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Term Paper: Realization of a unimolecular rectifier

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## **OBJECTIVE**

The objective of the project is to realize a unimolecular rectifier, capable of working under ambient condition. This rectifier will have very high rectification ratio for storing logical information. This device will have a size of only few nm, ideal for the nano-processor and nano-architect design.

Both electrical characteristics and conduction behaviour of different supramolecule molecules will be studied. Profound research on the different substrates and electrode materials will be carried out, for the development of real life novel nano-device. Novel fabrication techniques will be developed to place a single molecular nano-device on the substrate.

## MOTIVATION

Rectifiers are the basic active device necessary for realization of the complex digital circuit that will ultimately lead to the development of a nano-processor. Taking consideration of individual switch size (considering as 10nm) we can accommodate today available Intel Itanium microprocessor having 2 billion transistors [1] in an area of only  $1\text{mm}^2$ . Since, most of the supra-molecules have size in the order of the nanometre, there is a huge potential towards miniature circuit development that can accommodate inside an intracellular bodies (nucleus or ribosome or cell membrane). We can modulate the single supramolecule at different locations, also can realize multiple rectification centres within the same molecule, which helps in realizing complex logic circuit (fig. 1).

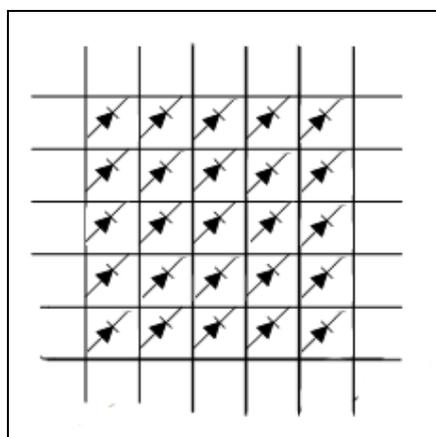


Fig. 1: Molecular rectifier array (inside single supramolecule) for the boolean algebra implementation

Providing a suitable potential at the ends of these rectifiers (terminal of the supramolecule) we can store and retrieve the logic '0' or '1' stored by each molecular centre. Interconnection of individual logic component (fig. 1) we can implement any type of complex logic function. Applying molecular electronics, an individual switching element can have maximum size of an individual rectifier only 10nm.

Molecular rectifiers have huge future potential towards development of high performance, nanoscale level electronic devices. Trillions of individual molecular rectifiers can be fabricated on small area, which makes organic rectifiers suitable for the future nano-processor. Ultimately, programmable nano-processors can be utilized in controlling the cellular function, single molecular reaction, DNA sequence manipulation e.t.c.

## PROBLEM STATEMENT

When the size of the devices goes smaller upto the nanoscale level then the quantum limitation of the system must be addressed. If an electron is confined to a small area (with capacitance-C) and charging energy is greater than the thermal energy, i.e the ratio  $e^2/2C > KT$  (K = Boltzman's constant and T is the absolute temperature) then, Coulomb blockade occurs: and no more charge can be added to the molecule. Coulombs blockade occurs only when temperature (K) is very small.

There occurs the Schottky barrier between the interface of the molecule and the electrode which impedes the electrical characteristics of the molecule [2]. Deposition of molecule on the electrode of unimolecular junction is rigorous task. Because, molecule forms very weak Van Der Waals bond with the electrode surface, the force of interaction is so small that we cannot measure the pure electrical characteristics of the molecule without deformation of the monolayer. During the formation of single molecule thickness, many molecules get destroyed and also during the electrical measurement because, dielectric of organic molecules are less than 10 and cannot withstand high potential [3].

Tunnelling of electron, property of electron at nano-scale level, is liable to occurs on the single molecule thick system, thus current depends exponentially on the supply potential, not linearly, in the single molecular device. If the electron travel along the single molecule at the speed of light ( $3 \times 10^8$  m/s), then its only  $6.7 \times 10^{-18}$ s to travel along the 2nm size molecule, which is very high, this must be slowed down before an electron knocks out the electron from the electrodes. Heat dissipation, major factor in the electronic circuit design, must be studied in the single molecular devices. Molecules are very delicates because the bonds between the molecules are so weak that UV rays, high temperature and pressure can easily destroy the molecule [3]. Effect of UV, heat, pressure on the electrical property of single molecule must be studied.

Connection of electrode with the organic molecule also demands rigorous research because as of today precise channel modulation of the electrodes has yet not been realized, but the advancement of AFM and STM has made our task slightly easy because we can create small channel upto 10nm using nanopore technique [2]. Despite the use of AFM and STM actual device realization is different from the laboratory conditions [15], the molecule must be bonded with the electrodes, properly on the substrate, which too needs to be studied. Next step is to peek through the conduction mechanism between the organic molecules and the electrodes so that efficient device can be fabricated on the substrate.

# INTRODUCTION

In 1965, Intel's co-founder Gordon Moore predicted, popularly known as Moore's law states that the number of transistor on a chip will double about every two year [4]. Entire electronics manufacturing industries are undergoing rigorous research in fabrication technology to follow this trend. As of today, Intel has demonstrated world's first 32nm logic processor consisting of 1.9 billion second generation high-k metal gate transistors [5]. Intel has somehow kept its pace with reference with Moore's Law. But a big question ahead arises - how far can we travel along the Moore's curve? Unfortunately, the answer will ultimately impede us in future from delivering high performance silicon based electronics devices due to the major demerit which arises when we reach at nanoscale level. Major draw back for CMOS technology at nanoscale is tunnelling of electron, disadvantage when barrier size drops upto few nanometre and also the lowest limit of oxide thickness, which is upto single atom thickness. Hence, 2010 is end of Moore's prediction, applying conventional silicon technology.

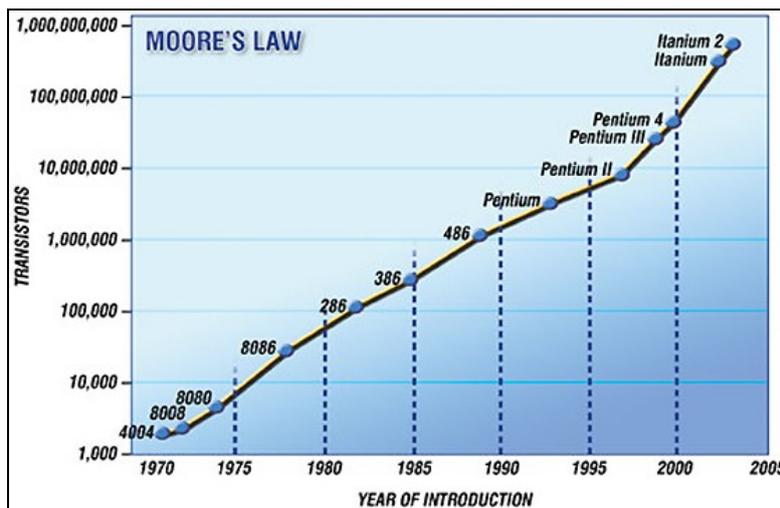


Fig. 2: Moore's Law depicting increment in the number of transistors per chip ever twice a year. (Courtesy: Intel.com)

On December 29, 1959, popular talk at Caltech delivered by famous physicist Richard Feynman- 'There is plenty of room at the Bottom' had showed us the novel pathway that will guide us towards new era of electronics technology. It is the exploration of the bottom world-nano and femto level technology, which will resolve every problem that will aid electronics in carrying along the Moore's curve. Molecular electronics is such novel solution which will not only avenue the new era of Terahertz speed but also TByte of information can be stored in tiny chip area. Single molecular rectifiers and transistors are the organic electronic two and three terminal active component for future electronics device, which sizes only upto few nanometres.

There are three distinct types of asymmetrical conduction i.e. rectification in metal-organic-metal system. First is due to Schottky barrier at metal-organic interfaces, where difference in the dipole will result in the different current for forward and reverse bias- termed as (S) or Schottky rectifier. The second type of rectification is termed as the asymmetrical (A) rectification. In this process the ‘chromophore’ (the part of molecule whose molecular orbital that takes part in conduction) is placed asymmetrically within a ‘metal-molecule-molecule’ sandwich. The third type of rectification is termed as Unimolecular rectification (U). When the current is flowing through a molecule or monolayer of molecule then, there involves electron transfers between the molecular orbitals. The significant probability amplitudes are asymmetrically placed within the chromophore. Most of the rectification involves all three different types of rectification [3]

As compared with conventional PN junction solid state rectifier, uni-molecular rectifier also consists of a molecule with an end very high electron affinity or electron poor (P-type) group attached with other end with electron rich group (N-type) separated with neutral molecule. Molecules having different  $\pi$ -electron density separated by the  $\sigma$ -electron system can function as the uni-molecular rectifier [6]. High electron dense region can act as electron donor to the electrode and low electron dense region can act as electron acceptor from the electrode and there occurs tunnelling of electron from electron rich (D) to electron poor region(A) which forms the complete conduction of electrical current along the single molecule (D- $\sigma$ -A). Unidirectional flow of charge along the single molecule is depicted below in fig. 3 for N-3- $\gamma$ -Pyrolyl aza[60]fulleroid (abv.  $C_{60}NPy$ ) D- $\sigma$ -A structure [7].

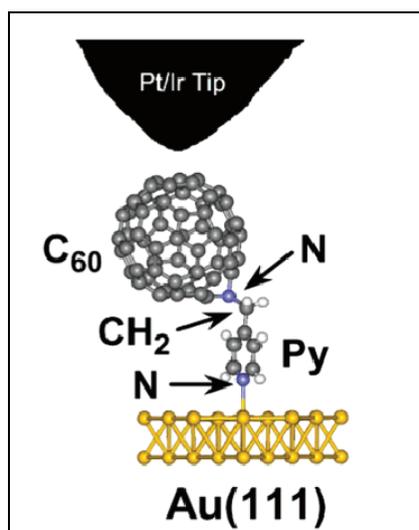


Fig. 3: Single molecular rectifier for  $C_{60}NPy$  oligomer, where gold and Platinum/Iridium are the corresponding contact terminals for electrical characterization [7].

Mathematically, we can express the inelastic electron transfer between a metal and a single molecule orbital of a molecule as [3],

$$I = I_0 [\tan^{-1} \{ \theta(E_0 + peV) \} - \tan^{-1} \{ \theta(E_0 - (1-p)) \} ] \dots\dots(1)$$

Where,  $E_0$  is the molecular orbital energy (LUMO or HOMO),  $V$  is the applied potential, and  $p$  is the fractional distance of the molecule from, say, the left electrode. If the molecule is centred in the gap, then  $p=1/2$  [3]. Thus, the rectification ratio (RR) can be written as the current at a positive bias  $V$  and the absolute of the current at the corresponding negative bias  $-V$  we get [3],

$$RR(V) = \frac{|I(V)|}{I(-V)} \dots\dots(2)$$

The charge transport in single molecule (Fig. 4 ) for rectification (unidirectional electron flow) takes only when LUMO (Lowest Unoccupied Molecular Orbital) of the acceptor region is slightly higher than the fermi level of the cathode and HOMO (Highest Occupied Molecular Orbital) of the donor region is slightly lower than the fermi level of the anode. On forward biasing when electrode connected with acceptor region is slight above the Fermi level (Fig. 4) then electron can easily jump to LUMO1 and tunnels to HOMO2 and finally to the anode. Due to high affinity level of electron acceptor region and the hole left on the ionized donor are sufficiently close in energy leads to tunnelling of electron from acceptor to donor side of the molecule [7] .

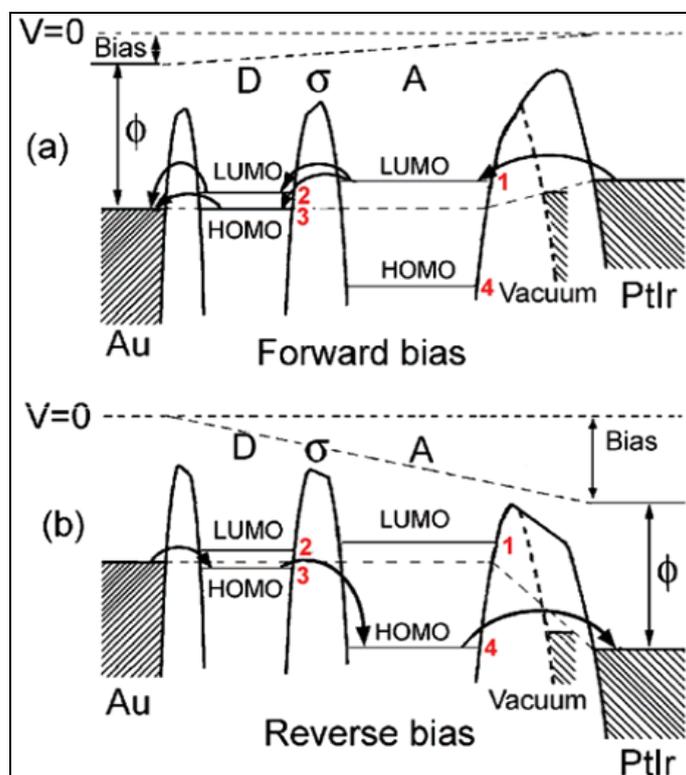


Fig. 4: Forward and reverse biased electron conduction in unimolecular rectifier system. Au and Pt/Ir forms the corresponding electrodes. D- $\sigma$ -A is the corresponding donor  $\pi$ -electron

group,  $\sigma$  electron cloud and acceptor  $\pi$ -electron region. 1,2,3,4 respectively are the LUMO for acceptor region, LUMO for donor region, HOMO for acceptor region and HOMO for donor region. Very low bias voltage is sufficient to transport the charge in forward biased condition (top) compared with reverse biased condition (bottom). [7]

For reverse conduction (Fig. 4), a very high reverse bias voltage is necessary no lower the fermi level of cathode by potential more than HOMO of acceptor region. The potential for reverse biasing is much higher than the potential needed to take fermi level of anode more than LUMO of acceptor (forward biasing potential). This system assures the unidirectional flow of electron along the molecular junction.

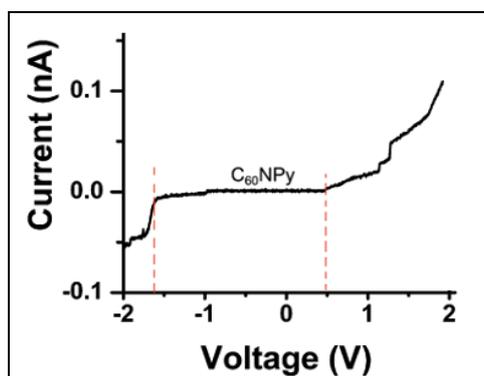


Fig. 5: Sample unimolecular rectifier for C<sub>60</sub>NPY, clearly shows the rapid increment of current for forward biased condition and no conduction for reverse biased condition [7].

Discovery of STM (Scanning Tunnelling Microscope) and AFM (Atomic Force Microscope) has evolved a new era of scanning probe method which can be precisely used to manipulate single molecules also study the electrical characteristics of nanoscale systems. Single molecular junction can be designed by using many approaches namely: Scanning Probe Method, Monomolecular film method, Nanopore construction, Mechanically Controlled Break Junction (MCB) and electromigration techniques.

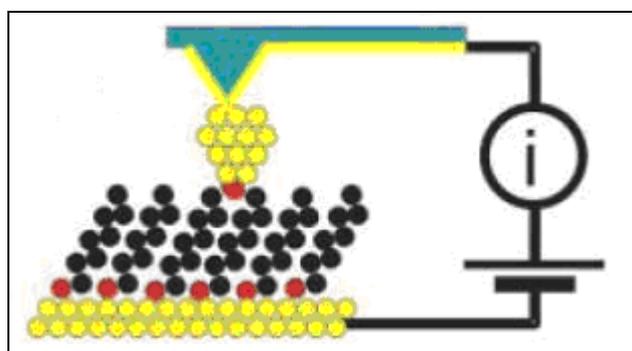


Fig. 6: Single molecular junction by scanning probe technique using AFM tip and gold electrode. [2]

In scanning probe method we can study the shape, size, diffusion and conductivity e.t.c of individual molecule on surfaces using very sophisticated devices like STM and AFM (Fig. 6). STM or AFM tip progressively [2]. Monomolecular film between two electrodes can be created by several technique like self-assembly, vapour deposition and Langmuir-Blodget (LB) films where organic mono layer of supra-molecule is sandwiched between the two metal surfaces (Fig. 7). A very tiny hole in a silicium membrane as the well-defined surrounding of self-assembled monolayers can act as nanopore between two electrodes [8]. In MCBJ, applying the force on the elastic substrate can ultimately create a nanosize hole (10-20nm) (Fig. 8, 9) on the metal film (Ag) which can hold a single molecule between the two electrodes [2]. Under the application of moderate electric current at the hyphenation point a small 1-3nm opening is created on the electrodes, on the fabricated metallic wire [2]. They can hold single supra organic molecule for unimolecular device realization is electromigration technique (Fig. 10).

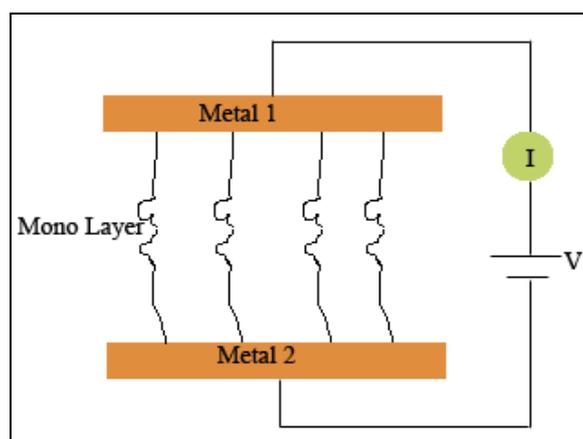


Fig. 7: Molecular junction using monolayer of the organic molecule

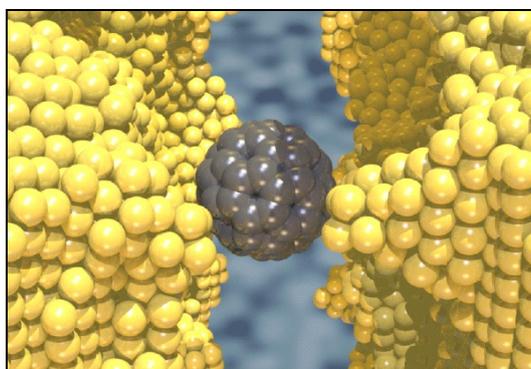


Fig. 8: Single supra molecule ( $C_{60}$ ) between two giant electrodes (Ag) depicting the concept of MCB for unimolecular junction realization [9].

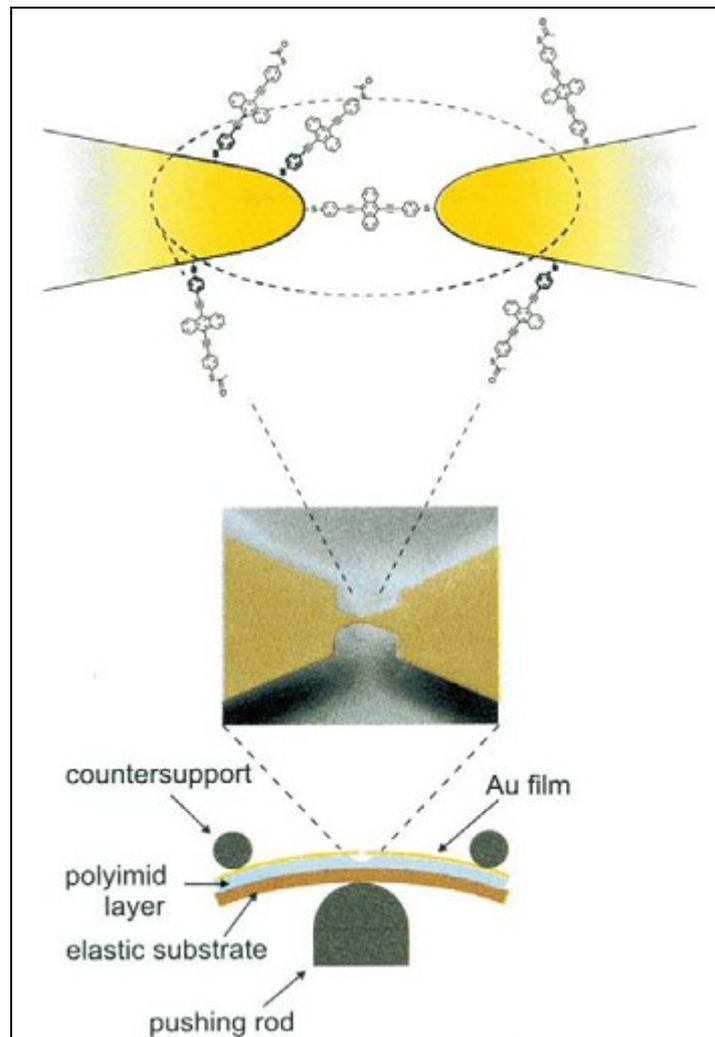


Fig. 9: By pushing a rod we can precisely create the nanoscale dimension equal to the size of the molecule using MCB technique [10].

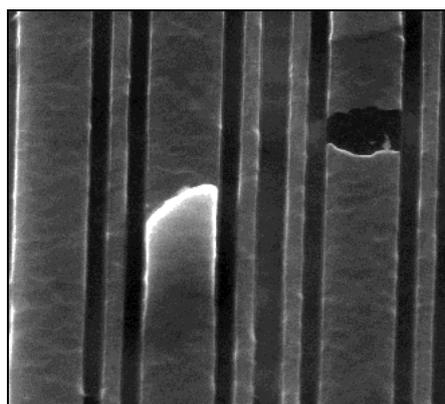


Fig. 10: A void and a hillock generated by electromigration [11].

## STATE OF THE ART

Arieh Aviram from IBM Thomas J. Watson Research Centre and Mark A. Ratner from New York University in 1974, first described the unimolecular rectification, which formed the basis of molecular conduction having D- $\sigma$ -A system [6], at molecular level. They first described the conduction mechanism in single molecule considering the four major steps taking place: cathode to acceptor region (A), acceptor region to sigma region ( $\sigma$ ), sigma to donor region (D) and finally donor region to the anode. The work got overwhelming response both from corporate and government level, and termed as the avenue of molecular electronic era.

Aviram and Ratner studied the conduction property taking reference of tetracyanoquinodimethane (TCNQ), tetrathiofulvalene (TTF) and triple methylene (-CH<sub>2</sub>-) bridge as the acceptor, donor and sigma bridge molecule.

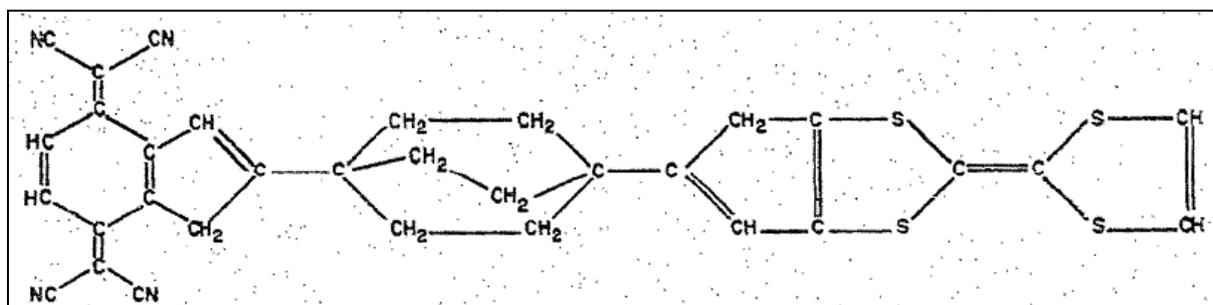


Fig. 11: A Rectifier molecule studied by Aviram and Ratner [6].

In 1992, researchers were able to study the asymmetric conduction behaviour of Aviram and Ratner model using a monomolecular Langmuir Blodgett film of a zwitterionic molecule, C<sub>16</sub>H<sub>33</sub>- $\gamma$ Q3CNQ between platinum and magnesium electrodes [12].

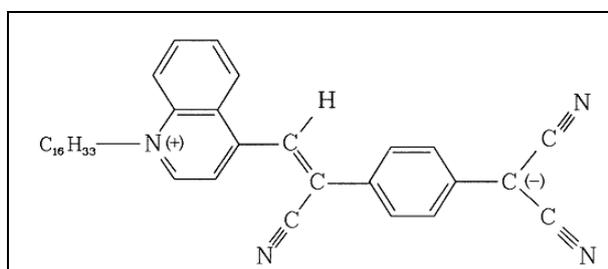


Fig. 12: C<sub>16</sub>H<sub>33</sub>- $\gamma$ Q3CNQ, Zwitterion molecule [12].

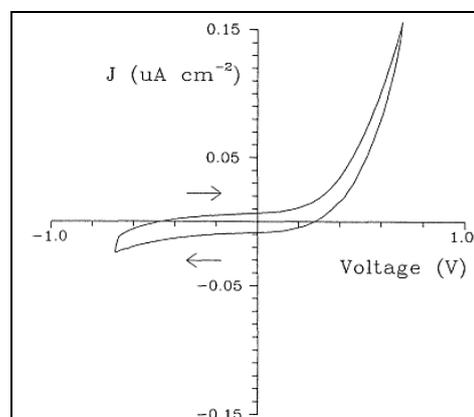


Fig. 13: Current density (J) voltage plot for AG - C<sub>16</sub>H<sub>33</sub>- $\gamma$ Q3CNQ – junction. [12]

First unimolecular diode was developed in 2004, where they have designed and synthesized in the form of the molecular rod which acts as the diode which exhibited rectification ratio (RR) equal to 1:4 for  $\pm 1.5\text{V}$  [13].

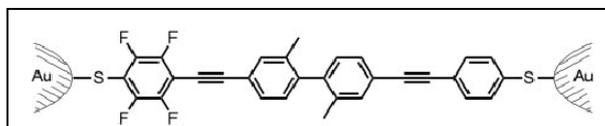


Fig. 14: Rectifying device between two gold electrodes. [13]

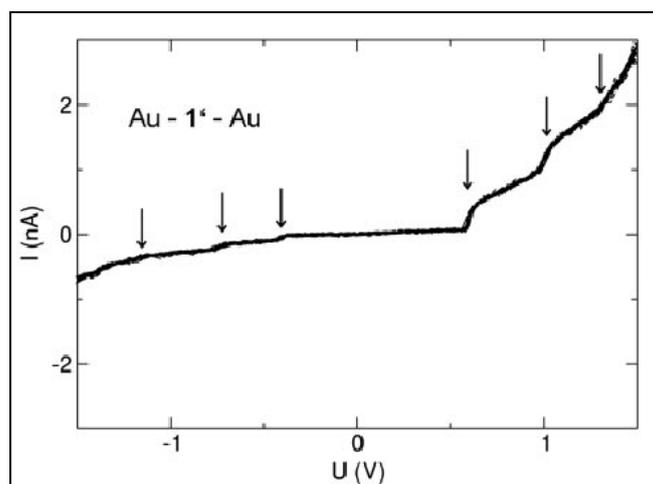


Fig. 15: Current vs voltage asymmetric curve for Gold-A-D-Gold MCB junction for above molecule and rectification property was visible at 30K temperature [13].

Since 1980, Prof. Robert M. Metzger has carried out tremendous research towards pure unimolecular rectification. His team has found rectification property of many molecules like: **1** ( $\gamma$ -hexadecylquinoliniumtricyanoquinodimethanide), **2** (2,6-dibutylaminophenylvinyl)-1-butylpyridinium iodide), **3** (dimethylanilinoaza[C]-fullerene), and **4** (fullerene-bis-[4-diphenylamino-4''-(N-ethyl-N-2''-ethyl)-amino-1,4-diphenyl-1,3-butadiene] malonate), **5** (N-(10-nonadecyl)-N-(2-ferrocenylethyl)pyrenyle-3,4,9,10-bis (dicarboxyimide)) and **6** (4,5-dipentyl-50-methyltetra-thiafulvalen-40-methyloxy2,4,5-trinitro-9-dicyanomethylene-fluorene-7-(3-sulfonylpropionate)) [2].

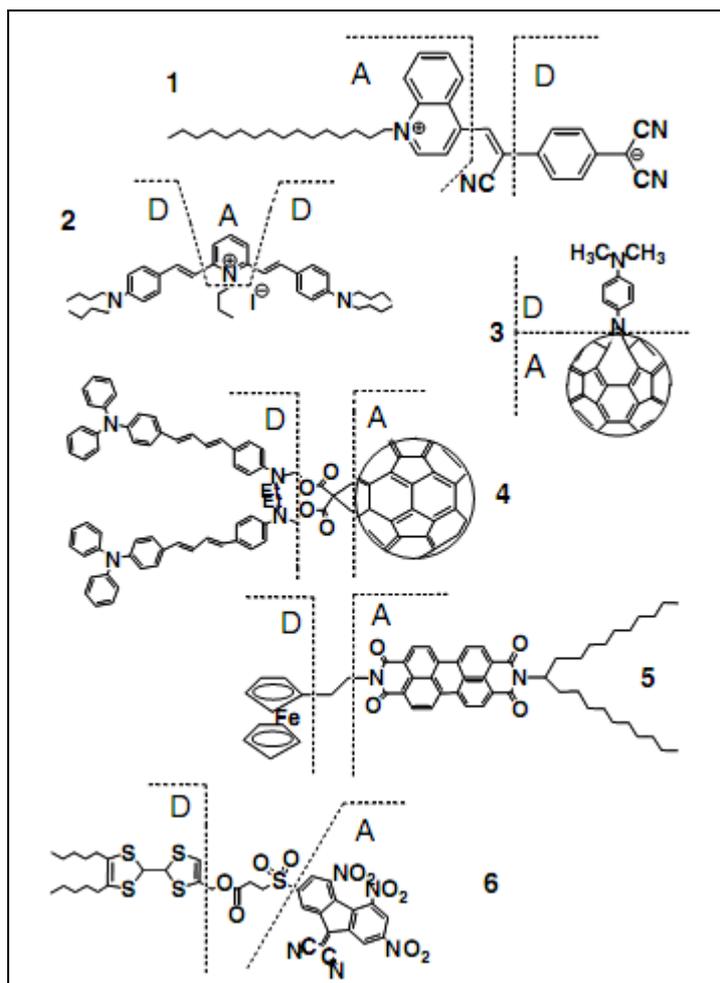


Fig. 16: Six different kinds of molecular rectifiers studied by Robert M. Metzger. D is the donor region and A is the acceptor region of the molecule separated by neutral sigma electron region [2].

When molecule **5** were present in one-molecular thick Langmuir Blodgett monolayer between Au electrodes (Au-D- $\sigma$ -A-Au) sandwich, it was found to be unimolecular rectifier with RR between 14 and 28 at  $\pm 1V$  [14]. He also found that using ‘nanopore’ technique molecule- 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitrobenzene-a-thiolate, attached to Au on one side and topped by a Ti electrode on the other, exhibits negative differential resistance (NDR) property, which was studied by STM [14]. NDR (29-amino-4-ethynylphenyl-49-ethynylphenyl-59-nitro-1-benzenethiol) was also visible in a molecule containing nitroamine redox center was used in the active SAM in an electronic device [16].

Rectification ratio upto 3000 at  $\pm 1V$ , has been reported by the researchers for self assembled monolayers (SAM) of cationic donor-( $\pi$  bridge)-acceptor dyes coupled with anionic donors contacted by Au (Gold) or Pt/Ir (Platinum or Iridium) probes for Au-S-C<sub>10</sub>-H<sub>20</sub>-A<sup>+</sup>- $\pi$ -D-|D<sup>-</sup> system, in which the cationic moiety is 5-(4-dimethylaminobenzylidene)-5,6,7,8-tetrahydro-

isoquinolinium and the counterion is copper phthalocyanine-3,4',4'',4'''-tetrasulfonate [17]. Some research groups has also developed the three terminal controlled molecular rectifier (CMR) same like those of solid state silicon controlled rectifier (SCR or thyristors) [19]. Both symmetric and asymmetric (rectification) current-voltage characteristics has been found for Bis[N-(-decyl)-5-(4-dimethylaminonaphthalenylmethylene)]-5,6,7,8-tetrahydroisoquinolinium]-disulfide diode. They forms self-assembled monolayers (SAMs) on gold substrates, where these diode-like molecules exhibit rectification ratios of 30–80 at  $\pm 1$  V, also display symmetrical current–voltage (I–V) characteristics when exposed to HCl and rectify again when exposed to NH<sub>3</sub>[18]. Ultimately, the new concept towards unimolecular amplifier has already paved the path towards unimolecular three terminal active devices.

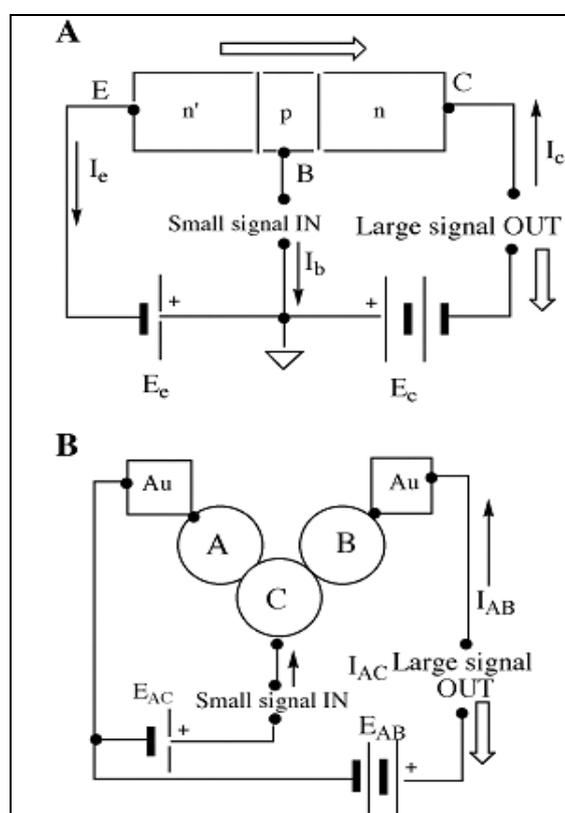


Fig. 17: Proposed unimolecular transistor, molecule with three sides as A ( $n'$ ), C(p) and B (n) region (bottom) respectively high  $\pi$ -electron cloud region separated from low-electron cloud from the  $\sigma$ -region analogous with the solid state bipolar junction transistor (BJT) (top) [15].

A research group has also proposed three terminal molecular transistor operating in wide range of bias voltage unlike single electron transistor (SET), operating under fixed biased condition, namely quantum interference effect transistor (QuIET) [20]. Benzene, biphenyl e.t.c molecules has also been studied as potential towards three terminal amplifier electronic circuit component [21] [22] [23] [24]. Multi-terminal parallel molecular processing has also been studied by few peoples [25], future scope towards molecular nano-processor [26] [27].

## REFERENCES

- [1] 'World's first 2 Billion Transistor-Breaking the performance barrier', [http://www.intel.com/technology/architecture-silicon/2billion.htm?id=tech\\_mooreslaw+body\\_2billion](http://www.intel.com/technology/architecture-silicon/2billion.htm?id=tech_mooreslaw+body_2billion), (2009).
- [2] Rainer Waser, 'Nanoelectronics and Information technology- Advanced Electronic Materials and novel devices', Wiley-VCH (2003).
- [3] Robert M. Metzger, 'Unimolecular Rectifiers: Present status', Chem. Phys. 326 (2006)
- [4] 'Excerpts from- A Conversation with Gordon Moore: Moore's Law', [ftp://download.intel.com/museum/Moores\\_Law/Video-Transcripts/Excerpts\\_A\\_Conversation\\_with\\_Gordon\\_Moore.pdf](ftp://download.intel.com/museum/Moores_Law/Video-Transcripts/Excerpts_A_Conversation_with_Gordon_Moore.pdf)
- [5] 'Introduction to Intel's 32nm Process Technology', [http://download.intel.com/pressroom/kits/32nm/westmere/Intel\\_32nm\\_Overview.pdf](http://download.intel.com/pressroom/kits/32nm/westmere/Intel_32nm_Overview.pdf), (2009).
- [6] Aviram, Mark A. Ratner, 'Molecular Rectifiers', Chem. Phys. Lett. 29, 277-283 (1974).
- [7] Bing Wang, Yunshen Zhou, Xunlei Ding, Kedong Wang, Xiapoing Wang, Jinlong Yang, J. G. Hou, 'Conduction mechanism of Aviram-Ratner Rectifier with single pyridine- $\sigma$ -C<sub>60</sub> Oligomers', J. Phys. Chem. B, 110, 24505-24512 (2006).
- [8] C Zhou, M. R. Deshpande, M. A. Reed, L. Jones II, J. M. Tour, 'Nanoscale metal/self-assembled monolayer/metal heterostructures', App. Phys., Vol. 71, 611 (1997).
- [9] T. Böhler, A. Edtbauer, and E. Scheer, 'Conductance of individual C<sub>60</sub> molecules measured with controllable gold electrodes', Phys. Rev. B, 76, 125432 (2007).
- [10] M. A. Reed, C. Zhou, C. J. Muller, t. P. Burgin, J. M. Tour, 'Conductance of a Molecular Junction', Sci., Vol. 278, 252 (1997).
- [11] A. Scorzoni, I. De Munari and H. Stulens, 'Non-Destructive Electrical Techniques as Means for Understanding the Basic Mechanisms of Electromigration', MRS Symp. Proc., Vol. 337, 515-526 (1994).
- [12] A. S. Martin, J. R. Sambles, 'Molecular Rectifier', The Am. Phys. Soc., Vol. 70, No. 2, 218- 221 (1993).
- [13] Mark Elbing, Rolf Ochs, Max Koentopp, Matthias Fischer, Florian Weigend, Ferdinand Evers, Heiko B. Weber, Marcel Mayor, 'A single-molecule diode', PNAS, vol. 102 no. 25, 8815-8820 (2004).
- [14] Robert M. Metzger, 'Unimolecular Electrical Rectifiers', Chem. Rev. 103, 3803-3834 (2003).

- [15] Gianaurelio Cuniberti, Klaus Richter, Giorgos Fagas, ‘*Introducing molecular electronics*’, Springer, 313-349 (2006).
- [16] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, ‘*Large On-Off Ratios and Negative Differential Resistance in a Molecular Electronic Device*’, *Sci. Mag.*, 286, 1550-1552 (1999).
- [17] Geoffrey J. Ashwell, Barbara Urasinska and Wayne D. Tyrrell, ‘*Molecules that mimic Schottky diodes*’, *Phys. Chem. Phys.*, Vol. 8 , 3314–3319 (2006).
- [18] Geoffrey J. Ashwell, Abdul Mohib, Christopher J. Collins, Amirreza Aref, ‘*Molecular rectification: Confirmation of its molecular origin by chemical suppression of the electrical asymmetry*’, *Syn. Met.*, Vol. 159, 2282–2285 (2009).
- [19] Marcos Allan Leite Reis, and Jordan Del Nero, ‘*Design of a Three Terminal NanoDevice: Controlled Molecular Rectifier*’, *Jou. Comp. Nano.*, Vol. 5, 1–4 (2008).
- [20] D. M. Cardamone, C. A. Stanord, S. Mazumdar, ‘*The Quantum Interference Effect Transistor*’, arXiv:cond-mat/0503540v1, (2005).
- [21] Haiying He, Ravindra Pandey, Shashi P. Karna, ‘*Electronic conduction in a three terminal molecular transistor*’, *2008 Nano.*, Vol. 19, 505203 (2008).
- [22] M. D. Ventra, and S. T. Pantelides, N. D. Lang, ‘*The benzene molecule as a molecular resonant-tunneling transistor*’, *App. Phy. Lett.*, Vol. 76, No. 23, (2000)
- [23] Paul M. Solomon and Norton D. Lang, ‘*The Biphenyl Molecule as a Model Transistor*’, *ACSNANO*, VOL. 2, NO. 3, 435–440 (2008)
- [24] Robert M. Metzger, ‘*Unimolecular Rectifiers and Proposed Unimolecular Amplifier*’, *Ann. N. Y. Acad. Sci.*, 1006, 252–276 (2003)
- [25] Anirban Bandyopadhyay, Somobrata Acharya, ‘*A 16-bit parallel processing in a molecular assembly*’, *PNAS*, Vol. 105, No. 10, 3668–3672, (2008).
- [26] M. R. Stan, P. D. Franzon, S. C. Goldstein, J. C. Lach, M. M. Zieleger, ‘*Molecular Electronics: From Devices and Interconnect to Circuits and Architecture*’, *Proc. IEEE*, Vol. 91, No. 11, 1940-1957 (2003).
- [27] S. Das, G. S, Rose, M. M. Ziegler, C. A. Picconatto and J. C Ellenbogen, ‘*Architectures and simulations for nanoprocessor systems integrated on the molecular scale*’, *Lect. Not. Phy.*, (2005).