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Nanogap Electrodes and Molecular Electronic Devices

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1.1 Introduction

The evolution of CMOS (complementary metal–oxide–semiconductor) technology has brought about unparalleled progress in semiconductor industry over the last 50 years. Today, the pace of exponential improvement on performance of digital electronics is still kept on. Integrated circuits (ICs) can be now made very compact, having up to several billion transistors and other electronic components in a fingernail-sized area. The proliferation of computers, communication, and other industrial and consumer electronics not only established a huge and ever-growing market of several hundred billion dollars per year [1], but also in an unanticipated way changed the world and our way of life. In August 2014, Intel formally unveiled its 14 nm manufacturing process, followed by Broadwell (Intel's codename for the 14 nm microarchitecture) based laptops available for sale in October. Subsequently, the 10 nm technique was released by Taiwan Semiconductor Manufacturing Company (TSMC) in 2016. And in April 2018, the company even has put the first generation of 7 nm processing technology into mass production. In this range, however, it will be more and more difficult to operate transistor structure that is utilizing MOS (metal–oxide–semiconductor) physics as the basic principle of operation. Moreover, manufacturing devices scaling to sub-10 nm dimensions goes beyond the capability of traditional lithography technologies. More advanced patterning techniques need to be developed, for example, the TSMC and Samsung are introducing extreme ultraviolet lithography (EUVL) to the subsequent products. Although it may very probably be too expensive and time-consuming for economics of chip production, the advanced technique can further decrease the power consumption and promote the operating frequency of the electronics.

How can we further increase the computation and memory capacity when the physical limits will be reached?

“There's plenty of room at the bottom” is a famous lecture given by American physicist Richard Feynman, who suggested that it should be possible to “arrange the

atoms one by one the way we want them” [2]. This talk is often linked to the “birth of nanotechnology,” as it inspired the conceptual beginnings of this field decades later. In view of his physical background, Feynman scored less strongly on the role of chemistry in nanoscale engineering, although it turned out that chemistry and molecular biology also play a crucial role on the engineering of small things, and Feynman himself conceded that chemists could, in principle, make anything from the bottom up. In the early 1970s, conductivity measurements through single layers of molecules were pioneered by Hans Kuhn and Dietmar Möbius [3]. More significantly, Arieh Aviram and Mark Ratner [4] in their theoretical work first suggested that a single molecule could mimic a semiconductor-like band structure by taking advantage of electron-rich and electron-poor moieties to achieve one-way conduction. In this sense, the possibilities for designing electronic functionality are proposed by bottom-up synthetic methods with atomically basic building blocks. It marks the origin of molecular electronics, which pointed out a possible way “beyond CMOS.”

Understanding charge transport properties of single molecules or a small collection of molecules is of fundamental importance in the field of molecular electronics. Even though single-molecule devices are conceptually simple – they consist of functional molecular components and two or three electrodes – it presents significant experimental challenges [5, 6]. A number of different experimental strategies have been developed in an effort to wire molecules into circuits [7–21], among which “nanogap electrodes,” namely a pair of electrodes with a nanoscale gap, are regarded as fundamental tools to study charge transport properties through single molecules and promisingly incorporate molecular components into electronic circuits. In this sense, the preparation of nanogap electrodes is as crucial as the design and synthesis of functional molecules for the construction of nanodevices.

1.2 Overview of Molecular Electronics

Molecular electronics is a relatively new while immensely vivid field, the major goal of which is to understand charge-transport properties of single molecules and their ensembles. Ultimately this will probably pave the way for electronic components made of molecular building blocks that can overcome the limits of conventional semiconductor technology [22, 23]. The research in molecular electronics is very much interdisciplinary (spans physics, chemistry, biology, computer technology, materials science, e.g.) and covers quite a broad range of topics. This chapter will begin with an overview of molecular electronics, including the origin and motivation of this field, materials and technologies involved, and fundamental challenges encountered, followed by the introduction of nanogap electrodes, which – as the main subject of this book – are the basic tools for studying molecular electronic properties and building blocks for manufacturing nanoelectronic devices. For a more comprehensive understanding of molecular electronics, several representative reviews [5, 24–27] and books [28–31] are recommended.

1.2.1 Why Molecular Electronics

It is widely accepted that we are now living in a period characterized by computer use and development, known as Computer Age (also known as Information Age or Digital Age). Capitalizing on computer-miniaturization advances has revolutionized almost every aspect of life, not only making it more efficient and convenient, but also changing the way people view the world. On the other hand, despite the great success, solid-state electronics faces a constant need for miniaturization in view of current and future technological developments, which is expected to approach fundamental limitations on further scaling based on MOS physics as the basic principle of operation. It is the basic motivation for developing beyond-CMOS devices. Molecular electronics is promisingly an option.

1.2.1.1 History of Computing

A computer is a general-purpose machine that can perform computations in a programmed way. The evolution of two separated techniques, automated calculation and programmability, is essential for the development of modern computers.

The Evolution of Calculator and Programmability in Embryo The history of computing can be traced back to the period of 2700–2300 BCE, when some data-processing tools in embryo came into being to meet the requirements of people's daily life (Figure 1.1a). Abacus, also called a counting board, was first devised by Sumerians and Egyptians. By using beans or stones moved in grooves in sand or on tablets of wood, stone, or metal according to some certain “programming rules” memorized by the user, simple operations such as counting, recording facts, addition, and subtraction can be made (Figure 1.1b). In the following thousands of years, various types of abacus were independently developed from ancient civilizations around the world and gradually matured as an important tool for merchants, traders, and clerks long before the adoption of the written modern numeral system. For example, the Chinese abacus, known as *suanpan*, usually has 13 rods and there are two beads on each rod in the upper deck and five beads each in the bottom for both decimal and hexadecimal computation. Skilled people can use *suanpan* to do addition, subtraction, multiplication, and division with very fast speed, handling numbers up to the tens of millions. It is still being in use by some old people nowadays.

Since 1600s, mechanical calculator came into being. Wilhelm Schickard, who was a universal scientist at the University of Tübingen, is known for his “calculating clock” evidenced by two letters from him to Johannes Kepler (well known for his eponymous laws of planetary motion) with a sketch drawing and building instructions of the calculating machine. Unfortunately, the design was considered to be incomplete and no Schickard's machine managed to survive to the present day. In 1642, Blaise Pascal designed and constructed a mechanical calculator capable of adding and subtracting numbers entered with dials to assist his farther, who had to do exhausting calculations as a tax collector. This machine, along with the ones modified for improvements by Pascal himself in the next following years, was generally recognized as the first digital

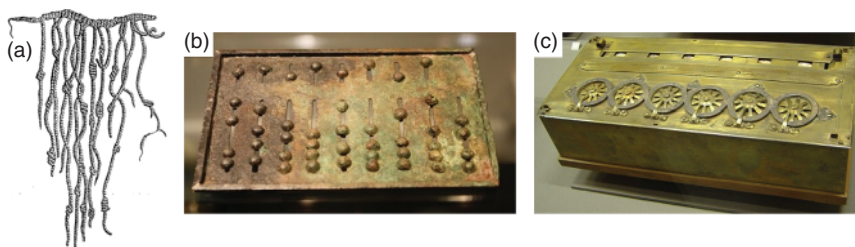


Figure 1.1 (a) A data-processing tool in embryo: keeping records by tying knots. Source: MKL online at Retro Bibliothek, work 149, 2009. Retrieved from: https://commons.wikimedia.org/wiki/File:Meyers_b13_s0522.jpg. (b) The rudiment of abacus. (c) Pascal's calculator. Source: [en.wikipedia.org/wiki/Pascal&percent;27s_calculator](https://en.wikipedia.org/wiki/Pascal%27s_calculator).

calculating machines, called Pascal's calculator or the Pascaline (Figure 1.1c). Although these machines were too expensive to be commercialized, they provided the basic principles for subsequent computer engineering. Pascal's work was followed by Gottfried Leibniz, who devoted himself to building a machine that could execute all four arithmetical operations since 1670s. He invented the Leibniz wheel in 1673 and built a machine called the Stepped Reckoner based on this design in 1694, which was the first calculator that can perform multiplications and divisions. In addition, Leibniz documented the binary numeral system in his early life, which is at the foundation of virtually all digital computers.

More than 100 years later, the nineteenth century saw the first commercially successful mechanical calculator. By making use of the designing ideas from previous mechanical calculators such as Stepped Reckoner, Charles Xavier Thomas invented the Arithmometer and patented it in 1820. The manufacturing of Arithmometer started from 1851 and in the next 37 years, it was the only type of mechanical calculator in commercial production. More than 2500 Arithmometers had been sold all over the world by 1890. As the first mass-marketed calculating machine, Arithmometer marks the beginning of the mechanical calculator industry. Many clone makers appeared during the period of 1887–1915, and there had been about 20 independent companies manufacturing machines based on Arithmometer's design by 1920s.

While Thomas and some other engineers were putting their efforts to develop more and more powerful calculators, in 1837, Charles Babbage first conceptualized and designed a fully programmable calculator, his Analytical Engine. The machine can be programmed by punched cards (pieces of stiff paper that contained digital information represented by the presence or absence of holes in predefined positions, first introduced by Joseph Marie Jacquard in 1801 enabling his loom to automatically weave defined patterns) and different types of punch cards responsible for different operations (e.g. arithmetical, load, store operations) were used. The architecture consisting of both processing elements and memory units is very similar to a modern computer. Although Babbage was never able to complete construction of the machine himself due to inadequate funding and personality

issues, he is credited with inventing the first general-purpose mechanical computer. The fusion of automated calculation with programmability started, which was one of the notable landmarks in the development of computers.

After Babbage's death, from late 1880s to early twentieth century, more and more interesting improvements came to the fore. Charles Babbage's son Henry Babbage built a simplified version of Analytical Engine in 1888 and gave a successful demonstration of how it worked in 1906. It to some extent made his father's design to become a reality, although not commercialized. Meanwhile, Herman Hollerith invented a mechanical tabulator based on punched cards and developed a tabulating machine to help process data for the 1890 United States Census. By using this machine, Hollerith's company accomplished the data-processing job, which was estimated to take around 13 years, in six weeks! Hollerith also introduced a machine-readable medium and the first key-punch machine (a punch operated by a keyboard). These inventions, together with the mechanical tabulator, were all among the foundations of the modern information processing industry. Hollerith's company merged with three other corporations to form the Computing Tabulating Recording Corporation (CTR) in 1911, which was renamed International Business Machines Corporation (IBM) in 1924. The tabulating equipment introduced by IBM in 1930s was capable of performing automatic sequences of advanced arithmetical operations in one second, enabling its clients (e.g. US Government) to process unprecedented amounts of data.

Timeline of Computer History On bases of the predecessors' achievements and promoted by the joint efforts of talents from almost all walks of life, the twentieth century witnessed the birth and explosive development of computer. It is generally accepted that there have been four generations of computers to date:

- (i) First generation of computers (1946–1959) used vacuum tubes as the basic components for memory and circuitry, supporting machine language only. They were huge and expensive. A lot of heat was produced by the tubes, giving rise to unreliable performances.
- (ii) Second generation of computers (1960–1964) were transistor based. They were cheaper, consumed less power, more compact in size, more reliable, and faster than the first generation. Assembly language and high-level programming language were used.
- (iii) Third generation of computers (1965–1970) were marked by the use of IC, which had many transistors, resistors, and capacitors along with the associated circuitry. As a result, computers became even smaller as more components were squeezed onto the chip. Multiprogramming operating system and high-level languages were used.
- (iv) Fourth generation of computers (1970–) used Very Large Scale Integrated (VLSI) and Ultra Large Scale Integration (ULSI) technology. The computers became more powerful, compact, and reliable, giving rise to personal computer (PC) revolution. They were also marked by advancement in parallel processing, networks, artificial intelligence, user-friendly interfaces with multimedia features, and so on.

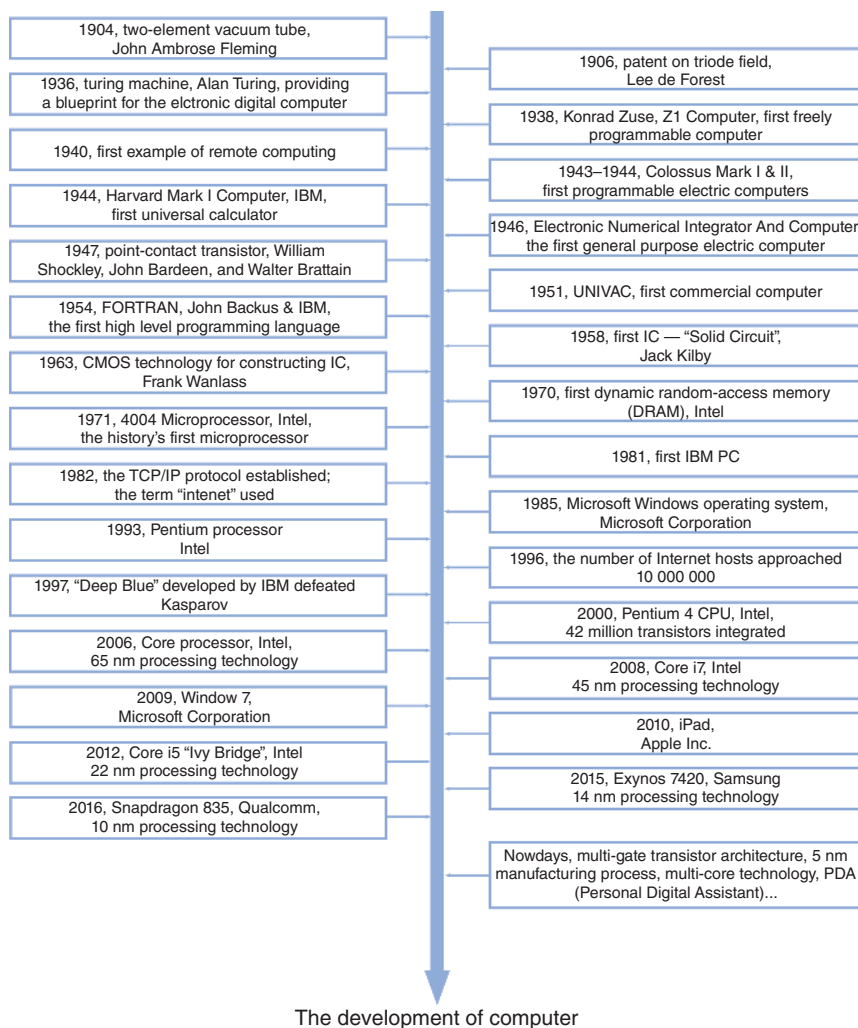


Figure 1.2 A general timeline of the important events in computer history.

A general timeline of the important events is provided in Figure 1.2.

1.2.1.2 Moore's Law

In 1965, only several years after the IC-based computer found its first customer, Gordon Moore, cofounder of Intel Corporation, noted that the number of transistors on a chip doubled approximately every two years. Therefore, he made a prediction that semiconductor technology will double its effectiveness every 18 months. This prediction was later named after his name, Moore's law [32]. It is not a physical or natural law; however, it has been held remarkably well for nearly 50 years (Figure 1.3) [33], in part because the law has been adapted as a driving force in the semiconductor industry to guide long-term planning for research and development.

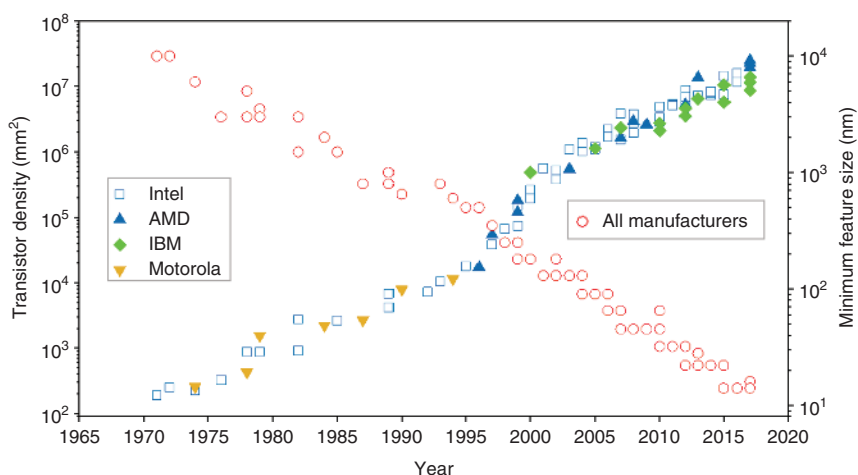


Figure 1.3 The density of transistors and the evolution of transistor gate length (minimum feature size) in microprocessors over time. Between 1971 and 2017, the gate length of metal–oxide–semiconductor field-effect transistors (MOSFETs) shrank from 10 000 to 14 nm (y axis, right), and the number of transistors per square millimeter increased from 192 to over 20 million (y axis, left). AMD, Advanced Micro Devices.

This exponential improvement has dramatically enhanced the impact of digital electronics in almost every aspect of the world.

On 2 May 2011, Intel announced its first 22 nm microprocessor, i.e. the average half-pitch (half the distance between identical features) of a memory cell shrank to the 22 nm level. Over 1 billion transistors were integrated on one single processor die. Then around one year later, on 23 April 2012, consumer-level CPU (central processing unit) based 22 nm technology went on sale worldwide. And in 2014, Intel released its Broadwell chips, the first CPUs manufactured using the 14 nm processing technology. Based on international technology roadmap for semiconductors (ITRS) roadmap, Intel and its rivals are promising to go even smaller, packing even more transistors onto each chip, making them more powerful while draining less battery charge or powers. Moreover, TSMC announced that the 7 nm technology has been put into mass production in 2018, and its 5 nm manufacturing process has been carried out tentatively in 2019, in which up to 14 layers employed the EUVL technique. By following this trend, many physical dimensions are expected to be crossing the 10 nm threshold in the following decade. However, it is predicted that as dimensions scale to sub-5 nm, physical limits such as source-to-drain leakage currents stemming from thermal diffusion of electrons and gate leakage currents caused by quantum-mechanical tunneling will make it difficult to operate any transistor structure based on MOS physics [34]. On the other hand, new levels of miniaturization would be for sure more and more challenging due to fundamental geometrical limits, although some technical solutions such as 3D (three-dimensional) integration, multi-gate structures, high- κ gate dielectrics have been proposed/underway [35, 36]. Furthermore, continuous scaling calls for more sophisticated lithographic techniques (EUVL, multiple patterning, etc.) [37, 38], resulting in an exponential

increase of the cost to manufacture chips (by a factor of 2 for every chip generation, sometimes known as Moore's second law). Therefore, the economics of chip production may also be a key issue that could bring Moore's law to an end.

1.2.1.3 Molecular Electronics: A Beyond-CMOS Option

It is widely acknowledged that Moore's law is approaching its threshold, as discussed earlier. On the one hand, many efforts have been devoted to the improvement of classical CMOS (e.g. ultrathin SOI (silicon-on-insulator) metal-oxide-semiconductor field-effect transistor (MOSFET) structure, high- κ gate dielectrics, strained silicon technology) [39], and expanding nonclassical CMOS technologies (e.g. multi-gate transistor, 3D integration, RF [radio frequency] interconnect) [36, 40]. On the other hand, people proposed many beyond-CMOS options, including spin device [41, 42], quantum computing [43], molecular device [14, 44, 45], nanotube transistor [46, 47], mechanical switch [48, 49], and so on. Although these emerging technologies are still very far from industrial maturity to replace CMOS architectures, they generally seek to use nanoscale components to build up more complex devices, namely in a bottom-up way, which is conceptually different from the well-established top-down approaches for the manufacture of products in silicon industry. These nanoscale building blocks, particularly molecules (dimensions could be as small as 1 nm), represent the ultimate limit that people can manipulate so far [50, 51]. If the new computing devices made up of these ultrasmall components (acting as channels and interconnects) do work, in principle, it can significantly extend Moore's law beyond the foreseen limit of integration.

The molecules are small enough to provide a spatial control that is currently impossible with top-down fabrication methods. We all know that. There is another thing we need to know, which is even more crucial: *will molecules compute?*

Conventional device for computing and information storage, put simply, is no more than an on-off switch. The switching between two (or more) clearly different states (normally characterized by electrical signal, i.e. high- and low-resistance states) defines binary "0" and "1" values (1 bit), the basic elements for information storage and complex logic operations. In 1974, Arieh Aviram and Mark Ratner [4] published their theoretical work entitled "Molecular Rectifiers" in the journal *Chemical Physics Letters*. They calculated charge transport through a single organic molecule consisting of donor and acceptor subunits separated by an insulating bridge (D-B-A system) and concluded that electrical conduction within this system would be favored from the donor subunit (electron rich) to the acceptor moiety (electron poor), while disfavored in the reverse direction. This work theoretically predicted the possibility of constructing a very simple electronic device, a rectifier/diode, based on single molecules, to potentially implement the basic on/off functionalities for computing (Figure 1.4) [52]. This is generally correlated to the origin of molecular electronics. More theoretical constructions came up afterward, including a detailed description of single-molecule field-effect transistor (FET) by Aviram [53] and the concept of single-molecule logic gates by Forrest Carter et al. in 1980s [54]. Concurrently, nature has been offering people much to learn. Taking human brain as an example, which is recognized as nature's computer,

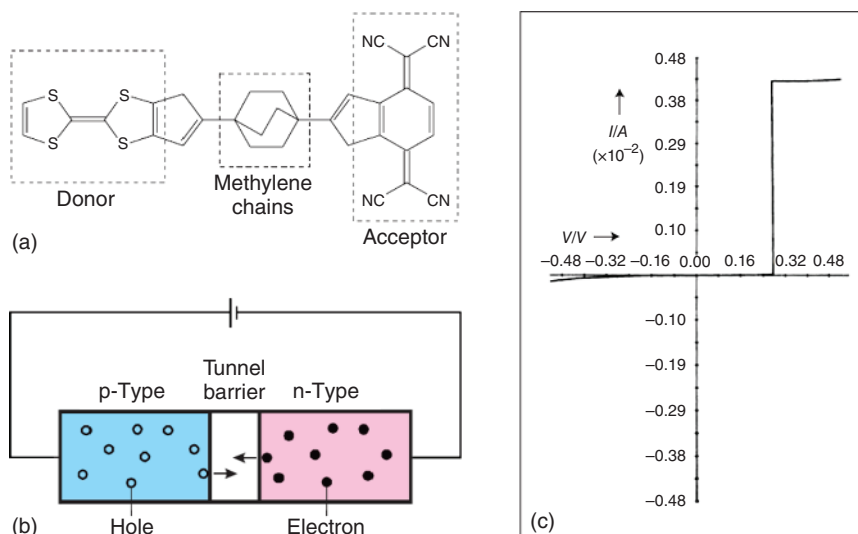


Figure 1.4 Aviram-Ratner single-molecule rectifier based on an acceptor tetracyanoquinodimethane (TCNQ) and a donor tetrathiofulvalene (TTF) separated by a triple methylene bridge. (a) Model molecule. (b) p-n-junction. (c) Calculated I - V characteristics. Source: (a, b) Kashimura and Goto [4]. (c) Aviram and Ratner [52]. Elsevier.

processing and storage of information (electrical and chemical signals) are executed by various biomolecular components (mainly nucleic acids and protein), thereby accomplishing complex physiologic processes. There are as many as 10^{11} neurons in this highly sophisticated system and each is connected to 10^3 – 10^4 others, giving a rough estimate of “bit count” up to 10^{15} . Although the working principle of a brain is different from solid-state microprocessors, the biological architectures inspired a wide range of ideas exploiting organic molecules in conjunction with electronics for the long-term perspective of molecular computers [55, 56].

In addition to the much smaller size of molecules for further scaling and promisingly higher efficiency compared to the electronic components currently used, as well as their potential capability for controllable charge transport and storage, several unique advantages are conducive to the incorporation of molecular components into microelectronic devices:

- (i) Synthetic methods offer a high degree of freedom for tailoring molecular geometry and composition, realizing diverse optical and electronic functions;
- (ii) Molecules have the ability to self-assembly and recognition, which is a key aspect of bottom-up approaches to nanotechnology. Well-organized structures for desired properties can be programmed with atomic precision by the specific interactions in between single molecules, which is previously unattainable with top-down methods;
- (iii) Manufacturing with molecules promises to be low-cost and environmentally benign. Molecular devices are expected to incorporate with lighter and flexible electronics with promisingly lower power dissipation under operation.

In spite of theoretical foundation, manipulation of single molecules is no easy task. It was not until late 1990s that researchers managed to wire a limited number of molecules between contacts for direct measurement of their electronic characteristics [57], after the advances of experimental means in the field of nanotechnology. The great challenges imposed by device fabrication as well as data analysis and interpretation will be discussed in the following sections and chapters. Nevertheless, the appearance of concrete devices accelerated the progress of molecular electronics and substantially confirmed the theoretical predictions. Until today, a wide range of intrinsic transport properties from molecules including nonlinear characteristics have been reported. Embryonic forms of molecular resistors [58, 59], rectifiers [60, 61], switches [62, 63], and transistors [64, 65] were on this basis realized.

In the last 15 years or so, a rapid progress in experimental research on molecular electronic devices has further pushed forward molecular electronics as one potential option of beyond-CMOS technologies. However, electronic circuits made up of only molecular components are still very far from being realized. Molecular electronics has not yet prepared well itself for devices capable of optimum performance, parallel processing, defect tolerant, and low cost, all that competitive with similar CMOS solutions. There would be a long way to go with numerous challenges and opportunities lying ahead.

1.2.2 Molecular Materials for Organic Electronics

Molecular materials for organic electronics, in a broad sense is another branch of molecular electronics. Different (but related) to molecular-scale electronics, it mainly focuses on exploiting the “bulk” properties of molecules for electronic applications. As mentioned in the previous sections, organic materials possess intrinsic advantages compared to their inorganic counterparts, including light weight, flexibility, ease of functionalization, and capability to be processed in large areas at low cost. Since the discovery of conducting polyacetylene in 1977 (Nobel Prize in Chemistry in 2000), organic semiconductors began to attract a worldwide interest in electronic devices [66]. Over the last 30 years, much effort has been devoted to design, synthesis, and characterization of molecular systems with desired optoelectronic properties. On this basis, a variety of active devices based on organic thin films have been successfully fabricated, including organic light-emitting diodes (OLEDs) [67, 68], organic field-effect transistors (OFETs) [69, 70], organic photovoltaics (OPVs) cells [71], photodetectors [72], memory cells [73], chemical sensors [74], and actuators [75], as well as organic thermal electrics [76] and nonlinear optics [77]. In addition, concurrent advances in biotechnology have allowed for integration of biomaterials into the structural components of organic electronic devices [78]. For instance, semiconducting active layers can be fabricated from a variety of small-molecule dyes and pigments [79, 80]; hydrophilic biopolymers are perfectly suitable for gate dielectrics while a wide range of natural and synthetic polymers are appropriate for use as flexible bulk substrates [81–84]. Due to the limitation of this book, here we only very briefly introduce the state of

the art of OLEDs, OFETs, and OPVs. For an extended discussion, we would like to refer the interested readers to some recent reviews and books [85–93].

1.2.2.1 OLEDs

OLEDs rely on organic materials (small molecules or polymers) that emit light in response to an electric current. The applications in displays and lighting are two dominant branches of OLED technology (Figure 1.5a). OLED display technology promises to deliver thin, flexible, power-efficient, and bright displays that will be competitive to mature LCD (liquid crystal display) technology. Substantial investments contribute to an increasing maturity in process technology, and today OLED technology has already been used in commercial applications as displays for computer monitors, television screens, and especially portable systems such as mobile phones. It is worth noting that, since Apple introduced OLED screens in its flagship smartphone iPhone X in the late 2017, almost all the cell phone companies, including Samsung, Huawei, and Apple, are launching new OLED produces in 2019. In addition to display, it is also possible to use the OLED technology to make white light panels for lighting. OLEDs can provide large area and hazard-free diffusing light sources and feature good color-rendering indexes and tunable color temperatures. They can be lightweight, flexible, transparent, energy-efficient, and recyclable [68, 94–96]. In 2013, Nippon Electronic Company (NEC) lighting Ltd. announced a new industry record for OLED efficiency as high as 156 lm/W at a color temperature of 2800–3000 K. In the first half of 2019, Jiangsu Yiguang Technology based in Liyang (China) upgraded its G2.5 OLED production line after taking the place of First-O-Lite in Nanjing (China), famous for its internal extraction strategy of OLED lighting panels. In the next three years, it will launch the world's only G6 OLED lighting production line, which further paves the way of OLED lighting technology to be a competitor in the general lighting markets.

1.2.2.2 OFETs

OFETs have received widespread interest since they were first reported by Tsumura et al. in 1986 using polythiophene as the semiconductor layer, because of their

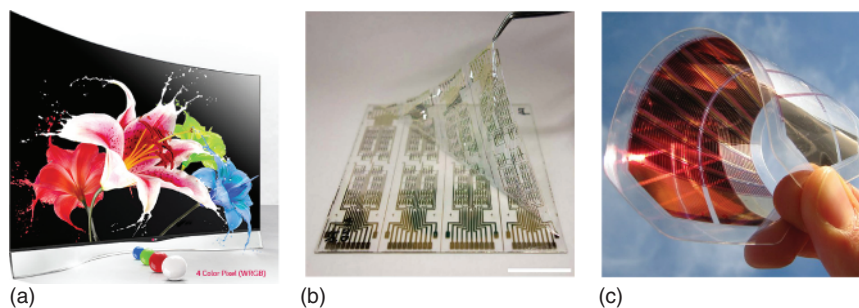


Figure 1.5 (a) A curved OLED TV model employing 4-Color Pixel technology, produced by LG Electronics. Source: LG Electronics USA Inc. www.lg.com. (b) The organic electronic circuit based on OFETs. Source: <http://en.wikipedia.org>. (c) The integrated OPV array. Source: Fraunhofer ISE.

potential applications in low-cost, large-area, flexible, and biodegradable electronic products [97]. To date, thousands of organic semiconductors have been reported to exhibit FET characteristics and impressive improvements in device performance have been achieved [98–104]. For example, the field-effect mobility has increased from low values $<10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $1\text{--}10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for thin-film transistors and to $15\text{--}40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for single-crystal transistors over the last three decades. Remarkably, In 2014, Zhenan Bao and coworkers reported thin-film transistor hole mobility up to $43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is a new record for all organic molecules [105]. Furthermore, Qian Miao and coworkers reported thin-film transistors electron mobility up to $27.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which sets a new record for n-channel OFETs [106]. These values are now exceeding those of benchmark amorphous silicon devices ($0.5\text{--}1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and there is little evidence that the progress in organic materials performance has reached fundamental limits [104]. On this basis, a wide range of applications can already be addressed, such as OFET-driven displays, mechanical sensors, and radiofrequency identification (RFID) tags (Figure 1.5b) [107–110]. Over the next few years, both materials' performance and processing methods (e.g. printing techniques) for OFET technology are expected to advance to the level that is compatible with full industrialization, allowing for more flexible electronic products, including the desired OFET-driven OLED displays [111–113].

1.2.2.3 OPVs

The development of photovoltaic (PV) cell that can transform inexhaustible solar energy into electricity represents one of the most promising solutions for providing clean and renewable energy (Figure 1.5c) [114]. Compared to the expensive silicon-based PV cells, solar cells based on organic materials (conductive polymers or small molecules) promise cost-effective PV applications, although OPVs generally suffer from relatively low efficiency and low stability. The first successful OPV device was reported as early as 1986 by Tang [115] with an impressive power conversion efficiency (PCE) of $\sim 1\%$ and high fill factor (FF) of 65%. Substantial progress has been made ever since in understanding the working mechanism of the OPV devices, molecular design, optimizing device architectures, and improving the device stability [116–118]. As a result, the maximum PCE of OPV cells has increased quickly to the level of over 15% [119, 120]. In January 2013, organic solar films developer *Heliatek* (Dresden, Germany) reported certified 12% PCE of a vacuum-processed small-molecule organic triple junction tandem solar cell with an active area of $>1 \text{ cm}^2$. What's more, *Heliatek* achieved a record PCE of 13.2% for an OPV multi-junction cell in 2016. Remarkably, Zou and coworkers reported a high-performance single-junction organic solar cell with the PCE of 15.7% and FF of 74.8% in 2019. The work in this field is exciting, and undoubtedly there is still room for improving OPV technology to promote its industrial application. The challenge of its commercialization has always been the development of products with high efficiency, long operational lifetimes, high production yields, and low cost.

1.2.3 Molecules for Molecular-Scale Electronics

Molecular electronic devices (or junctions) are qualitatively similar to organic thin-film devices. The difference is molecular junctions only incorporate a limited number of molecules in electrical contact with two (or more) conductors (mostly metal). The molecular components within the junction could be either single molecules or molecular monolayers, whose feature size is generally no larger than a few nanometers. The overall performance of the molecular device is determined by the electrode/molecule interface and the electronic structure of the molecular kernel. For such tiny devices, the measured properties can also be largely influenced by variations of molecular geometries inside the junction and small changes of external environment. In order to operate these devices in a relatively controllable manner, chemical design and synthesis of molecular systems are of paramount importance.

Anchoring group and molecular backbone are two main parts of a molecular system [6, 121]. The anchoring group with an affinity for specific substrates (metals or other electrode materials) is responsible for binding the molecular backbone with electrodes. Both of its mechanical stability and electronic transparency (weak or strong coupling) are important considerations. A detailed discussion of anchoring groups can be found in the following chapters.

The molecular backbone is the key unit of the molecular system, which to a large extent defines the electronic functionality of the molecular device. Tailor-made molecules could function as resistors, diodes, or transistors depending on their electronic structures [122–124]. Linear alkanes, π -conjugated molecular wires, molecular switches, and biomolecules are major classes of molecules that have been widely studied [125–129]. Detailed descriptions of their specific electronic properties will be dispersed into the upcoming chapters that separately focus on charge transport mechanisms, testbeds, and analyzing methods. This section provides a broad overview of molecular wires.

In this book, the term “molecular wires” is used to describe rigid, linear, and highly conjugated molecules, although alkane chains as a benchmark molecular system are also “wire-shaped.” Charge transport through molecular wires is more efficient because electrons can move freely in the delocalized orbitals over “long” distances [130, 131]. Typical molecular wires (Figure 1.6) are semiconducting oligomers with narrow HOMO–LUMO gaps (HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital), such as oligo(*p*-phenylene ethynylene)s (OPEs) [14, 132], oligo(*p*-phenylene vinylene) [133], oligothiophenes [134], oligophenyleneimines (OPIs) [135], oligofluoreneimines (ONIs) [136], oligophenylenetriazoles (OPTs) [137], oligo(aryleneethynylene)s (OAEs) [138], oligoynes [139], and oligoanilines [140]. Measurements on these wires with a variety of testbeds revealed apparently smaller conductance decay coefficient ($0.1\text{--}0.5 \text{ \AA}^{-1}$) compared to that of nonconjugated alkanes ($0.7\text{--}1.0 \text{ \AA}^{-1}$) [141, 142]. The capability of delivering higher conductivities makes molecular wires potential candidates as building blocks in molecular electronic circuits.

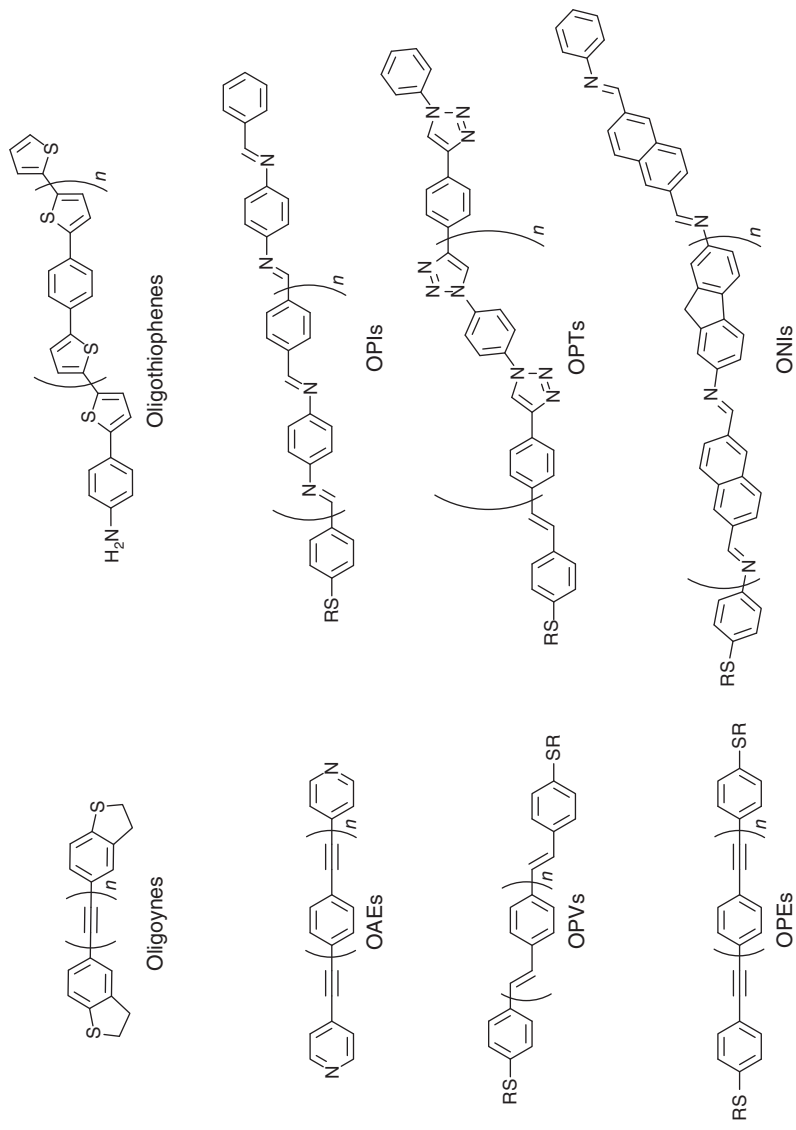


Figure 1.6 The structures of several typical molecular wires.

The length of the wires can be systematically changed by modulating the number of repeating units that constitute the molecular backbone. In general, within a given molecular series, the HOMO–LUMO gap of π -conjugated molecules decreases with an increase in conjugation length. It is thus possible to “manually” adjust the alignment of energy levels between contact electrodes (the Fermi level) and molecular components for ease of charge injection [14, 143]. More importantly, measurements on length-variable transport have been proved feasible to examine the charge transport mechanism for the molecular junction. This method was first proposed by Frisbie and coworkers, who synthesized a series of OPI wires (ranging in length from 1.5 to 7.3 nm) bonded to Au substrates via a thiolate anchoring group and measured their conductance using conducting probe atomic force microscope (cpAFM) [144]. The study indicated a clear transition of transport mechanisms from nonresonant tunneling for short molecules to thermally activated hopping for longer molecules (for the OPI system, the transition happens at around 4 nm), agreeing well with theoretical predictions. This phenomenon was observed in other molecular systems as well, independent of platforms and methods employed [136, 145].

In addition to oligomers, polymeric molecular wires with good conductivity and rigidity have also been reported [146]. A representative work was done by Hu and coworkers, who used poly(*p*-phenylene ethynylene)s (PPEs) (24 polymerization units, up to 18 nm in length) for the fabrication of molecular junctions [147]. It was interesting to see the long polymer has quantized electronic structures and charge hopping has been observed. Compared to the extensively studied short molecular wires, molecular-scale electronics calls for more attention on polymer wires with more extended conjugation length for potentially even larger charge transport capabilities.

Wires incorporating metal complexes are another group of interesting molecules [148–150]. Metal centers in the backbone can lead to multiple redox and spin states that can afford unusual current–voltage characteristics. Furthermore, gate control on molecular junctions is possible by directly modulating the specific optical, redox, and magnetic properties of the complex via external stimuli [151]. In this way, functional molecular junctions and logic gates can be potentially developed. At the present stage, there is still plenty of room for improvement of multifunctional molecular devices integrating organometallics as well as coordination compounds [152]. A recent review focusing on metal complexes in molecular junctions is recommended [153].

A molecular wire occurring in nature is DNA (deoxyribonucleic acid), which is a long polymer encoding the genetic instructions used by all living organisms and many viruses. Double-stranded DNA is a well-ordered, closely spaced (3.4 Å) arrangement of conjugated bases (adenine, thymine, guanine, and cytosine), suggesting its potential use as a bridge for charge transport [154]. Furthermore, the nature of DNA endows it with unique molecular self-assembly properties [155, 156]. It also exhibits good chemical and mechanical properties such as stability and rigidity. Today, advances in synthetic chemistry not only allow DNA to be synthesized in high yield with high purity, but also permit adding functionalities to it. What's more, the order of DNA bases can be sequenced to create arbitrary two- and

three-dimensional architectures on the nanoscale. The challenge of implementing DNA as a molecular wire lies in reading its chemical and biological information based on electrical measurements [157]. Many groups have attempted to couple DNA with probing electrodes for conductance measurements, but the reported characteristics of DNA vary from insulator, semiconductor to conductor and superconductor. The reasons for these contradictory findings might be multiple. In addition to the DNA sequence and length, the measured conductance is also influenced by different experimental conditions (e.g. test environment and testbeds) [158, 159]. In recent years, researchers from different groups gradually reached a consensus that good coupling of electronic contacts to the DNA and preservation of the DNA π -stacking by maintaining physiological conditions are prerequisites to be met for observing high conductivity. What's more, DNA can also act as template for the seed-mediated growth of metal nanowires and nanogap architectures for the fabrication of nanodevices [160]. Collectively, understanding mechanisms of charge transport through DNA is fundamental for rational design of conductive DNA wires and programmable multistate DNA memory systems [161, 162]. For more complete discussions on biomolecules in the field of molecular electronics, several reviews and books are recommended [163–168].

1.3 Introduction to Nanogap Electrodes

At the current level of knowledge, a molecule is recognized as the smallest bit of substance that retains its chemical properties [51]. In the context of molecular electronics, synthetic molecules as small as 1 nm are expected to perform a variety of electronic tasks, aiming at the next limit of miniaturization of electronic devices when conventional silicon technology is foreseen to face fundamental limitations within a decade [50, 169]. As introduced in previous sections, molecular electronics has matured over the last 40 years since a paper from Arie Aviram and Mark Ratner illustrated a theoretical molecular rectifier in 1974 [4]. However, in the first 20 years or so, research progresses in this field were all theoretical constructs [170] without concrete devices, because direct measurement of individual molecules is no easy task, awaiting the development of techniques for making molecular-scale contacts. The first experiment that successfully probed the conductance of a single molecule was reported by C. Joachim and J. K. Gimzewsky on a single C_{60} molecule in 1995 [171], followed by Mark Reed et al. on a limited number of self-assembled benzene molecules in 1997 [57]. Since then, the experimental branch of molecular electronics has developed rapidly, marked by much more reported testbeds for measuring the electronic characteristics of single molecules and their ensembles [57, 172, 173].

Nanogap electrodes are a big class of the testbeds featured by nanometer-sized spaces between paired (or more) contact electrodes, the architecture of which is well suited for molecular components to reside in [174]. Compared to the scanning probe microscopy techniques such as scanning tunneling microscopy (STM) [175] and cpAFM [176] that are powerful to address single molecules with precisely

manipulated tips, the significance of nanogap electrodes lies in they facilitate the fabrication of solid-state devices for potentially practical applications besides fundamental research [17–19, 177]. Moreover, most nanogap electrodes present a planar configuration, making it easier to realize high-density integration of molecular devices and to take the underlying substrate as a gate contact to tune the electrical properties of the molecular components. Furthermore, nanogap electrodes are generally fabricated before the molecular components are subsequently inserted in, therefore they can be characterized with and without molecules in place, helping to distinguish intrinsic molecular properties from artifacts.

Despite the superiorities, the preparation of nanogap electrodes is a very challenging mission. Firstly, typical molecules are only several nanometers in size. This dimension is so small that it goes beyond the capability of traditional microfabrication technologies. Secondly, the size of different molecules largely varies from each other, thus for specific molecules, specific control on the nanogap is required, in case the molecules are posited in an undesired stretched/distorted state between the electrodes. Lastly but not least, from a practical point of view, nanogap electrodes should be reproducible and robust, preferably manufactured by reliable and cheap means. On this basis, mass production is a key issue that needs to be addressed for potential integration solutions.

Because of the major challenges, it was not until late 1990s that researchers managed to measure single-molecule transport in a predefined nanogap as introduced earlier [171]. The pioneering work has inspired a lot more experimental devices based on nanogap electrodes to come [57, 178, 179]. In the recent 15 years or so, a number of elaborate and creative methods for manufacturing nanogap electrodes have been reported [21, 180–182]. These methods cover a variety of techniques ranging from the state-of-the-art lithography techniques to chemically driven self-assembly techniques. Different methods are also frequently combined to use in order to obtain a desired dimension and configuration. For example, electron-beam lithography is often utilized to firstly prepare paired electrodes with spaces at 20–50 nm, and then other techniques, such as shadow mask evaporation, are implemented to further narrow the gap width to a 1–5 nm scale.

Today, nanogap electrodes have become fundamental tools for the construction of solid-state single-molecule devices and the research on charge transport mechanisms through the molecules of interest. Interesting functions performed by molecular components, including diodes [183, 184], switches [185, 186], and transistors [64, 65], have been successfully explored by using nanogap electrodes, and some of the theoretical predictions of the early researchers have been substantially confirmed. More significantly, both experimental and theoretical advances gradually open up a set of exciting possibilities of understanding and manipulating single-molecule properties beyond simple descriptions of electronic transport. Recent research on quantum interference [43, 187], spintronics [41, 188], electromechanics [48, 49], and thermoelectronics [189, 190] at the single molecule level could promisingly lead to fundamentally new concepts for device function beyond CMOS-like logics (Figure 1.7) [191]. On the other hand, although there have been plenty of publications on nanogap electrodes, development of an agreed-upon

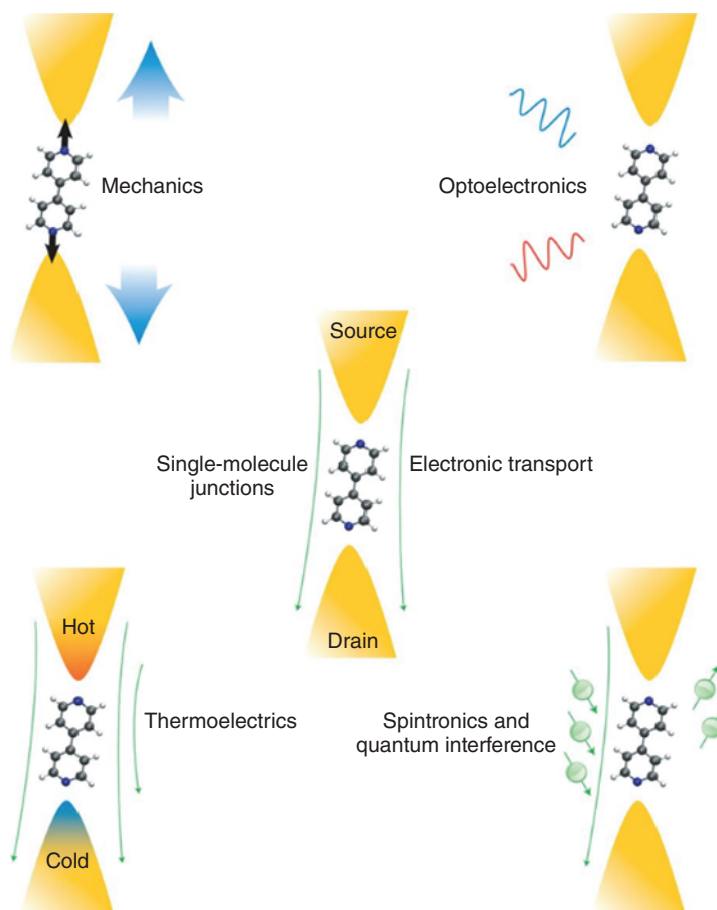


Figure 1.7 Probing multiple properties of single-molecule junctions. Beyond the electronic transport that led to their initial interest, recent studies are beginning to explore the rich physics of metal–molecule–metal junctions through measurements of mechanics, optical effects, and thermoelectric phenomena in addition to demonstrations of quantum mechanical spin- and interference-dependent transport concepts for which there are no analogues in conventional electronics. Source: Aradhya and Venkataraman [191]. 2013, Springer nature.

standard strategy for device fabrication and operation is still lacking. Only when such a standard junction can be reliably manufactured by different laboratories, are the researchers able to focus more on contact interface, molecular kernel, geometry, etc. and correlate their effect with electronic behavior. In the long run, mass production of robust molecular junctions for high-density device integration is a main issue awaiting to be addressed.

A thorough review of the techniques for the fabrication of nanogap electrodes and characteristics of various types of nanogap electrodes is a main focus of this book. Techniques for data collection and analysis, as well as physical phenomena observed in single-molecule devices, are involved. We will also include descriptions on contact

methods for monolayered molecules (generally prepared by self-assembly process or Langmuir–Blodgett method) and in a broad sense view the vertical junctions based on monolayered molecules as a special type of nanogap devices.

1.4 Summary and Outlook

The visionary idea of molecular electronics has been sketched out for decades. If it comes true, the next generation of circuit elements made of molecular components is expected, preferably with lower power consumption, higher speed, and most importantly, an unprecedented level of integration. This chapter offers an overview of this cutting-edge interdisciplinary field, including its origin, motivation, and challenges, followed by a brief summary of molecular materials for electronics, which is an important branch of this field and closely related to the main topic of the book. On this basis, a general introduction to nanogap electrodes is made. The remaining chapters are set up around this theme.

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