

The very first organic material based electronic device was envisioned by a German physiologist Ewald Hering in his lecture of 1870 “Memory as a general function of organized matter” (Hering, 1870). The physiology behind his argument was the transfer of knowledge/memory from the parents to their offspring. This phenomenon is mostly observed in all living organisms. This idea was very crude and requires a significant advancement in state-of-the-art engineering on DNA. Nearly a decade later in 1974 Aviram and Ratner introduced to us the first single organic molecule rectifier (Aviram and Ratner, 1974). The giant molecule used by the team of Ratner consists of Tetra-cyanoquinodimethane (TCNQ) acting as electron acceptor, Tetra-thiofthalvalene serves as electron donor and to insulate both of them multiple methylene groups make sigma bonded bridge between the acceptor and donor. This combination of the acceptor and donor type organic materials are radially available and had been cited very frequently by scientific community, working on organic materials. The acceptor-donor molecular structure resembles with p-n junction devices in silicon technology which has been the backbone of electronics industry ever since the invention of transistor in late 1948 at Bell Labs (William, 1951). Silicon technology has gained pace after the development of Metal oxide semiconductor field-effect transistor (MOSFET) (Dawon, 1963) and Complementary metal oxide semiconductor (CMOS) (Wanlass, 1967) in the year 1960 and 1963 respectively. Looking at the popularity and potential of silicon technology Gordon Moore, the co-founder of intel corporation, predicted the roadmap of the future of integrated chip as the rise in the number of transistors per unit area at a rate of twice per year (Moore, 1965). Though he has to revise his prediction of rate of rise of number of transistors per unit area from twice per year to twice every two years in year 1975 (Moore, 2006). From all these years till now silicon technology evolved heavily in other aspects as well like cost, power consumption, speed of operation (Max Roser, 2019).

However, according to International roadmap for devices and systems (IRDS) IEEE, by 2033 the node range maybe reduce to 1nm by the introduction of Vertical gate all around (VGAA), Lateral gate all around (LGAA) and 3D VLSI which is 7nm with FinFET in 2019. This indicates how difficult it is to further reduce the feature size of devices due to significant rise in short channel effects. Therefore, engineers and scientists are looking for its alternative to replace typical silicon technology in pursue of higher density of integration, low power consumption and flexible electronics. With the advancement in various lithography and other deposition techniques organic materials are gaining huge attention. In this chapter, importance of organic materials in electronics and physics behind electron transport will be discussed alongside their development from 1974 till 2019.

## 1.1 Motivation

Challenges arise in silicon technology due to quantum tunneling and short channel effects are the main source of motivation to carry out research in organic molecular electronics. One of these challenges is high density of integration of transistors in an IC. Till now electronic industry was following the trend set by Moore’s law but it is high time to think about More Moore (MM) or More-than-Moore (MtM) to further enhance the higher density of integration per unit area. Another big challenge in current silicon technology is power consumption and heat dissipation

per unit cell. A recent study (Shafaei et al., 2015) predicted the leakage power consumption of around 53nW in a 6T 7nm FinFET based SRAM cell. The main contribution to this power is because of high value of ON current (0.1-10mA) and OFF current (0.5-5uA). This value could further be reduced by two orders by the introduction of organic materials based devices because in organic materials based memory device the typical ON current (1nA) and OFF current (0.1nA) values are very low under low applied bias condition (Mativetsky et al., 2008). Both of these factors will cumulatively further reduce down the power requirement. In another recent study change in heat measured due to self-heating in FinFET fabricated on SOI technology node was as high as 141° C above the room temperature (Stellari et al., 2015). The huge rise in temperature within such a tiny region has tremendous potential for lots of anomalies. This can be overcome by reducing the operating voltage and current values much further. Organic materials are strong candidates in this perspective as well.

Though single molecule electronics seems very lucrative in terms of density of integration, power consumption and performance but there are some challenges that needs to be addressed. First and foremost, challenge is development and functionalization of molecular devices. A base organic molecule like benzene can have various electrical properties depending upon the type of functional groups attached to it. From a single molecule-based device design this is bit of a concern as it requires atomic precision to functionalize selective molecules with desired functional groups. So far chemical and physical roots of molecule functionalization have been adopted by researchers. For single molecule characterization both of these roots are very adequate but it is still a challenge in mass production. Another big challenge in single molecule-based devices is the proper arrangement of individual molecule. Though atom manipulation has been practiced several times for desired arrangement of molecules with remarkable precision but it is a very slow process and needs significant boost.

Self-assembled monolayers of organic molecules dazzled scientific community because of their unique property to make a supramolecular structure. A recent study reveals the influence of self-assembly in solar cell (Choi et al., 2019). Another similar study reveals the wide spectrum usability of molecular junction diodes and the role of interatomic interaction among molecules in self-assembled monolayer on the conductivity (Vuillaume, 2019). All these studies gave us a hope to work on More-than-Moore's approach via self-assembly of molecules in an electronic device. Scanning tunneling microscopy has proven its heavy applicability in designing and characterization of single molecule devices (SMD) and self-assembled monolayers (SAM).

## **1.2 Single Molecule Organic Electronics (SMOE):**

Organic materials are widely used in many application specific areas like OLED, photodetectors, electronic rectifier, memory switching etc. So far organic materials have been used as thin film in electronics components. In thin films spread of charge within organic molecules is delocalized which is very useful in electronic components but charge among molecules is localized because of that organic materials lack in some critical aspects like device endurance, repeatability, reliability and speed of operation. Nowadays, the most demanding parameter in logic devices is high density of integration and fast switching. But both of these demands come with a trade-off of heat generation. The main objective of scientific community working on single molecule electronic devices and some emerging industries has been to identify the organic molecules those can operate at low voltages and induce leakage current upto few nA/pA ranges for single molecule cell. Another important hurdle could be contact resistance between metal electrode and molecule but some research studies shows that contact resistance also helps in negative difference resistance behavior which is also an important characteristic for designing of electronic oscillators. But organic materials haven't spread their wings in electronic industry other than flexible or wearable gadgets. The main reason behind this is lack of advanced technology that can fabricate and characterize single molecule with atomic precision. Mechanically controlled break junctions (MCBJ) (Ke et al., 2019; Yasuraoka et al., 2019) and Conductive Atomic Force Microscopy (C-AFM) (Cui et al., 2001; Ho Choi et al., 2008) based

systems managed to illustrate the single molecule devices. But Scanning Tunneling Microscopy (STM) system brings great advantage when it comes to fabrication, designing and testing of single molecule devices.

### 1.2.1 Applications

Higher density of integration is a very common requirement for each electronic application. A brief categorization of single molecule organic devices based on electronic application is illustrated in fig. 1.1.

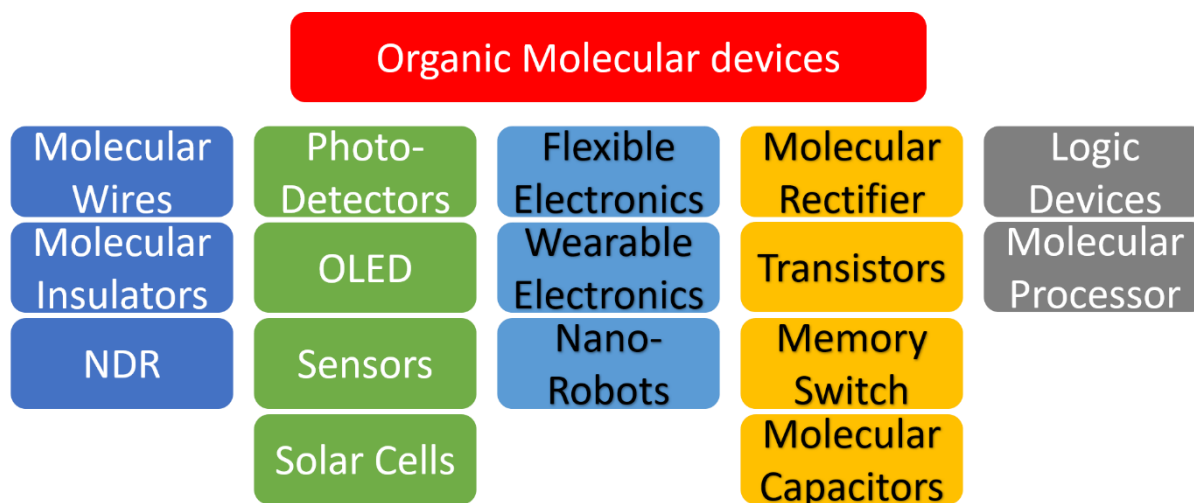


Fig.1.1 Schematic representation of various applications of organic molecular devices as electronic component.

In early studies conductivity of self-assembled monolayers of molecular wires was tested (Bumm et al., 1996; Reed et al., 1997). Among these molecular wires carbon nano tubes (CNT) have very unique characteristics. Small length CNT shows low resistance and are mostly conductive while long length CNT are semi-conductive and show comparatively high resistance (Collins and Avouris, 2008). A set of theoretical studies also point out the negative differential resistance (NDR) induced due to contact resistance between electrode and molecule (Dagar et al., 2019; Geng et al., 2007). Organic molecular optoelectronic devices (Lee et al., 2005) have also studied by many groups including absorption in photodetectors at room temperature (Celebrano et al., 2011; Kukura et al., 2010), light emitting diodes (LEDs) and logic gates (Lee et al., 2003). A review study (Gooding and Gaus, 2016) described various near-field and wide-field measurements illustrated the advancement in single molecule nanopore sensors. Apart from all these applications molecular rectifiers and memory switches are stand out studies which are explored extensively. The early proposed models of molecular diodes were based on donor-acceptor type supra-molecule along with a linker between them. Similar mechanism in redox based molecules give memory switching.

### 1.2.2 Types of organic molecules

Organic compounds can be classified into two types based on their structures as shown in fig. 1.2. The two main sections of organic compounds are whether they are open chain or cyclic. The open chain compounds are usually hydrocarbon chains. Langmuir-Blodgett systems were heavily used for creating self-assembly of functionalized hydrocarbon chains. The potential application of these open chain compounds has been seen in molecular wires (Donovan et al., 1991; Leatherman et al., 1999; Ward, 2001) and molecular insulators (Kaun and Guo, 2003)

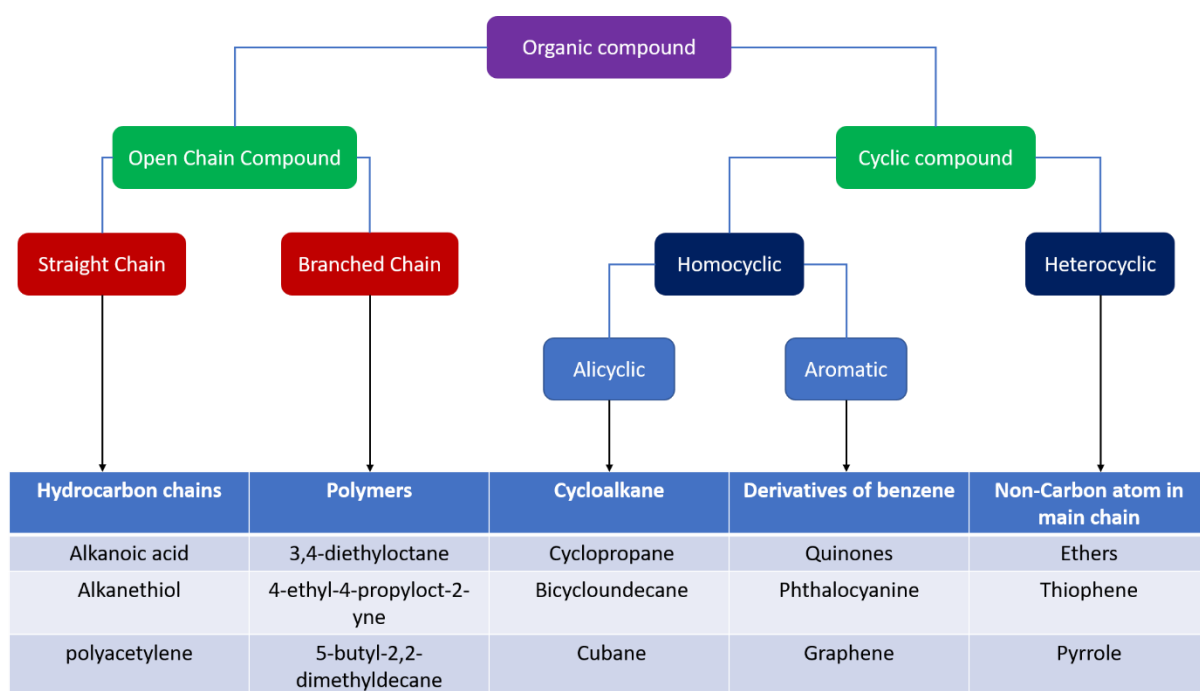


Fig.1.2 Classification of organic molecules based on their structure.

On the other hand, cyclic compounds especially those which possess aromaticity are proven to be immensely helpful in molecular electronics because of their conjugated structure. The driving factor in conjugated structure of aromatic molecules like graphene is  $sp^2$  hybridization among carbon atoms which makes them not just strong but very good conductor of electronic charge. Researchers are trying to observe superconductivity in graphene layers near to room temperature (Chen et al., 2019; González, 2008). Though high conductivity is desirable in electronic components through electrodes to reduce transmission losses but for logical operations semi conductive nature of the molecule is required. To achieve that, graphene has been functionalized with various other reactive groups for desirable applications (Englert et al., 2011; Kuila et al., 2012). Similar experiments have been performed on other organic molecules which have one or more aromatic components in its structure (Anthony, 2006; Calhoun et al., 2008; Katz and Willner, 2004). This brings a huge success in categorizing organic molecules based on their potential application in molecular electronics.

### 1.2.3 Electronic charge transportation in molecular devices

The electronic charge transportation in molecular devices is different from macroscopic electronic devices and therefore they do not follow traditional ohm's law. To understand the electronic devices at nano scale several conduction mechanisms have been illustrated.

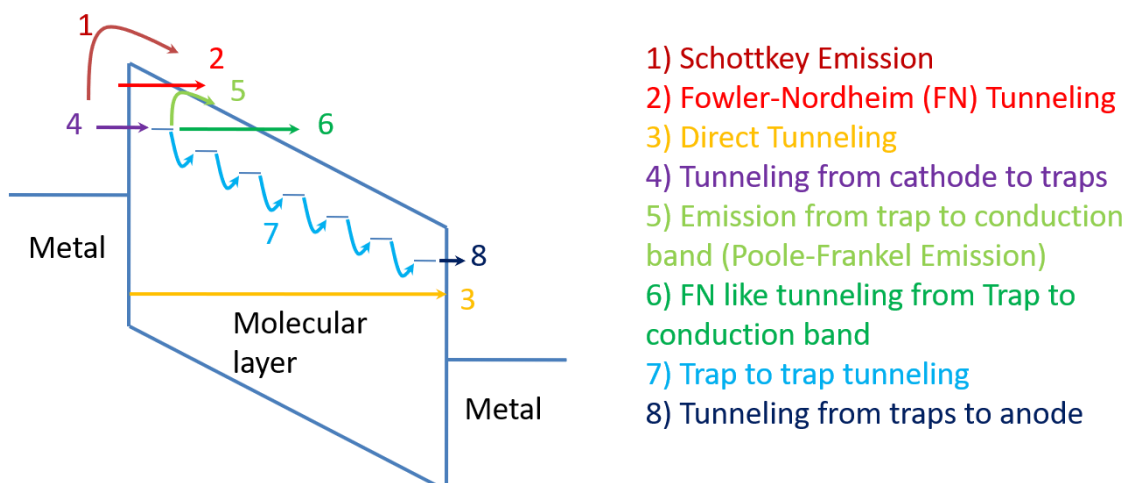


Fig 1.3. Schematic representation of various conduction mechanisms (Yu et al., 2011).

First of these effects is Schottky emission which enhances the emission of charge by lowering the barrier because of room temperature condition. The impact of temperature in macroscopic devices is not observable because of huge amount of charge scattering but at quantum level temperature effects are directly observable. Apart from that charge tunneling phenomenon is very popular at atomic scale which deals with the probability of transfer of charge from one electrode to another electrode through insulating barrier without gaining ionization energy at its source. The tunneling current mainly depends upon the applied biasing and the width of the barrier instead of height of the barrier. Besides them there is another conduction mechanism where electric field is solely responsible for the excitation of electrons from trap sites to conduction band in a quantum regime. It is Frenkel-Poole emission, named after their inventors Yakov Frenkel and Horace Hewitt Poole. The charge hopping conduction mechanism is peculiar among all other quantum mechanical conduction mechanism and mostly observed among organic molecules. The nature of charge transfer is inter-molecule instead of intra-molecule in this type of conduction. In organic molecules charge is usually localized within the molecule therefore a single molecule may act as charge trapping sites. The charge hopping conduction mechanism deals with the conduction of the electrons from one trap site to another.

Table 1.1 Mathematical relation between current voltage and temperature for various conduction mechanism in molecular devices.

Conduction Mechanism	Current Equation	Temperature dependency	Voltage dependency
Direct Tunneling (Low Bias)	$I = V \frac{q^2 \sqrt{2mq\Phi_B}}{4\pi\hbar^2 d} e^{-\frac{2d}{\hbar} \sqrt{2mq\Phi_B}}$	None	$I \propto V$
Fowler-Nordheim Tunneling	$I = \frac{q^3}{16\pi^2 \hbar (q\Phi_B)} V^2 e^{-\frac{4\sqrt{2m^*} (q\Phi_B)^{3/2}}{3q\hbar V}}$	None	$\ln\left(\frac{I}{V^2}\right) \propto \frac{1}{V}$
Thermionic Emission	$I = \frac{qm^*}{2\pi^2 \hbar^3} (k_B T)^2 e^{-\frac{\Phi_B}{k_B T}} e^{\frac{q\sqrt{4\pi\epsilon d}}{k_B T}}$	$\ln\left(\frac{I}{T^2}\right) \propto \frac{1}{T}$	$\ln(I) \propto C_1 V^{1/2} - C_2$
Schottky Emission	$I = \frac{4\pi qm^*}{\hbar^3} (k_B T)^2 e^{-\frac{\Phi_{eff}}{k_B T}} e^{\frac{q\sqrt{4\pi\epsilon d}}{k_B T}}$	$\ln\left(\frac{I}{T^2}\right) \propto \frac{1}{T}$	$\ln(I) \propto V^{1/2}$
Poole-Frenkel Emission	$I = V \sqrt{N_{eff}} \sqrt{N_D} q \mu e^{\frac{E_T}{2k_B T}} e^{\frac{\sqrt{q^3 V}}{\sqrt{4\pi\epsilon}}}$	$\ln\left(\frac{I}{V}\right) \propto \frac{1}{T}$	$\ln\left(\frac{I}{V}\right) \propto V^{1/2}$
Hopping Conduction	$I = VAe^{-\left(\frac{B}{\tau^{1+d}}\right)}$	$\ln\left(\frac{I}{V}\right) \propto \frac{1}{T}$	$I \propto V$

Due to reduced distance between the metal contacts in molecular devices the rules of quantum mechanics start dominating at this scale. Therefore, molecular devices comply with Schrödinger's equation. The atoms within a molecule are bounded to each other with an attractive force also known as bonds. Briefly there are three types of bonds: ionic, metallic and covalent bonds. Out of these covalent bonds has been proven very useful in semiconductors and insulators. After the invention of graphene, covalent bonds secure their spot among conductors as well. The state of the molecular orbital can be determined with Schrodinger's wave equation, Pauli's exclusion principle, Hund's rule, molecular orbital (MO) theory and principle of lowest energy. The molecular orbital theory is very helpful in describing conjugated structure of organic molecules like benzene which have alternately single and double bonds whereas the valance band theory was failed to do so. Molecular orbital theory has advantageous linear combination of atomic orbitals (LCAO) which include bonding orbitals and anti-bonding orbitals.

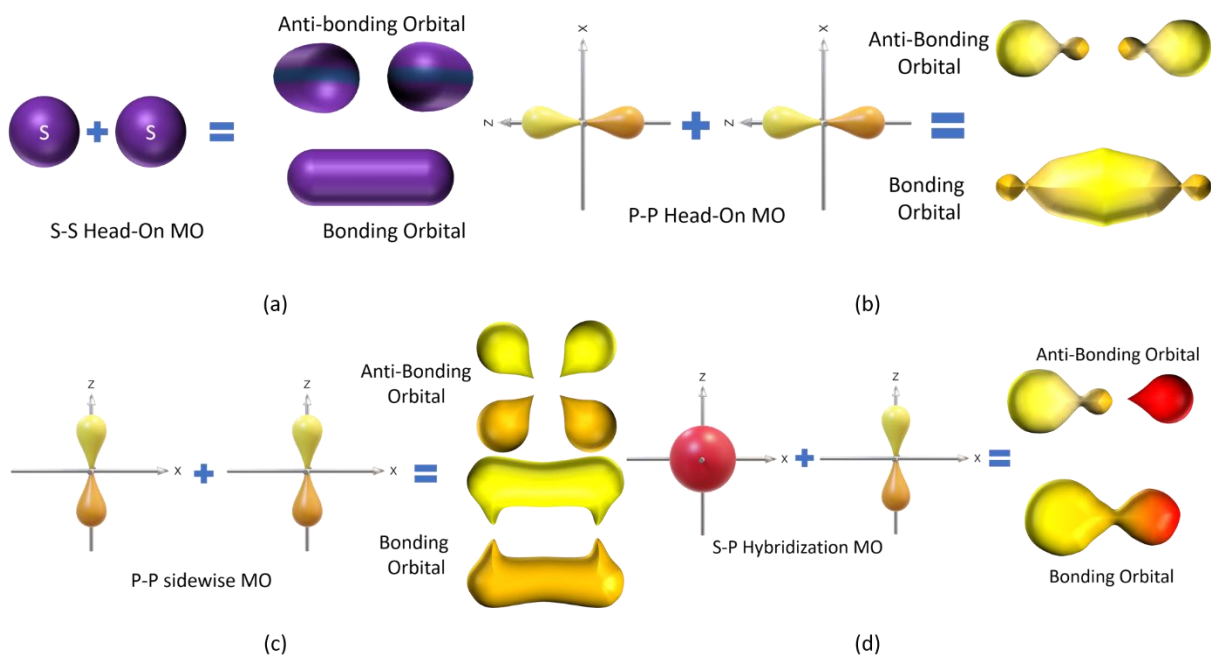


Fig. 1.4. Schematic representation of bonding and anti-bonding orbitals derived from linear combination of atomic orbital (LCAO) of s and p orbitals.

In Fig. 1.4, the application of LCAO illustrates the bonding and anti-bonding orbital structure when two similar or different types of orbitals interact with each other. Fig. 1.4(a) shows the dense electron cloud in resultant bonding( $\sigma$ ) orbital between two atoms when a s-orbital of an atom interacts with s-orbital of another atom head on. While in anti-bonding orbital structure electron cloud moves away from center of two atoms. Similar is the case with p-p head on orbital interaction as shown in fig. 1.4(b). But when two p orbitals interact sidewise with one another instead of head-on an interesting bonding orbital comes into picture. The electron cloud in this case is above and below the two atoms instead of being in-between as shown in fig. 1.4(c). This in conjunction with sp hybridized molecular orbital (fig. 1.4(d)) will make flow of electrons delocalized within the molecule. Graphene structure makes use of this delocalization of charge to reduce the scattering of electrons for relatively long distances.

### 1.2.4 Effect of conjugation on charge transport mechanism

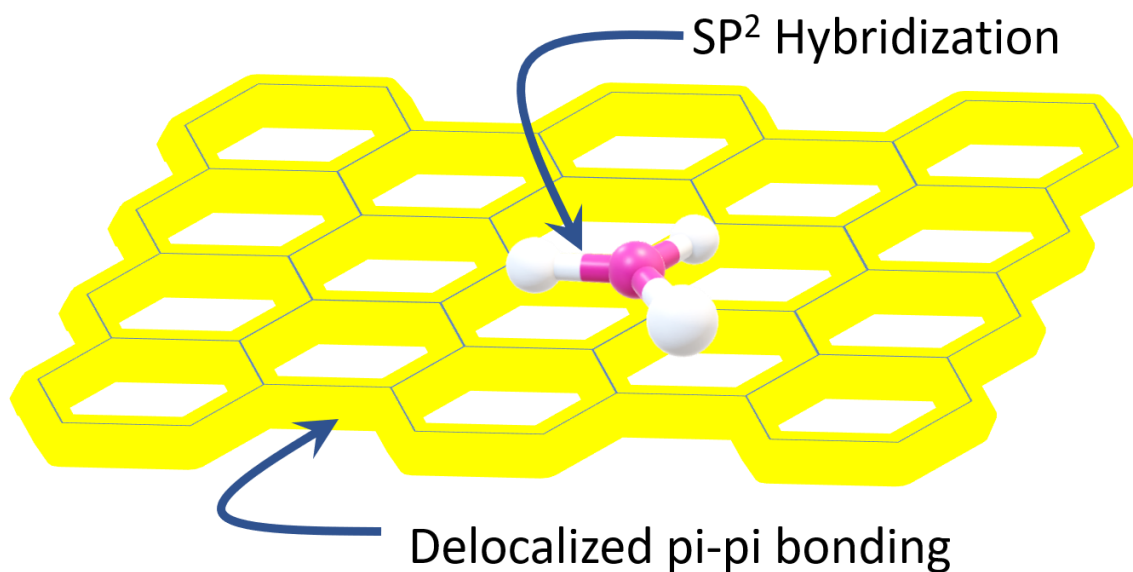


Fig. 1.5. Schematic representation of delocalization of electrons in a graphene structure.



Conjugation is mainly observed in  $sp_2$  hybridized molecular orbitals of carbon atom along with an additional  $p_z$  orbital. Both of these orbitals lead to alternate single bond and double bond formation. The interesting thing in conjugated structures is isomerization of the molecular structure with nearly same energy level. The floating  $p_z$  orbital helps in high mobility and conduction of electrons with less scattering. Other molecules which experiences conjugation are fullerene and its co-polymers, members of polythiophenes, quinones, oligomers and many more. Some of these molecules are proven to be very useful in various electronics applications at molecular and thin film levels.

### 1.2.5 Device Structure

The molecular device structure for organic materials is very fundamental. It consists of two conducting electrodes at two ends and a single organic molecule laying between them in desired geometry. The primary requirement in molecular devices is atomic uniformity in substrate materials. The Langmuir-Blodgett method of monolayer deposition is based on surface tension of self-assembled molecules (SAM) when squeezed in a confined area. Similarly, e-beam evaporation of small organic molecules on atomically flat substrate yield better results compared to a rough substrate.

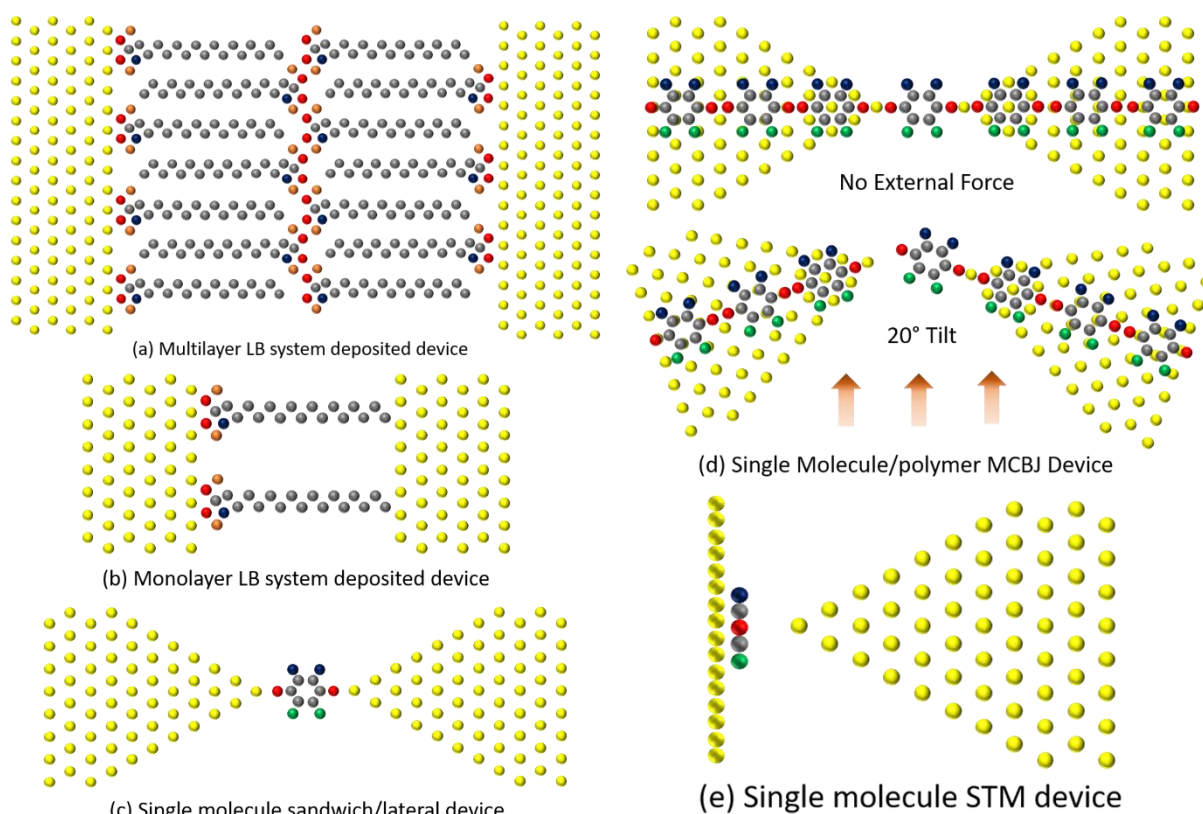


Fig. 1.6. Schematic representation of molecular devices. (a & b) corresponds to self-assembly of multilayers and monolayers of functionalized hydrocarbon chains/oligomers/polymers. (c) represents a typical theoretical 2 terminal modal device to characterize electrical properties of a molecule. (d) shows the characterization module used in mechanically controlled break junction system. (e) gives the typical modal of material characterization in scanning tunneling microscopy by means of an atomically sharp tip.

Fig 1.6 shows schematic representation of various types of molecular device structures. The depicted structures can be prepared by using LB system, MCBJ system, STM system and theoretical designs.

### 1.2.6 Quantum effects in molecular devices

Quantum mechanics is the only tool available to us to understand the properties of molecules at nano and sub-nano scale. Scanning tunneling microscope (STM) is a very useful tool

to sense these quantum effects experimentally with the help of highly sensitive piezo materials. The charge conduction in STM systems comprise of three parts. First part is bulk charge conduction which usually corresponds to charge flow within tip or substrate. Second part is tunneling of charge, which is only possible when certain conditions met. The tunneling current depends mainly on two parameters, applied biasing and separation between tip and substrate. Last part is quantum conductance, which corresponds to the charge conduction through the molecule. The main phenomenon behind quantum conductance is local density of states of molecule which when interact with tip atom yield discrete conductance value depending on the interacting quantum state of the molecule.

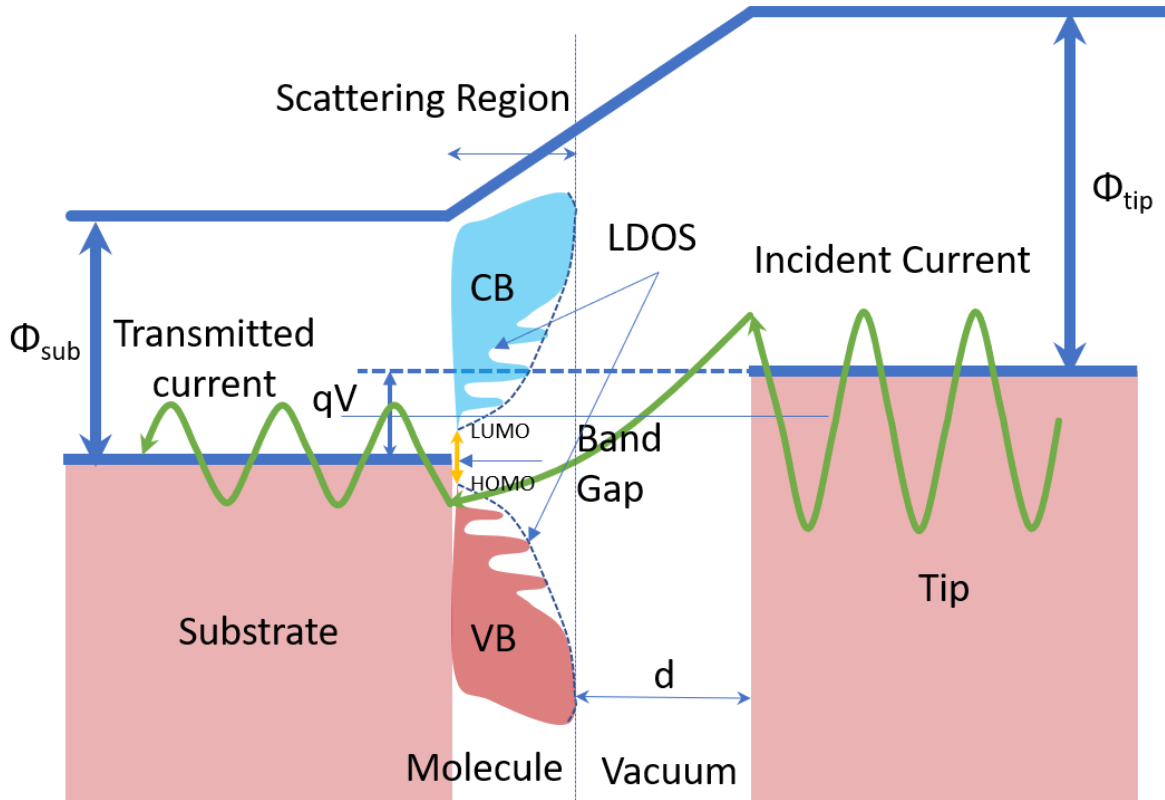


Fig. 1.7. Energy band diagram representation of an organic molecule deposited on a metal surface separated from a metal tip few angstroms apart in an STM system (Schouteden et al., 2013).

$$\Psi(d) = \Psi(0)e^{-kd} \quad 1.1$$

Where,  $k = \frac{\sqrt{2m(\Phi-E)}}{\hbar}$

$$I \propto V\rho(d, E) \quad 1.2$$

Where,  $\rho(d, E) \equiv \frac{1}{\varepsilon} \sum_{E_n=E-\varepsilon}^E |\Psi_n(d)|^2$

$\Psi$  is electronic wave function,  $k$  is decay constant,  $d$  is separation between tip and substrate/molecule,  $\Phi$  is average of work function of tip and substrate and  $\rho$  is local density of states (LDOS).

The substrate and tip have crystalline pattern therefore charge distribution is uniform throughout the bulk but organic molecules cause distortion in that symmetry because of their structure. Therefore, molecular region in single molecule devices is also referred as scattering region because of varied electron scattering of electrons in molecule as compared to crystalline metal contacts. The local density of states in scattering matrix provide the transmission probability and hence the value of transmission current.



### 1.3 Advancement towards organic molecular devices

Earlier the primary advancement in organic molecular devices was mainly focused on either theoretical studies or thin film based organic devices. Later, Langmuir-Blodgett systems help in self-assembly of monolayer and multilayers of functionalized hydrocarbon chains. Various applications of such devices include molecular wires, rectifiers and LED devices. Recently due to advancement in fabrication techniques and introduction of highly precise e-beam lithography/evaporation systems and atomic layer deposition (ALD) system it became possible to deposit very thin layers of active materials. Moreover, Mechanically Controlled Break Junction (MCBJ) and Scanning Tunneling Microscopy (STM) make it possible to characterize electrical properties of single molecule. A state-of-the-art research progress is shown in table 1.2.

Table 1.2 A brief comparative summary of rise of organic materials-based electron devices from theoretical studies to most recent molecular studies. The brief study includes the change in the performance of the organic devices, the device type, the techniques used for device preparation, device structure and electronic application of organic devices.

Molecule Name	Performance	Device Type	Device Preparation method	Device structure	Application	Reference
Tetra-Cyano quinodimethane (TCNQ) – 3(CH <sub>2</sub> ) – Tetra-Thiofulvalene (TTF)	--	Molecular	Theoretical study	MIM	Rectifier	(Aviram and Ratner, 1974)
Phthalocyanines	Thermal conductivity	Crystalline	--	--	Semiconductor	(Eley, 1948)
Anthracene, Tetracene	--	Thin film	Material sublimation	MIM	Electroluminescence	(Pope et al., 1963)
Polysulfur Nitride	--	Thin film	Material sublimation and polymer growth	Standard procedure	Conductive polymer	(Walatka et al., 1973)
Copper phthalocyanine and perylene tetracarboxylic	1% power conversion efficiency	Thin film	Vacuum evaporation	MIM	Photovoltaic cell	(Tang, 1986)
Polythiophene	$I_{ON/OFF} > 10^2$	Thin film	electrochemical	Back gated	FET	(Koezuka et al., 1987)
Polyacetylene	$I_{ON/OFF} > 10^5$	Thin film	Spin coating and thermal heating	Back gated	MISFET	(Burroughes et al., 1988)
Alpha-Sexithienyl	Carrier mobility = $10^{-3}$ cm <sup>2</sup> /V/s	Thin film	Vacuum evaporated	Back gated	MISFET	(Horowitz et al., 1989)
8-hydroxyquinoline aluminum, diamine	EL quantum efficiency = 2.5% phonons/electrons	Thin film	Vapor deposition	MIM	Electroluminescence	(Tang et al., 1989)
poly(2-methoxy, 5-(2'-ethyl-hexoxy)-1,4-	Rectification ratio $> 10^4$	Thin film	Spin casting	MIM	LED	(Braun and

phenylenevinylene) MEH-PVP						Heeger, 1991)
PEDOT, MEH-PPV, PPP-NEt <sub>3</sub> <sup>+</sup> , PVK, PVA	Brightness = 200 cd/m <sup>2</sup>	Thin film	Ink Jet Printing	MIM	PVED, OLED	(Yang et al., 2000)
poly(3-hexylthiophene), (6,6)-phenyl C61 butyric acid methyl ester	Power efficiency > 4%	Thin film	Doctor blading	MIM	Solar cell	(Schilinsky et al., 2006)
poly-(ethylene dioxythiophene) : polystyrene sulphonic acid ,(PEDOT:PSS)	Power conversion efficiency > 4.3%, surface roughness = 2.6 nm	Thin film	Screen printing	MIM	Solar cell	(Shaheen et al., 2001)
P(NDI2OD-T2) and P3HT	Electron Mobilities 0.45–0.85 cm <sup>2</sup> /V/s, Gain 25-65	Thin Film	Spin coating, Gravure, Flexo, Inkjet Printing	Top gate	Organic Thin-Film Transistor (OTFT)	(Yan et al., 2009)
7,8,9,10 - tetrafluoro-5,12-bis(TIPSethynyl)tetraceno[2,3-b]thiophene, and 7,8,9,10-tetrafluoro(2,3-b)thiophene	Charge Mobility of 0.12 and 0.37 cm <sup>2</sup> /V/s In air and N <sub>2</sub>	Thin film	--	Top gate	OTFT	(Tang et al., 2008)
pentacene and hexadecafluorocopperphthalocyanine (F <sub>16</sub> CuPc)	Static current < 100pA/logic gate, Static power consumption < 1nW/logic gate	Thin film	Dip coating, plasma treatment , evaporation	Patterned structure	OTFT, complimentary invertors, NAND gate, ring oscillator	(Klaauk et al., 2007)
cyclopentadithiophenebenzothiadiazole copolymer (CDT-BTZ)	Hole mobility around 0.67 cm <sup>2</sup> /V/s, On/Off current ratio of 2x10 <sup>4</sup>	Thin film	Spin coating	Top contact gate	OFET	(Tsao et al., 2009)
Polydivinylbenzene	Film thickness = 10-50 nm	Thin film	Glow discharge	MIM	Resistive Memory device	(Gregor, 1968)
Styrene	Resistance ratio = 10 <sup>7</sup>	Thin film	Glow discharge polymerization	MIM	Bistable Memory device	(Carchano et al., 1971)
styrene, acetylene, benzene, and aniline	high-voltage switching regime (HVSR) >20V,	Thin film	Glow discharge polymerization	MIM	Memory device	(Pender and Fleming, 1975)

	Low-voltage switching regime (LVSr) = 1-5V					
vinylidene fluoride (VDF), trifluoroethylene (TrFE)	Remnant polarization = $8\mu\text{C}/\text{cm}^2$	Multilayers of polymer	Langmuir-Blodgett method	MFIS capacitance memory	nonvolatile ferroelectric random-access memory	(Ducharme et al., 2005)
squarylium dye	Number of layers dependent On/OFF current ratio	Multilayer sandwich	Langmuir – Blodgett method	MIM	Memory device	(Kushida et al., 2003)
Multi-layer graphene (MLG), polyimide (PI)	ON/OFF Ratio = $10^6$ , Retention time $> 10^4$	Thin film	e-beam evaporator, conductive AFM, spin coating, CVD	Al/PI/MLG/PI/Al	Crossbar Memory array	(Ji et al., 2012)
bipyridyl-dinitro oligophenylene-ethynylene dithiol (BPDN-DT), bipyridyl oligophenylene-ethynylene dithiol (BP-DT)	Reversible switching	Single molecule	MCBJ	MIM	Memory	(Lörtscher et al., 2006)
2,3,5,6-tetramethyl-1,4-Benzoquinone (DRQ)	--	Single molecule	Evaporation, STM	MIM	NDR, Memory	(Bandyopadhyay et al., 2006b)
Fe(1,10-phenanthroline) <sub>2</sub> (NCS) <sub>2</sub> molecules (Fe-phen)	--	Single molecule	e-beam evaporation, STM	MIM	Delayed Switching	(Miyamachi et al., 2012)
metal-oxide phthalocyanines	Excitonic emission change due to chemical reaction	Single molecule	HR-AFM, STM-LE, atomic manipulation	MIM	Induced light emission	(Kaiser et al., 2019)
2,3,5,6-tetramethyl-1,4-benzoquinone (DRQ)	16-bit molecular processor	Supramolecular structure	Atomic manipulation, e-beam evaporation	MIM	CCU machine	(Bandyopadhyay and Acharya, 2008)

From the above table, the tremendous transformation of scale of organic devices and their performance can be observed due to advancement in fabrication and characterization techniques. The most recent advancements are mainly focused on single molecule characteristics with the help of high-resolution atomic force microscopy (HR-AFM) and low temperature scanning tunneling microscope (LT-STM).

## 1.4 Research focus and thesis organization

A rising demand of higher density of integration of logic devices in an integrated circuit, low power consumption and enhanced operating speed is forcing the scientific community to identify and implement logic devices from small sized organic molecules. Though, many such organic molecules have already been identified as mentioned in table 1.2 above which are useful as electronic component at molecular level. But mass production of such highly packed molecular devices has not been implemented commercially because of lack of advanced fabrication instruments. Therefore, industry level production of single molecule electronic devices is a challenge for both instrumentation engineers (to design fast molecule manipulation system) and scientists to identify the set of molecules which are capable to work as logic cell in a single molecule device.

In this study, our main focus is on the identification of organic molecules which can act as a unit cell in single molecule device. For identification, both theoretical and experimental studies were performed on the organic molecule. Virtual NanoLab - Atomistik Toolkit (VNL-ATK) was used as density function theory (DFT) tool to study electrical properties of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) molecule. The DDQ molecule was further studied experimentally with the help of STM system under Ultra High Vacuum (UHV) conditions. The electrical behavior of single DDQ was verified experimentally and theoretically. The choice of DDQ molecule was based on few critical parameters. Firstly, the DDQ molecule is aromatic therefore the molecule has potential to undergo conformational isomerization because of conjugated structure. Secondly, the molecule has multiple functional groups which can make it a better contender as a redox active material. And lastly, the molecule is planar therefore it can form self-assembly with other DDQ molecules. Similar to DDQ molecule, a newly synthesized polydentate Schiff's based ligand was also studied at molecular level. The ligand molecule form dative bonds with tip and show rectification under negative biasing as well as memory switching in positive biasing.

The thesis has been organized as following:

Chapter 2 presents the background concept of fabrication techniques and characterization instruments in brief.

In chapter 3 basic concept of density functional theory (DFT) in conjunction with non-equilibrium Green's function (NEGF) used in VNL-ATK tool is explored to understand concept of charge transportation mechanism at molecular scale.

Chapter 4 provide the theoretical study of bidirectional multiple negative differential resistance (BM-NDR) behavior of DDQ molecule.

Chapter 5 proves BM-NDR behavior of DDQ molecule experimentally by STM system. In this chapter self-assembly of DDQ molecules is also discussed along with their application in molecular electronic devices.

Chapter 6 cover the rectification and memory switching observed in newly synthesized polydentate Schiff's based ligand. The study also shows polymer structure of the ligand.

Chapter 7 summaries the whole work from a single molecule organic electronic device point of view and conclude the results. Also, a brief discussion on the future single molecule electronic devices.