

Introduction

An exponential rise is evidenced in our dependency on portable and affordable smart systems in last couple of decades, such as smartphones, laptops, wearable devices, displays, lighting, energy harvesting devices, and various handheld devices. The rapid evolution and upgradation of technologies for the progress of economy of the world, have drastically shortened the lifespan of consumer electronics, leading to a significant increase in electronic waste (E-waste) after their utilization. As reported by the United Nations in 2021, each person is predicted to produce approximately 7.6 kg of E-waste, resulting in a whopping amount of E-waste of 57.4 million metric tons (MMT) (Murthy & Ramakrishna, 2022), and estimated to reach 74 MMT by 2030 if it is not controlled. According to the United States Environmental Protection Agency, out of these, only 15-20 % of waste is properly recycled, and remaining goes directly into landfills and incinerators (Hsu et al., 2019). Moreover, E-waste comprises a combination of valuable recyclable materials and hazardous substances, including lead, mercury, and cadmium (Babu et al., 2007). Hence along with extraction of valuable materials as far as possible, safe disposal is one of the major requirements for E-waste management. In addition, landfills may cause the contamination of toxic and hazardous components into soil and natural resources in that particular region and hamper the ecological system due to the existence of non-decomposable solid e-waste components (Murthy & Ramakrishna, 2022). Moreover, e-waste imposes extreme risks to the environment as well as the health of humans and related habitats. There will undoubtedly be serious repercussions if the issue of increasing E-waste is not addressed soon.

In order to suppress the burdens on environment, organic electronics is emerging as a potential low-cost technology for the development of eco-friendly and biodegradable electronics (Di Mauro et al., 2021; Lee et al., 2017), by incorporating nature-inspired materials in devices that offer inherent benefits of eco-friendliness, biodegradability, green processing, helping to reduce electronics-waste (E-waste) (Torricelli et al., 2022). After a certain amount of time, these naturally occurring polymers can be broken down into non-toxic byproducts when exposed to environment. Organic field effect transistors (OFET) are crucial devices of organic and flexible electronics for use in various circuit and sensing applications (Li et al., 2019; Yan et al., 2022). Further, multi-functionality offered by OFETs makes them a versatile choice for exploration by researchers for wide range of applications with reduced cost and complexity for a system (Maddirala et al., 2022). There have been numerous efforts to increase eco-friendliness of organic devices, specifically OFETs, such as the use of low-temperature and solution processing techniques, utilization of natural polymers as gate dielectric materials (Irimia-Vladu, 2014), nature-derived semiconductors (Fallon & Bronstein, 2021), fabrication on biodegradable substrates (Kumar et al., 2020; Lee et al., 2018a), and use of biocompatible electrodes (C. Wang et al., 2021). Regarding the stated requirements, this chapter briefly discusses the importance of organic electronics and their advantages in developing biodegradable and green electronics.

1.1 ORGANIC ELECTRONICS

From the last few decades, "Organic electronics" has attracted substantial attention where carbon-based compounds and organic molecules are used to fabricate electronic devices. The utilization of organic materials with their unique properties makes this a revolutionized technology field for next-generation electronics. Though the electrical performance of these

devices is not comparable to traditional Silicon technology, this field offers solutions which is limited in conventional electronics such as flexibility, stretchability, and bendability along with eco-friendliness. The market of organic electronics experienced huge growth due to the mechanical, electrical, and optical properties of organic materials and their potential to be employed in a variety of applications. This has facilitated cost-effective production on various flexible substrates such as plastics, paper, and textiles with large-area processing at low temperatures, facilitating wearable and stretchable devices. Moreover, the possibility of implementing environmentally sustainable and biodegradable electronics corresponds with the development of eco-sustainable systems, addressing ongoing E-waste issue. The replacements of toxic and hazardous substances with safer alternatives and lower energy usage during fabrication offer potential environmental advantages over traditional rigid electronics (Kokare et al., 2022), however, evidence on end-of-life environmental impact remains limited.

1.1.1 Historical Development of Organic Electronics

Though some initial explorations had earlier happened, in 1977, a demonstration of electrical conductivity in polyacetylene, a conjugated polymer, played a huge role in revolutionizing organic electronics (Shirakawa et al., 1977). In the year 2000, the Chemistry Nobel Committee awarded A. J. Heeger, A. G. MacDiarmid, and H. Shirakawa Nobel prize in chemistry (Shirakawa et al., 1977) for the discovery of conductive polymers. First organic field-effect transistors (OFETs) were demonstrated by researchers Mitsubishi Electric researchers H. Koezuka, A. Tsumura and Tsuneya Ando with polythiophene (Koezuka et al., 1987; Tsumura et al., 1988) and small conjugate oligomers in the late 1980s (Garnier et al., 1990). On the other hand, development for the fabrication of devices on flexible substrates had started much earlier in 1960s, when the first flexible solar cell arrays were demonstrated by thinning a single crystal silicon wafer up to 100 μm and then integrating on a plastic substrate to offer flexibility (Crabb & Treble, 1967; Ray, 1967). Brody and colleagues developed the first flexible thin film transistor (TFT) in 1968, when they fabricated a tellurium TFT on a strip of paper for displays (Brody, 1969). Further, they had developed TFTs on a wide range of flexible substrates, including polyethylene, mylar, and anodized aluminium foil. Moreover, in the early 1980s, solar cells on organic polymer substrates were also demonstrated with inorganic active materials (Okaniwa et al., 1982). For organic electronics, Burroughes and coworkers demonstrated the first conjugated polymer-based light-emitting diode (PLED) in year 1990 (Burroughes et al., 1990). Apart from organic light-emitting diodes (OLEDs), other devices like organic field effect transistors (OFETs) (Mannsfield et al., 2010; Meager et al., 2014) and circuits based on organic FETs (Chong-an Di et al., 2013; Khim et al., 2013; Li et al., 2018), solar cells (Chen et al., 2017; Liu et al., 2016), photodiodes (Lamprecht et al., 2005; Ng et al., 2008; Rauch et al., 2009), and lasers (Gaal et al., 2003) with organic materials have been demonstrated, leading the organic and flexible electronics to the commercial level. Developments towards flexible inorganic electronics excelled mid-1980s for the display industry in Japan. Backplane driving circuitry for flexible displays with Si:H TFTs sparked huge interest in flexible electronics. Since then, various research groups and industries have started to explore technologies for flexible electronics extensively. As compared to rigid technology, factors including ruggedness, portability, light weight, and low production costs contribute to growth of this area. Later researchers demonstrated high performance flexible transistors with various vacuum evaporated semiconductors making these devices a real competitor to Si:H TFTs which were earlier considered to be suitable for flexible transistors. Moreover, high processing temperatures required for inorganic semiconductors made it more challenging for flexible electronics. Printed electronics, polymer electronics, plastics electronics, flexible large-area electronics, etc. are some of the common names used today for flexible organic electronics. The idea of the integration of biodegradable materials in organic electronics was initiated in early 2000s, further it was emerged from 2010s utilizing silk-fibroin as biodegradable substrate to implement Si device on it for implantable applications (Kim et al., 2009). From then, the biodegradable electronics area has witnessed significant advancements for the development of biodegradable electronic components, including transistors, sensors, and energy storage devices. In addition, foldable displays, flat panel display drivers, radio frequency identification (RFID)

tags, solar cells, printable batteries, smart packaging, flexible sensors, printable circuits are examples of the advancement of flexible electronics (R. Singh et al., 2017; Sirringhaus, 2014). Moreover, today's flexible electronics has reached to a stage where heterogeneous integration of inorganic and organic devices can be utilized to develop a flexible system for various smart applications (Cunha et al., 2022; Kumaresan et al., 2021). These demonstrations range from developing large-area displays to high-performance CMOS like circuits and multi-functional devices suitable for real-time health monitoring (Park et al., 2021; B. Yang et al., 2020). Though high performance, stability, and flexibility are demonstrated from many of these devices, multiple implementation challenges are faced at system level when multiple devices are connected together. The evolution of organic electronics from the first theoretical studies to actual implementations illustrates a significant progression in scientific and technological developments.

1.1.2 Advantages of Organic Electronics

Organic electronics has offered numerous advantages compared to traditional silicon-based electronics, distinguishing it as an attractive domain for new and eco-sustainable applications. One of the primary advantages of organic electronics is the ability to fabricate them on flexible light weight substrates along with solution-processability, low-temperature processing, large-area processing, multi-functionality, and cost-effectiveness. Crucial advantages are briefly discussed below:

(a) Solution Processability

Solution processability of organic materials is the key advantage for organic electronics, enabling to fabrication of devices with high-throughput and cost-effective techniques. Different organic materials, such as conductive polymers, organic semiconductors, and insulators, typically consist of carbon-based backbones with functional groups, which provide solubility in appropriate solvents. Solution processability allows organic materials to be dissolved to form inks, which can then be easily patterned using different simple processes like spin-coating, dip-coating, blade-coating, and printing. Consequently, organic electronics can avoid the requirement of expensive and energy consuming deposition methods such as thermal evaporation, sputtering, and electron-beam deposition. Furthermore, accurate material deposition and patterning in devices are feasible due to the solution processing property. Such processing techniques can be handled easily without any prior knowledge about sophisticated instruments.

(b) Low-temperature Processing

Organic materials can be easily processed at low temperatures ($<100\text{ }^{\circ}\text{C}$), making them compatible with flexible and heat-sensitive substrates like plastic, fabric, paper, or various thin film polymers. Most of the traditional electronics technologies such as single-crystalline silicon ($>800\text{ }^{\circ}\text{C}$), polycrystalline silicon ($\sim 600\text{ }^{\circ}\text{C}$), or hydrogenated amorphous silicon ($\sim 300\text{ }^{\circ}\text{C}$) require extremely high processing temperatures during fabrication. In contrast to this, organic devices can be fabricated at room temperature or below $150\text{ }^{\circ}\text{C}$, which is the glass transition temperature for most of the flexible plastic substrates. This technology lowers energy consumption and supports the production of sustainable electronics by minimizing the environmental impact of fabrication processes. While solution processability and low-temperature processing offer distinct advantages, these benefits are often accompanied by certain trade-offs such as lower charge carrier mobility, higher sensitivity towards environmental, and limited operational stability compared to their inorganic counterparts.

(c) Flexibility and Roll-to-roll Processing

The soft nature of organic materials and the presence of long chains in polymers facilitate flexibility and stretchability which is possible to fabricate devices on various flexible substrates. This feature is mainly important in various applications like foldable displays, wearable sensors, electronic skin, and e-textiles, where devices should perform effectively without losing their

functionalities even after bending, twisting, or stretching according to human motions. The property of flexibility also allows roll-to-roll processing in which batch fabrication is possible at a high speed through various printing techniques for large-area fabrication. This approach reduces overall cost of organic electronics than conventional electronics, where batch fabrication is limited by the size of the wafer. Figure 1.1 shows a circuit on a flexible plastic substrate and the roll-to-roll processing for printing technology.

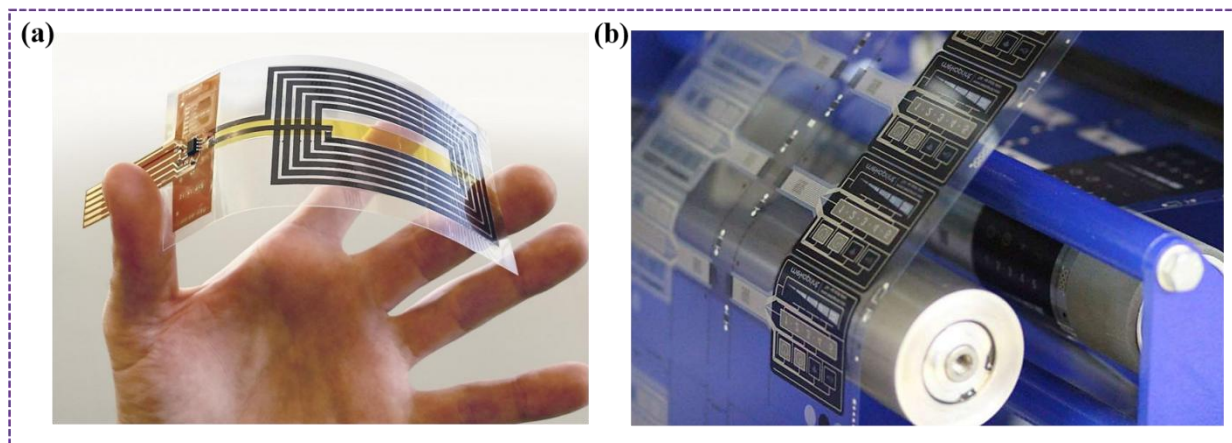


Figure 1.1 : (a) Example of a printed circuit on a flexible substrate (Source: Phys.org / Article by Mary Vogt), and (b) Roll-to-roll processing technique used for large area fabrication in organic electronics (Source: mekoprint.com)

(d) Low-cost Fabrication

The cost of fabrication processes in organic electronics is cheap as compared to the conventional rigid technology. It is a cost-effective technology where simple processing techniques along with reasonable tools are used to fabricate the devices. The carbon-based organic materials are abundant and less expensive as compared to materials used in traditional Si electronics. The use of simple solution processing techniques with low-temperature processing such as inkjet printing and roll-to-roll processing is more affordable than the high-energy processes required for manufacturing Si-based devices. In addition, flexible substrates like plastic, paper, or metal foils can be produced in large quantities and are also cheaper than rigid silicon wafers. All these factors make organic electronics particularly attractive for large-scale production of devices such as organic solar cells, flexible displays, and wearable electronics, where cost efficiency is crucial for widespread adoption. Moreover, this cost-effectiveness allows to manufacture of organic electronics in a resource-limited regions within their budget.

(e) Biodegradability and Eco-friendliness

Environment friendliness is one of the most important advantages of organic electronics. Due to the possibility of solution processability and low-temperature processing, organic electronics allow to integration of various nature-originated materials in device fabrication to suppress the adverse consequences associated with E-waste on the environment and ecology (M. Irimia-Vladu et al., 2010). In comparison with non-degradable inorganic materials, these nature-inspired materials are non-toxic, eco-friendly, and easily degradable in nature without creating any harmful substances (W. Li et al., 2020). Moreover, the introduction of biodegradable materials enhances the functionality of conventional technologies across various fields including environmental monitoring, biomedical applications, agricultural applications, wearable technology, smart packaging, and military applications. In medical field, the transient nature of nature-originated materials-based devices enables them to function as implantable medical diagnostic and therapeutic devices with electronic capabilities (L. Wang et al., 2021). Moreover, the possibility of edibility of these polymers enhances the usage of such eco-friendly devices in emerging biomedical ingestible and edible applications, as most of the material components remained inactive or break down into non-toxic, environmentally safe byproducts. The

biodegradable materials along with energy-efficient green processing techniques support the development of green electronics. Moreover, the degradation time of organic and natural materials is influenced by several factors, including their chemical structures, environmental conditions (ex: temperature, humidity, and microbial activity), and the presence of specific additives. The complete decomposition typically occurs within a few weeks to several months under composting or soil burial conditions. Additionally, the incorporation of additives like plasticizers or enzyme-sensitive linkers can also facilitate faster degradation. Figure 1.2 shows the example of a flexible and biodegradable circuit along with an implantable device that was successfully decomposed in an animal body.

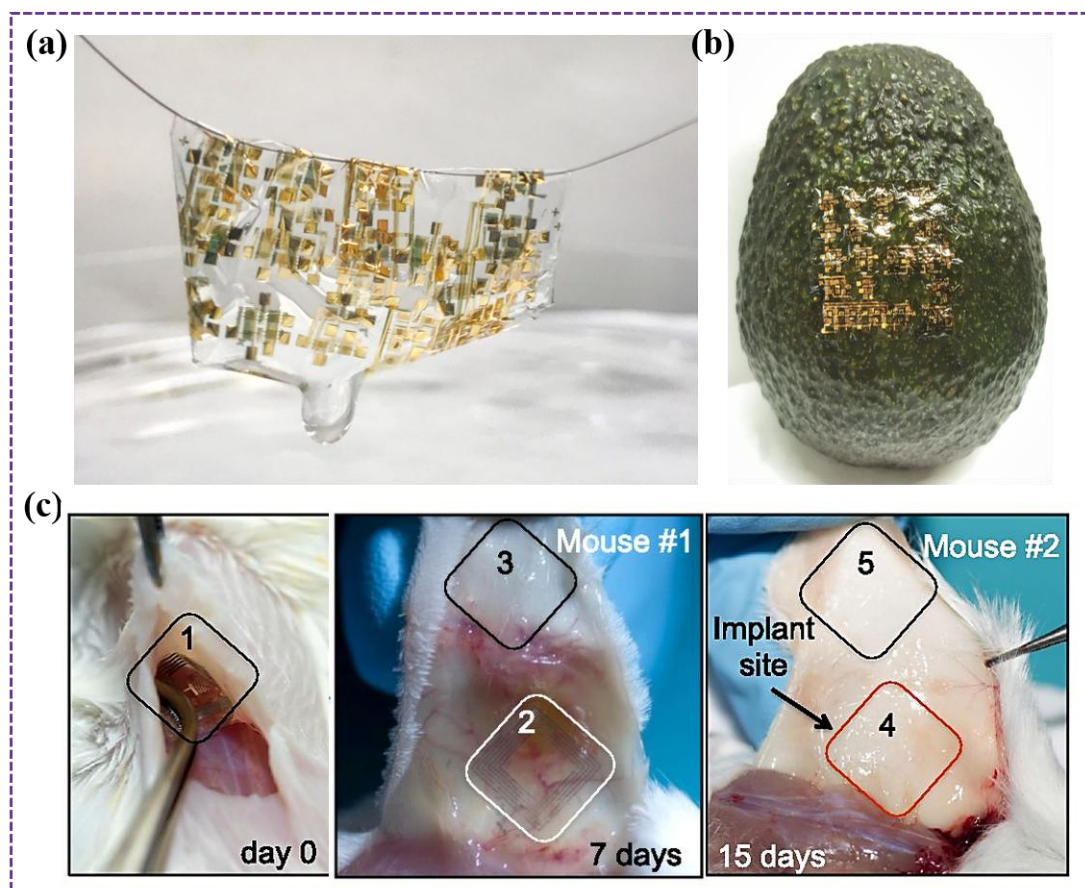


Figure 1.2 : (a) Flexible and biodegradable semiconductive polymer developed by Stanford University researchers (Source: Bao lab, news.stanford.edu). (b) A biodegradable circuit on an edible avocado substrate (Source: inhabitat.com). (c) A silk-based resorbable electronic device implanted on a mouse for *in vivo* infection reduction, which was successfully dissolved in the surrounding tissues within 15 days (Source: pnas.org) (Tao et al., 2014).

1.1.3 Applications of Organic Electronics

Organic and printed electronics offer a wide range of applications due to their unique properties including flexibility or stretchability, lightweight, and cost-effective production. In addition, the organic electronics market is enhanced in a significant way for the requirements of flexible emerging applications in the automotive and healthcare fields. Some of the major applications of organics electronics are flexible OLED displays, organic photovoltaics (OPVs), thin film transistors (TFTs) or organic field-effect transistors (OFETs), bendable sensors and arrays, smart cards, flexible circuitry, organic memory devices, radiofrequency identification tags (RFIDs), artificial skin, intelligent packaging, and smart-textile, etc. OLEDs are the revolutionary advancement for organic electronics which are widely used in high-resolution displays for different applications like smart phones, tablets, laptops, televisions, smartwatches, etc. The thin, flexible, and lightweight properties of OLEDs make them an ideal candidate for portable and foldable devices like fitness trackers, smart glasses, and high-quality imaging and diagnostic devices. These are also useful for energy-efficient lighting systems for homes, vehicles, and

different decorative lighting systems. Few examples of commercially available flexible displays are in smartphones, tablets (Samsung and Huawei introduced flexible OLED technology), smartwatches and fitness trackers (e.g., Fitbit and Samsung Gear), rollable OLED TVs (e.g., LG Signature Rollable TV), etc. In January 2021, TCL CSOT launched two innovative flexible displays: the 17-inch Printed OLED Display and the 6.7-inch AMOLED Rollable Display, containing touch module display panels and can be utilized across a variety of applications including interactive whiteboards, gaming monitors, automotive displays, and video walls. In 2019, Samsung launched the first commercially available foldable smart phones. In 2023, LG introduced a foldable laptop by launching the LG Gram Fold Laptop, incorporating folding features with a touchscreen display that functions both as a tablet and as a laptop when it is completely extended. OPVs are another important device for organic electronics, providing the possibility to be used as portable solar chargers, in green house to generate sufficient light for plant growth, and in indoor light systems for smart homes and industries. The integration of printed organic electronics in smart packaging is useful in food and pharmaceutical industries for real-time monitoring of freshness, temperature, humidity, etc. Moreover, flexible printed RFIDs offer various benefits of energy autonomy and IoT capabilities. Among all organic devices, OFETs are the most important component which is suitable for various applications like sensors, circuitry, and memory. Figure 1.3 shows examples of few applications of organic electronics on flexible substrates.

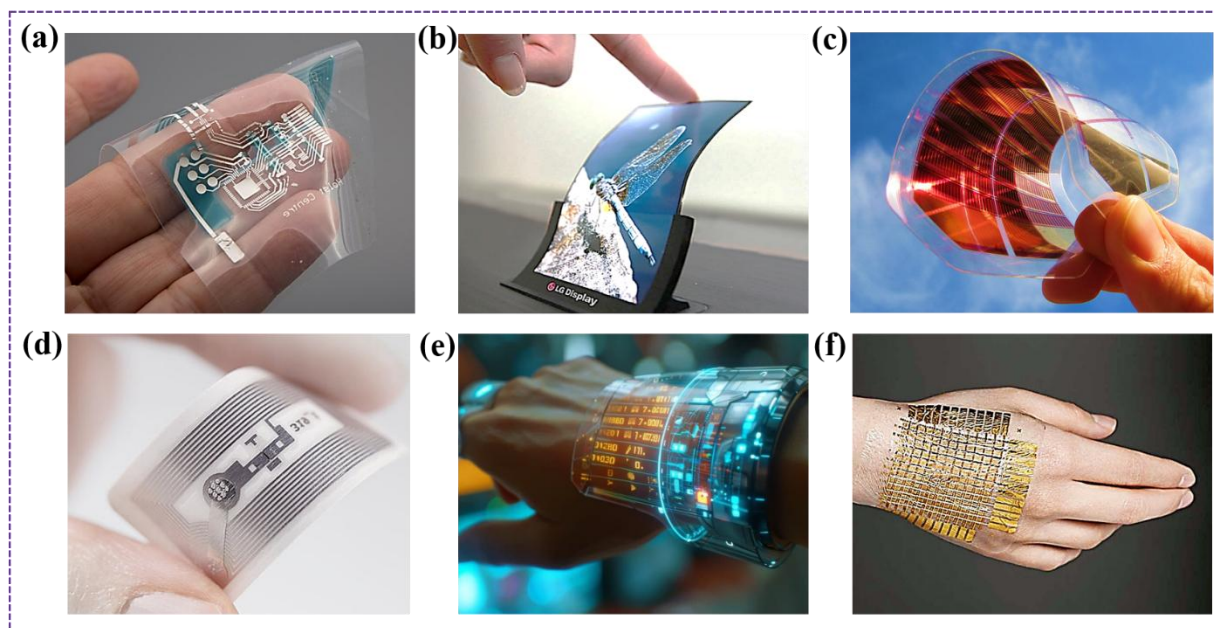


Figure 1.3 : Few examples of organic electronics for different flexible application areas. (a) A complete circuit on flexible substrate by Holst Centre (Source: loomia.com). (b) flexible emerging OLED display by LG (Source: oled-info.com), (c) an innovative thin film flexible solar cell panel (Source: materialdistrict.com), (d) RFID label by Schreiner Group (Source: schreiner-group.com). (e) wearable smart health care device (Source: htworld.co.uk), (f) self-healing electronic-skin by Ulsan National Institute's for detection of temperature and pressure (Source: techeblog.com)

1.2 ORGANIC SEMICONDUCTORS

Organic semiconductors (OSCs) are derived from carbon compounds with π -conjugated aromatic backbone for charge transportation which efficiently interacts with light. Charge transportation in OFETs, OLEDs, and OPVs is primarily dependent upon the OSC layer. In the conducting organic materials list, OSCs are the most significant class of materials with a diverse array of applications. In 1977, the groundbreaking discovery of highly conducting organic material was made by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid, who synthesized chemically doped polyacetylene during the early stages of organic conducting polymers. Subsequently, numerous organic semiconductors are being created, advanced, and presented for application in a variety of industrial goods. The delocalization of π -electrons within the molecules

enables the movement of electrons. The electrical and optical properties of organic semiconductors are primarily governed by their molecular orbitals: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These levels are determined by the delocalized π -electron systems within conjugated molecular structures. When conjugated molecules are brought into close proximity, their π -orbitals can overlap, leading to the formation of extended electronic states. According to the Pauli Exclusion Principle, this orbital overlap results in the splitting of energy levels, forming bonding and antibonding orbitals, which significantly influence charge transport properties. A suitable alignment of HOMO/LUMO levels with electrode work functions is essential for efficient charge injection and minimal contact resistance in organic transistors, as depicted in our book chapter (Gargi Konwar & Shree Prakash Tiwari, 2024). The conducting properties of OSCs can be modified to meet the specific requirements of a given application, which is one of their primary advantages over their inorganic counterparts. Despite their advantages, organic materials face inherent challenges such as low charge carrier mobility and environmental instability, which can hinder device performance and durability. To overcome these, various strategies such as molecular design optimization, interface engineering, and effective encapsulation methods, are being investigated to enhance the overall performance, and lifespan of such devices.

1.2.1 Charge Transport Mechanism

Charge transport in OSCs is intrinsically dependent on their chemical structure and combination of molecules within the thin films. The arrangement of molecules determines the efficacy of molecular orbitals overlapped with nearby objects, creating the paths for charge transmission between intra-polymers and inter-polymers. In traditional semiconductors, band transport is facilitated due to presence of highly delocalized conduction and valence which is not possible in OSCs. The overlap of p-orbitals between neighboring carbon atoms leads to the formation of π -bonds and resulting in the conductivity of OSCs. Furthermore, the delocalization of electrons in these pi-bonds influences conductivity and their mobility between neighboring moieties. There are several transport mechanism models such as hopping model, small polaron or energy transfer model, grain boundary model, and multiple trap and release model. Among these, hopping is the most dominant model for charge transport between localized states. This transport mechanism results from weak van der Waals interactions and structural instability in organic semiconductors, which restrict charge carriers to discrete molecules or polymer segments. The charge transports between two molecules via phonons or lattice vibrations. Charge carriers "hop" between localized sites via a thermally induced mechanism, necessitating adequate energy to surmount energy level discrepancies between sites. The hopping rate is influenced by the spatial overlap of molecular orbitals, the inter-site distance, and the extent of energetic and structural disorder. The process is contingent upon temperature, as elevated temperatures enhance hopping by supplying the necessary thermal energy. The hopping model is essential for comprehending charge transport in OFETs.

1.2.2 Classification

Based on their basic building units, OSCs are broadly classified into two categories: small molecules and polymers. Benzene is the typical basic unit in small molecule organic semiconductors, and their chemical structure is highly specific due to the accurate determination of the HOMO and LUMO energy levels. It does not possess any energy disorders like polymer OSCs because of their simple structure and no inter-intra chain interactions, providing relatively better crystal structure and lattice parameters. Moreover, the molecular weight of these OSCs is often below 1000g/mol. Typically, it has better carrier mobility due to high crystallinity, high purity, low trap states, and defects. These can be deposited both by thermal evaporation and solution-processed methods. The controlled evaporation process enhances the film quality with good morphology and uniformity, which reduces the device-to-device variations. On the other hand, polymer organic semiconductors have extended chains due to the repeated use of a single

monomeric unit. The mechanisms of intra-chain and inter-chain charge transfer in polymers are complex due to substantial structural disorder inside the semiconducting chains, hence lower mobility than small molecules OSCs. It can be easily deposited using solution processing methods like drop casting, spin coating, blade coating, spray coating, and other similar procedures. However, variation can be seen in the device performance due to the non-uniformity of films over a certain area. Therefore, it is essential to choose a material with better film quality and simple deposition process. Depending upon the conductivity, OSCs are classified as p-type, n-type, and ambipolar. In real applications, p-type conductivity is preferred to their high stability under ambient conditions than n-type materials, which are often more reactive with oxygen and water. Examples of few most widely used p-type small molecules OSCs are Pentacene, 6,13-Bis(triisopropylsilyl)ethynyl)pentacene (TIPS-Pentacene), dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT), rubrene, copper phthalocyanine (CuPc), 2,7-Bis(thien-2-yl)benzo[1,2-b:4,5-b']dithiophene (BTBT) derivatives, etc. Figure 1.4 shows some of the examples of solution-processable OSCs utilized in OFETs. Investigation of solution-processed OSCs offers multiple advantages including low-temperature processing, extensive area coverage, cost-effectiveness, and flexibility. Moreover, solution-processing techniques are becoming very effective for large-scale roll-to-roll (R2R) fabrication through multiple film deposition methods and adjustable coating parameters, such as solvent, concentration, coating speed, solution temperature, substrate temperature, and annealing conditions. By utilizing different coating techniques and adjusting these parameters, the thickness of the thin film can be changed from micrometers to nanometers, allowing changes in the morphology of film surface and its properties and performances.

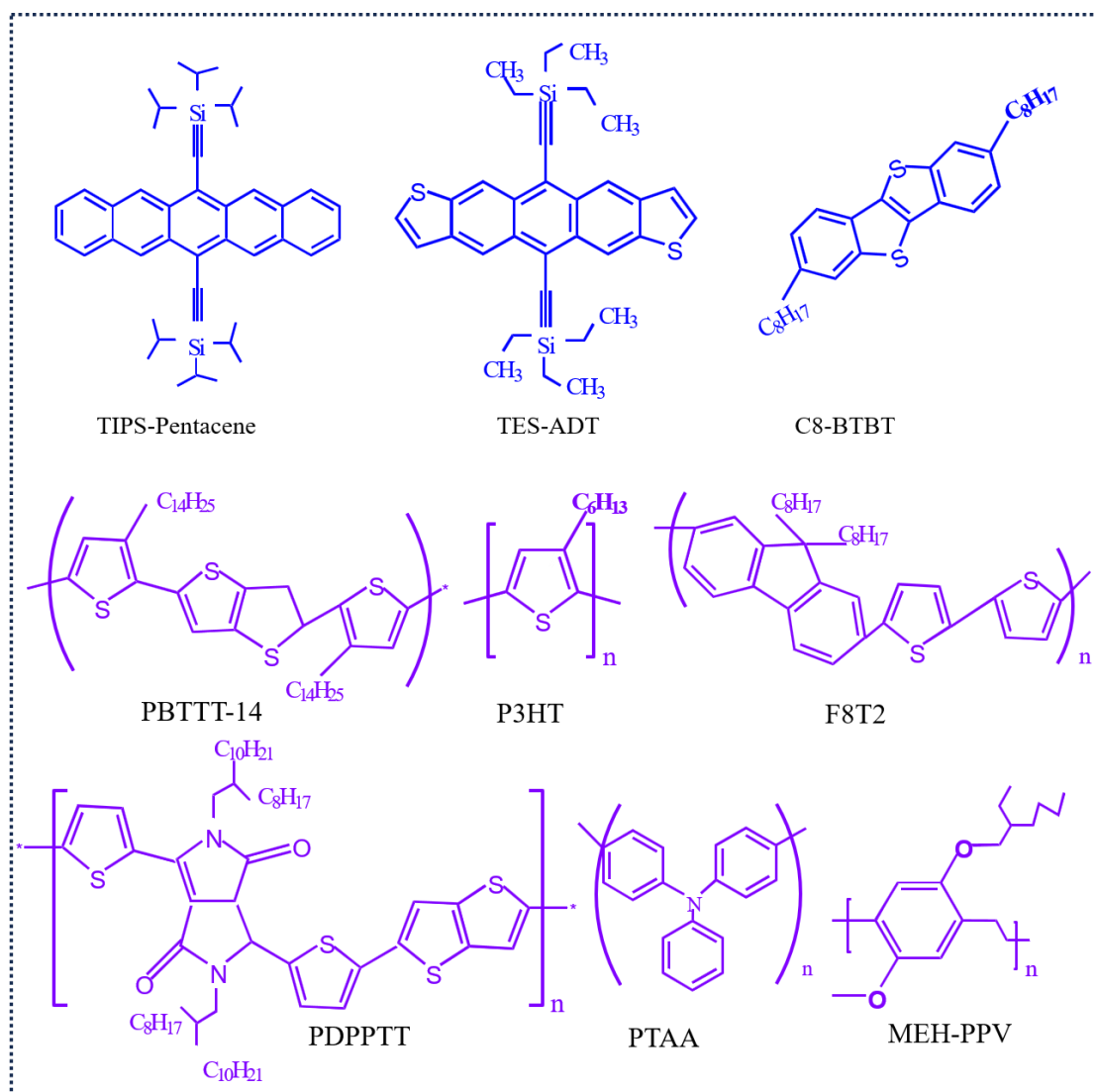


Figure 1.4 : Chemical structures of various solution-processable organic semiconductors. Small-molecule: TIPS-Pentacene, TES-ADT, and C8-BTBT; Polymers: PBTTT-14, P3HT, F8T2, PDPPTT, PTAA, and MEH-PPV

In this thesis, most widely used p-type small molecule semiconductor TIPS-Pentacene was used as the example semiconductor in all devices due to its easy solution processability, high carrier mobility, and air stability (Raghuwanshi et al., 2018; Raghuwanshi, Bharti, & Tiwari, 2016). All the fabricated devices were characterized in ambient conditions; thus, the use of air-stable semiconductors is crucial to achieve consistent performance throughout the studies. To achieve high crystallinity with low trapping states, an optimized semiconductor polymer blend of TIPS-Pentacene and polystyrene (PS) was utilized to form an active layer for high performance in OFETs. However, the pristine TIPS-Pentacene layer is preferred for light sensing applications due to the availability of high trapping states for light absorption exhibiting better photoresponsivity in OFETs (D. Bharti et al., 2017; Mahato, Bharti, Saxena, et al., 2021). Our work mainly focuses on the exploration and utilization of biodegradable dielectrics and substrates for the development of eco-friendly OFETs.

1.3 ORGANIC FIELD-EFFECT TRANSISTORS

Organic field-effect transistor (OFET) is an electronic device that employs organic semiconductor (OSC) material as the active layer to control the flow of current. OFET is considered to be the key component in flexible electronics, providing several applications including active-matrix displays, sensors, circuitry, memories, and various smart wearable devices. The initial research on OFETs commenced in 1983 by Ebisawa, who utilized polyacetylene as the active semiconductor in the device. Even though OFETs have shown a lot of advantages, achieving high carrier mobility with environmental stability is still a critical challenge. Although OFETs have lower performance compared to conventional Si devices, this emerging technology is in high demand due to its wide range of applications and its ability to integrate natural materials in fabrication, making them suitable for eco-friendly devices with minimal environmental impact.

The device structure of OFETs is significantly simpler than traditional metal oxide semiconductor field-effect transistors (MOSFETs) consisting similar three-terminals including gate, source, and drain. Depending on the position of these electrodes with respect to the OSC films, OFETs have four possible structures resulting in either coplanar or staggered architectures. The structures are called bottom gate top contact (BGTC), bottom gate bottom contact (BGBC), top gate bottom contact (TGBC), and top gate top contact (TGTC). Device geometry plays an important role in OFETs' electrical performance and each device structures have their own advantages and disadvantages. Top contact structures are preferred for better contact formation and low contact resistance by introducing a large uniform area for charge injection into semiconductor channel. In this configuration, OSCs were deposited over the smooth dielectric surface and did not face many dissimilarities in interfaces hence able to grow better semiconductor film. Among all these, BGTC structure is preferred in this work due to its simple fabrication process and better performance in comparison with others.

1.3.1 Working Principle of OFETs

The operation of OFET is dependent on two major mechanisms i.e. charge injection at electrode/OSC interface and charge transport at dielectric/OSC interface. It is important to note that OFETs work in accumulation mode, whereas the conventional MOSFETs are operated in either depletion or inversion mode and the characteristics obtained in these devices are identical to those of conventional enhancement mode MOSFETs. Since the source-drain electrodes are mostly metals, the charge injection from source to semiconductor is very crucial for operation of these devices. Unlike crystalline silicon which has conduction and valance bands, the energy levels of organic semiconductors are termed as lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) corresponding to these levels. For the injection of electrons, the work function of the metal has to be aligned with LUMO level of semiconductor. Similarly, for injection of holes, the work function of the metal has to be aligned with HOMO level of semiconductor. In ideal case, the work function of the metal is aligned with the fermi level (E_F) of semiconductor. Moreover, these energy

levels are shifted and bend bending occurs depending upon the applied bias. For p-type OSC, on applying negative gate voltage ($V_{GS} < 0$), bend shifts in upward direction and the HOMO level comes closer to E_F , resulting in the accumulation of holes at the interface of dielectric: semiconductor. For applying a positive voltage, band shifts downward and charge carriers start to deplete. Similarly, for n-type OSC, above phenomenon happened for opposite polarities of voltages (Gargi Konwar & Shree Prakash Tiwari, 2024).

The charge conduction for both p- and n- types of charge transport is summarized through schematic diagrams in Figure 1.5. On varying the input gate voltage V_{GS} , the level of HOMO and LUMO were changed to match with the fermi level of source metal contact as explained in Figure 1.5. Initially, when $V_{DS} = V_{GS} = 0$ V, p-type OFET is in an equilibrium state where no current flows between source and drain, and device is in OFF condition as shown in Figure 1.5 (a). When $V_{DS} < 0$; $V_{GS} = 0$ V, holes present in p-type OSC migrate toward negative biased drain contact. However, the current at this condition is very negligible since no mobile charges are present due to zero V_{GS} .

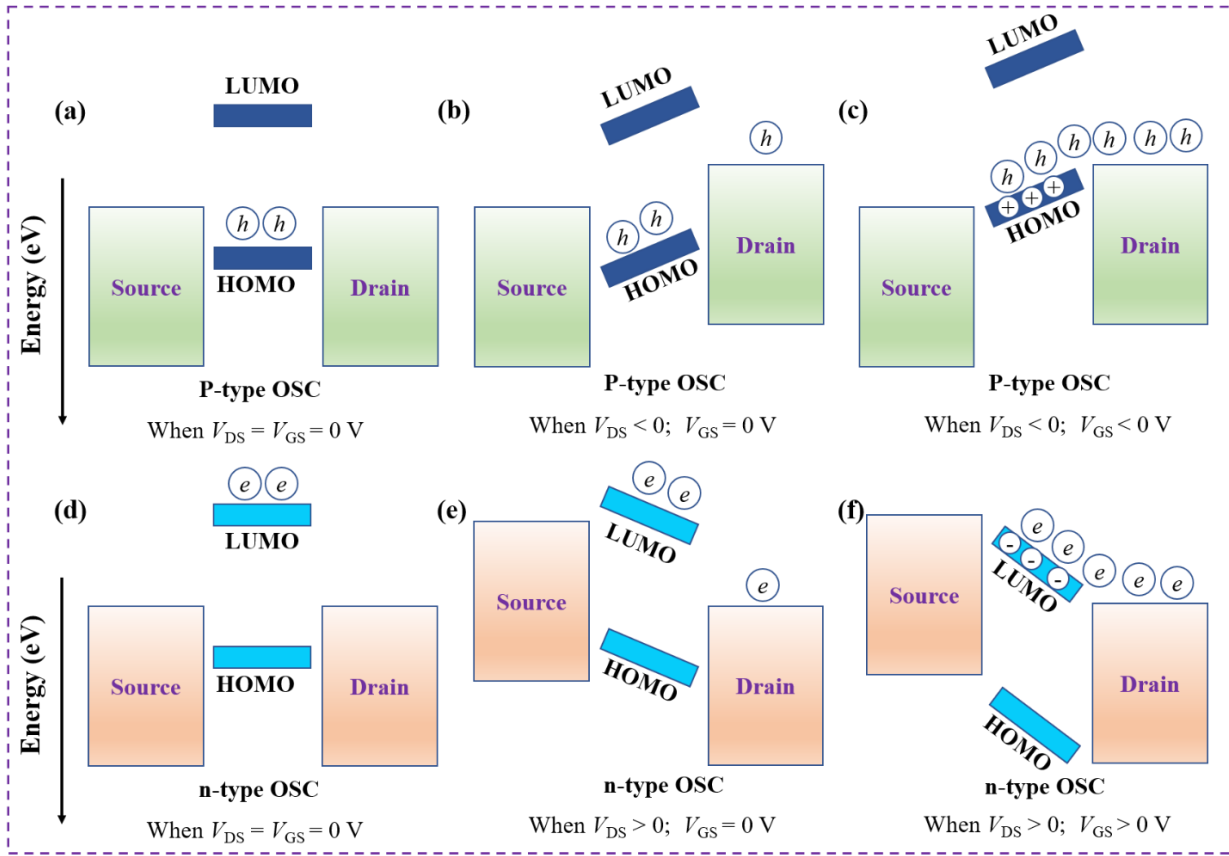


Figure 1.5 : Demonstration of the charge transportation in OFETs with p-type OSC (a-c) and n-type OSC (d-f) depending on applied V_{GS} .

On applying negative gate voltage, mobile charges accumulate at the dielectric: semiconductor interface through the dielectric layer, and the transistor starts to conduct. These mobile charges resulted in a high electric field at the interface and shifted HOMO and LUMO levels upward to match the fermi energy level of drain contact with HOMO level. Similarly, for n-type OSCs (Figure 1.5 (d-f)) positive bias is applied to turn ON the transistor. In a transistor, a sufficient voltage is required before it is turned ON to fill the various traps present at the at the interface. This voltage is denoted as threshold voltage, after that a noticeable drain current is observed in OFETs. Due to similarity of achieved characteristics of OFETs with conventional MOSFET, the standard drain current equations are used to model the operation of TFTs in linear and saturation regime. For a small applied drain voltage, transistor current is directly proportional to applied V_{DS} , indicating that the transistor operates in the linear regime:

$$\text{Linear regime, } I_{DS, \text{Lin}} = \frac{\mu C_i W}{L} (V_{GS} - V_{TH}) V_{DS} ; V_{DS} < (V_{GS} - V_{TH}) \quad (1.1)$$

As the drain voltage increases beyond $V_{DS} > |V_{GS} - V_{TH}|$, the channel begins to pinch off from the drain side, resulting in current saturation. The device is reported to function in the saturation regime and the current in this region is primarily depend upon the gate bias.

$$\text{Saturation regime, } I_{DS,sat} = \frac{\mu C_i W}{2L} (V_{GS} - V_{TH})^2 ; V_{DS} > (V_{GS} - V_{TH}) \quad (1.2)$$

where C_i is gate capacitance density; L and W are length and width of conducting channel, V_{GS} is applied gate input, V_{DS} is drain to source voltage and V_{TH} is threshold voltage.

1.4 APPLICATIONS OF OFETs

OFETs have received tremendous popularity for next-generation flexible electronics due to their inherent advantages of flexibility, lightweight, low-power consumption, and ease of integration on different substrates along with a wide range of applications in different fields. Most importantly OFETs are used as sensors for various applications, RFID tags, memory devices, energy harvesting devices for improving energy efficiency as well as different circuits, and artificial skins (Benas et al., 2020; Janasz et al., 2021; Yan et al., 2022). OFET-based sensors exhibit excellent selectivity and sensitivity than the two-terminal-based sensors, due to the amplification of small electrical changes, providing precise detection even at low concentrations. Highly sensitive sensors towards physical signals, biosensors, and chemical gasses have been demonstrated for detection of pressure, temperature, gas, ions, proteins, nucleic acids, drug molecules, etc (Li et al., 2019; Shi et al., 2016).

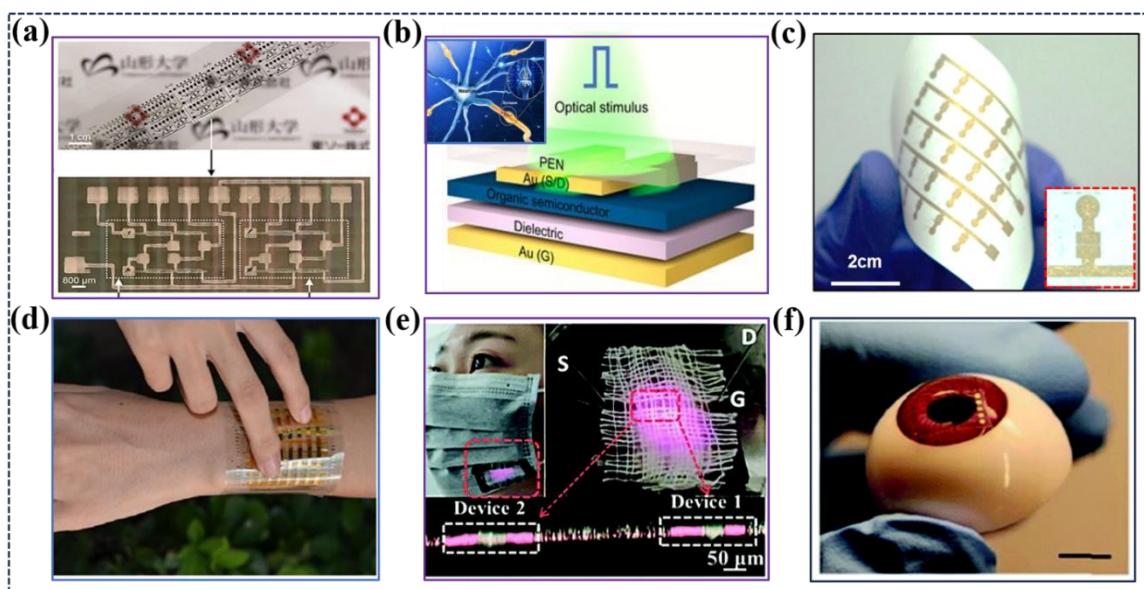


Figure 1.6: Applications of OFETs: (a) Inverter based circuit signal amplification of K⁺ sensor. Reuse with permission (Yan et al., 2022) copyright 2021, Wiley online library, (b) Photonic synaptic transistor (Source: sioc-journal.cn) (Sun et al., 2022), (c) Transistor array on paper substrate for tactile sensing (Source: Cambridge.org) (d) Pressure sensing array (CC BY 4.0) (Zang et al., 2015), (e) A wearable NIR phototransistor for e-textile. Reuse with permission (Zheng et al., 2021) copyright 2013, Royal Society of Chemistry, (f) Glucose sensor embedded on artificial eye for real-time health monitoring. Reuse with permission. (Yuvaraja et al., 2020) copyright 2018, American Chemical Society.

Both chemical and biosensors have garnered significant attention due to their applications in electronic noses, environmental monitoring, medical diagnostics, and real-time health monitoring as well. In addition, OFET functions as memory elements by incorporating charge storage layers or functional materials, enabling the multi-bit storage and erasing of information (Lien et al., 2014). OFETs are also crucial to implement different logic circuitry to be used in smart applications. One of the promising circuit applications is their usability as driver circuits in flexible and foldable OLED displays. In contrast to traditional silicon-based transistors, displays

with OFET-based circuitry can bend, fold, or roll while maintaining their functionalities. Moreover, due to presence of different functionalized layers, OFETs exhibit multifunctionality which can perform more than one function in a single device, reducing the material requirements and processing cost (Zhao et al., 2023). Furthermore, the utilization of natural materials in OFETs will enhance the eco-friendliness of the devices, making them a suitable candidate for smart biodegradable systems. Figure 1.6 shows examples of different OFET based applications reported in the literature.

1.5 EFFORTS TOWARD BIODEGRADABLE ELECTRONICS

E-waste is increasing significantly due to the excessive production of consumer electronic products, along with continuous enhancement in product specification and models, requiring replacement and disposal of a large number of unused products. Most of the conventional devices are typically fabricated using non-degradable and hazardous materials, which substantially contribute to global pollution through the emission of harmful toxic heavy metals into the environment upon disposal, leading to considerable environmental and health risks. To address this challenge, the development of biodegradable electronics has emerged as a probable solution to minimize their negative impact through recycling and using biodegradable materials as device components in fabrication. For the fabrication of any active electronic device, substrates, conductors, dielectrics, and semiconductors are primary ingredients, which have been explored for biocompatibility and biodegradability in recent years. Many nature-derived materials have been demonstrated to offer performance similar to those of conventional inorganic, or organic materials, including advantages of added functionalities in some cases. To induce eco-friendliness, one or many of the material components of a device can be replaced with nature-derived or biocompatible alternatives.

Substrate is a very important component for any device which usually accounts for the majority of the device's weight, upon which other various functional layers are deposited or coated. Replacement of non-degradable rigid or plastic substrates with a variety of synthetic and natural polymers as potential biodegradable film-like substrates will certainly reduce the issue of E-waste. Polylactic-co-glycolic acid (PLGA), polylactic acid (PLA), polycaprolactone (PCL), polyglycolic acid (PGA), polyvinyl alcohol (PVA), and polybutylene succinate (PBS), are the few examples of most commonly used synthetic substrates (M. Irimia-Vladu et al., 2010). Natural polymers such as cellulose and its derivatives, starch, chitosan, natural rubber, gelatin, silk-fibroin, agar, ecoflex, caramelized glucose, etc., are the primary contenders for biodegradable substrates. Among all, paper is one of the most used cost-effective biodegradable substrates, employing effectively in high-efficiency printing technologies for large-area applications (Bonacchini et al., 2018; Casula et al., 2020; Cunha et al., 2021). For natural dielectrics, various proteins, and polysaccharides such as gelatin, silk fibroin, chicken albumen, cellulose, starch, etc., have been reported as suitable candidates for application in various devices (Hsieh et al., 2013; Kim et al., 2010; Ko et al., 2017; Wang et al., 2011; Zhu et al., 2016). In addition, nature-originated semiconductor materials such as indigo dye and β -carotene, vat orange 3, and perylene diimide have been explored for demonstration of organic devices though their performance is very limited (M. Irimia-Vladu et al., 2010). Moreover, conjugate polymers such as polypyrrole (PPy), polyaniline (PANI), and poly(3,4-ethylenedioxythiophene) (PEDOT) with poly(styrenesulfonate) (PEDOT:PSS) along with nano composite integrated natural polymers were demonstrated as suitable biocompatible electrodes for the development of a complete eco-friendly device.

Although various biodegradable electronic devices have been proposed, special focus is given to the advancement of biodegradable OFETs, as they act as the essential building blocks for numerous applications of flexible electronics. In 2009, a silicon transistor was successfully implemented on a bioresorbable silk substrate for the first time (Kim et al., 2009). Bettinger et al. reported the first biodegradable OFETs on PLGA substrate and completely degraded in water within 70 days (Bettinger & Bao, 2010). Further, fully edible OFETs were demonstrated with DNA gate dielectric and perylene diimide as semiconducting layer on a biodegradable hard gelatin capsules substrate. Chang et al. reported a electrolyte-gated OFETs (EGOFETs) utilizing biodegradable major ampullate silk electrolyte harvested from gigantic wood spiders and a small

molecule OSCs (Chang et al., 2014). A significant study on biodegradable OFET was demonstrated by Seck et al., utilizing different gums as gate dielectric with solution-processed DPPTT semiconductor, however, flexibility of these OFETs was not studied (Seck, Mohammadian, Diallo, Faraji, Erouel, et al., 2020; Seck, Mohammadian, Diallo, Faraji, Saadi, et al., 2020). In addition, a fully degradable organic synaptic transistor was demonstrated using renewable chlorophyll gate dielectric (Ou et al., 2021). Similarly, OFETs were fabricated on various degradable substrates like bandages and commercial papers, highlighting their significant progress towards biodegradable and eco-friendly electronics (Bonacchini et al., 2018; Gao et al., 2016b; Lien et al., 2014). Though nature-inspired materials are widely explored in OFETs, realizing these devices in real applications is still challenging due to their high operating voltage and instability in electrical characteristics. Natural materials exhibit significant sensitivity towards environmental factors such as humidity, pressure, temperature, and light, causing difficulties in fabricating highly stable devices with long shelf-life capabilities. Moreover, limited studies are reported in the literature for demonstrating multifunctionality in OFETs using natural polymers, which is an important aspect of the advancement of intelligent biodegradable and eco-friendly systems.

This dissertation is an effort to address some of these aspects by demonstrating low-voltage operated eco-friendly flexible OFETs for various applications. Different dielectric strategies were introduced to accomplish high performance with excellent electrical, operational, and environmental stability. More than one function was accomplished in a single device to confirm the multifunctional capability of OFETs. In addition, fully decomposable devices were also demonstrated to minimize the negative aspect of E-waste on the environment.

1.6 RESEARCH FOCUS AND ORGANIZATION OF THESIS

The field of organic electronics has seen remarkable progress in recent decades, with extensive research on developing eco-sustainable smart biodegradable systems. OFETs play a pivotal role in organic electronics offering many applications due to their low processing temperatures, solution processibility, and compatibility nature originated materials in fabrication. The utilization of such non-toxic, biodegradable, and biocompatible, materials make these devices crucial to use in biomedical applications with multifunctional capabilities, which is not possible by traditional silicon-based technology. Despite their advantages, there are still some crucial challenges such as achieving high performance with operational and electrical stability, and addressing these issues are important for the commercialization of flexible organic devices in real-world applications.

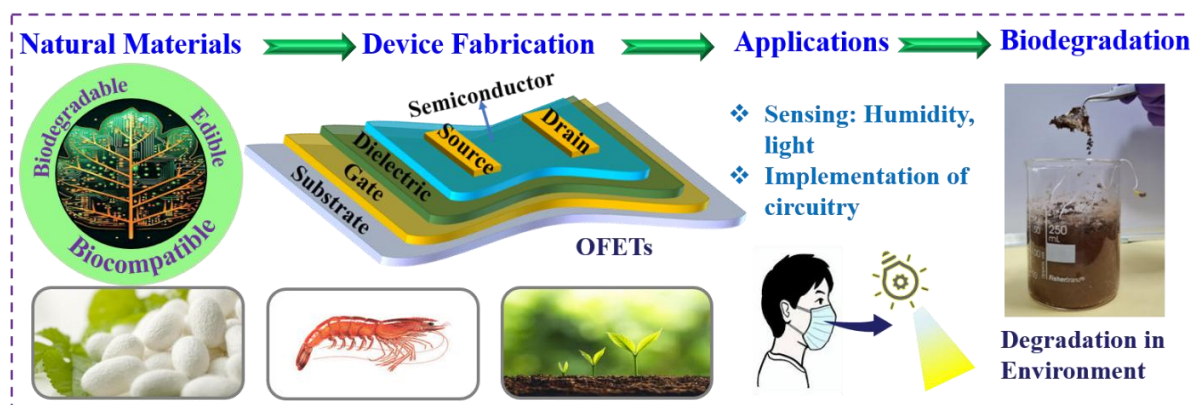


Figure 1.7 : Schematic representation of research objectives of this thesis from choosing natural materials as device component in transistors to performing various applications and finally investigated their biodegradability in environment.

The main focus of the thesis is to explore various nature originated materials as gate dielectrics and substrates to demonstrate high performance OFETs for sustainable electronics

with excellent electrical and operational stability at low voltage operation. For gate dielectrics, both natural protein and polysaccharides were employed on different substrates including glass, plastic, and biodegradable cellulose-based substrates. Different dielectric engineering techniques such as introduction of thin high-k inorganic gate dielectric with pristine layer of natural polymers and composite of bio-polymers were explored to enhance the overall device performance, and stability. Moreover, the inherent properties of natural materials add more functionality to transistors, making these devices suitable for multifunctional applications. Here, a widely explored organic semiconductor TIPS- Pentacene and its blend with polystyrene polymer were used as active layer due to their air stability and high carrier mobility. These devices were studied in harsh environments like high humidity and exposed to environment for long term to investigate their suitability in real applications. The following research aims are set with suitable natural gate dielectric and substrates:

- Exploration of different biocompatible and natural polymers such as gelatin, chitosan, silk fibroin, egg albumen, and cellulose as gate dielectrics in OFETs.
- Achieving high performance in OFETs by performing various dielectric engineering like integrating a thin high-k inorganic layer of hafnium oxide (HfO_2) with pristine polymer layers, and forming bilayers and composites of polymers to enhance overall properties of dielectrics.
- To achieve low voltage operation by exploring natural protein dielectric gelatin with a blend of TIPS-Pentacene: polystyrene active layer with high electrical stability.
- Exploring the multifunctional capability in OFETs utilizing the natural protein as gate dielectric with performing multiparameter sensing and implementing circuits, for the development of smart eco-friendly systems.
- To enhance the eco-friendliness, plastic substrate was replaced by commercially available paper substrate to realize high-performance devices with natural gate dielectric.
- Realizing cellulose derivative as a potential dielectric material to achieve high performance with very stable characteristics under different conditions. Moreover, a unique material combination consisting of cellulose as gate dielectric on paper substrate was successfully decomposed in soil, to confirm their biodegradability after the lifespan of devices.

The thesis has been organized as follows:

Chapter 1 presents concise information about the need for biodegradable and sustainable electronics and provides a brief introduction about organic electronics and its advantages and applications. The further section mainly focuses on various organic semiconductors and the working principle of OFETs followed by applications and advancement towards biodegradable electronics. The importance of gate dielectric and the utilization of natural polymers in OFETs are summarized.

Chapter 2 provides the process flow for the fabrication of organic transistors starting from the cleaning of the substrates. Basic working principles of all fabrication and characterization tools along with processes are briefly discussed. Moreover, this chapter includes the important performance parameters for OFETs with their extraction methods.

Chapter 3 represents a brief overview of various organic and natural polymers and their mechanism in OFETs as electrolyte gate dielectrics. Different materials such as polyvinylpyrrolidone, silk fibroin, egg albumen, chitosan, gelatin, and a cellulose derivative were explored as gate dielectrics. These materials were demonstrated either as a single layer or combined with other polymers and inorganic gate dielectric to fabricate high-performance OFETs.

Chapter 4 focuses on the advancement of low-voltage operated OFETs using a pristine gelatin gate dielectric and a TIPS-Pentacene: PS active layer. Multiple stability analysis, including bias-stress, repeatability, cyclic stability, long-term ambient stability, and effect of bending were

examined in these devices. The applicability of the circuit was further evaluated by realizing a resistive load inverter.

Chapter 5 demonstrates multifunctionality in flexible OFETs using a hybrid gate dielectric combination of HfO_2 /gelatin and TIPS-Pentacene active layer. Circuit and multi-parameter sensing capabilities such as for visible and UV light, as well as the humidity and breath rate monitoring were successfully demonstrated from these devices. Moreover, the electrical, operational, and bending stability were studied for these devices.

Chapter 6 discusses the dielectric composite of gelatin: chitosan to tune and enhance the electromechanical stability of flexible transistors. Chitosan was proposed as a tuning agent in composite with gelatin to modulate the dielectric properties. The electrical, and operational stability along with the effect of bending were discussed for all four dielectric composites. Among all, devices with 10:5 composite exhibited better performance in transistors even after application of 100 continuous bending cycles. Circuit applicability and shelf life of these devices were also discussed.

Chapter 7 demonstrates biodegradable OFETs on a paper substrate with cyanoethyl cellulose as gate dielectric and TIPS-Pentacene: PS to form the active layer. The formation of EDL capacitance was discussed by measuring the gate capacitance density at low frequencies (0.1 Hz). The unique material combinations of cellulose-based gate dielectric and substrates improve the biodegradable and decomposable capability of OFETs. These devices exhibit excellent p-channel transistor characteristics with high electrical and operation stability. The variation in transistor performance under different conditions such as high humid environment, after the application of bending, and increasing the annealing temperature to the devices, was discussed. Most importantly, devices were decomposed in soil due to the presence of microorganisms, confirming their excellent biodegradability. This shows a significant step toward the development of fully biodegradable flexible electronics to minimize the effects of e-waste on environments.

Chapter 8 briefly presents an overview of the research work conducted in this thesis, summarizing the all findings and addressing possible directions for future investigation.

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