applied science and technology. Part 1 presented the background scenario of the emergence of molecular materials. We dwelt at length on the basic philosophy of the two-stage development of molecular materials that enables a systematic approach to the attainment of material properties. This idea was developed further in Parts 2, 3 and 4 using illustrative examples from liquid crystals and molecular conducting, magnetic and nonlinear optical materials. These discussions can, by no means, be exhaustive since the growth of literature on these subjects has been phenomenal. Our attempt has been to highlight just enough examples to illustrate the relevant basic concepts and the versatility of these functional

Factors such as fragility of crystals and low thermal stability have impeded the deployment of these interesting materials in practical devices.



## Suggested Reading

- [1] C A Mirkin and M A Ratner. Molecular electronics. *Ann. Rev. Phys. Chem.* 43. 719, 1992.
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materials. The same approach applies to the subsequent discussion of molecular devices in the latter parts (5 and 6) of the series. We have encountered several examples where single molecules or bulk materials developed from molecular building blocks are put to use as conventional or unconventional devices. These examples are suggestive of the direction in which things are likely to move in future. They also illustrate perhaps the ultimate in miniaturisation of practical active devices.

We have focused throughout this series of articles on the versatility of functional molecular solids. One should however take cognisance of the handicaps of these materials which has limited their technological applications so far. We have alluded to some of them in Part 4 during the discussion of nonlinear optical materials. Though the 'soft nature' of these materials can be advantageous in terms of their processability, the same can turn out to be their undoing when hostile environments demand robustness of the materials. Factors such as fragility of crystals and low thermal stability have impeded the deployment of these interesting materials in practical devices. In this context polymer based systems and glassy materials offer greater promise. We should also note that the changing trends in the outlook on modern materials, with emphasis being placed on the so-called 'soft materials', augurs well for molecular materials.

The overview of functional molecular solids that we have presented in these articles demonstrates that the field of molecular materials brings together a wide variety of scientific disciplines. Synthetic organic and inorganic chemistry, polymer science, crystallography, spectroscopy, condensed matter physics, electronics, photonics, material science and engineering, and several allied fields contribute to this area. The recognition of the critical role played by these varied subjects in the development of molecular solids leads to an appreciation of the versatility of these materials. We hope that this series of articles imparts at least a hint of the fascination that this area of scientific endeavour holds.