

Molecular Switches: A Review

Asha Lather¹

Department of Electronics & Communication
Engineering
Haryana College of Technology management
kaithal, Haryana, India.

V.K. Lamba², Himani Malik³

Department of Electronics & Communication
Engineering
Haryana College of Technology management
kaithal, Haryana, India.

Abstract : Nanotechnology is the engineering of functional systems at the molecular scale. Generally, nanotechnology deals with developing materials, devices, or other structures with at least one dimension sized from 1 to 100 nanometer. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. Molecular nanotechnology is especially associated with the molecular assembler, a machine that can produce a desired structure or device atom-by-atom using the principles of mechanosynthesis. The emphasis of this paper to study of molecular nanotechnology, some of its applications, desired properties in molecular nanotechnology, development of molecular electronics, nano-structured materials, molecular nanoelectronics switches and some future scope of it.

Keywords : *molecular electronics, nanotechnology, molecular nanotechnology, nano-structured material, molecular switch, nano-molecular switch*

I. INTRODUCTION

A basic definition: Nanotechnology is the engineering of functional systems at the molecular scale. This covers both current work and concepts that are more advanced. As small as a nanometer is, it's still large compared to the atomic scale. An atom has a diameter of about 0.1 nm. An atom's nucleus is much smaller -- about 0.00001 nm. Atoms are the building blocks for all matter in our universe. You and everything around you are made of atoms. Nature has perfected the science of manufacturing matter molecularly. In 1959, the promise of nanotechnology was outlined by Nobel Prize laureate Richard Feynman in his famous talk,

“There's Plenty of Room at the Bottom”. Since then, the concepts of molecular nanotechnology have extended to such as “molecular engineering” by Eric K. Drexler [1] and “molecular electronics” by Mark A. Ratner, [2] etc. Recently, the area of molecular nanotechnology has rapidly developed because enormous possibilities have opened to manipulate the molecular synthesis and movement. A lot of devices and applications have been demonstrated. [3] It is now not an impractical dream to fabricate molecular devices and molecular machines with atomic precision. There are several highly active fields of molecular nanotechnology such as molecular electronics, carbon nanotube technology, organic electronics, self-assembly and its application, molecular machine and nano-structured materials. It is becoming acceptable that molecular nanotechnology will be the next industrial breakthrough. Most obviously a molecular manufacturing capability will be a prerequisite to the construction of molecular logic devices. It is necessary to be able to economically manufacture device at large scale with atomic precision. This capability will also require materials with expected properties that border on the limits imposed by natural law. A broad range of other nanofunctionalized materials beside electronics materials will also benefit from a manufacturing process that offers atomic precision at low cost. Fortunately, with nowadays dramatic developing of computational technology at both hardware (computation speed) and software (parallel computation), our current understanding of chemistry and physics should be sufficient to simulate such nano systems that involves millions of atoms.

II. SEVERAL HIGHLY ACTIVE FIELDS OF MOLECULAR NANOTECHNOLOGY

There are several highly active fields of molecular nanotechnology such as molecular electronics, carbon nanotube technology, organic electronics, self-assembly and its application, molecular machine and nano-structured materials.[1][2][3]

A. Molecular Electronics

Molecular electronics as depicted Figure1, sometimes called moletronics, involves the study and application of molecular building blocks for the fabrication of electronic components. This includes both bulk applications of conductive polymers as well as single-molecule electronic components for nanotechnology. Molecular scale electronics, also called single molecule electronics, is a branch of nanotechnology that uses single molecules, or nanoscale collections of single molecules, as electronic components.

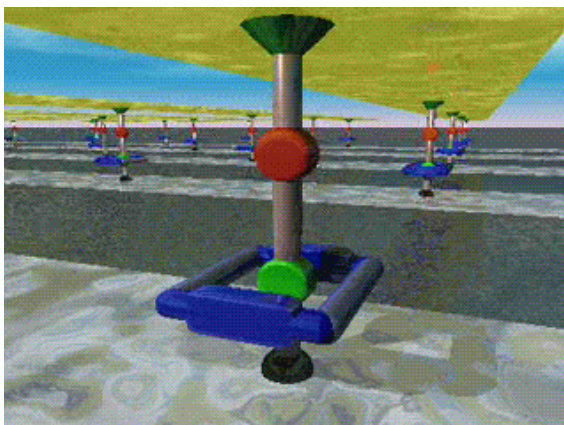


Figure1 : Molecular electronics [1]

B. Carbon Nanotube technology

Carbon nanotubes as shown in Figure 2 are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibres known, and have remarkable electronic properties and many other unique characteristics. For these reasons they have attracted huge academic and industrial interest, with thousands of papers on nanotubes being published every year. Commercial applications have been rather slow to develop, however, primarily because

of the high production costs of the best quality nanotubes.

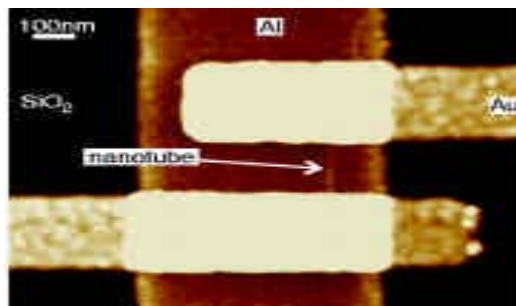


Figure 2: Carbon Nanotube[1]

C. Nano Organic electronics

An 'organic' revolution is unfolding in the electronics industry. From flat-screen TVs and flexible displays to windows, lighting and solar panels, organic electronic components are offering unprecedented features, design flexibility and versatility at relatively low financial and environmental cost, therefore nano organic as shown in Figure3 are boon to electronics.

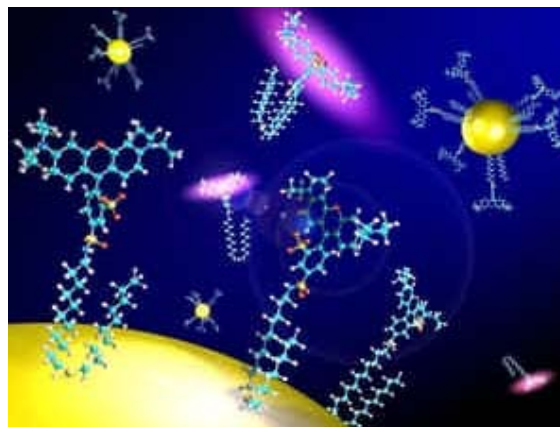


Figure 3 : Nano Organic electronics [1]

D. Nano-machine

A nanomachine as shown in Figure 4, also called a nanite, is a mechanical or electromechanical device whose dimensions are measured in nanometers (millionths of a millimeter, or units of 10^{-9} meter). The first useful applications of nanomachines will likely be in medical technology, where they could be used to identify pathogens and toxins from

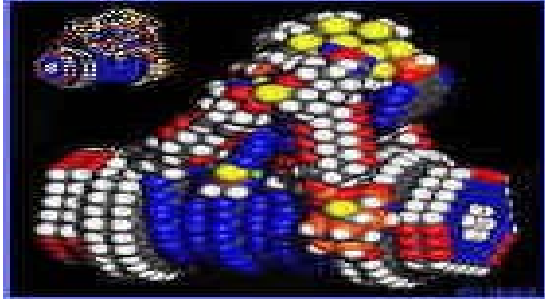


Figure 4 :Nano-machine [2]

samples of body fluid. Another potential application is the detection of toxic chemicals, and the measurement of their concentrations, in the environment. Specialized nanomachines called nanorobots might be designed not only to diagnose, but to treat, disease conditions, perhaps by seeking out invading bacteria and viruses and destroying them. Another advantage of nanomachines is that the individual units require only a tiny amount of energy to operate. Durability is another potential asset; nanites might last for centuries before breaking down. The main challenge lies in the methods of manufacture. It has been suggested that some nanomachines might be grown in a manner similar to the way plants evolve from seeds.

E. Nano-structured materials

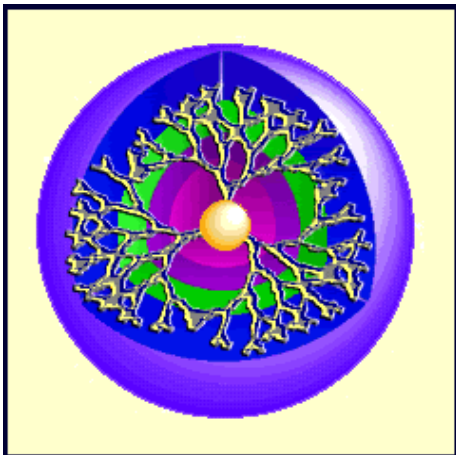


Figure 5 : Nano-structured materials [2]

Nanostructured as shown in Figure5 Materials are a new class of materials which provide one of the greatest potentials for improving performance and extended capabilities of products in a number of industrial sectors, including the aerospace, tooling, automotive, recording, cosmetics, electric motor, duplication, and refrigeration industries. Nanostructured materials may be defined as those materials whose structural elements - clusters,

crystallites or molecules - have dimensions in the 1 to 100 nm range. Encompassed by this class of materials are multilayers, nanocrystalline materials and nanocomposites. Their uniqueness is due partially to the very large percentage of atoms at interfaces and partially to quantum confinement effects.

F. Self-assembly

Self-assembly as shown in Figure 6 is a well-established concept in physics, chemistry, and molecular biology, and is an important factor in high-volume production of systems made of heterogeneous sub-millimeter components. Molecular self-assembly is the process by which molecules adopt a defined arrangement without guidance or management from an outside source.

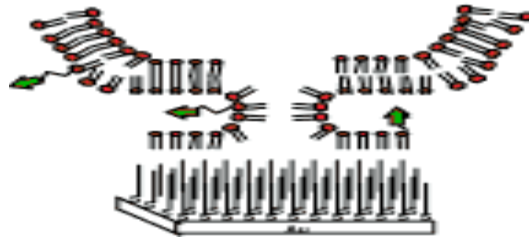


Figure 6 Self-assembly [3]

Molecular self-assembly is an important aspect of bottom-up approaches to nanotechnology. Using molecular self-assembly the final (desired) structure is programmed in the shape and functional groups of the molecules. Self-assembly is referred to as a 'bottom-up' manufacturing technique in contrast to a 'top-down' technique such as lithography where the desired final structure is carved from a larger block of matter. In the speculative vision of molecular nanotechnology, microchips of the future might be made by molecular self-assembly. An advantage to constructing nanostructure using molecular self-assembly for biological materials is that they will degrade back into individual molecules that can be broken down by the body.

III. MOLECULAR AND NANO-ELECTRONICS SWITCH

Molecular scale electronics is developing rapidly [4] because of advances in the synthesis of suitably tailored organic structures, bringing us closer to the ultimate miniaturization of nano-electronic devices.[5-6]

A. *Stoddart-heath bistable rotaxane molecular switch*

Some of the success got by the Stoddart and Heath groups utilized rotaxanes, which have a ring component encircling the dumbbell-shaped component, function as a programmable electronic switch.[7] The ring is a cyclobis(paraquat-p-phenylene) tetracationic macrocycle (CBPQT4+). In order to provide the molecular level understanding necessary to design and optimize such nanoelectronic devices, they initiated theoretical studies on the mechanism of conduction for the bistable rotaxane. This structure is based on a known compound [8]. A molecular switch based on a bistable rotaxane consisting of a ring and a backbone component was proposed and demonstrated, where the writing voltage triggered the ring movement along the backbone between two stable states, leading to a dramatic change in the conductivity of the system that can be ascertained under a much smaller reading voltage. Although appealing as a memory device, the response time scale of this switch is too slow, ~ microseconds, limiting its application for ultra-fast processes required by information technology for its next generation electronic devices.

B. *Ultrafast proton-hopping molecular switch*

For a rational design of a molecular switch, two issues have to be considered: an ultrafast response time scale and a switchable conductivity with changes of voltages. The need of such switches are because they can work ultra fastly as compare to the other switches of that time. The previous switches are too slow, ~ microseconds, limiting its application for ultra-fast processes. It is well known that proton hopping in aqueous solutions can occur at subpicoseconds or faster; [9][10] and that the conductivity of conducting polymers can change dramatically as a function of pH (On/Off ratio can be up to 10^{11}), implying that proton motion may play an important role in changing electronic conductivity.[11] Therefore, it is possible to design an ultra-fast molecular switch triggered by proton migration.

C. *Tuning the conductance of a molecular switch*

The ability [12] to control the conductance of single molecules will have a major impact in nanoscale electronics. Azobenzene, a molecule that changes

conformation as a result of a trans/cis transition when exposed to radiation, could form the basis of a light-driven molecular switch. It is therefore crucial to clarify the electrical transport characteristics of this molecule. Here, we investigate, theoretically, charge transport in a system in which a single azobenzene molecule is attached to two carbon nanotubes. In clear contrast to gold electrodes, the nanotubes can act as true nanoscale electrodes and we show that the low-energy conduction properties of the junction may be dramatically modified by changing the topology of the contacts between the nanotubes and the molecules, and/or the chirality of the nanotubes (that is, zigzag or armchair). We propose experiments to demonstrate controlled electrical switching with nanotube electrodes.

D. *Nanoscale molecular-switch crossbar circuits*

Molecular electronics offer an alternative pathway to construct nanoscale circuits in which the critical dimension is naturally associated with molecular sizes. They describe the fabrication and testing of nanoscale molecular-electronic circuits that comprise a molecular monolayer of rotaxanes sandwiched between metal nanowires to form an 8×8 crossbar within a $1 \mu\text{m}^2$ area. The resistance at each cross point of the crossbar can be switched reversibly. By using each cross point as an active memory cell, crossbar circuits were operated as rewritable, nonvolatile memory with a density of $6.4 \text{ Gbits cm}^{-2}$. By setting the resistances at specific cross points, two 4×4 subarrays of the crossbar were configured to be a nanoscale demultiplexer and multiplexer that were used to read memory bits in a third subarray.[13]

E. *Nanoengineering a single-molecule mechanical switch using DNA self-assembly*

The ability to manipulate and observe single biological molecules has led to both fundamental scientific discoveries and new methods in nanoscale engineering. A common challenge in many single-molecule experiments is reliably linking molecules to surfaces, and identifying their interactions. We have met this challenge by nanoengineering a novel DNA-based linker that behaves as a force-activated switch, providing a molecular signature that can eliminate errant data arising from non-specific and multiple interactions. By integrating a receptor and ligand into a single piece of DNA using DNA self-

assembly, a single tether can be positively identified by force–extension behavior, and receptor–ligand unbinding easily identified by a sudden increase in tether length. Additionally, under proper conditions the exact same pair of molecules can be repeatedly bound and unbound.[14]

F. Tunable nanoswitches based on nanoparticle meta-molecules

They introduce ultra-fast tunable nanoswitches based on the transition between states of nanoparticle meta-molecules. These molecules are formed (activated) when hybrid systems consisting of metallic nanoparticles and semiconductor quantum dots interact with coherent light sources (laser fields). The switching process occurs via minuscule changes of the refractive index of the environment or the distance between the quantum dots and metallic nanoparticles. These changes stimulate the transition between the states of the meta-molecules in nanosecond timescales, setting up dramatic optical events that can be observed easily. These nanoswitches can be tuned by varying the intensity of the activating laser field, allowing us to adjust the switching process to occur at different values of refractive indices. The results open a new horizon for chemically, biologically, or physically triggered optical nanoswitches and nanosensors that are sensitive to ultra-small changes in the environment. [15]

G. The Smallest Molecular Switch

Electronic devices that switch between high and low resistance states are at the heart of the modern information technology. As miniaturization of this technology continues to progress, the long-standing fundamental problem of identifying and understanding the smallest physical systems that are capable of switching behavior is attracting growing interest. They proposed that Total energy calculations reveal benzene-dithiolate molecules on a gold surface, contacted by a monatomic gold STM tip to have two classes of low-energy conformations with differing symmetries. Lateral motion of the tip or excitation of the molecule cause it to change from one conformation class to the other and to switch between a strongly and a weakly conducting state. Thus, surprisingly, despite their apparent simplicity, these nanowires are shown to

be electrically bistable switches, the smallest two-terminal molecular switches to date.[16]They have shown that one of the simplest and most studied molecular wires, surprisingly, becomes a bistable molecular switch if one of its two metal contacts is a monatomic scanning tunneling microscope tip. This is the smallest two-terminal molecular switch to date. The switching mechanism that we have introduced here relies on the coupling between the molecule and contacts and thus should be broadly applicable. They have proposed experiments with a conventional or novel selfassembled STM to test our predictions, and hope that the ideas put forward here will facilitate bridging the gap between theory and molecular switching experiments.

H. Nanoelectromechanical contact switches

Nanoelectromechanical (NEM) switches are similar to conventional semiconductor switches in that they can be used as relays, transistors, logic devices and sensors. However, the operating principles of NEM switches and semiconductor switches are fundamentally different. These differences give NEM switches an advantage over semiconductor switches in some applications — for example, NEM switches perform much better in extreme environments — but semiconductor switches benefit from a much superior manufacturing infrastructure. Here we review the potential of NEM-switch technologies to complement or selectively replace conventional complementary metal-oxide semiconductor technology, and identify the challenges involved in the large-scale manufacture of a representative set of NEM-based devices.[17]

I. Spatial periodicity in molecular switching

The ultimate miniaturization of future devices will require the use of functional molecules at the nanoscale and their integration into larger architectures. Switches represent a prototype of such functional molecules because they exhibit characteristic states of different physical/chemical properties, which can be addressed reversibly. Recently, various switching entities have been studied and switching of single molecules on surfaces has been demonstrated. However, for functional molecules to be used in a future device, it will be necessary to selectively address individual molecules, preferentially in an ordered pattern. Here, they show that azobenzene derivatives in the

trans form, adsorbed in a homogeneous two-dimensional layer, can be collectively switched with spatial selectivity, thus forming a periodic pattern of *cis* isomers. They find that the probability of a molecule switching is not equally distributed, but is strongly dependent on both the surrounding molecules and the supporting surface, which precisely determine the switching capability of each individual molecule. Consequently, exactly the same lattices of *cis* isomers are created in repeated erasing and re-switching cycles. Their results demonstrate a conceptually new approach to spatially addressing single functional molecules. [18]

J. Flipping a single proton switch

The basic idea of molecular electronics using molecules as components in electrical circuitry has been verified experimentally by using molecules as diodes, switches and transistors. The use of molecules in electronics is conceptually appealing because the required function can be encoded into the molecule through chemical synthesis, making molecules an ideal tunable nanoscale building block. However, the molecular components have to be interfaced with the macroscopic world and this places a number of constraints on their design.

In molecular switches, for example, the switching action should not change the overall size of the molecule because this will disturb the external contacts to the switch. Ideally, small changes of the atomic structure of the molecule should lead to changes in the electronic properties of the whole molecule that are large enough to allow the different states to be distinguished from each other by measuring the electric current through the molecule. The switching unit should also be protected in some way so that the switch is not affected by changes in its immediate environment. In addition to these strict requirements, it might also be beneficial to have access to more than two levels (states) in a switch. Furthermore, if the switching unit is part of a molecule that already has a well-developed chemistry, this could help broaden the range of different molecular architectures that the switch can be incorporated into. A four-level conductance switch can be created by using a scanning tunnelling microscope to remove a hydrogen atom from the central cavity of a porphyrin molecule.[19]

IV. IMPACT OF MOLECULAR NANOTECHNOLOGY

Impact of molecular Nanotechnology is discussed in term of benefits and risks are followings:-

A. Benefits

It will let us make remarkably powerful molecular computers. It will let us make materials over fifty times lighter than steel or aluminium alloy but with the same strength. Molecular surgical tools, guided by molecular computers and injected into the blood stream could find and destroy cancer cells or invading bacteria, unclog arteries, or provide oxygen when the circulation is impaired. It will let us make materials over fifty times lighter than steel or aluminium alloy but with the same strength.

B. Risks

Molecular nanotechnology is one of the technologies that some analysts believe could lead to a Technological Singularity. Some feel that molecular nanotechnology would have daunting risk as described by Center for Responsible Nanotechnology. It conceivably could enable cheaper and more destructive conventional weapons. Also, molecular nanotechnology might permit weapons of mass destruction that could self-replicate, as viruses and cancer cells do when attacking the human body. Commentators generally agree that, in the event molecular nanotechnology were developed, mankind should permit self-replication only under very controlled or "inherently safe" conditions. A fear exists that nanomechanical robots, if achieved, and if designed to self-replicate using naturally occurring materials (a difficult task), could consume the entire planet in their hunger for raw materials, or simply crowd out natural life, out-competing it for energy. Some commentators have referred to this situation as the "grey goo" or "ecophagy" scenario.

V. CONCLUSION

Nanotechnology researchers have developed a molecule-sized switch which means that data storage can be dramatically increased without the need to increase the size of devices. The chemical switch is some one million times smaller than the current silicon switches, creating the potential for further miniaturization of computers. Not only

would the machines be appreciably smaller than anything possible at present, but such molecular computers would be far more powerful than those available now using silicon-based logic gates.

REFERENCES

- 1) Drexler, K. E. (1981) “*Molecular engineering: An approach to the development of general capabilities for molecular manipulation.*” Proc. Natl. Acad. Sci. U.S.A. 78:5275-5278, 1981.
- 2) Aviram A. and Ratner M. A. “*Molecular rectifiers*” Chem. Phys. Lett. 29: 277-283, 1974.
- 3) Heath J.R.; and Ratner M.A.; “*Molecular electronics*” Physics Today (5): 43-49, 2003
- 4) Tseng, G.Y.; Ellenbogen, J.C.; Science 2001 294, 1293
- 5) Feynmann, R. P. In Miniaturization; Gilbert, H. D., Ed.; Reinhold: New York,1961; p 282.
- 6) Aviram, A.; Ratner, M. A. Chem. Phys. Lett. 1974, 29, 277
- 7) Collier C.P.; Mattersteig G.; Wong E.W.; Luo Y.; Beverly K.; Sampaio J.; Raymo F.M.; Stoddart J.F.; Heath J.R.; Science 2000, 289, 1172.
- 8) Luo Y., Collier C. P., Jeppesen, J. O., Nielsen K. A., Delonno, E. and et. Al Chemphyschem 2002, 3, 519
- 9) Mauerhofer, E. and Ro`sch, F. Phys. Chem. Chem. Phys., 2003, 5, 117–126. 0.69ps reported.
- 10) Horsewill, J.; Jones, N. H. and Caciuffo, R. Science 2000, 291, 100
- 11) Miller, L.L.; Bankers, J. S.; Schmidt, A. J. and Boyd, D. C. J. Phys. Org. Chem. 2000; 13, 808–815
- 12) M. Del Valle, R. Gutiérrez, C. Tejedor, G. Cumiberti, “*Tuning the conductance of a molecular switch*”, Nat. Nanotechnol. 2, 176 (2007)
- 13) Yong Chen, Gun-Young Jung, Douglas A Ohlberg, Xuema Li, Duncan R Stewart, Jan O Jeppesen, Kent A Nielsen, J Fraser Stoddart and R Stanley Williams ,” *Nanoscale molecular-switch crossbar circuits* ,” Nanotechnology, Vol 14 Issue, Number 4 ,pp-462,(2003).
- 14) Ken Halvorsen, Diane Schaak1 and Wesley PWong ,” *Nanoengineering a single-molecule mechanical switch using DNA self-assembly* “, Nanotechnology Vol 22 ,Issue Number 49, (November 2011).
- 15) S M Sadeghi , ” *Tunable nanoswitches based on nanoparticle meta-molecules* “Nanotechnology Volume 21 ,Issue Number 35 ,(6 August 2010)
- 16) Eldon G. Emberly¹ and George Kirczenow²,” The Smallest Molecular Switch “*PHYSICAL REVIEW LETTERS* ,VOL 91, Issue NUMBER 18 (27 October 2003)
- 17) Owen Y. Loh & Horacio D. Espinosa ,” *Nanoelectromechanical contact switches* ” ,Nature Nanotechnology ,Vol 7,pp:283–295(29 April 2012)
- 18) Carlo Dri, Maiké V. Peters, Jutta Schwarz, Stefan Hecht & Leonhard Grill ,” *Spatial periodicity in molecular switching*“Nature Nanotechnology 3, 649 - 653 (14 September 2008)
- 19) Peter Liljeroth,” *Flipping a single proton switch* ” , Nature Nanotechnology vol 7,5–6 (2012)