Chapter 1
Molecular Electronics: A Brief Overview of the Status of the Field

Jan M. van Ruitenbeek

Abstract The developments in the field of molecular electronics have seen many successes and many setbacks, but the field continues to inspire scientists around the world, now more than ever. The interest is, certainly, for a large part in the fundamental issues: molecules as conducting elements bring together questions from various fields of study and lead to profound new questions. However, this interest alone would not suffice to explain the large efforts in research. Indeed, the prospects of developing electronics with better performance, higher density, and new functionality are what motivates most of the research. In this introductory chapter, I will attempt to take stock of the field, to evaluate what has been achieved, and to identify the interesting challenges that lie ahead.

Keywords Molecular electronics • Organic electronics • Applications of molecular electronics • Fundamental questions of molecular electronics

1.1 Definition of Molecular Electronics

Before we do so, we need to specify what we mean by the words molecular electronics. Polymers [1] and organic molecular compounds [2] have been studied widely for applications in electronics. Polymer and printable electronics are already commercially available, and organic compounds are found in many commercial organic light-emitting diode (OLED) displays. Plastic photovoltaic cells are in production and are continuously improving in performance. Organic layers can be spin coated or drop casted, where the organic matter in these structures is randomly packed in the form of thin films, usually in contact with a metallic electrode at the top and bottom of the layers. The thickness of these films is many times the molecular diameter, so that only a small fraction of the molecules is in contact with the electrodes.

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M. Kiguchi (ed.), *Single-Molecule Electronics*, DOI 10.1007/978-981-10-0724-8_1

We will refer to this wide field of study and technology as *organic electronics*. The applications mentioned above illustrate the relevance of these developments, but there is a prospect for more advanced exploitation of the properties of molecular building blocks when we connect just a single molecule, or a self-assembled single layer of molecules, between metal electrodes. This adds serious technical challenges, but provides access to the full quantum mechanics of electron transport at the molecular scale, even at room temperature. This is expected to provide new opportunities, e.g., in terms of functionality and miniaturization of electronics, and opens up new areas of study of electron transport at the interface between chemistry and physics.

In order to specify this latter field of study, we will call this *molecular electronics*, or *single-molecule electronics*, which we consider as a subfield of organic electronics. Molecular electronics is concerned with devices which have each of the molecules connected to electrodes at both their ends. This can be either in a single-molecule configuration (for a comprehensive review, see [3]) or in large assemblies of molecules, i.e., self-assembled monolayers (SAMs) [4]. In such SAMs, each molecule is connected to both the top and bottom electrodes placed above and below the layer. In contrast to the many concrete applications already found in organic electronics, the subfield of molecular electronics is still in an earlier, exploratory phase. Although first niche applications are entering the market here, for its full potential to be developed, a lot of research is still needed, as I will argue below.

1.2 A Brief History

1.2.1 Molecular Monolayers: Langmuir-Blodgett Technique

As early as 1974, ideas were discussed of using organic molecules as electronic circuit elements. The theoretical ideas outlined in the seminal paper by Aviram and Ratner [5] could not be tested in experiments on individual molecules until much later, because the technology had not yet been developed. On the other hand, many steps had already been taken for studying the electrical transport properties of monolayers of molecules. Based on earlier work by Lord Rayleigh and by Agnes Pockels, Langmuir [6] and Blodgett [7, 8] had shown in the 1920s and 1930s that it is possible to form ordered monolayers of amphiphilic molecules at the liquid-air interface and that these layers can be homogeneously transferred to cover solid surfaces. By this Langmuir-Blodgett (LB) technique, Mann and Kuhn [9] first succeeded in reproducibly measuring the electrical resistance of a monolayer of a fatty acid on top of aluminum bottom contacts. The top contact was applied, either in the form of a liquid Hg electrode or it was formed by evaporation and deposition of metals such as Au, Pb, and Al.

Aviram and Ratner had considered a σ bridged donor-acceptor molecule, with TTF (tetrathiafulvalene) as the donor and TCNQ (7,7,8,8-tetracyano-p-quinodimethane) as the acceptor. This combination has never been realized literally in this form but many donor-σ-acceptor molecules have since been synthesized and tested for diode characteristics. The first experimental observations of rectification by an LB monolayer were reported in 1990, using hexadecylquinolinium tricyanoquinodimethanide as the active molecular layer between Mg and Pt electrodes [10] and even between Al electrodes on both sides [11]. The mechanism for the observed effects has remained under debate because the direction of rectification does not match that of the mechanism proposed by Aviram and Ratner.

One of the central concerns in the experiments has been the role of the metal contacts, notably the top contact. This remains also one of the challenges in more recent experiments, as will be discussed below. The problems are threefold. First, any defects in the LB film are likely to lead to the formation of a metallic short-circuit connection between the top and bottom electrodes. By careful preparation of the LB film and the metallic contacts, this problem can be controlled [12]. Second, once a defect-free device has been achieved, the atoms in the metallic leads have a tendency to migrate under the influence of the very strong electric fields. Indeed, the electric field for an LB film thickness of 2 nm at an applied bias of 2V is as high as 10^9 V/m. As a result, shorts develop after one or more current-voltage cycles. The problem arises for metals with a high room-temperature atom mobility at the surface such as gold, but also for Ti top contacts [13]. The third problem relates to the deposition of metals by evaporation: under-coordinated metal atoms landing from a hot source onto the top of the molecular layer are very reactive and likely to damage the molecular structure of the LB film. Although many experiments suggest that the results are independent of the method of applying a top contact, this is a critical issue that should be considered.

Concerning the latter problem, several solutions have been tested over the years. Metzger and his team have developed a system that allows cold deposition of metals from the vapor phase [14]. The trick they introduced was to have the hot source facing the reverse side of the sample, inside a chamber filled with an inert gas that serves to thermalize the metal vapor and to allow the metal to deposit by diffusion on the farside. The efficiency of this process is very low and this is perhaps the reason why it has not been widely employed. The use of liquid Hg electrodes, as already pioneered by Mann and Kuhn [9], was further developed into a versatile method by Rampi and Whitesides [15]. The latter group elaborated the Hg electrode into a mechanically adjustable microdrop and improved the technique by substituting Hg with a Ga-In eutectic (EGaIn) [16], which marries the advantages of the flow of a metal with the stability of a solid. Although Hg-drop and EGaIn electrodes are very well suited for testing of the molecular layer conductivity, it is not a proper solution for building microfabricated devices.

In order to circumvent the first two problems listed above, Akkerman et al. have introduced the use of conducting polymers (PEDOT:PSS) as top contacts [17]. The junctions show very high stability and reproducibility and a long shelf life. Another original approach was taken by McCreery and colleagues [18], using sp^2 carbon as electrode material.

A first demonstration of a device structure presented by Collier et al. [19] attracted wide attention to the field. They used the LB technique to deposit a layer of rotoxanes, which were expected to switch between two conductance states upon applying a suitable bias voltage. The LB layer was deposited on top of microfabricated Al/Al_2O_3 wires and covered by crossed wires in a second lithography step, by deposition of a Ti/Al layer. Although the device showed the expected switching behavior, follow-up experiments showed that similar switching effects can be obtained in devices containing LB monolayers of nonspecific molecules, including alkanes [20]. The mechanism of switching has been attributed to migration of metal atoms in the electrodes, highlighting one of the main problems mentioned above. The observed switching effect is interesting by itself for application purposes, but it is not a specific molecular device property that we want to discuss here.

1.2.2 Molecular Monolayers: Self-Assembly

A chemistry-based method for growing molecular monolayers introduced in the 1980s has become very popular in recent years. In their 1983 paper, Nuzzo and Allara [21] showed that sulfides adsorb onto Au surfaces from solution and form densely packed coverages. Through later work as reviewed, e.g., by Love et al. [22], the method of forming self-assembled monolayers (SAM) was extended to many different substrate materials and many different anchoring groups. Under proper conditions, many combinations of metal substrates, anchoring groups, and molecular structures allow the formation of regular two-dimensional lattice structures on metal surfaces. The molecules can be deposited from the gas phase as well as from solution and bind by proper choice of a functional head group that has specific affinity for the exposed surface. The functional head group is commonly referred to as the anchor group, and molecules can be synthesized to have anchor groups at both ends, such that binding to the top surface of the SAM is enabled. Specifically the combination of Au surfaces with thiol anchoring groups has been very popular due to the low chemical activity of the gold surface for most contaminants and the specificity of the thiol binding.

Some of the first electrical measurements on SAM were done for *n*-alkyltrichlorosilane molecules, which form a dense layer on oxidized Si substrates [23]. While electron transport appeared to be extremely low, which was suggested to be of use for improving insulation in silicon electronics, later experiments using metal substrates showed a more systematic dependence of conductance as a function of length of the molecules [24, 25]. We will return to this systematics below.

1.2.3 Single Molecules

The development of scanning tunneling microscopy (STM) by Rohrer and Binnig in 1981 [26] has largely shaped many areas of nanoscience. Looking back it seems a natural and logic step to study individual molecules by STM, but it still took about 15 years before the first experiments were performed by Joachim, Gimzewski, and coworkers [27]. They succeeded in imaging and contacting individual C_{60} molecules, employing an STM operating at room temperature under ultra-high vacuum (UHV).

The fullerene C_{60} is a rather unusual molecule, which does not have a specific functional group for anchoring to the metal electrodes. In order to broaden the spectrum towards a wider range of molecular wires, the formation of SAM was combined with STM [28–31] and conducting-tip atomic force microscopy (AFM) [32]. In the approaches by Bumm et al. [28] and by Leatherman et al. [32], a suitable substrate, usually Au(111), was covered by self-assembly with a dense layer of alkanethiolate. The length of the alkanethiolate is tuned to match the length of the molecule of interest, and the latter is inserted as isolated molecules, again by self-assembly, at defect positions in the alkane lattice. Since the alkanethiolates have a very low electronic conductance, the molecules of interest, usually conjugated molecular wire structures having delocalized π-electrons, are observed as points of high conductance in the STM images. Although the interface between the molecules and the metal substrate is well-defined and stable by the self-assembly process, the top contact is only made by tunneling over an ill-defined barrier distance. In order to remedy this problem, Cui et al. [33] introduced a second self-assembly step, where the top thiol group was allowed to bind with Au nanoparticles. The Au nanoparticles are clearly visible in the AFM images and can be contacted by the conducting tip of the AFM. Although this approach improves the measurements of the single-molecule characteristics, the contact between the AFM tip and the Au nanoparticles remains a source of variability.

The essential feature of STM and AFM is the capability to adjust the tip-sample distance to the size of a molecule. The molecules of interest have a size in the range from 0.5 to 10 nm, which is too small for standard lithographic techniques. Several other methods have been developed to solve the problem of creating nanogaps between two electrodes to match the size of the molecules, out of which the mechanically controllable break junction (MCBJ) technique and the electromigration break junction (EBJ) technique are the most popular. Since the gap size between the electrodes and the positioning of the molecule cannot be done top down, some form of self-assembly process is involved in all the techniques. The MCBJ technique was originally developed in my group for the study of metallic and superconducting atomic contacts [34, 35]. It was first applied by Reed et al. for the study of single-molecule transport, by measuring the conductance across a junction formed by breaking a gold wire in a solution of benzenedithiol [36]. The MBCJ technique was later refined by introducing microfabrication [37, 38], which made it more widely applicable.

The EBJ technique was invented by Park et al. and first applied for the study of electron transport across a single C_{60} molecule [39]. The technique makes use of the electromigration force, by which a large current density is capable of displacing the atoms of the current-carrying wire. Breaking a microfabricated wire by control of the current through the wire creates a small tunneling gap, and when molecules have been introduced to the surface of the wire, they are frequently found to bridge this gap. A more elaborate discussion of single-molecule techniques will be presented in Chap. 2.

Although the 1997 work by Reed et al. [36] is regarded as the first single-molecule conductance experiment, in the strict sense of having a single molecule that is chemically bonded between two metallic leads, for several years, it remained difficult to demonstrate unambiguously that the observed signals are associated with a single molecule of the type targeted in the experiment. In 2002, within a year's time, several papers appeared that clarified this problem using all three mayor single-molecule techniques and opened new avenues for research. Employing the EBJ technique, Park et al. [40] and Liang et al. [41] independently published data on a metal-organic complex between metallic leads, where the doped Si substrate serves as a gate electrode. By control of the gate potential, it was possible to control the charge state of the molecule, and a conductance peak appeared at the crossing point between charge states. In experiments employing the MCBJ technique, Smit et al. [42] studied the simple model system of a single H_2 molecule bound between Pt electrodes. The simple structure and low mass of the H_2 allowed identifying its presence uniquely by vibration mode signals in the differential conductance and by isotope shifts of these signals. Although the hydrogen molecule will not be useful for electronics applications, the experiment provides a model system for which the junction can be characterized in great detail.

Finally, employing an STM setup at ambient conditions in a solution of bipyridine molecules, Xu and Tao demonstrated a method for statistically identifying the conductance of a single molecule [43]. The procedure relies on making and breaking cycles of contact between a Au tip and a Au sample immersed in a solution of the molecules. During the breaking process, a single molecule frequently bridges the gap between the metal electrodes, which is identified as a peak in histograms of conductance values.

1.2.4 Present Status of the Field

The three experimental techniques described in the last paragraph have been at the basis of most of the experiments that followed. The repeated breaking of atomic contacts by STM in the presence of molecules allowed Venkataraman et al. [44] to demonstrate a beautiful systematic exponential decrease of the electronic conductance of alkanediamines. The conductance decreases as $\exp(-\beta N)$, where N is the number of carbons in the molecular chain and the factor β was determined as $\beta = 0.91 \pm 0.03$. Many similar experiments have confirmed this exponential dependence with length, at least up to $N = 12$ [45]. There is wide consensus that the factor β for alkanes lies close to 1, which also agrees with results from DFT-based theoretical analysis [46]. For conjugated molecular chain structures, β is significantly smaller [47].

The same experimental technique was also successfully employed for demonstrating other systematics. In a series of molecules synthesized such that the angle ϕ between the planes of two adjacent phenyl rings could be varied, controlled by chemical substitutions, it was shown that the conductance increases as $\cos^2(\phi)$ and that this agrees with the results from model calculations [48, 49].

Once the methods were developed to introduce molecules with specific anchor groups at both ends into the gap between the electrodes in an MCBJ setup [50], this opened the way for detailed experiments and investigation of molecule-specific properties. Among many other works, it led to the discovery of single-molecule conductance switching under the influence of light by Dulić et al. [51]. The combination of optics and molecular junctions was further exploited by detecting the Raman signal associated with the molecule in a junction for which the conductance was measured simultaneously, either in an EBJ setup [52] or an MCBJ device [53].

The later experiments provide examples of the many new tools that have been developed for characterizing the molecular junctions and investigating their properties. Indeed, it was soon realized that the main limitation of most MCBJ, STM, or EBJ experiments is that the information obtained is limited to values of conductance only, which leaves a lot of ambiguity in interpretation. Additional properties that have been explored, illustrated in Fig. 1.1, include vibration mode spectroscopy [42, 54–56], shot noise [57], mechanical force spectroscopy [59], thermopower [60], electrostatic gating [61, 62], redox chemistry at the single-molecule level monitored by conductance [63, 64], and local thermometry [65].

While most of the STM experiments are performed under ambient conditions or in solution, recent work shows a promising development of more sophisticated STM experiments under UHV conditions at helium temperatures [66–69]. These techniques will be described in more detail in Chap. 2.

All this work starts with the design and synthesis of the appropriate molecular compounds, which has advanced very rapidly as will be presented in Chaps. 4, 5, and 6. Theory has progressed at equal pace, where concepts and techniques from Landauer theory and mesoscopic physics were married with those from theoretical chemistry [70–74]. Many predictions have been made of interesting new phenomena that are uniquely uncovered by single-molecule junctions, including the prediction [75] and observation [76] of Franck-Condon blockade, large negative differential conductance [77], and the prediction [78, 79] and observation [80, 81] of quantum interference between molecular orbitals. A more extensive discussion of theoretical progress is given in Chaps. 7 and 8.

Summarizing, as a field of science, molecular electronics is starting to mature. Robust probes have now been developed to study molecular conductance, both in SAM and on the single-molecule level. Results on the same molecular species are now being reproduced in different labs, and the toolbox of the research field is

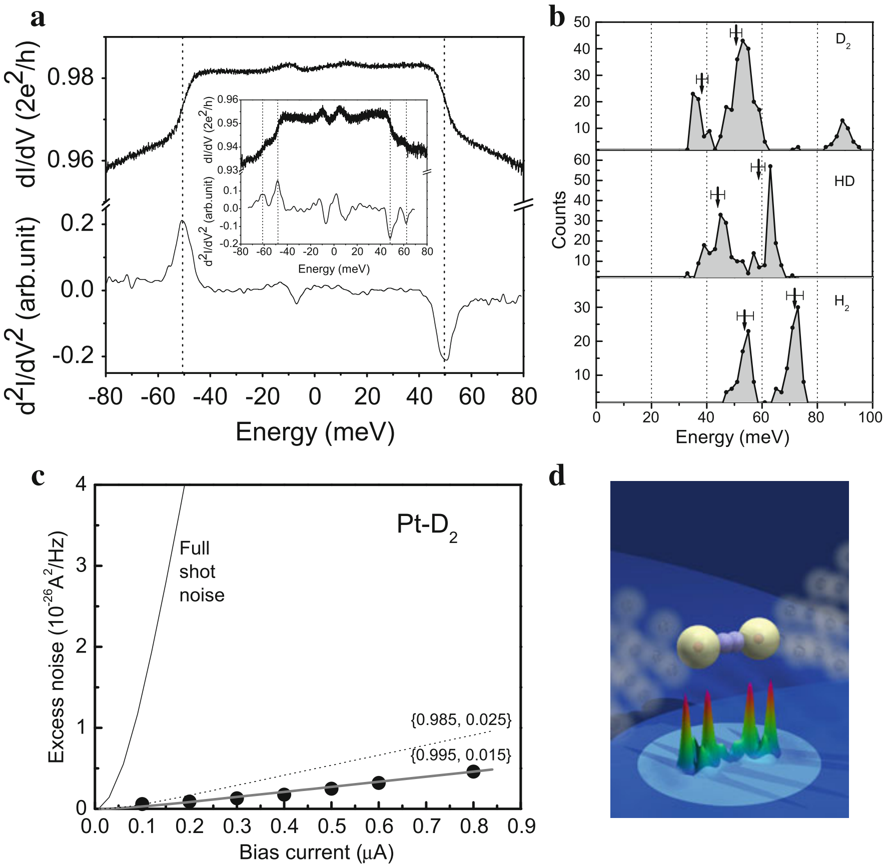

Fig. 1.1 A single hydrogen molecule bridging two Pt electrodes forms a model system that permits many detailed tests. The differential conductance (**a**) shows sharp drops at characteristic frequencies associated with the vibration modes of the molecule. The *inset* shows an example where two modes are observed for the same molecular junction. The position of the steps in the conductance for many experiments is shown in (**b**), and the interpretation of the features in the differential conductance as vibration mode energies can be tested using isotope substitutions of the molecule. The shift of the modes between H_2 and D_2 is close to the value of $\sqrt{2}$, as expected. This permits verifying that the molecule forming the bridge is indeed hydrogen. By further experiments exploiting shot noise (**c**), it is possible to show that the conductance is carried by a single conductance channel. More precisely, the total conductance for this particular junction is $1.01G_0$, which is the result of a dominant conductance channel with transmission 0.995 and a small additional tunneling contribution of 0.015. This demonstrates that the bridge is formed by just a single hydrogen molecule. Panel (**d**) illustrates the configuration that matches the data, together with a calculation of the local density of states on the bridge (Reproduced by permission from Refs. [42, 57, 58])

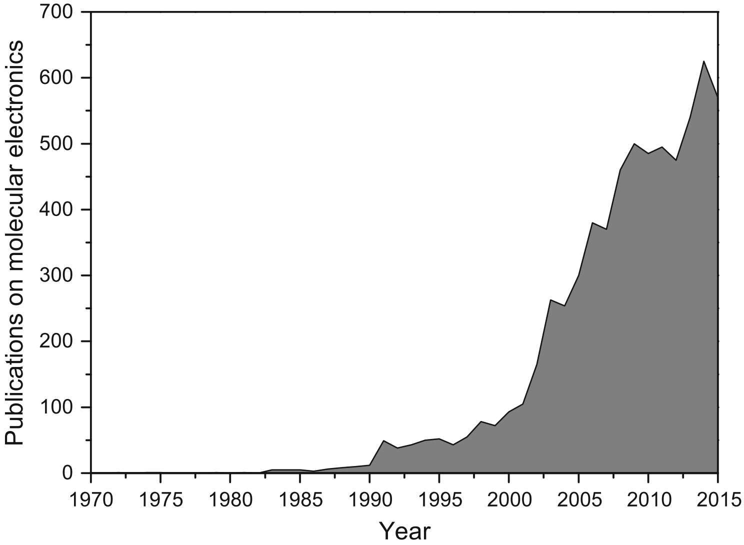

Fig. 1.2 Number of publications on molecular electronics in each year of publication (Data based upon ISI Web of Science, Thomson Reuters)

rapidly expanding. Figure 1.2 shows the evolution of the numbers of publications each year having "molecular electronics" as topic. The total number exceeds 6500, making molecular electronics one of the large research areas of nanoscience, and the interest clearly continues to grow.

Before we continue to discuss which are the attractive issues for further studies towards deeper fundamentals understanding and for developing applications, I will first argue against the widespread suggestion that molecular electronics may one day replace silicon electronics. This is not intended as discouragement, but intended to highlight the realistic prospects for applications.

1.3 Will Self-Assembled Molecular Circuits Replace Silicon?

Semiconductor technology is driving a large part of the word economy, and the fact that there are many signs that we are arriving at the end of the roadmap underlying Moore's law is making the industry nervous [82]. The industry is in urgent need of new ideas and possibly revolutionary approaches. Molecular electronics is one of the possible ways to go forward, but as I will argue here, it will not proceed by simply replacing silicon transistors by molecular equivalents.

The initial excitement around molecular electronics derived from the vague notion that molecules would someday replace transistors in today's complementary metal-oxide-semiconductor (CMOS)-based silicon technology, an idea that was sometimes even voiced explicitly. Design of the proper links between the molecular building blocks and choice of proper processing conditions would permit self-assembly of the complete circuit. Furthermore, the tools of organic chemistry would allow design of the properties of all circuit elements, they could be produced such that they are all identical at mole quantities, and they would represent the ultimate limit in miniaturization. The self-assembly process would obviate the need for investments in wafer-stepper machines, for which the costs explode as the sizes of the smallest circuit details shrink. Although many of these attractive aspects of molecules in electronics remain true and may be exploited in applications of some form, as I will argue below it is useful to be aware that the initial dream in this sense will never become a reality. This has been admitted by many, but has only seldom been stated very explicitly.

One of the main reasons why this scheme cannot work, even in principle, is the fact that the electronic wave functions on a molecule are phase coherent. This is one of the reasons why many believe that molecules may be very attractive in electronics, but phase coherence also implies that the properties of two circuit elements coupled in series do not simply behave as the connection of two classical circuit elements in series. When coupling two molecules together, the wave functions of the two combine into a coherent superposition that modifies the properties of both [83]. In general, the electronic transmission of a molecule is only defined in combination with the properties of the connections and the strength of the coupling.

One possibility of circumventing this problem would be offered by reducing the strength of the coupling of the molecule to its surrounding circuit. A molecule will normally have a single conductance channel that dominates transport, which provides a conductance of one quantum unit, $2e^2/h$, or about 0.1 mS under conditions of perfect transmission. When we want to decouple the molecule enough to prevent modification of its wave functions, we will need to introduce barriers that reduce the transmission by typically three orders of magnitude at all connections. The net conductance between any two leads then becomes of the order of 0.1 nS. When, in addition, we want to conserve the operating voltage at about 1 V and the clock frequency of silicon electronics to values of several GHz, we notice that the amount of charge transmitted within a clock cycle is of the order of a single electron. This will produce unwanted statistical fluctuations of the results of the computing operations, will be extremely difficult to control the next circuit elements reliably, and will impose a serious limitation on the fan-out, i.e., the number of next-stage circuit elements that can be controlled be the present one.

The strategy of reducing the coupling between molecular circuit elements to such a degree also implies that the single-electron description of coherent transmission breaks down and that electron-electron interactions need to be taken into account. Coulomb blockade will be important, even at room temperature. This means that the properties of the circuit cannot be described by combining independent circuit elements, but can only be described at the level of the complete circuit, which brings us back to the problem that we started from.

Another approach for decoupling the molecular circuit elements could be provided by placing metallic islands between each molecular stage, large enough to provide decoherence of the phase of the wave functions. This has two serious drawbacks: First, we lose most of the small-size advantage of the molecules.

Second, we would need to arrange for the coupling between the molecules and the metal islands to be strong in order for the electron current to remain large enough to drive the next stage, as argued above. This will result in significant broadening of the molecular level, which will wash out a lot of the specific molecular energy level structure that we would like to exploit for the active device-specific operations.

Even if we were able to find solutions to handle these problems, the difficulty remains of catching up with all the technology invested in CMOS in circuit design taking care of heat dissipation, capacitive cross talk, and much more. For all of these reasons, it seems obvious that molecular electronics can only work if we consider entirely different circuit architectures or different applications that permit relaxing some of the requirements and take advantage of the specific properties of molecular circuit elements. Some of these ideas are briefly outlined below.

1.4 Intrinsically Quantum

After these critical remarks, it is important to emphasize that there are many application perspectives and that between the present time and future applications, there is fascinating science on our path. A large part of the fascination lies in the fact that molecules are intrinsically quantum objects and that we may explore and exploit this fact, even at ambient conditions.

An exciting aspect of molecular conduction is the fact that the energy scales involved are such that quantum effects are expected at room temperature. In this sense, single-molecule electronics forms a natural extension of mesoscopic physics. An illustrative example is the observation of quantum interference in charge transport. In mesoscopic physics, interference has been shown to govern the conductance in gold rings with a diameter of 1 micrometer at cryogenic temperatures [84]. In molecules with sizes as small as 1, nanometer interference effects are expected at room temperature. This has first been recognized in theoretical works [79] and very recently, the first experiments have been done [80]. New switchable devices or sensors come within reach once destructive interference (with low conductance) can be turned on and off in a controlled way. However, the consequences of quantum interference reach much further as it may govern thermoelectric properties or spin-spin interaction, enabling new functionality [85].

A molecular wire is maximally exposed to its environment, which poses challenges in incorporating the environment in the description. A molecule exchanges energy with its surroundings through the exchange of vibration modes (phonons), electromagnetic modes (photons), electronic excitations, and composite excitations such as plasmons. It is also influenced by static and dynamic electric fields, magnetic fields, pH and chemical composition in general, temperature, and more. Their influence on transport properties is not understood in detail and provides one of the main challenges of the field. On the other hand, the strong interaction with the environment also creates a lot of opportunities. Some molecular devices show switchability, while the molecule in the junction has no built-in functionality [85].

In this case, the interaction with the electrodes, either via the electric field or via the current, induces the necessary bistability for switch operation. By control of the environment, a fully symmetric molecule can function as a strongly asymmetric diode [86].

Another tantalizing possibility arises from non-conservative current-induced forces. Such forces are held responsible for electromigration in microscopic metal wires. However, more recent work by Tchavdar Todorov and others suggests an interesting connection with the presence of nearly degenerate vibration modes that could be engineered for switching properties in an organic molecule or even for driving nanoscale motors by a dc current [87, 88].

The intrinsic quantum nature of molecules highlights two legitimate goals for further research: fundamental understanding and applications. Below a sketch of promising developments for both directions is given.

1.5 Challenges for Applications

Self-assembly will be an essential part of most molecular electronics applications, and this process needs to be optimized for success rates at the single-molecule level. A clear advantage of SAM devices is that the molecular building blocks are all identical, while the variations in coupling of the individual molecules are averaged away. In addition, functionalities can be built in by chemical design, examples of which include switches, rectifiers, and sensors. However, to fully exploit this potential, a good understanding of the molecule-electrode interface is crucial. Single-molecule devices serve as model systems to study these interfaces, as they do, for instance, not suffer from pinhole shorts that SAMs may have. Importantly, single-molecule devices can provide the feedback loop to make the required steps in our understanding and control. In an ideal feedback loop, synthesis of molecules is followed by experimental characterization of single-molecule junctions, for which by now various approaches are available. The experimental results form the input for theoretical modeling and the latter would dictate the synthesis of a new class of molecules with improved performance. In this way, single-molecule electronics becomes an enabling field for large-area device applications based on molecules. These include both SAM-based devices and organic electronic devices, as will be illustrated below.

The metal-molecule interface plays a crucial role in understanding molecular device behavior. This holds not only for the mechanical coupling but also for the electronic coupling, governing charge transport through the junction. The mechanical coupling is based on the stability of chemical bonds, which provide the driving force for self-assembly. Traditionally, the Au-S bond has been the most popular one, but recent research focuses on alternative binding schemes. In fact, this has become an active field of current research that has seen a strong development in the last couple of years [89]. Apart from the mechanical stability, the binding configuration also determines the electronic properties of the junction. Coupling a molecule to metallic electrodes has two important effects on the molecular energy levels. First, the molecular levels are broadened and, generally speaking, the broader the levels, the higher the off-resonance conductance. Second, charge transfer near the interface may lead to significant shifting of the molecular levels. This shifting has important implications for transport, as the position of the molecular levels with respect to the Fermi energy of the electrodes determines its charge transport properties. In fact, this is used in current organic devices to optimize injection barriers by a methodology that we call interface engineering. For example, an SAM sandwiched between an organic layer and a metal electrode acts as an intermediate, reducing the injection barrier [90].

The perspectives for applications naturally separate into short-term and long-term perspectives. The first applications of molecular electronics have started to appear [91] and, just as this example illustrates, the earliest applications will most likely not rely on single-molecule junctions. In addition, applications of single-molecule layers formed by self-assembly are already being explored for the engineering of work functions of metallization layers. Charge injection into organic conducting layers, such as those being developed for solar cells, can be optimized by a proper choice of molecular surface coating [92]. Although the principles of the process are now reasonably well understood, the optimization and detailed understanding require still a large effort. A third promising application near the horizon is the use of redox-active molecules to improve properties of flash memory in combination with standard silicon transistors [93, 94].

One of the most attractive proposals for employing molecules in electronics is the use of cross-bar array architectures [95, 96], as illustrated in Fig. 1.3. It opens the way towards high-density memory, which could be implemented initially as

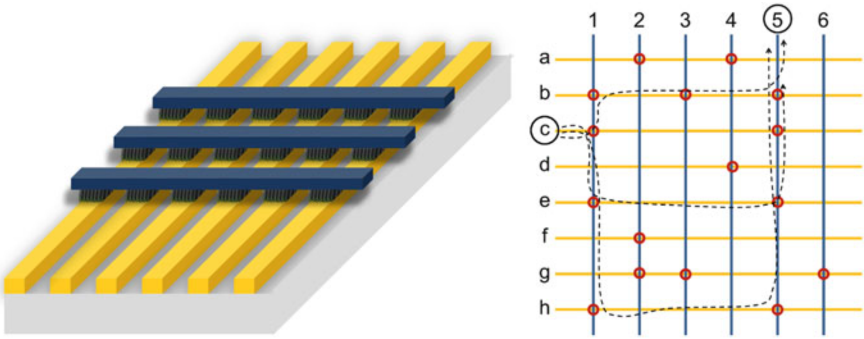

Fig. 1.3 Schematic structure of a cross-bar array structure employing a layer of molecules as active components at the nodes. Ideally the molecules switch between high-conductance and low-conductance states above a threshold value of the applied bias. The *right panel* illustrates the need for blocking current through parallel paths. When the *circled* nodes are in the high-conductance state and we want to read the information in node C5, the information read will be confounded by parallel current paths as shown by the *dashed lines*. The larger the array, the more abundant are such parallel paths

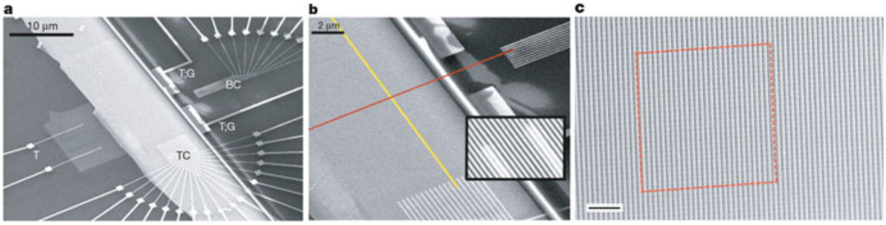

Fig. 1.4 Scanning electron micrographs of a 160 kbit molecular memory device. It contains 400 Si bottom nanowire electrodes having a 33 nm pitch, seen as the *light gray area* connected by "T" in (**a**), and 400 Ti nanowires on top with the same pitch, visible as the light band diagonally stretching the image. The nodes are formed by about 100 rotoxane molecules deposited as an LB layer. Panel (**b**) is a zoom of the central area with a top wire highlighted as red and a bottom wire as yellow. The further zoom in (**c**) shows the central area of about 2500 bits, where the scale bar is 200 nm (Reproduced by permission from [96])

relatively small arrays incorporated into and added onto standard CMOS circuits. A test structure containing 160,000 molecular junctions was fabricated by Green et al. [96] using an LB monolayer of rotaxanes as the active component; see Fig. 1.4. Although only 25 % of the junctions tested showed an on/off ratio larger than 1.5, the work demonstrates that some of the hurdles can be taken. Apart from the application as memory, such cross-bar arrays can be used for processing, using reconfigurable logic [95].

In its simplest implementation, each node is connected to a single bottom wire and a single cross wire on top. The problem of defective molecular junctions can be accommodated by the embedding structure into a fault-tolerant architecture. Nevertheless, reducing the number of defective junctions will greatly enhance the success of the devices, and this problem is probably predominantly associated with improvement of the deposition and bonding of the top contact wires to the molecular layer and the quality of the SAM.

The schematic in Fig. 1.3 shows the basic structure. The minimal requirements are the need for a molecule that can be self-assembled into a densely ordered layer and deposited on the bottom wires and a molecule that behaves as a well-defined switch between a low-conductance and a high-conductance state upon application of a bias voltage above a suitable threshold value. Although the rotaxanes demonstrate some intrinsic switching behavior, there is much room to improve the on/off ratio and the reliability by searching for other molecular components.

For a practical device, we will need to add further components, which could also be implemented as molecular layers. First, it will be necessary to add a diode in series with the switches at each node [97]. The need for such diodes is illustrated in the right panel of Fig. 1.3. Without diodes, a large cross-bar array would have a multitude of parallel conduction paths that would mask the information for individual bits. We further need to demand a high rectification ratio R_{rr} between forward and reverse bias for these diodes because the number of parallel current paths scales with the size of the array. In the worst case, when all nodes have their switch closed (i.e., “on”), the ratio of the signal current to the current through parallel paths is $2/(N-1) + R_{rr}/(N-1)^2$ for an $N \times N$ array. Even for a modest 1 MBit memory, the requirements would be $R_{rr} > 10^6$, which is quite demanding. The solution will be to implement large numbers of smaller arrays embedded into CMOS electronics.

Finally, when we introduce a diode, it impedes the process of writing information to the molecular switch by a current bias of either polarity. This could be taken care of by a molecular Zener diode. Although such Zener diodes have not been discussed widely in the context of molecular electronics, the principle may also be implemented by combining two resonant tunneling diodes [98].

Apart from considering different computer architectures, there are ample further possibilities for which optimization in speed is not required, such as for disposable or wearable electronics. As argued above, electronics based on such molecular SAM are not expected to outperform existing silicon devices, but they will be complementary, will profit from cheap processing technologies, and will enable new applications and functionality. ” For electronics applications that rely less on dense packing of bits and high switching speed, such as disposable electronics, the requirements will be different than those for high-density computing and memory applications. The former will typically make use of SAM of molecules over relatively large areas. It will, then, be important to reduce defects in the SAM or make the device structure insensitive to them.

An aspect that is seldom discussed is the fact that the molecular compounds that have been studied to date at the single-molecule level have a conductance that is far too high for such applications. The conductance for single-molecule junctions usually covers a range down to 10^{-7} of the conductance quantum or 10^{-7} S. SAM of molecules having a conductance at this bottom end of the range and covering an area of 1 mm^2 would make a total conductance of 10 S. In other words, at a bias of only 1 V, this device would draw a current of 10 A. The conclusion should be that for such applications, it will be necessary to extend the range of investigation of molecular conductance towards much smaller values.

For the longer term, it remains very attractive to investigate truly single-molecule electronics applications. One of the main difficulties that we will need to address is that of keeping single molecules stable at a reproducible transmission. It is likely that metal electrodes will not be the best choice to deal with this problem. Possibly covalent bonds can be explored for bonding to other electrode materials such as Si [99, 100] or graphene [101, 102]. While single-molecule junctions are ideal for testing concepts, for applications, it will be necessary to solve the problem of interfacing the molecules with lithography or find other solutions for creating stable gaps between the electrodes. A lot of progress in this direction has already been made as recently reviewed by Cui et al. [103]. Such single-molecule devices will also need to be forgiving in the variability and fluctuations in the molecular anchoring and conformations.

Most of the research directions discussed above are connected to electronics in some way. However, there are important developments that connect to very different fields such as microbiology and medicine. Sequencing and read-out of DNA and other biopolymers has evolved into a main field of research and development. The techniques currently in use in sequencers rely almost exclusively on biochemical methods. The advantages of a direct read-out of biopolymers by physical methods are obvious, and several groups are working towards these goals [104–108]. One of the approaches taken is the read-out of sequences of monomers by differentiating the levels of tunneling current [105, 106, 108]. Ideally one would like to controllably drag a biopolymer past a nanometer-size gap between two metallic electrodes and read off the nature of each of the building blocks passing by. Many steps in this direction have been taken, and larger consortia are now being formed for bringing this application to the market. A more extensive discussion is given in Chap. 9.

1.6 Challenges for Fundamental Understanding

Obviously, as applies to all of the discussions in this chapter, it is not possible to give an exhaustive list of all points of interest. The items given below are inevitably colored by personal preference, but should still serve to outline the scope of challenges open for research.

Starting with one of the most fundamental issues, the question of whether an accurate prediction of electronic conductance of a molecular junction can be given is still open. For molecules having a strong hybridization of the molecular orbitals with the metallic states of the leads, a coherent transport description works very well [42]. At the other end of the spectrum, molecules that have only a weak tunnel coupling to the leads can be understood within the framework of Coulomb blockade of discrete charge states of the molecule [109]. The intermediate regime has been understood at the level of idealized models, but experiments on individual molecules are usually compared with theory for one of the two extreme conditions. For most molecules for which the off-resonant zero-bias conductance is measured, the results are compared with DFT-based calculations that take electron-electron interaction into account only at a mean field level. Equally important, the role of image charges is very large and has only started to be included in the discussion [61, 110]. For a more extensive discussion of these open problems, I recommend the book by Cuevas and Scheer [3].

The nature of the bond between the molecule and the metal electrodes is of obvious importance. We have only partial understanding of the nature of the binding of the molecules to electrodes (anchoring) in terms of bond strength and electronic transport. The interesting question is whether these two are correlated in any way. This is a critical question for interface engineering and well-defined SAM for applications. The answer to this question will depend on the nature of the electrode material, where metals should probably be distinguished from materials such as graphene, which allow for covalent bonding.

In regular metallic transport experiments, it is very difficult to set up an electron distribution that is locally very far from equilibrium. Molecular junctions open this window toward electron transport far from equilibrium. Under these conditions, we can probe the details of electron-phonon interactions, dissipation, and relaxation. As a result of the large voltage bias and the associated large current density, electrons have access to many types of relaxation mechanisms, including vibration modes, photons, plasmons, and spin excitations. This coupling works also in the other direction: because the molecule is exposed to the environment, electron transport is sensitive to fields of all these types. These effects can be further amplified by quantum effects such as interference of transport through multiple atomic orbitals [81].

In this way, single molecules form an exceptional platform for testing many phenomena under extreme conditions. There is a wide interest in spin transport, and interaction of the electron spin with the electronic and nuclear spins on the molecule, where the research connects to the field of spintronics [111, 112]. Seebeck coefficients and thermal transport can be engineered and investigated at the single-molecule scale, which will boost progress in thermoelectric energy conversion [113]. Electrochemistry can be investigated down to the single-molecule level [64], and more generally the specificity of the interaction of the molecule with its chemical environment can be investigated through its electronic conductance. The extreme current densities open the way for microscopic investigations of electromigration, where recent predictions suggest that such forces could be harnessed for developing dc-current driven nanomotors, acting as waterwheels in the electron flow [87].

Finally, many important challenges connected to applications stand out: molecular junctions having diode characteristics [114], voltage-controlled switching [85], and negative differential conductance [77] have been demonstrated, but in view of the applications discussed above, there is much need for improvement of these properties and for investigation of other principles leading to the desired properties.

1.7 Outlook and Conclusions

Many of the points mentioned above have been widely discussed and are part of active research worldwide. Thinking further into the future, it will be attractive to consider the possibilities of building three-dimensional networks by self-assembly. Can we come up with mechanisms and architectures to do this? Some inspiration may come from the self-assembly of two-dimensional networks that employ the recognition and selective bonding of engineered strands of DNA [115]. Although DNA serves the purpose of self-assembly very well, it is a very poor conductor, if not a very good insulator. We would need, instead, to use flexible conducting molecular wires and find new avenues for targeted self-assembly. Examples of such long self-assembling conducting wires have been demonstrated by Tuccitto et al. [116], and other examples are discussed in Chaps. 5 and 6. Ideally, the target connections would be controllably activated by setting its electrical potentials or by reversible chemical modifications. Such 3D reconfigurable networks would have very interesting properties and offer perspectives for signal processing through neuromorphic networks. The challenge is clearly formidable and the time scale for achieving this is likely longer than any of the other applications discussed.

From a scientific point of view, as well as from an applications perspective, the conclusion should be that the future of the field of molecular electronics is bright. At which point we find ourselves in the development of the field, we can only answer with certainty much later, but Fig. 1.2 and the list of interesting open problems discussed here suggest that the field will continue to grow for some time to come.

Acknowledgements I have profited from many discussions with Sense Jan van der Molen, Herre van der Zant, Ferdinant Evers, Mehdi Tahoori, Alfredo Levy Yeyati, Dago de Leeuw, Juan Carlos Cuevas, Duncan Stewart, and Manabu Kiguchi.

References

1. Skotheim TA, Elsenbaumer RL, Reynolds JR (eds) (1998) Handbook of conducting polymers. Marcel Dekker, New York/Basel
2. So F (ed) (2010) Organic electronics, materials, processing, devices and applications. CRC Press, Boca Raton
3. Cuevas JC, Scheer E (2010) Molecular electronics, an introduction to theory and experiment. World Scientific, Hackensack
4. Gooding JJ, Ciampi S (2011) The molecular level modification of surfaces: from self-assembled monolayers to complex molecular assemblies. Chem Soc Rev 40:2704–2718
5. Aviram A, Ratner MA (1974) Molecular rectifiers. Chem Phys Lett 29:277–283
6. Langmuir I (1920) The mechanism of the surface phenomena of flotation. Trans Faraday Soc 15:62
7. Blodgett KB (1934) Monomolecular films of fatty acids on glass. J Am Chem Soc 56:495–495
8. Blodgett KB (1935) Films built by depositing successive monomolecular layers on a solid surface. J Am Chem Soc 57:1007–1022
9. Mann B, Kuhn H (1971) Tunneling through fatty acid salt monolayers. J Appl Phys 42:4398
10. Geddes NJ, Sambles JR, Jarvis DJ, Parker WG (1990) Fabrication and investigation of asymmetric current-voltage characteristics of a metal/Langmuir-Blodgett monolayer/metal structure. Appl Phys Lett 56:1916
11. Metzger RM, Chen B, Höpfner U, Lakshmikantham MV, Vuillaume D, Kawai T et al (1997) Unimolecular electrical rectification in hexadecylquinolinium tricyanoquinodimethanide. J Am Chem Soc 119:10455–10466
12. Metzger RM (1999) Electrical rectification by a molecule: the advent of unimolecular electronic devices. Acc Chem Res 32:950–957
13. Lau CN, Stewart DR, Williams RS, Bockrath M (2004) Direct observation of nanoscale switching centers in metal/molecule/metal structures. Nano Lett 4:569–572
14. Metzger RM, Xu T, Peterson IR (2001) Electrical rectification by a monolayer of hexadecylquinolinium tricyanoquinodimethanide measured between macroscopic gold electrodes. J Phys Chem B 105:7280–7290
15. Rampi MA, Whitesides GM (2002) A versatile experimental approach for understanding electron transport through organic materials. Chem Phys 281:373–391
16. Chiechi RC, Weiss EA, Dickey MD, Whitesides GM (2007) Eutectic Gallium-Indium (EGaIn): a moldable liquid metal for electrical characterization of self-assembled monolayers. Angew Chemie 120:148–150

17. Akkerman HB, Blom PWM, de Leeuw DM, de Boer B (2006) Towards molecular electronics with large-area molecular junctions. Nature 441:69–72
18. Yan H, Bergren AJ, McCreery R, Della Rocca ML, Martin P, Lafarge P, Lacroix JC (2013) Activationless charge transport across 4.5 to 22 nm in molecular electronic junctions. Proc Natl Acad Sci 110:5326
19. Collier CP, Wong EW, Belohradsky M, Raymo FM, Stoddart JF, Kuekes PJ, Williams RS, Heath JR (1999) Electronically configurable molecular-based logic gates. Science 285:391–394
20. Stewart DR, Ohlberg DAA, Beck PA, Chen Y, Williams RS, Jeppesen JO, Nielsen KA, Stoddart JF (2004) Molecule-independent electrical switching in Pt/Organic Monolayer/Ti devices. Nano Lett 4:133–136
21. Nuzzo RG, Allara DL (1983) Adsorption of bifunctional organic disulfides on gold surfaces. J Am Chem Soc 105:4481–4483
22. Love JC, Estroff LA, Kriebel JK, Nuzzo RG, Whitesides GM (2005) Self-assembled monolayers of thiolates on metals as a form of nanotechnology. Chem Rev 105:1103–1169
23. Boulas C, Davidovits JV, Rondelez F, Vuillaume D (1996) Suppression of charge carrier tunneling through organic self-assembled monolayers. Phys Rev Lett 76:4797
24. Wold DC, Frisbie CD (2001) Fabrication and characterization of metal-molecule-metal junctions by conducting probe atomic force microscopy. J Am Chem Soc 123:5549–5556
25. Cui XD, Zarate X, Tomfohr J, Sankey OF, Primak A, Moore AL, Moore TA, Gust D, Harrias G, Lindsay SM (2002) Making electrical contacts to molecular monolayers. Nanotechnology 13:5
26. Binnig G, Rohrer H, Gerber Ch, Weibel E (1982) Surface studies by scanning tunneling microscopy. Phys Rev Lett 49:57
27. Joachim C, Gimzewski JK, Schlittler RR, Chavy C (1995) Electronic transparence of a single C_{60} molecule. Phys Rev Lett 74:2102
28. Bumm LA, Arnold JJ, Cygan MT, Dunbar TD, Burgin TP, Jones L, Allara DL, Tour JM, Weiss PS (1996) Are single molecular wires conducting? Science 271:1705–1707
29. Datta S, Tian W, Hong S, Reifenberger R, Henderson JI, Kubiak CP (1997) Current-Voltage characteristics of self-assembled monolayers by scanning tunneling microscopy. Phys Rev Lett 79:2530–2533
30. Han W, Durantini EN, Moore TA, Moore AL, Gust D, Rez P, Leatherman G, Seely GR, Tao N, Lindsay SM (1997) STM contrast, electron-transfer chemistry, and conduction in molecules. J Phys Chem B 101:10719
31. Donhauser ZJ, Mantooth BA, Kelly KF, Bumm LA, Monnell JD, Stapleton JJ, Price DW Jr, Rawlett AM, Allara DL, Tour JM, Weiss PS (2001) Conductance switching in single molecules through conformational changes. Science 292:2303
32. Leatherman G, Durantini EN, Gust D, Moore TA, Moore AL, Stone S, Zhou Z, Rez P, Liu YZ, Lindsay SM (1999) Carotene as a molecular wire- conducting atomic force microscopy. J Phys Chem B 103:4006–4010
33. Cui XD, Primak A, Zarate X, Tomfohr J, Sankey OF, Moore AL, Moore TA, Gust D, Harris G, Lindsay SM (2001) Reproducible measurement of single-molecule conductivity. Science 294:571
34. Muller CJ, van Ruitenbeek JM, de Jongh LJ (1992) Conductance and supercurrent discontinuities in atomic-scale metallic constrictions of variable width. Phys Rev Lett 69:140–143
35. Muller CJ, van Ruitenbeek JM, de Jongh LJ (1992) Experimental observation of the transition from weak link to tunnel junction. Physica C 191:484–504
36. Reed MA, Zhou C, Muller CJ, Burgin TP, Tour JM (1997) Conductance of a molecular junction. Science 278:252–254
37. van Ruitenbeek JM, Alvarez A, Piñeyro I, Grahmann C, Joyez P, Devoret MH, Esteve D, Urbina C (1996) Adjustable nanofabricated atomic size contacts. Rev Sci Instrum **67** 108–111
38. Kergueris C, Bourgoin J-P, Palacin S, Esteve D, Urbina C, Magoga M, Joachim C (1999) Electronic transport through a metal-molecule-metal junction. Phys Rev B 59:12505–12513

39. Park H, Park J, Lim AKL, Anderson EH, Alivisatos AP, McEuen PL (2000) Nanomechanical oscillations in e single C60 transistor. Nature 407:57–60
40. Park J, Pasupathy AN, Goldsmith JI, Chang C, Yaish Y, Petta JR, Rinkoski M, Sethna JP, Abruña HD, McEuen PL, Ralph D (2002) Coulomb blockade and the Kondo effect in single-atom transistors. Nature 417:722–725
41. Liang W, Shores MP, Bockrath M, Long JR, Park H (2002) Kondo resonance in a single-molecule transistor. Nature 417:725–729
42. Smit RHM, Noat Y, Untiedt C, Lang ND, van Hemert MC, van Ruitenbeek JM (2002) Measurement of the conductance of a hydrogen molecule. Nature 419:906
43. Xu B, Tao NJ (2003) Measurement of single-molecule resistance by repeated formation of molecular junctions. Science 301:1221–1223
44. Venkataraman L, Klare JE, Tam IW, Nuckolls C, Hybertsen MS, Steigerwald ML (2006) Single-molecule circuits with well-defined molecular conductance. Nano Lett 6:458–462
45. Haiss W, Martin S, Scullion LE, Bouffier L, Higgins SJ, Nichols RJ (2009) Anomalous length and voltage dependence of single molecule conductance. Phys Chem Chem Phys 11:10831–10838
46. Picaud F, Smogunov A, Dal Corso A, Tosatti E (2003) Complex band structures and decay length in polyethylene chains. J Phys Cond Mat 15:3731
47. Choi SH, Kim B, Frisbie CD (2008) Electrical resistance of long conjugated molecular wires. Science 320:1482–1486
48. Venkataraman L, Klare JE, Nuckolls C, Hybertsen MS, Steigerwald ML (2006) Dependence of single-molecule junction conductance on molecular conformation. Nature 442:904
49. Michenko A, Vonlanthen D, Meded V, Bürkle M, Li C, Pobelov IV, Bagrets A, Viljas JK, Pauly F, Evers F, Mayor M, Wandlowski T (2010) Influence of conformation on conductance of Biphenyl-Dithiol single-molecule contacts. Nano Lett 10:156–164
50. Reichert J, Weber HB, Mayor M, Löhneysen Hv (2003) Low-temperature conductance measurements on single molecules. Appl Phys Lett 82:4137
51. Dulić D, van der Molen SJ, Kudernac T, Jonkman HT, de Jong JJD, Bowden TN, van Esch J, Feringa BL, van Wees BJ (2003) One-way optoelectronic switching of photochromic molecules on gold. Phys Rev Lett 91:207402
52. Ward DR, Halas NJ, Ciszek JW, Tour JM, Wu Y, Nordlander P, Natelson D (2008) Simultaneous measurements of electronic conduction and raman response in molecular junctions. Nano Lett 8:919–925
53. Konishi T, Kiguchi M, Takase M, Nagasawa F, Nabika H, Ikeda K, Uosaki K, Ueno K, Misawa H, Murakoshi K (2013) Single molecule dynamics at a mechanically controllable break junction in solution at room temperature. J Am Chem Soc 135:1009–1014
54. Osorio EA, O'Neill K, Stuhr-Hansen N, Nielsen OF, Bj ornholm T, van der Zant HSJ (2007) Addition energies and vibrational fine structure measured in electromigrated single-molecule junctions based on an oligophenylenevinylene derivative. AdV Mater 19:281–285
55. Tal O, Krieger M, Leerink B, van Ruitenbeek JM (2008) Electron-vibration interaction in single-molecule junctions: from contact to tunneling regimes. Phys Rev Lett 100:196804
56. Kim Y, Pietsch T, Erbe A, Belzig W, Scheer E (2011) Benzenedithiol: a broad-range single-channel molecular conductor. Nano Lett 11:3734–3738
57. Djukic D, van Ruitenbeek JM (2006) Shot noise measurements on a single molecule. Nano Lett 6:789–793
58. Djukic D, Thygesen KS, Untiedt C, Smit RHM, Jacobsen KW, van Ruitenbeek JM (2005) Stretching dependence of the vibration modes of a single-molecule Pt-H_2-Pt junction. Phys Rev B 71:161402
59. Aradhya SV, Frei M, Hybertsen MS, Venkataraman L (2012) Van derWaals interactions at metal/organic interfaces at the single-molecule level. Nat Mater 11:872–876
60. Reddy P, Jang, S-Y, Segalman RA, Majumdar A (2007) Thermoelectricity in molecular junctions. Science 315:1568–1571
61. Perrin ML, Verzijl CJO, Martin CA, Shaikh AJ, Eelkema R, van Esch JH, van Ruitenbeek JM, Thijssen JM, van der Zant HSJ, Dulić D (2013) Large tunable image charge effects in single-molecule junctions. Nat Nanotechnol 8:282–287

62. Xiang D, Jeong H, Kim D, Lee T, Cheng Y, Wang Q, Mayer D (2013) Three-terminal single-molecule junctions formed by mechanically controllable break junctions with side gating. Nano Lett 13:2809–28113
63. Li Y, Baghernejad M, Qusiy, Al-G, Zsolt Manrique D, Zhang G, Hamill J, Fu Y, Broekmann P, Hong W, Wandlowski T, Zhang D, Lambert C (2015) Three-state single-molecule naphthalenediimide switch: integration of a pendant redox unit for conductance tuning. Angew Chem Int Ed. 54:1–5
64. Osorio HM, Catarelli S, Cea P, Gluyas JBG, Hartl F, Higgins SJ, Leary E, Low PJ, Martin S, Nichols RJ, Tory J, Ulstrup J, Vezzoli A, Zeng Q, Costa Milan D (2015) Electrochemical single-molecule transistors with optimized gate coupling. J Am Chem Soc 137:14319–14328
65. Lee W, Kim K, Jeong W, Zotti LA, Pauly F, Cuevas JC, Reddy P (2013) Heat dissipation in atomic-scale junctions. Nature 498:209–213
66. Temirov R, Lassise A, Anders FB, Tautz FS (2008) Kondo effect by controlled cleavage of a single-molecule contact. Nanotechnology 19:065401
67. Schull G, Dappe YJ, González C, Bulou H, Berndt R (2011) Charge injection through single and double carbon bonds. Nano Lett 11:3142–3146
68. Schmaus S, Bagrets A, Nahas Y, Yamada TK, Bork A, Bowen M, Beaurepaire E, Evers F, Wulfhekel W (2011) Giant magnetoresistance through a single molecule. Nature Nanotechnol 6:185–189
69. Kitaguchi Y, Habuka S, Okuyama H, Hatta S, Aruga T, Frederiksen T, Paulsson M, Ueba H (2015) Controlled switching of single-molecule junctions by mechanical motion of a phenyl ring. Beilstein J Nanotechnol 6:2088
70. Lang ND (1995) Resistance of atomic wires. Phys Rev B 52:5335–5342
71. Galperin M, Ratner MA, Nitzan A, Troisi A (2008) Nuclear coupling and polarization in molecular transport junctions: beyond tunneling to function. Science 319:1056–1060
72. Emberly E, Kirczenow G (1998) State orthogonalization by building a Hilbert space: a new approach to electronic quantum transport in molecular wires. Phys Rev Lett 81:5205–5209
73. Tröster P, Schmitteckert P, Evers F (2012) Transport calculations based on density functional theory, Friedel's sum rule, and the Kondo effect. Phys Rev B 85:115409
74. Thygesen KS, Rubio A (2007) Non-equilibrium GW approach to quantum transport in nano-scale contacts. J Chem Phys 126:091101
75. Koch J, von Oppen F (2005) Franck-Condon Blockade and Giant Fano Factors in Transport through Single Molecules. Phys Rev Lett 94:206804
76. Burzurí E, Yamamoto Y, Warnock M, Zhong X, Park K, Cornia A, van der Zant HSJ (2014) Franck–Condon blockade in a single-molecule transistor. Nano Lett 14:3191–3196
77. Perrin ML, Frisenda R, Koole M, Seldenthuis JS, Celis Gil JA, Valkenier H, Hummelen JC, Renaud N, Grozema FC, Thijssen JM, Dulić D, van der Zant HSJ (2014) Large negative differential conductance in single-molecule break junctions. Nat Nanotechnol 9:830–834
78. Lee H-W (1999) Generic transmission zeros and in-phase resonances in time-reversal symmetric single channel transport. Phys Rev Lett 82:2358–2361
79. Solomon GC, Andrews DQ, Goldsmith RH, Hansen T, Wasielewski MR, Van Duyne RP, Ratner MA (2008) Quantum interference in acyclic systems: conductance of cross-conjugated molecules. J Am Chem Soc 130:17301
80. Guedon CM, Valkenier H, Markussen T, Thygesen KS, Hummelen JC, van der Molen SJ (2012) Observation of quantum interference in molecular charge transport. Nat Nanotechnol 7:305–309
81. Ballmann S, Härtle R, Coto PB, Elbing M, Mayor M, Bryce MR, Thoss M, Weber HB (2012) Experimental evidence for quantum interference and vibrationally induced decoherence in single-molecule junctions. Phys Rev Lett 109:05680
82. Guha S (2015) Moore's Law turns 50, but will it soon cease to exist? Fortune 19 Apr 2015 http://for.tn/1PYZsVa
83. Joachim C, Gimzewski JK, Aviram A (2000) Electronics using hybrid-molecular and mono-molecular devices. Nature 408:541–548

84. Webb RA, Washburn S, Umbach CP, Laibowitz RB (1985) Observation of h/e Aharonov-Bohm oscillations in normal-metal rings. Phys Rev Lett 54:2696
85. van der Molen SJ, Liljeroth P (2010) Charge transport through molecular switches. J Phys Condens Matter 22:133001–133001
86. Capozzi B, Xia J, Adak O, Dell EJ, Liu Z-F, Taylor JC, Neaton JB, Campos LM, Venkataraman L (2015) Single-molecule diodes with high rectification ratios through environmental control. Nat Nanotechnol 10:522–528
87. Dundas D, McEniry EJ, Todorov TN (2009) Current-driven atomic waterwheels. Nat Nanotechnol 4:99–102
88. Lü J-T, Brandbyge M, Hedegård P (2010) Blowing the fuse: Berry's phase and runaway vibrations in molecular conductors. Nano Lett 10:1657–1663
89. Kaliginedi V, Rudnev AV, Moreno-García P, Baghernejad M, Huang C, Hong W, Wandlowski T (2014) Promising anchoring groups for single-molecule conductance measurements. Phys Chem Chem Phys 16:23529–23539
90. Cahen D, Kahn A (2003) Electron energetics at surfaces and interfaces: concepts and experiments. Adv Mater 15:271–277
91. http://www.chem.ualberta.ca/~mccreery/media.html
92. Ho PKH, Kim J-S, Burroughes JH, Becker H, Li SFY, Brown TM, Cacialli F, Friend RH (2000) Molecular-scale interface engineering for polymer light-emitting diodes. Nature 404:481–484
93. Busche C et al (2014) Design and fabrication of memory devices based on nanoscale polyoxometalate clusters. Nature 515:545–549
94. Zhu H et al (2015) Redox-active molecular nanowire flash memory for high-performance and high-density non-volatile memory applications. ACS Appl Mater Interfaces 7:27306–27313
95. Heath JR, Kuekes PJ, Snider GS, Williams RS (1998) A defect-tolerant computer architecture: opportunities for nanotechnology. Science 280:1716–1721
96. Green JE et al (2007) A 160-kilobit molecular electronic memory patterned at 10^{11} bits per square centimetre. Nature 445:414–417
97. Parkin SSP et al (1999) Exchange-biased magnetic tunnel junctions and application to nonvolatile magnetic random access memory. J Appl Phys 85:5828–5833
98. Perrin ML, Galan E, Eelkema R, Grozema F, Thijssen JM, van der Zant HSJ (2015) Single-molecule resonant tunneling diode. J Phys Chem C 119:5697–5702
99. Li Q, Mathur G, Gowda S, Surthi S, Zhao Q, Yu L, Lindsey JS, Bocian DF, Misra V (2004) Multibit memory using self-assembly of mixed ferrocene/porphyrin monolayers on silicon. Adv Mater 16:133–137
100. Zhao Q, Luo Y, Surthi S, Li Q, Mathur G, Gowda S, Larson PR, Johnson MB, Misra V (2005) Redox-active monolayers on nano-scale silicon electrodes. Nanotechnology 16:257–261
101. Ullmann K, Coto PB, Leitherer S, Molina-Ontoria A, Martín N, Thoss M, Weber HB (2015) Single-molecule junctions with epitaxial graphene nanoelectrodes. Nano Lett 15:3512–3518
102. Jia C, Ma B, Xin N, Guo X (2015) Carbon Electrode–Molecule junctions: a reliable platform for molecular electronics. Acc Chem Res 48:2565–2575
103. Cui A, Dong H, Hu W (2015) Nanogap electrodes towards solid state single-molecule transistors. Small 11:6115–6141
104. Xiao X, Xu B, Tao N (2004) Conductance titration of single-peptide molecules. J Am Chem Soc 126:5370–5371
105. Ohshiro T, Matsubara K, Tsutsui M, Furuhashi M, Taniguchi M, Kawai T (2012) Single-molecule electrical random resequencing of DNA and RNA. Sci Rep 2:501
106. Ohshiro T, Tsutsui M, Yokota K, Furuhashi M, Taniguchi M, Kawai T (2014) Detection of post-translational modifications in single peptides using electron tunnelling currents. Nat Nanotechnol 9:835–840
107. Livshits GI et al (2014) Long-range charge transport in single G-quadruplex DNA molecules. Nat Nanotechnol 9:1040–1046
108. Zhao Y et al (2014) Single-molecule spectroscopy of amino acids and peptides by recognition tunnelling. Nat Nanotechnol 9:466–473

109. Kubatkin S, Danilov A, Hjort M, Cornil J, Brédas J-L, Stuhr-Hansen N, Hedegård P, Bjørnholm T (2003) Single-electron transistor of a single organic molecule with access to several redox states. Nature 425:698–701
110. Kaasbjerg K, Flensberg K (2008) Strong polarization-induced reduction of addition energies in single-molecule nanojunctions. Nano Lett 8:3809
111. Wolf SA, Awschalom DD, Buhrman RA, Daughton JM, Molnár S, von Roukes ML, Chtchelkanova AY, Treger DM (2001) Spintronics: a spin-based electronics vision for the future. Science 294:1488–1495
112. Vardimon R, Klionsky M, Tal O (2015) Indication of complete spin filtering in atomic-scale nickel oxide. Nano Lett 15:3894–3898
113. Murphy P, Mukerjee S, Moore J (2008) Optimal thermoelectric figure of merit of a molecular junction. Phys Rev B 78:161406
114. Yuan L, Nerngchamnong N, Cao L, Hamoudi H, del Barco E, Roemer M, Sriramula RK, Thompson D, Nijhuis CA (2015) Controlling the direction of rectification in a molecular diode. Nat Commun 6:6324
115. Braun E, Eichen Y, Sivan U, Ben-Yoseph G (1998) DNA-templated assembly and electrode attachment of a conducting silver wire. Nature 391:775–778
116. Tuccitto N, Ferri V, Cavazzini M, Quici S, Zhavnerko G, Licciardello A, Rampi MA (2009) Highly conductive $\sim$40-nm-long molecular wires assembled by stepwise incorporation of metal centres. Nat Mater 8:41–46