

Molecular Electronics

1 Introduction

The evolution of microelectronics into nanoelectronics and the requirements for future developments of logic circuits have been discussed in the Introduction to Part III. As we have seen there, the ongoing feature size reduction of Si-based technology will run into severe physical and economic limitations in the long term. Several potential alternatives to supplement or to replace this technology have been described in Chapters 13 to 19, each of which is based on a typical class of materials. The subject of this chapter is the ultimate miniaturization of logic circuits by utilizing single molecules which would act as electronic switches and storage elements [1]. Molecules in this context are considered as small, typically organic molecules. These molecules are several orders of magnitude smaller than present feature sizes. They may be tailor-made by chemical synthesis and their physical properties are tunable by their structures (see Chapter 5). In addition, they have the potential to organize themselves on surfaces to regular 2-D patterns as well as to well-defined 3-D supramolecular objects. In fact, they appear to be the ideal building blocks for designing future high-density electronic devices. Therefore, in visionary concepts it has already been predicted that complete systems for information processing may be built from basic functional units consisting of molecules acting as logic devices. This idea of using molecules to perform electronic functions was born in 1974. Aviram and Ratner suggested that a molecule with a donor-spacer-acceptor structure would exhibit a diode-like I - V characteristic similar to a traditional semiconductor pn-diode (in which the *spacer* is given by the depletion space charge region at the pn interface) [2]. At this time, any realization of a molecular device was completely unfeasible and their suggestion was solely based on theoretical assumptions. However, it marks the origin of the progressively developing research area entitled today *Molecular-Scale Electronics* or *Molecular Electronics*. In the literature the latter term is used for two very different approaches, which must be distinguished to prevent possible confusion. The main differences are sketched in Figure 1.

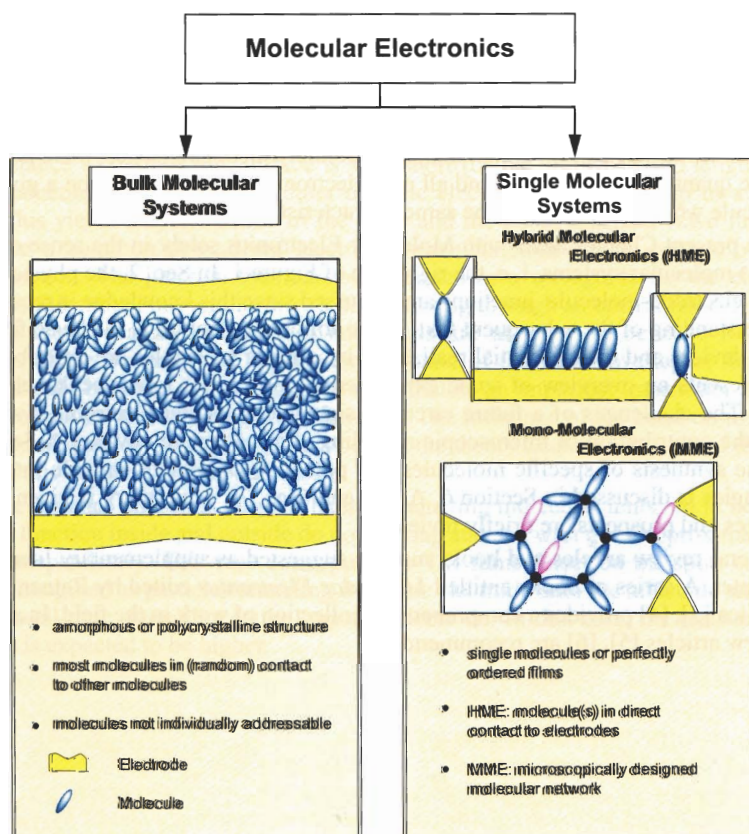


Figure 1: Sketch of the definition of conventional bulk molecular systems and single molecular systems. Only the latter is treated in this Chapter.

Bulk Molecular Systems for electronic devices are based on organic compounds with specific dielectric or electronic conduction properties. The organic compounds consist of small molecules, oligomers, or polymers and have found application in devices such as liquid crystal displays (Chap. 37), organic light-emitting diode displays (Chap. 38), and soft plastic transistors (Introduction to Part III). The volume of the organic compounds in these devices shows an amorphous or polycrystalline, often textured structure. The characteristic dimensions are much larger than the sizes of the molecules (as sketched in Figure 1, left side). Consequently, most of the molecules are in (arbitrary) contact to other molecules, instead of being directly contacted by external electrodes. At the electrode interface, a huge ensemble of molecules is contacted by a typically inorganic, electronically conducting phase.

Single Molecular Systems, in contrast, aim at individual contact to single molecules or small arrays of identical and perfectly ordered molecules. This approach differs radically from the bulk molecular system approach, as it tries to utilize the physical properties of single molecules for nanosized electronic devices. Due to the extreme difficulties in contacting and manipulating single molecules, research work during the first period according to the suggestions of Aviram and Ratner was focused on theoretical models and on studies of the electronic properties of molecular structures in solution or in bulk material. In recent decades, the invention and development of scanning probe techniques and many advances in micro- and nanotechnology have allowed the manipulation and operation on the level of small numbers or even a single molecule. The single-molecular systems approach (as sketched in Figure 1, right side) may be subdivided into hybrid molecular electronic (HME) devices and mono-molecular electronic (MME) devices [5]. HME systems are characterized by organic molecules directly contacted by inorganic electrodes. In the case of three-terminal devices, the gate electrode are of an inorganic nature, too. The HME approach is used to study and to manipulate individual molecules in test devices (see Section 4) and may provide the first platform for the integration of single molecular systems into contemporary high-density circuits. The vision of the MME approach reaches much further. It is based on the idea that all major functions of logic circuits can be integrated into molecules which are individually connected to each other. MME systems would need electrode contacts only for data exchange with the outside world and for an energy supply.

It should be mentioned that the use of small *organic* molecules shows an inherent advantage over small *inorganic* clusters, i. e. nanosized clusters of metal or semiconductor. Any object of few nm in size or smaller shows discrete (quantum) energy levels instead of energy bands which characterize the solid-state on a large scale. These energy levels will be crucial for the electronic properties of the nanosized devices made from these objects. Inorganic clusters made by self-assembly techniques or cutting-edge lithography and patterning will differ slightly in the number of atoms they consist of, and this scatter will be reflected in a scatter of their quantum energy levels. For future nanoelectronic devices, this scatter may be too large to be tolerated. On the other hand, organic molecules of a given compound are absolutely identical. Hence, there is no scatter in the quantum energy levels and all nanoelectronic functions based on a given type of molecule would show exactly the same characteristics.

The present Chapter deals with Molecular Electronics solely in the sense of single (organic) molecular systems, i. e. the right side of Figure 1. In Sec. 2, the physical properties of electrode-molecule junctions are discussed since this knowledge is required for the understanding of the subsequent text. In the following Section 3, the basic functions of logic devices and their potential realization by organic molecules are described. Section 4 presents an overview of some experimental approaches to molecular electronic devices. The challenges of a future circuit design for molecular electronic systems as well as the contribution of microscopic modeling and theory are covered in Section 5, while the synthesis of specific molecules and potential routes into suitable integration technologies is discussed in Section 6. At the end (Sec. 7), a summary is given and the challenges and prospects are briefly reviewed.

Several review articles and books may be suggested as supplementary literature to this chapter. A series of books entitled *Molecular Electronics* edited by Ratner, Aviram and Mujica [3], [4] provides a comprehensive collection of work in the field. In addition, the review articles [5], [6] are recommended.

2 Electrodes and Contacts

A basic requirement for molecular electronics is the connection of the molecule to the outside world. If we want to drive a current through individual molecules, we need an electrode pair with nanometer-sized spacing to contact them. If we are interested in molecular films, again we need contact electrodes which must be controlled on the scale of atomic length scales. The usual way is to use metallic or semiconducting electrodes, which yield hybrid (HME) devices. In the future, the replacement of metallic electrodes by molecular wires might be investigated (MME).

It turns out that the nature of the electrodes is also of importance for the electronic properties of the device. A molecule which is closely connected to an electrode has very different properties from a molecule in solution. Two main groups of links between molecules and solids can be distinguished: **covalent bonds** and **van der Waals interaction**.

A frequently used and up to now probably the best investigated covalent link is the bond between a thiol (sulfur) group on the molecule and a Au substrate. Au is favorable due to its proper and non-oxidizing surface. The thiol endgroup is one of the rather rare functionalities which form covalent bonds with the noble metal gold. Further requirements are good stability of the bond at room temperature, which must be, however, loose enough to allow for self-assembly (i.e. to rearrange continuously until finally a completely ordered monolayer of molecules is formed). Other combinations like Se-Au or S-Ag have already been investigated as members of this family. Molecules with hydroxy groups are used on SiO₂ and TiO₂ substrates. Such couplings are of particular interest due to the use of these materials in traditional microelectronics and hence may form a bridge between the fields. However, they lack the advantage of subsequent self-organization of the molecules, due to the large stability of the covalent bond formed. Covalent bonds lead to a mechanically fairly stable and resistant connection between the molecule and the substrate.

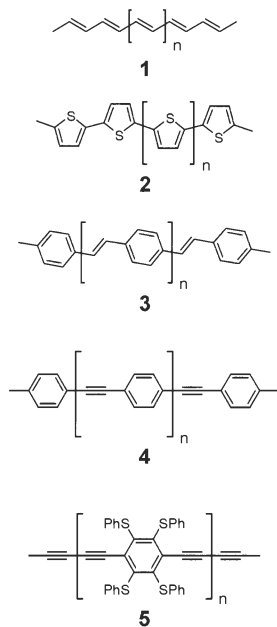
Van der Waals interaction acts in particular between Langmuir-Blodgett (LB) films of organic lipophiles and planar substrates. This technique results in very well organized films with the advantage of substrate diversity: the only requirement is a planar surface with appropriate wetting properties, i.e. a designated lipophilic or hydrophilic characteristic (depending on the type of molecules and the desired orientation). While for some types of molecules LB films might be suitable, in other cases they suffer from poor long-term stability due to the weakness of the Van-der-Waals interactions. A successful example will be discussed in Section 4.2: a LB-film sandwiched between two electrodes displays the characteristics of a (reconfigurable) switch. In other cases, electronic components with molecular building blocks require the stability of covalent linkages rather than the weak van der Waals bound interfaces.

These different contacts types also correspond to different electron transport mechanisms. Imagine a molecule with a *conductive* inner part (this can be realized with extended, *delocalized* π -electron systems, see Chapter 5) connected to a gold electrode. If the distance to the metallic surface is very short (of the order of bond lengths), the inner conducting orbitals and the outer metallic electronic states overlap to a certain extent. This yields a hybridisation of the inner and the outer extended wave functions and hence a common delocalized electronic wave function which extends over the whole junction. The junction then can be imagined as a waveguide for the electrons which are transmitted in a similar way to light passing through an optical fiber. This case is, for example, realized when thiol endgroups are attached to benzene rings: the π -orbitals of the benzene and the conduction band of the metal overlap at the sulfur atom. It should be noted that the sulfur is nevertheless an imperfect transmitter and acts as a bottleneck for the extended wave function. The influence of the bond on the molecule is complicated and not fully understood. In the theory Section 5.1 some of the challenges of this question will be addressed.

If the distance chosen is large or badly-conducting molecular units are in between, the wave function inside and outside do not overlap and can with good approximation be treated independently. This case corresponds to LB films. Electron transport can then better be imagined as particles tunneling from one electrode onto the molecule and, after a short dwell time, tunneling to the opposite electrode. In this case, the resistance per molecule is expected to be higher.

3 Functions

Wires:
conjugation active motives



Insulators:
conjugation passive motives

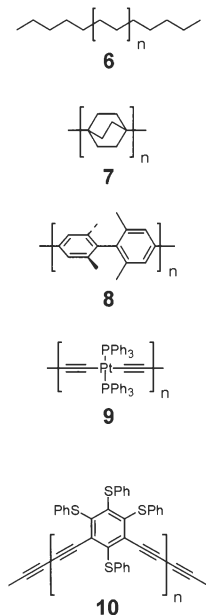


Figure 2: Molecular structural motives described in the text. Motives 1-5 are delocalized conjugated systems with the potential to act as molecular wires. Motives 6-10 are barely conjugated - even so in the case of 7-10 still rigid - systems, rather acting as insulating spacers.

The visionary concept of *Molecular Electronics* in terms of HME and MME is more than the usage of molecular structures in electronic circuits. The perspective that the electronic properties of a device may be adjusted by design of the chemical structure is the real beauty of the approach. Early investigations have already demonstrated the strong interdependence of chemical structure and electronic transport properties of integrated molecules. Further, a more molecular junction should also be tunable by other stimuli e.g. voltage, light, or magnetic fields. Thereby a whole set of functions can be embedded in a circuit by appropriate choice of the molecule. This section gives a first impression of the functions and properties that are approachable by molecular structures. These functions based on electron transport properties through molecular structures have already been investigated without integrating molecules into electronic circuits, but in solution or in the solid materials. In the last decades numerous compounds consisting of a functional unit bridging two redox-active centers have been synthesized and investigated spectroscopically and electrochemically. Most of the chemical structural knowledge and working principles of the functional units presented in this chapter has been gathered by such experiments in solution and only a few experiments have shown the validity of the same concepts for individual contacted molecules.

3.1 Molecular Wires, Insulators, and Interconnects

The most basic electronic function is a wire, a one-dimensional object that allows the transport of electric charge [7]. Transferred to a molecular scale, of particular interest are rod-like structures that transport electrons from one end to the other [8]. Electron transport is expected to take part through the frontier orbitals of a molecule, as these should be closest to the Fermi levels of the electrodes (see Sec. 5.1). In general, with increasing size of the π -system the energy difference between the frontier orbitals decreases and hence the energy difference to the Fermi level of the electrode. Promising candidates as molecular wires are therefore large delocalized π -systems. Structural motives that allowed the design of chains with delocalized π -systems were studied extensively in solution [9]. The simplest example of such a chain is polyene 1 (for the following molecules, cf. Figure 2) consisting of an alternating sequence of single and double bonds leading to a π -system over the whole length [10]. Many other examples consisting of aromatic building blocks like polybenzene [11], polythiophene 2 [12], polypyrrole and combinations of aromatic building blocks with conjugated double or triple bonds like polyphenylenevinylene 3 [13] or polyphenyleneethynylene 4 [14] were extensively studied. The enormous developments in nanoscale manipulations down to a single atom level, made it possible to investigate the electric current through selected π -systems, on surfaces or between electrodes, as will be discussed in detail in section 4 of this chapter. An experiment that illustrates the concept nicely is the incorporation of protruding rigid π -systems as molecular rods out of a self-assembled monolayer (SAM) of an thioalkane in Ref. [15] (Sec. 4.3). This first conductance investigations of single molecules demonstrated substantial differences in electron transport properties between the rod and the thioalkane SAM emphasizing the concept of delocalized π -systems as molecular wires.

Conductance is not always the property which has to be optimized. The opposite property, a rather insulating molecular structure, is of similar importance for particular applications. The very first HME-device considered, the rectifier by Aviram and Ratner, is based on a donor and an acceptor π -system linked together by a spacer [2]. They suggested a rigid adamantyl cage 7 as a non-conjugating linker between both π systems which was expected to behave as an insulating molecular unit. The choice of the spacer will be very important, as it has to be sufficiently insulating to preserve the energy differences between the π systems, but still allows to some extent electron transport. In this particular case, the authors suggested electron transport by tunneling through the insulating structure. Structural motives not consisting of delocalized π -systems are in general poor conductors but reasonably good insulators. However, on a molecular scale, the rigidity of the structure is of similar importance to prevent short circuiting of the separated units through space. Rigid molecular structures restricted to non-conjugating systems are rather limited. The above-mentioned adamantyl structure meets the conditions but is synthetically quite demanding. Alkanes 6 are known for their insulating properties, but lack the required rigidity. π -Systems meet the rigidity conditions but have already discussed as good conductors. However, the delocalisation of the π -system depends strongly on the torsion angles between the subunits. Two neighboring subunits with perpendicular π -systems reduce their electronic communication and, hence, the

connecting single bond between them becomes a rigid and insulating connection on a molecular scale, as is the case for the tetramethylsubstituted biphenyl building block **8**. The transparency for electrons through a benzene core also depends on the relative positions of the linkages. While *ortho*- and *para*-connections are conjugation-active linkers, the *meta*-position is conjugation-passive [16]. This has been shown, for example, in the comparison of *para*-diacetylene connected thiophenyl-substituted benzenes **5** and the corresponding *meta*-connected building block **10** [17]. Another approach to meet the required rigidity and electronic passivity is the use of metalorganic complexes as linkers. The potential of this approach has already been demonstrated on a single-molecule level by the investigation of a *trans*-acetylene platinum(II) molecule **9**, which turned out to display the characteristics of a single molecule insulator, as will be discussed below (Section 4.2) in detail [18]. An additional motivation for using metal centers as connectors is the adaptability of the electronic transparency by the choice of the linking metal center, raising hopes of a rich future construction kit consisting of tailor-made linkages based on metal ions. An overview of molecular building blocks for rigid rods is given by Schwab, Levin and Michl [19].

3.2 Diodes

As already mentioned several times in this chapter, the field of *Molecular Electronics* is closely related to the function of a diode, as was the first hypothetical function described of the field. In 1974 Aviram and Ratner described their visionary HME device as a molecule **11** between a pair of electrodes, performing the function of a rectifier. The working principle they suggested is based on the difference in energy of the frontier orbitals of two separated donor- and acceptor- π -systems, as shown schematically in Figure 3. To transfer electrons from the cathode to the acceptor and subsequently from the donor to the anode should be feasible at a smaller applied voltage than to transport electrons in the opposite direction. As discussed in the section 3.1 above, the donor- and acceptor π -system of the molecule is separated by a spacer, that preserves the energy differences of the frontier orbitals between both π -systems but allows to some extent electronic transport, as an electric conduction through the device shows a preferential direction.

The realization of this concept however, turned out to be difficult. The suggested molecule has a defined working direction and therefore its orientation between the electrodes is essential. This may be neglected with a test system based on a single molecule approach, as the orientation of a single molecule in an HME device may be adjusted by the wiring of the electrodes. However, to contact single molecules is still a challenge, as we will see in section 4. Therefore, first efforts were focused on films consisting of a single molecular layer. In these films it is crucial, that all molecules are lined up in the same direction, as a random orientation would equalize the directional effects from the individual molecules. Packing effects in a Langmuir-Blodgett (LB) film results in perfectly oriented molecules. With this technique, LB-films consisting of donor-spacer-acceptor molecules **12** (Figure 4) were deposited on metallic surfaces as electrodes and subsequently covered by a second metallic top electrode, as will be discussed in more detail in section 4.3 [20]. Such devices displayed rectifying properties, but lacked the required stability due to the weak van-der-Waals interaction between the electrode and the molecules. However, it was the first attempt to verify the principle of an electronic device with its functionality based on a molecular structure. But was the difference in voltage threshold really due to the molecular structure? These devices consist of a tailor-made molecular structure consisting of donor-spacer-acceptor-alkyl chain. The alkyl chain is required for the LB-film formation. While in the final device the donor is deposited directly onto the electrode surface, the acceptor is separated from the top electrode by a layer of alkyl chains. The observed differences could be explained as a consequence of the different contacts of the LB-film to the two electrodes as well as by an effect of the separated donor and acceptor in the molecular structure. Moreover the two electrodes consisted of different metals and only very recently were findings on such a device published, that was made of two Au electrodes [21]. The nature of the contact realisation is at least of equal importance as the molecular structure in between [22]. In the case of sandwiched LB-films between two electrodes, the contacts to both electrodes are Van-der-Waals interactions, but to rather different molecular substructures. Is the interaction with the electrode on either sides of a different nature, an even stronger dependence on the current direction through the device is expected.

Another interesting device was proposed by Reed and Tour [23]. The rod like molecule **13** (cf. Figure 4) with a thiol function at one end was immobilized on a small Au surface in a Si_3N_4 pore – which yielded a self-assembled molecular film (SAM). This

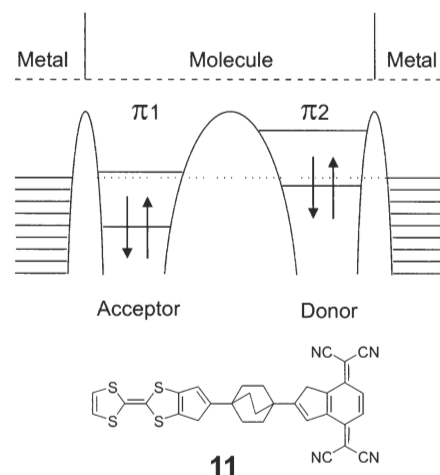


Figure 3: The first approach to molecular electronics [2]. Molecules with a donor and an acceptor group, separated by an insulating spacer, are predicted to behave as diodes. The upper panel displays the electron energies in the system, when no bias voltage is applied: In the metallic electrodes outside, electrons are filled up to the Fermi energy. The π -systems of the donor and acceptor units are confined in two potential wells. If a positive voltage is applied, the potential of the left lead is slightly increased and the potential of the right lead is correspondingly lowered: current can flow from the left to LUMO1, then to HOMO2 and further to the right electrode, going towards lower energies at each step. If the opposite voltage is applied, conduction takes place only at much higher voltages. This is the behavior of a diode with the favourable current direction from the acceptor to the donor.

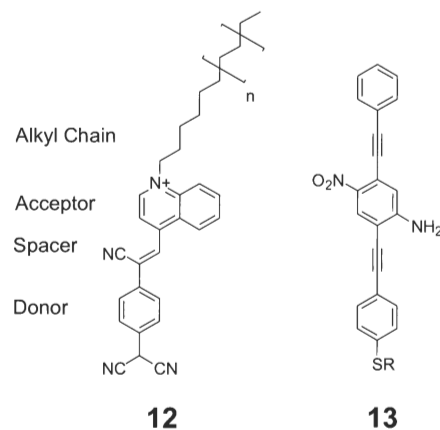


Figure 4: The LB-Film molecule **12** and the rod-like molecule **13**.

processes	example of bistable systems
redox process	
configuration change	
conformation change	
electronic excitation	
magnetic spin orientation	
logic states	"0" "1"

Figure 5: Illustration of bistable molecular structures.

- (a) redox states, where A denotes an acceptor group and D is a donor group of the molecule;
 (b) configurations obtained by a re-arrangement where Z is the wandering group;
 (c) example of cis and trans conformations;
 (d) ground state A and excited state A* of a molecule;
 (e) parallel and anti-parallel spin states within a molecule.

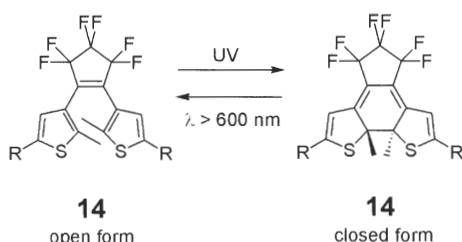


Figure 6: The light-triggered switch by Masahiro Irie [26].

SAM was subsequently covered with a Au electrode. The molecular rods were covalently bonded through the S-group to the Au bottom electrode while the linkage to the Au top electrode was undefined. In addition to the diode characteristic, the device displayed a **negative differential resistance (NDR)** in the electric current. A NDR is a decrease in current caused by an increase in voltage above a certain threshold. The observed effect was temperature-dependent, reversible and reproducible. The substituents on the molecular rods turned out to be crucial for the effect. Even though the device demonstrates the potential of the concept, the nature of the effect is not fully understood yet and is the topic of current investigations.

3.3 Switches and Storage Elements

There are classes of molecules, which are stable in two different states (so-called **metastable**). As a consequence physical properties like the conductance will differ for these two states. If this difference in the conductance is sufficiently high, these molecules may be used as *molecular storage elements* if good control of the addressing and switching of the molecules is realized. Figure 5 illustrates some possibilities of such **bistable molecular switches**. (a) A reduction-oxidation (redox) process may change between neutral and ionized acceptor/donor groups of a given molecule. (b) A configuration change may take place through a reversible re-arrangement reaction. (c) A conformation change may be controlled in such a manner that both conformations are sufficiently stable at the operation temperature of the designated storage element. (d) Electronically excited states may be used in the same way, if the lifetime of state A* is made sufficiently high. (e) The idea may also be applied to spin magnetic moments, as has been shown for Mn acetate [24]. In all cases of Figure 5, the bistable switches are characterized by double well potentials concerning their energy and exhibit a **hysteresis** when driven between the two states. In many cases, more than one of the above mentioned mechanisms must cooperate to achieve the hysteretic properties. Below, for example, we will report on a molecule which undergoes a conformational change due to a redox reaction. To control (meta-) stable physical properties of molecular structures by external stimuli has fascinated researchers for a long time and several structural motives as molecular switches have been published in the last decades. The book *Molecular Switches* edited by Feringa is recommended [25] as an overview for the interested reader.

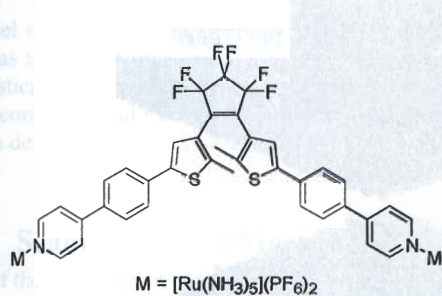
In general, molecular switches may be classified by

- the stimulus that *triggers* the switch and
- by the *property* or function that is switched.

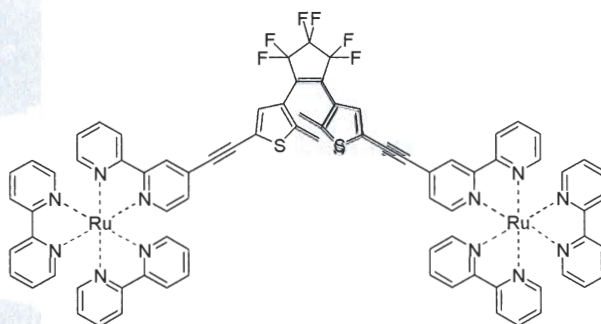
Frequently light or chemical parameters such as pH, for example, are used as **triggers** and the switched property is often a structural feature. Of particular interest in view of molecular electronic applications are systems, in which the two states of the switch display different current transport properties.

One of the best-studied examples in chemistry is the light-triggered switch by Masahiro Irie **14** [26], which is shown in Figure 6. Two methyl-thiophene units are linked with a hexafluorocyclopentene bridge in the open form of the switch. Irradiation with light in the wavelength range 200 – 380 nm leads to the closed conjugated form on the right side which is more favorable for charge transfer. Irradiation with light in the range 450 – 720 nm opens the switch back again. The potential of the switch has been studied extensively by synthetic systems possessing redox and/or photo-active units located at the thiophenes which allowed the investigation of electron delocalization over the switching structure (see Figure 7). Even though this system has been carefully studied and provides promising properties like excellent addressability and conversion into the desired switching state, the main drawback of the system is the use of light as switching trigger. For electronic applications switches that are addressable by voltage or charges are of much greater interest, as this would allow the integration of such a switching device into a nanoelectronic circuit.

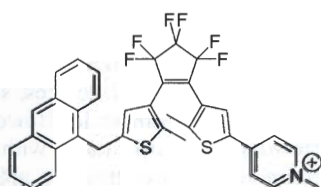
So far, only few switches fulfill these boundary conditions. An interesting approach comes from supramolecular chemistry. Rotaxanes and catenanes have been synthesized to switch as a function of an applied potential between two different states. An overview is given in the review article [27]. In particular, the catenane **15** shown in Figure 8 [28] has already been used to build up electronic memory devices [29], as we will see in Section 4.2. A catenane consists of two interlocked rings. In this particular case of two different rings, one is functionalized with two viologene units and the other with a dioxynaphthalene and a tetrathiafulvalene (TTF) unit. The interaction of the different redox



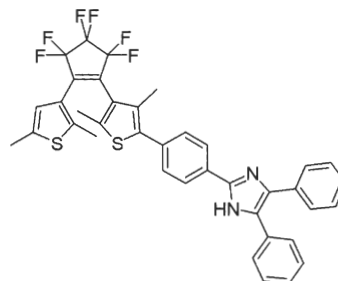
A. Fernández-Acebes, J.-M. Lehn, *Chem. Eur. J.*, **5**, 3285 (1999)



S. Fraysse, C. Coudret, J.-P. Launay, *Eur. J. Inorg. Chem.*, 1581 (2000)



J. M. Endlner, F. Effenberger, A. Hartschuh, H. Port, *J. Am. Chem. Soc.*, **122**, 3037 (2000)



K. Yagi, C. F. Soong, M. Irie, *J. Org. Chem.*, **66**, 5419 (2001)

states of these units make it possible to rotate one ring within the other. Therefore this molecule is bistable at zero voltage: it may exist in two configurations. By applying a positive potential pulse to the solution it can be set into one configuration (dioxynaphthalene unit in the viologene ring) while applying a negative potential pulse results in the other configuration (TTF unit in the viologene ring). The switching mechanism is explained in details in Figure 8. The states of the molecule can be regarded as memory bits which can be written and erased.

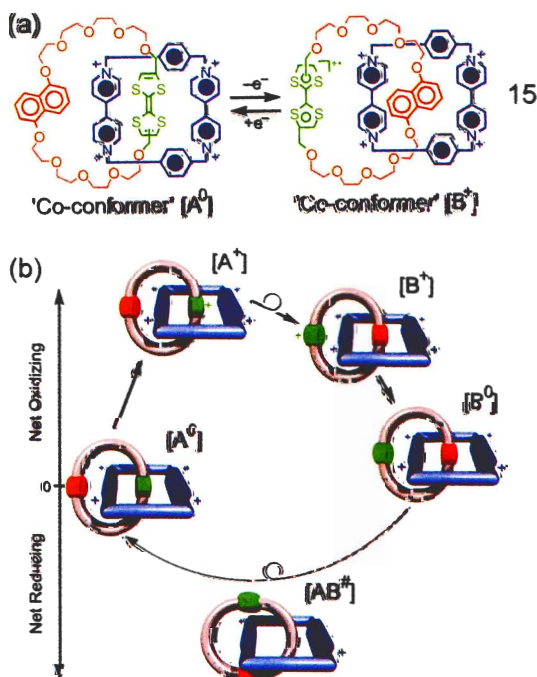


Figure 7: Examples of redox and/or photo-active units connected to the switching unit discussed in Fig. 6. The extent of interaction between the peripheral units depends on the state of the switch.

Figure 8: Hysteretic redox-triggered rearrangement of the catenane **15**. At zero bias the molecule is in the ground-state $[A^0]$ with the TTF unit between the two doubly charged viologenes. Biasing the system into the net oxidizing direction by +2V leads to an ionization of the TTF unit into state $[A^+]$. Because of electrostatic repulsion, the ring will mechanically rotate into state $[B^+]$. Reducing the bias back to zero will remove the ionization and, hence, the ground-state $[B^0]$ with the dioxynaphthalene between the two doubly charged viologenes is established. A bias pulse into the net reducing direction with an amplitude of -1.5 V reduces the two viologenes into the monocharged state $[AB^{\#}]$ which causes a preference for the TTF unit between the viologenes. Resetting the bias to zero results again in the state $[A^0]$ with the two positively charged viologenes surrounding the neutral TTF unit. (Reproduced from Collier et al. [29] with permission; copyright © 2000 by the American Association for the Advancement of Science).

Figure 9: SEM picture of a Au electrode pair on top of an Al gate electrode, which is covered by an Al_2O_3 insulator. Such a setup was used as a molecular field effect transistor [48].

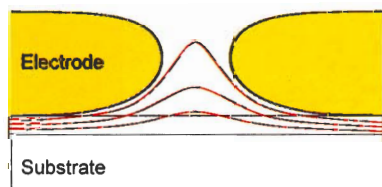
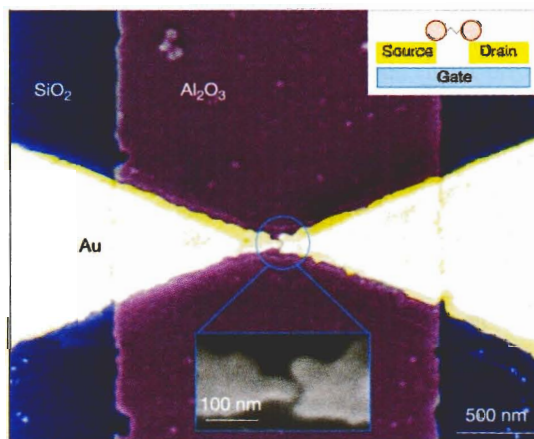


Figure 10: Scheme of an electrode gap with a buried gate electrode formed by the substrate (covered by an insulating layer). When a gate voltage is applied, the equipotential lines (red) are not homogeneous in the gap region. If the molecule is far away from the surface, high gate voltages are needed to affect the potential at the molecule's position. If the distance from the gate electrode is not well controlled, this will result in strongly varying switching voltages.

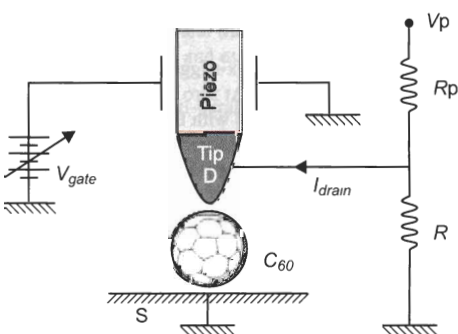


Figure 11: A nanomechanical three-terminal device [42]. The C_{60} molecule is contacted by the metallic substrate on one side, and by the STM tip from the opposite side. The steering parameter which replaces the third electrode is the force which acts on the STM tip. By pushing on the C_{60} molecule, the conductance varies by two orders of magnitude per nano-newton.

3.4 Three-Terminal Devices

While the implementation of two-terminal devices like diodes or resistive memory switches can be made on a very small scale of few nanometers or even with single molecules, it is much more difficult to obtain three-terminal devices, simply because three independent leads have to be structured on a few-nm scale. However, if one wants to build up integrated circuits (ICs) performing logic operations with traditional architectures, transistor-type devices are important because they are able to provide power amplification to the signal.

There are two possible approaches to solving the problem. One is to make a molecule with three branches, which are independently contacted by three leads. This would fit into the MME concept. However, it is an enormous challenge for lithography and will certainly involve physical phenomena much more complex than for a two-terminal molecular device. So far, no meaningful concept has been developed for this case. An HME-type approach is to place the third lead relatively far away (for example, buried in the substrate, see Figure 9), not in contact with the molecule, but able to modify the electrostatic potential inside the molecule by field effects. This has already been demonstrated [46], [48] in low-temperature experiments. The conductivity of single organometallic molecules was tuned by electrostatic gate electrodes and the properties of a *Single Electron Transistor* (cf. Chapter 16) were observed (Figure 22). The junction was switched from the Coulomb blockade regime with a strong suppression of the current to a conducting mode (which has still a high resistance: $R \sim 100 \text{ M}\Omega$). The gate voltage dependence demonstrates that indeed a single molecule could be selected in a few cases. A key issue is to make this third gate electrode sufficiently close to the molecule to enable operation at small voltages. One of the emerging problems which can be seen in Figure 10 is the reproducibility of the transistor, as the exact distance of the molecule with respect to the gate will affect the voltage necessary to switch the molecule's conductance. If, however, the molecular junction comprises of a large number of molecules, the tuning by electrostatic gating will be complicated by screening effects. The polarizability of the external molecules will weaken the field which acts on the inner molecules and the gate effect will be smeared out. This problem might be overcome by molecules which react to external stimuli with changes in the conformation, which might allow a cooperative switch of all molecules as soon as the external field reaches a certain threshold. This would involve nucleation statistics as an uncertainty.

A completely different approach was reported in Ref. [42]. C_{60} molecules were deposited on a metallic substrate and investigated with an STM. After imaging the surface and detecting where C_{60} could be found, the tip was used to simultaneously squeeze the C_{60} and measure the conductance (Figure 11). Though only two terminals (tip and surface) were present, the mechanical force on the tip added a third parameter. It turned out that the conductance could be tuned by two orders of magnitude per nano-newton. Whether this setup is able to provide power amplification to a signal depends on the development of an appropriate nano-electromechanical system used to apply the force.

4 Molecular Electronic Devices - First Test Systems

Parallel integration of single molecular structures as functional units in electronic circuits as the long-term aim of molecular electronics is still unattainable. However, first sophisticated experimental setups allow controlled assemblies or even single molecules to be contacted and their properties investigated in an applied electric current. This section is devoted to these first test systems.

4.1 Scanning Probe Methods

One of the main triggers for the enormous boom in nanoscience was the development of the scanning probe methods. Properties such as shape, size, diffusion, conductivity etc. of individual molecules on surfaces could be achieved for the first time [34]. Scanning tunneling microscopes (STM), atomic force microscopes (AFM) and similar instruments provide an enormous variety of experimental applications (Chapter 12).

If we wish to study the conduction along a rod-like single molecule on a surface, while the surface acts as one electrode and the STM tip as the opposite electrode, we have to prepare the molecules such that they stand up right on the surface. However, isolated molecules often prefer to lie flat on surfaces due to Van-der-Waals interaction. To force configurations perpendicular to the surface, tripodal attachments to the molecules has been proposed such as tetrahedral-shaped molecules in which three of the four *legs* are terminated by S-groups as 'alligator clips' [35]. Another approach makes use of a carpet of upright standing *insulating* alkanethiols to embed the *conducting* molecules under investigation. A stabilization of the position and the orientation of the sample molecules at angles between 60° and 90° to the surface was thus achieved. It should be noted that most of these experiments are in the tunnel regime, where the tip-molecule contact is not a chemical bond.

As an example, the molecular rod **16** (cf. Figure 12) is a fairly good electronic conductor, due to its conjugated π -system. To investigate its conduction properties it was embedded in a SAM matrix of electrically insulating molecules, such as dodecylmercaptan ($C_{12}H_{26}S$) as a long-chain thioalkane [30], [36]. The film preparation started with the preparation of the pure alkane SAM layer. As observed by STM, the SAM layer is organized in domains, which resemble 2-D crystals. Within one domain, the molecules are perfectly ordered. Subsequently, the SAM layer is treated in a diluted solution of **16**, which leads to a partial exchange at the Au surface. STM studies show that the exchange takes place at domain boundaries and triple points while **16** is not observed within the domains. Since STM is based on the tunneling current, which is determined by both, the thickness of the SAM layer (i.e. the length of the molecules) and the conductance of the molecules, additional physical information is needed to separate the contribution of the two properties. The combination of conventional DC-voltage STM with a microwave AC-STM (alternating current-STM) technique allowed at the same tip the two properties to be distinguished [36]. Based on this method, the topography of the SAM film was separated from the conductance mapping. In many spots (but not always), the topography maxima attributed to molecules **16**, which are approx. 0.7 nm longer than the dodecane molecules, coincide with conductance maxima.

Scanning probe methods are not limited to imaging and electrical measurements. They may also be used as a working tool in the nanometer range, as is illustrated by the following example. To circumvent the arbitrary placement of **16** in the SAM matrix, the SPM tip was used to pattern the SAM layer as sketched in Figure 13 [37]. After SAM formation on gold, the specimen was inserted into a dilute solution of **16** and NH_3 in an STM liquid cell with the exclusion of oxygen. The SAM layer can be locally removed at the tip position by applying a short voltage pulse to the substrate (Figure 13 b) in an area of 10 nm diameter. After patterning a few sites, the film was monitored by STM imaging and a filling of the pits by **16** was observed. Each pit hosts approx. 400 molecules **16**.

Another approach to direct the placement of molecules by scanning probe methods is the manipulation by mechanical forces in nanometer dimensions by AFM (Atomic Force Microscopy). Single atoms, clusters and molecules can be moved and manipulated on the sample surface by this technique [38], [39], [40]. Electrochemical deposition makes it possible to create designed and defined structures in the few nanometer regimes using an AFM-tip as the local writing electrode [41]. Such structures may soon reach molecular length scales.

Altogether, scanning probe techniques are amazingly powerful tools to investigate substrates coated with molecules. They can be used for manipulating, imaging and measuring nano-objects with the same tip. While their contribution to the comprehension of the correlation between molecular structure and physical property is outstanding, the potential of the system for upscaling to parallel integration is still currently under investigation (Chapter 28).

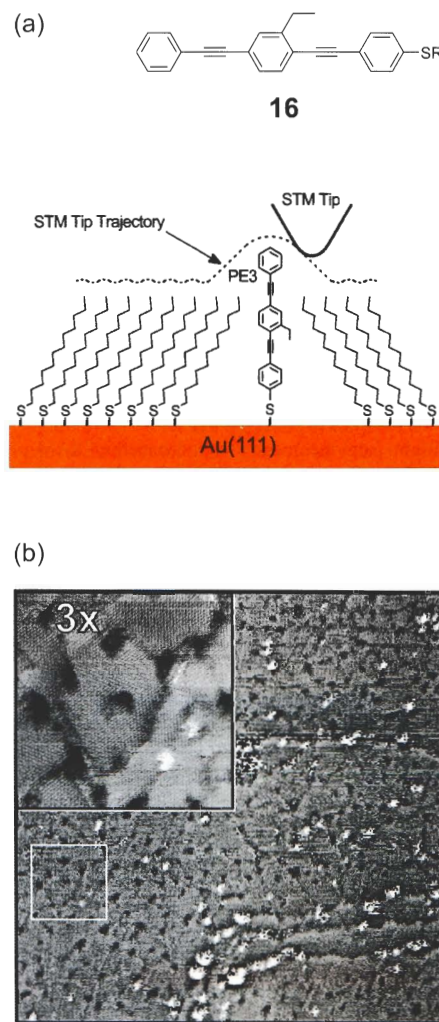


Figure 12:

(a): Protruding molecular rod **16** out of a SAM layer of dodecylmercaptan.

(b) STM picture of the sample displaying protruding rods **16** as brighter spots. Correlated maxima in the conductivity and the topology indicate the increased conductance through the molecular rods **16**. [36]

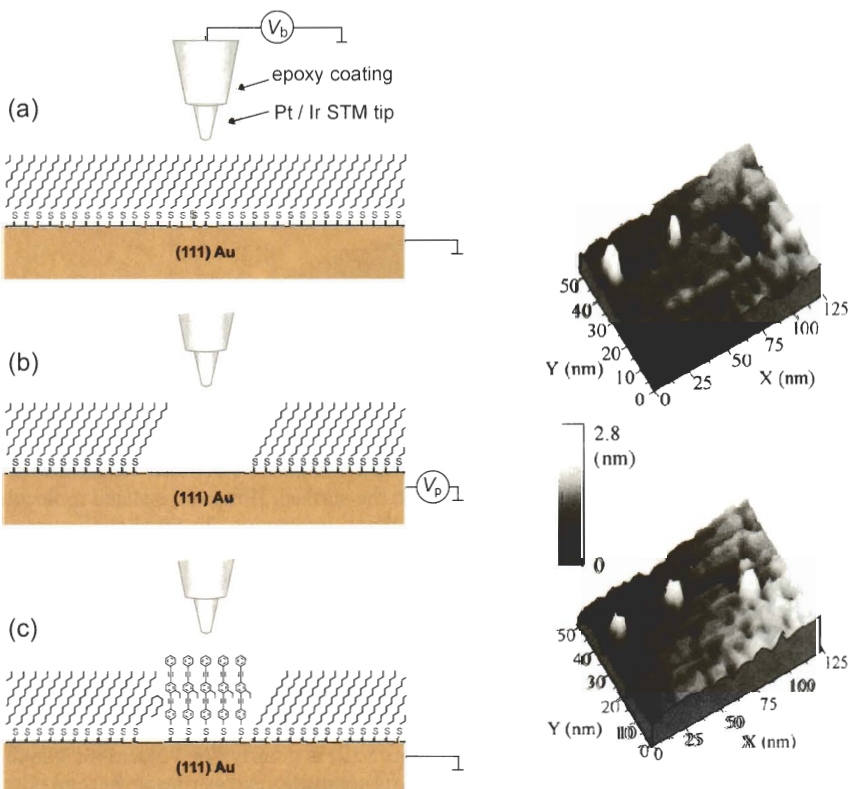


Figure 13:

Left: Illustration of the patterning of the SAM layer and the placement of electronically conducting **16** molecules in the alkanethiol matrix:

(a) normal STM imaging of the SAM surface with a tip bias V_b ;

(b) SAM removal by applying a pulse V_p to the substrate;

(c) filling of the pit by **16** molecules from the solution (adapted from Ref. [37]).

Right: (top) the image of a dodecanethiol SAM surface after consecutive patterning, three pits show two peaks indicating adsorbed **16** and one pit without adsorption; (bottom) image taken few minutes later showing adsorption onto the third remaining pit.

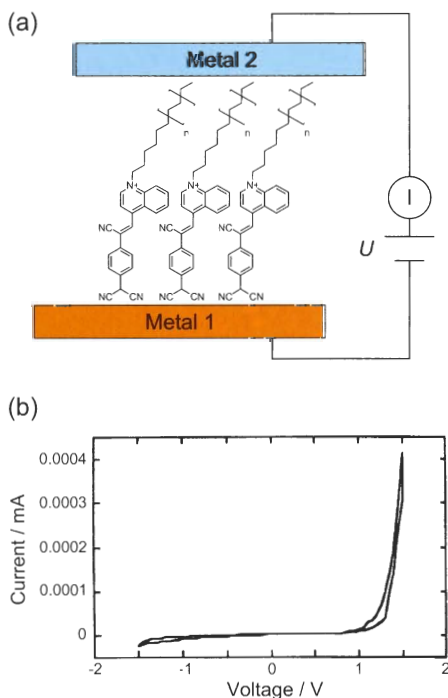


Figure 14:

(a) Schematic presentation of a rectifying device based on an LB-film of the donor-acceptor molecule **12**.

(b) The I - V curve of the sandwiched LB-monolayer displaying rectifying character.

4.2 Monomolecular Film Devices

While future devices based on single molecules are still highly challenging, devices based on molecular films are much more promising for the near term. The required films of molecules can be made available by numerous different techniques like self-assembly, vapor deposition techniques or LB films. The film may be sandwiched between two metallic leads (a bottom electrode and a subsequently evaporated top electrode). This allows a patterning of the leads by standard lithography techniques. The outcome is a 2-D architecture which can easily be combined with conventional circuits. The device can in principle be scaled arbitrarily to a few-nanometer lateral sizes. Having a large number of molecules, the I - V properties of the individual molecule are averaged out which enhances the reproducibility. A major problem with molecular film devices is defects. When the second electrode is evaporated on top of the molecular film or due to diffusion processes during the device's lifetime, metal atoms may penetrate the film and short-circuit the device. There is a need for elimination of this problem by appropriate engineering of the films. Experiments have revealed that with decreasing area covered by an electrode the probability of a defect is reduced. Several demonstration devices based on molecular films displaying a variety of physical properties like rectifying, negative differential conductance and switchable memories have been proposed. This section is only a short overview based on some prominent examples.

One of the very first examples of a device based on molecular films was the realization of the rectifying principle predicted in the seventies and demonstrated in the 1990s [49], [50], as has already been mentioned in Section 3.2. A LB film of molecules **12** consisting of an electron rich π -system as donor D linked to an electron-poor π -system as acceptor A decorated with a long alkyl tail has been sandwiched with a second top electrode (Figure 14, a). A torsion angle between the A and D π -systems reduces the overlap of the two π -systems and allows a zwitterionic ground state, $T-D^+-\pi-A^-$, where T is the hexadecyl 'tail' to support the LB film formation. It exhibits a pronounced different conductivity depending on the polarity of the voltage applied to it in an LB film as shown experimentally (Figure 14, b) [49], [50], [51] and studied theoretically [52]. A negative bias at the acceptor side triggers an intramolecular electron-transfer from the A^- side to the D^+ side of the zwitterion as the initial step of the conduction process. This is energetically more favorable than electron injection from the metal contact into the D^+ side of the molecule under reverse bias

as the initial step. The device impressively demonstrated the potential of molecular films as electronic components, but, lacked sufficient stability: The applied electric fields between the electrodes caused a reorientation of the molecules thus destroying the device.

An approach towards real integrated devices is based on the deposition of supramolecular systems like catenanes and rotaxanes on a substrate with prefabricated nanowires as bottom electrodes. For example, the electrochemically active components on the catenane rings make it possible to switch between two configurations by voltage pulses, as discussed in Section 3.3. As both configurations (which may serve as the two states of a single bit of information) differ in their tunnel currents the state of the switch can subsequently be read out with the tunnel current at low voltage (see Figure 15). This approach aims at a cross-bar random access memory with hysteretic, non-volatile molecular switches.

As explained in the Introduction to Part III, cross-bar arrays can be impressively utilized as RAM devices as well as field-programmable gate array (FPGA) based wired-logic devices. Since the cross-bar itself can not provide gain, it has to be supplemented by active devices outside or underneath the cross-bar system. Based on their cooperation on the molecular electronic variant of the Teramac concept [62], Heath [63] and Williams [64] presented different demonstrators of this concept. The fabrication starts by the deposition of either poly-Si [63] or Pt bottom electrodes [64] as parallel wires using e-beam lithography or nano-imprint techniques. Thereafter, a monomolecular film is deposited by the LB technique followed by a Ti layer as a top contact and to protect the molecular film from the subsequent integration steps. The final top electrodes (Al, Au or else) again are deposited by e-beam lithography or nano-imprint techniques. Finally the protective Ti layer is removed by etching between the top electrodes to avoid short-circuits.

In Figure 16 a section of a cross-bar array made by these technique is shown. Electrochemical switchable supramolecular systems like rotaxanes [63] and catenanes [29] have been deposited between these electrodes as LB-films. In both cases, the configuration of the supermolecules is switched by applied voltage pulses. Similar as in solution (see Section 3.3), the relative position of an interlocked ring as part of the supermolecules is assumed to be the different states of the switch. It was found that the rotaxanes employed in this concept need a relatively large footprint to show well-defined switching voltages. Obviously, the rings can not move individually if the footprint is too small. Voltages in the range from approx. 1 V to 2 V are required in the *write* operation to set the molecule into the high-resistive and low-resistive state. The *read* operation is executed at much lower voltages which do not change the resistive state of the switch and, in addition, contribute to a low power consumption of the device. The $R_{\text{on}}/R_{\text{off}}$ ratio of individual nodes ranges from approx. 3 to 10 for the Si/molecule/Ti system. The integration of pn diode junction in the Si bottom electrode wires led to a considerable suppression of cross-talk. In addition to a small memory matrix, the demultiplexer and the multiplexer for the row and column lines have been realized by wired-AND and wired-OR in order to demonstrate the successful operation of a complete system (see Figure 29 in Sec. 6.2). Furthermore, using an EXOR gate (Figure 17) in combination with the (simpler) AND gate indicated that a half-adder function can be configured from a cross-bar circuit

Between Pt bottom electrodes and Ti/Al top electrodes the series of as LB film deposited molecules were supplemented by long alkyl chain carboxylic acid. These devices displayed very promising switching properties with $R_{\text{on}}/R_{\text{off}}$ ratio of individual nodes up to 10^4 . Although in the latter case, the R_{on} value as well as the R_{off} value shows a variation of up to one order of magnitude, still a $R_{\text{on}}/R_{\text{off}}$ ratio of 10^2 remains in the worst case. However, the nature of this switching behavior is not clarified yet. As it works with rather simple molecules as well, the switching obviously is not due to a configuration change of the supermolecule in this case and the role of the molecules in this setup is not understood at the publishing date of this book.

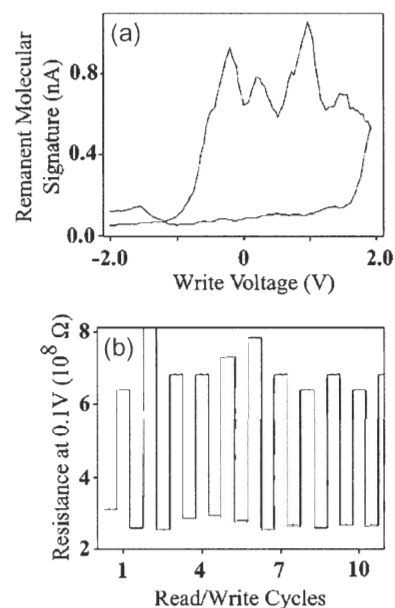


Figure 15: Switching of the catenane [56] (Figure 8). a) Molecular signature of the device upon stepwise variation of the writing voltage and read out at -0.2 eV. b) Repetitive switching of the device at room temperature. Switched with voltage pulses of -2 V and +2 V respectively and read out at +0.1 V.



Figure 16: An SEM image of a semiconductor crossbar structure utilizing molecular switch tunnel junctions. Each junction has an area of $0.007 \mu\text{m}^2$ and contains about 5000 molecules. The inter-wire separation distance was kept large so as to simplify the task of contacting this circuit to external devices for testing [63].

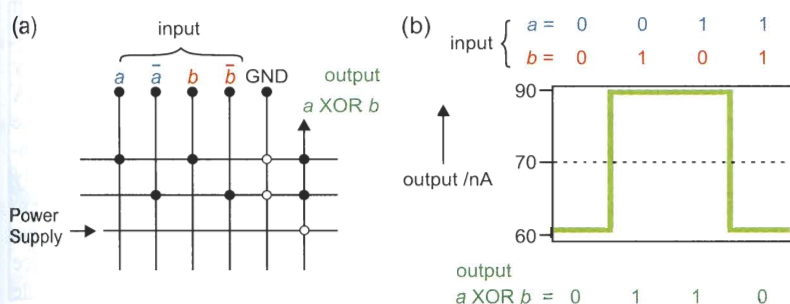
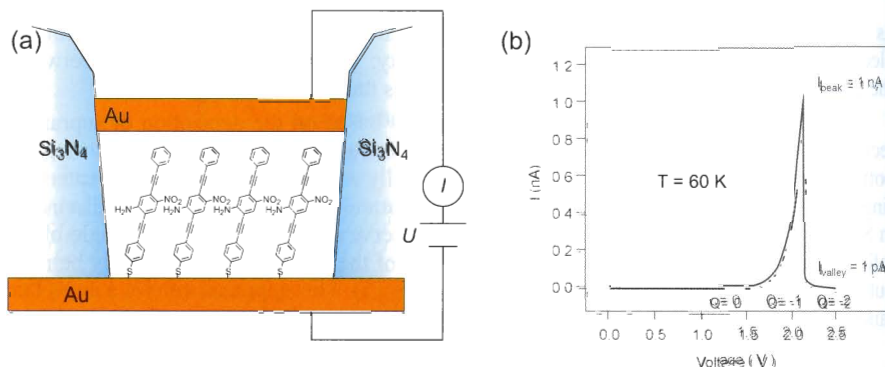


Figure 17: (a) The wiring diagram and (b) truth table of an EXOR gate. In the wiring diagram, ● represents closed switches and ○ represent open switches. The junctions that are not dotted, which would be diodes in an ideal molecular-switch crossbar circuit, are not connected. \bar{a} and \bar{b} are the complements of a and b . An AND (which is a simpler structure) and an EXOR function combine to yield a half-adder, with the EXOR representing the sum of two 1-bit numbers and the AND representing the carry. In the truth table, the green trace is the output signal recorded corresponding to four different input combinations [63].

Figure 18:

(a) Schematic presentation of the NDR-device. SAM of **13** between two Au electrodes laterally limited by Si_3N_4 walls.

(b) The I - V characteristics of the device displaying an negative differential resistance (NDR). The Q values are suggested to refer to charge (in electrons) set by the bias voltage according to the theoretical studies [55].



4.3 Nanopore Concept

Another interesting device architecture is the use of tiny holes in a silicium membrane as the well-defined surrounding of self-assembled monolayers. The processing is based on standard microtechniques [53] and starts with the formation of a suspended Si_3N_4 membrane. A 50 nm low-stress Si_3N_4 is deposited by chemical vapour deposition on both sides of a double-side polished Si-wafer, followed by an opening of the nitride coating on the back surface in an area of $400\text{ }\mu\text{m} \times 400\text{ }\mu\text{m}$. An anisotropic etch (KOH solution at 85°C) was used to remove the Si wafer and to obtain a Si_3N_4 membrane, $40\text{ }\mu\text{m} \times 40\text{ }\mu\text{m}$ in size. 100 nm SiO_2 was grown on the Si sidewalls to improve the electrical insulation. By means of e-beam lithography and RIE, a single hole of approx. 40 nm in nominal size was introduced into the membrane. The RIE rates were adapted to achieve a bowl shaped hole into the membrane, which led to a further reduced diameter of the pore on the bottom of the membrane. A Au top electrode was placed on the membrane by evaporation to fill the pore with Au. The specimen was immersed in a solution containing **13** leading to a SAM on the Au surface. After careful (low-temperature) application of the bottom Ti/Au or Au electrode, the specimens were electrically characterized. It was found that an amino and nitro substitution in the middle aryl ring leads to a strong NDR effect at 60 K with an $I_{\text{peak}}/I_{\text{valley}}$ -ratio of approximately 1000 [23], exceeding the corresponding values of semiconductor tunneling diodes (Figure 18, b). Molecules without the amino group exhibit a NDR effect at room temperature, with a peak/valley ratio of 1.5 [54]. The I - V curve is fully reversible. The nature of this strong effect is still under debate.

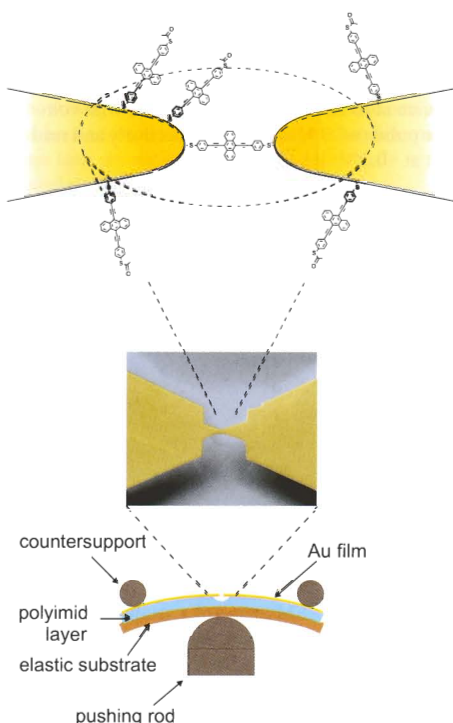


Figure 19: Scheme of a mechanically controlled break junction. On top of a bendable substrate a Au film is patterned with a freely suspended bridge in the center (see SEM micrograph in the middle panel). By bending the substrate in a three point support (lower panel: the pushing rod is driven by a motor), the Au bridge can be broken into two electrodes. By bending the substrate back and forth, the gap between the electrodes can be tuned with a distance resolution much better than Angstroms. This setup can be used to match the electrode gap precisely to the length of a molecule and finally to contact a molecule from two sides via well defined chemical S-Au bonds.

4.4 Mechanically Controlled Break Junctions

Scanning Probe methods can in principle be used to make chemical contacts to both sides of the molecule. The advantage is that images and contacts can be made with the same instrument. However, the contacts are not symmetric, because the tip and the planar surface differ in both shape and (often) material. Another disadvantage is a lack of drift stability as soon as the distance-control feedback-loop is switched off. Complementary techniques to make stable test electrode pairs are required. The use of high-resolution lithography and shadow mask techniques allows the fabrication of metallic structures with a width in the order of 10 to 20 nm. These structures are still about one order of magnitude too large for single molecules, but can serve as a starting point for new methods. The goal of further processing is to reduce the size of the lithographically fabricated structures in a controlled manner. Metallic wires with predetermined breaking points are fabricated and subsequently treated to open the hyphenation points to tiny voids. Two examples of this type are the mechanically controlled break junction technique and the electromigration technique.

First attempts to immobilize molecules between a pair of electrodes of a mechanically controlled break junction (MCB) are reported by the groups of Tour and Reed [31]. A notched gold wire was mechanically broken while it was exposed to a 1,4-dithiobenzene solution. The gold surfaces are soon covered with strongly adhering self-assembled monolayers (SAM) of the dithiol compound. After the solvent evaporated, the tips were slowly moved together until the onset of conductance was achieved. Non-linear I - V curves were measured repeatedly. Unfortunately, up to now no microscopy technique is able to observe the molecules in the junction. Hence, the only information available is the conductance data. In this case, the authors suggested that the junction is formed by only one molecule bridging the gap. However, a final proof of this hypothesis was lacking.

The use of high-resolution e-beam lithography provides access to metallic structures such as wires with much better defined predefined breaking-points than a notched gold wire. These high-quality MCBs were originally used and designed to observe single-atom junctions between metals at low temperatures [43]. Bourgoïn and co-workers first reported the immobilization of molecules in such advanced MCBs [32]. They immobilized molecular rod-like structures consisting of three thiophene units functionalized at the ends with thiols. In comparison to a rather simple theoretical model, the number of investigated molecules is assumed to be very small or even a single one. However, there are no convincing experimental arguments with regard to the number of molecules.

To resolve this ambiguity, a systematic comparison of measurements with different molecules was very useful. In this experiment, the electrode pair was prepared in the following way (similar to the previously mentioned experiment): A flexible substrate was covered with an insulating polyimide layer. A gold structure consisting of two large areas connected with a thin gold bridge has been deposited lithographically on top. Reactive ion etching removes the polyimide around the gold structure, underetches the gold bridge and leaves it freely suspended. The final structure on the substrate is shown in Figure 19. The substrate is fixed in a three point set-up that makes it possible to mechanically bend the substrate (Figure 19). In a vacuum chamber the substrate is carefully bent while the electric resistance between the two large gold areas is monitored. In this way, the thin gold bridge is elongated until it finally breaks, which is observed as an immediate increase of the resistance. Release of the bending tension allows to approach the two broken ends of the gold structure. The extremely flat architecture results in a distance resolution of the two electrodes better than a tenth of an Ångström. The set-up turned out to be ideal to immobilize molecular rods with the length in the order of a few nanometers [33].

Two molecular rigid rods **17** and **18** consisting of *para* acetylene-connected aromatic cores as delocalized π -systems, with thiol functions at each end and a length of 2 nm have been synthesized as shown in section 6.1 [44]. Both molecules were very similar concerning their length, functional endgroups, and polarizability. The main difference of both structures, however, is their spatial symmetry. Because of the symmetry plane in the center of rod **17** perpendicular to its axis (cf. Figure 20) the conductance properties are expected to be independent of the current direction and hence the differential conductance $dI/dV(V)$ should be symmetric with respect to positive/negative voltages. This symmetry is absent for rod **18** due to the acetamine and the nitro substituents at the central aromatic core. Thus, asymmetries in $dI/dV(V)$ are expected. The conductance data observed in the experiment reflected indeed the symmetry properties of the molecules (see Figure 21). This lead to the following important conclusions: First, it was proven that the junction was formed of the sample molecules (and not, for example, of undesired adsorbates). Further, the asymmetric shape of $dI/dV(V)$ which appeared randomly in approximately mirrored shape, indicated that only one molecule was contacted: an ensemble of many molecules would have resulted in a symmetric $dI/dV(V)$ because of averaging over randomly oriented molecules. Together with further considerations, this showed that indeed single molecules were observed. A very important property of single-molecule junctions was also reported in these experiments: all stable junctions displayed conductance curves which had a couple of common features, but differed nonetheless substantially. This is not surprising: as the molecule is chemically connected to both electrodes, the limitations of the molecule are not clear: the organic molecule, but also the randomly arranged metal atoms in its vicinity form the molecular wave function and determine the electronic properties of the junction. Because of small random variations in the atomistic electrode arrangements, sample-to-sample variations are observed, which are a typical and expected feature of a single-molecule experiment.

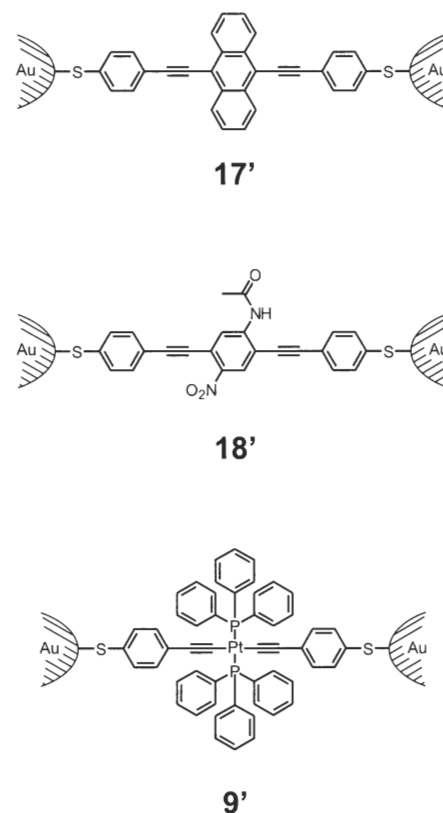


Figure 20: Rigid molecular rods **17'**, **18'** and **9'** immobilized between two gold electrodes with terminal sulfur groups.

Figure 21: I - V curves (red) and differential conductance dI/dV (blue) for a) Au-**17'**-Au and b) Au-**18'**-Au. c) I - V curve (red) for Au-**9'**-Au and simulated current with a barrier height of 2.5 eV (blue circles) are shown.

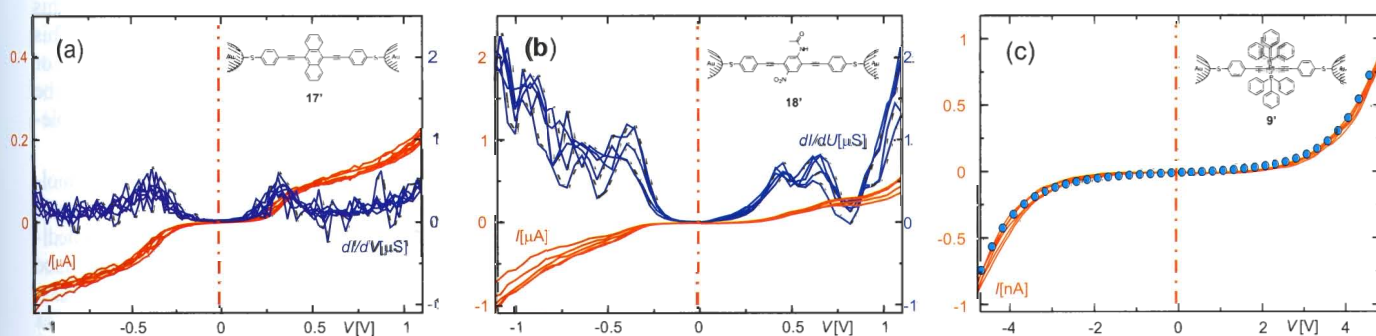
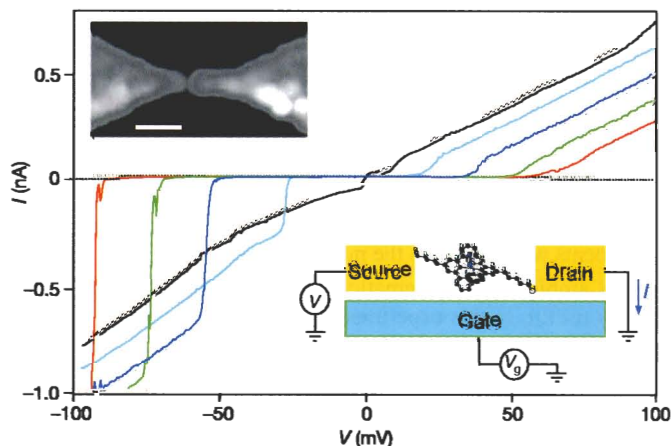


Figure 22: A single molecule transistor with an organometallic molecule [46]. The electrode pair with ~ 2 nm spacing has been manufactured by the electromigration technique (see SEM picture in the inset). The Si substrate served as gate electrode, separated by a SiO_2 insulating layer. If the charge of the central Co ion is fixed to either Co^{2+} or Co^{3+} , no current can flow at small bias voltage due to Coulomb blockade (colored lines). If the gate is tuned such that Co^{2+} or Co^{3+} have the same energy, the ion can be continuously charged or uncharged: current can flow even at small bias voltages (black line).



These findings, displaying the potential of the MCB technique to investigate single molecules, encouraged further research to control the electronic properties by careful design of the molecules structure. The first example is the adjustment of the resistance caused by the molecular structure in the MCB device. Both molecular rods discussed above are delocalized π -systems of very similar structural features like connections of the subunits and length. The similar overall resistance ($\sim 1\text{M}\Omega$) of the device with both structures is not surprising. If the conjugation of the molecular rod is interrupted, an increase of the overall resistance is expected. As *trans*-platinum(II) ethynyl complexes are known as conjugation-passive but rigid spacers, this motive was chosen to design the molecular rod **9** [18]. Its stiffness allows the design of rod-like structures and the pure σ -character of the Pt-C(sp) bonds is expected to divide the molecules' π -system. A single molecule junction formed with this rod-like molecule in a MCB displayed an increase of the overall resistance by several orders of magnitude ($\sim 5\text{G}\Omega$) compared with the conjugated structures **17** and **18**. The entire I - V curve displays the properties of an insulator and was best fitted with a simple model of a rectangular barrier (height 2.5eV). Remarkable is that both, the insulating effect and the experimental set-up, survives up to a bias voltage of 5 V, displaying the stability and therewith the interesting application potential of such molecular units as electronic components. In future HME and MME devices, such *trans*-platinum(II) complexes may serve as insulating linkers and as well defined tunnel junctions on a single molecule level.

4.5 Electromigration Technique

Another experimental set-up to observe transport features through single nanoscaled object is the electromigration technique. It benefits as well from the weakness of a hyphenation point in a fabricated metallic wire. Here, the hyphenation point is opened to a tiny void by application of a moderate electric current. The current flow causes electromigration of metal atoms and the metal wire breaks up at the bottleneck. The electrodes thus resulting have a distance of about 1 to 3 nm, which can easily be estimated by the resistance. In the experiment, several electrode pairs are fabricated and the most appropriate ones are selected. As these gaps can be made on a chip with a conducting substrate (covered with an insulator) which can serve as additional gate electrode, this set-up is suitable to make a nanoscale field effect transistor. Indeed, transistor properties have been described with colloidal cadmium selenide nanocrystals [45], [47], fullerene (C_{60}), and inorganic complexes (see Section 3.4 and Figure 22). The advantage of this method is that the electrode gap is close to the surface and the electrodes are stable. This allows for systematic studies like gate voltage dependence, temperature dependence or magnetic field dependences. In contrast to MCB experiments, the distance can not be manipulated further after the junction has formed. Hence, both methods give complementary opportunities for experiments.

The investigations described so far enable the conductance properties of single molecules to be investigated. The wealth of phenomena observed as well as the accuracy of the investigations are constantly increasing. One main focus of these activities was dedicated to the understanding of how different molecules generate different conductance properties. Thus a picture evolves which allows to design the electronic properties of a device by tailor-made molecules. The applicability of these experimental concepts as interface in a future hybrid device remains disputable.

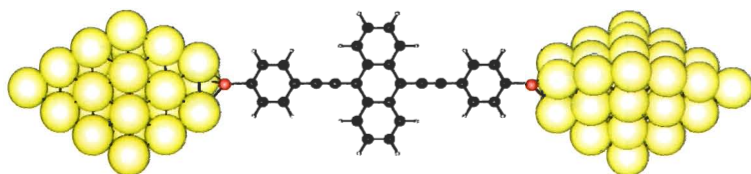


Figure 23: Quantum chemistry can only be used in a finite system with a fixed electron number. To compute not only the organic molecule, but also the interaction with the electrode, one considers a *super-molecule*, including parts of the metallic electrode.

5 Simulation and Circuit Design

5.1 Theoretical Aspects

To understand electron transport through molecules a better theoretical description of the processes is required.

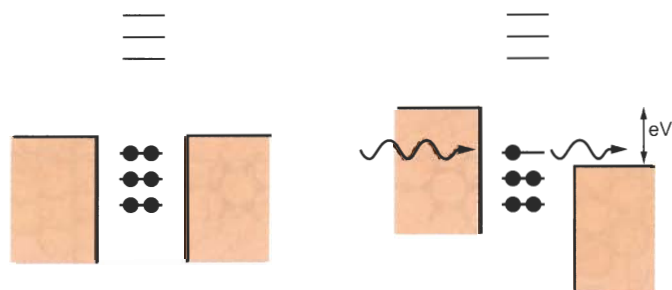
If the molecules are attached to the surface only by weak van der Waals forces, the molecule and the electrode can be treated independently in good approximation. In this case of weak coupling, electron transport is manifested by tunneling processes: an electron from one electrode is tunneling on the molecule, remains there for a while and continues to tunnel to the opposite electrode. A possible description of the current can be given by rate equations. Electrons are charged particles and Coulomb blockade comes into play (see Chapter 16), which is able to suppress the current at small bias voltages. The description is then similar to the description of a *quantum dot* with a large level spacing (of the order of 1 eV). In such a set-up equivalent effects like in weakly coupled quantum dots can be found, such as single-electron tunneling [46].

The description becomes much more challenging when the molecule is better coupled to the electrodes. Then the molecular orbitals hybridize with the metallic states in the leads, which yields a broadening of the energy levels and a higher conductance. This occurs, for example, in thiol-ended molecules chemically connected to two metal electrodes. The electron transport adopts a more wave-like character which can be handled according to the following procedure.

The first task is to compute the wave function of the junction in equilibrium (i.e. when no current is flowing). This is already very difficult because traditional quantum chemistry has been developed to compute the wave function of an isolated molecule with fixed integer electron number. In our case, both requirements are not fulfilled: the molecule is chemically connected to the semi-infinite metallic leads and electrons are continuously exchanged between them. Thus, we have rather an open system with no fixed electron number and no borders. The usual workaround is that one separates the system into three separate parts: the two leads and the molecular junction itself. But where should the borderline between the lead and the molecule be drawn? The best approach is to involve the first metal atoms into the quantum chemical computation, forming a super-molecule, which describes the metal-molecule coupling on the well-controlled quantum chemistry level (Figure 23). At this point, some assumptions have to be made about the atomic form of the molecule-metal bonds as well as the shape of the electrodes (plane surfaces or sharp tips). It should be noted, that this choice strongly affects the results [44], [57]. Then, the coupling of the super-molecule to the leads can be done between metal and metal, which is less critical. The more metal atoms are involved in the super-molecule, the more accurate are the results with respect to the interaction between the molecule and the electrode surface.

We have so far only described how to calculate the equilibrium wave function at zero voltage. If we are interested in the conductance, some methods developed for the physics of nanostructures can be applied. In particular, the Landauer-Büttiker picture has successfully been used to describe the electronic conductance (cf. Chapter 3). Essentially, electrons are considered as plane waves, coming e.g. from the left side and which may be transmitted through the molecular junction to the right side with a certain proba-

Figure 24: Simplified picture of the conductance process: At low voltages, no molecular orbital contributes to the current (left). As soon as the first molecular orbital comes in the energy window spanned by the bias voltage, conductance is possible (right).



bility or alternatively be reflected. The system is thus treated as a scattering object. The scattering matrix t can be computed when the wave function is known. The **transmission function** T (or transparency) results from

$$\text{Tr}(t^\dagger t) \quad (1)$$

where t are the scattering matrix elements which describe the scattering from the states on one electrode to those of the opposite electrode.

Now the current I can be calculated by means of a Landauer-type formula [58], [59], [60]

$$I(V) = \frac{2e}{h} \int T(W, V) f(W + eV/2) - f(W - eV/2) dW \quad (2)$$

where f is the Fermi-Dirac distribution function, W the energy, and V the applied voltage.

Some results of the theory:

- The potential difference V of the electrons in the left and the right electrode spans an energy window. The basic mechanism is shown in Figure 24, where the levels are for simplicity drawn as sharp levels. At low voltage V , the conductance is poor because no molecular level can carry electrons. When V is further increased, the first molecular orbital will enter into the energy window: the molecule starts to conduct. Hence, one would expect a step-like increase of the current as a function of the voltage. Due to the hybridisation of the molecule and the metallic states in the leads, however, all these molecular orbitals are strongly broadened in energy, which yields a rounding of the current steps and might also contribute to conductivity even at lowest voltages.
- The thiol-bonds, which are the anchor group between the molecule and the metal surface, act as tunnel barriers and suppress the amplitude of the current. When a finite voltage is applied, a large fraction of the voltage drops along these barriers. Therefore, the chemical environment of the tunnel barriers is very important for the transport properties: the conductance varies strongly, if the molecule-metal-bond is arranged differently.
- The contribution of the current through different molecular orbitals may strongly vary. This is illustrated by calculations shown in Figure 25. In this example, the contribution of the HOMO or LUMO is in certain examples not dominating because the charge of the HOMO is accumulated in the center of the molecule, while that of the LUMO is depleted in the center. Other MOs, although being far away in energy may carry much more current due to a favourable regular spatial structure.
- This procedure can now be refined in several aspects. For example, the influence of the applied voltage on the electronic structure and even the atomic structure of the molecule can be considered by recomputing the (super-)molecule at each voltage in the corresponding electric field. Furthermore, the current flowing at finite voltage may cause some stationary redistribution of the charge. This requires a so-called non-equilibrium transport theory, which has to be adapted to the special situation of a molecular junction.

Consequently, it makes no sense to assign a conductance to a molecule. The conductance can only be defined for the compound electrode-molecule-electrode system. A lot of interesting questions have not yet been answered by theory. One important example is the heat arising in the molecule when a current is flowing and inelastic scatter processes become important. Where does the heat occur? How does the molecule carry the heat, i.e. the vibrational energy away? Of course, too much heat will inevitably destroy the organic molecule and therefore, this is a crucial problem for all technical applications.

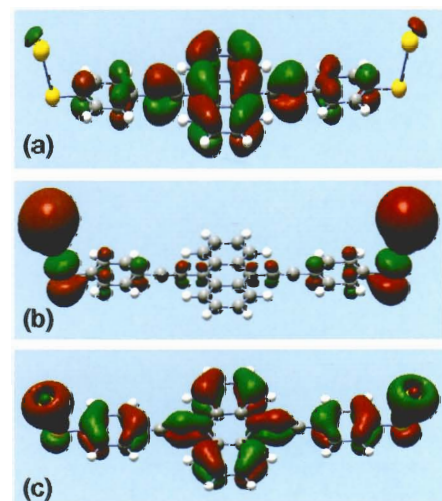


Figure 25: Spatial distribution of the charge density of three different molecular orbitals (MO's), calculated with DFT for the example of the same molecule as in Figure 1. In this calculation, only one gold atom was considered to model the influence of the electrodes [67]. The HOMO (a) as well as the LUMO, (b) concentrate in the center / at the ends of this supermolecule and contribute little few to the current. The MO (c) although being ~ 1 eV below the HOMO, contributes considerably to the current due to its homogeneous charge distribution along the junction.

5.2 Design Rules for Molecular Nanocircuits

In general, circuit design and analysis is based on the application of Kirchhoff's laws: (1) The charge conservation implies that the sum of all currents I_k into a circuit node must be zero

$$\sum_k I_k = 0 \quad (3)$$

(2) The fact that the electrostatic potential is path-independent (in the absence of time-dependent magnetic fields) implies that the sum of all voltages in a mesh must be zero

$$\sum_i V_i = 0 \quad (4)$$

In conventional solid state circuits, the impedances of the components in a circuit are independent of each other because the coherence lengths for electron transport in metals and semiconductors at room temperature are much smaller than the overall device dimensions. Therefore, the components are treated as lumped elements and the circuit design and analysis exploits the principle of superposition of the impedances of the individual components. In conventional electronics, the applicability of this **superposition principle** is restricted to frequencies below which the wavelength of the electromagnetic fields becomes comparable to device dimensions. At microwave frequencies this condition is not valid any more and, hence, microwave circuit design and analysis treat the components as distributed elements which make it necessary to take into account the geometrical layout and a simultaneous modeling of the entire circuit using the electromagnetic field theory.

Similarly, components can not be treated independently when molecules are connected in MME devices parallelly or serially. If, for example, two molecular branches are connected in parallel, the wave function of one branch hybridizes with the other branch and modifies thus the properties of both branches (Figure 26). This is fully consistent with the statement in the former section that it makes no sense to define the conductance only of a molecule, but rather of the compound junction. The following points may explain some mechanisms, as to why the *conductance* of one molecular subunit depends strongly on the other molecular subunits around and is thus badly defined:

1. effects on the density of states and the geometry of molecular orbitals (MOs),
2. Coulomb blockade effects due to the discrete nature of the electric charge,
3. interference effects.

Category 1. Adding a branch in a given molecule modifies the electronic structure of the entire molecule, i.e. the geometry and the energy levels of the MOs will be changed. We already pointed out in the last section (cf Figure 25) that the conductance is very sensitive to small details of the spatial electronic distribution.

The influence on the energy levels of the MOs upon changes of the structure are well known from traditional molecule spectroscopy. A very simple example of this fact is presented in Chap. 5 / Figure 17 in which the MO energy diagram is shown for polyenes of different chain length. The addition of each chain element (ethenyl group) increases the density of states and decreases the HOMO-LUMO gap.

Category 2. The Coulomb blockade effect of nano-sized capacitors and their impact on the charge transport through nanostructures are described in Chap. 16. In molecules, due to their smallness, these effects are particularly important. Hence, molecular subunits which are in close proximity, have very strong mutual capacitive interaction. This affects not only the static wave function, but in particular electronic transport: the *conductance* of a molecular subunit depends strongly on whether the next subunit is temporarily charged or not.

Category 3. If a wave-like current is flowing through different parallel branches of a molecule, the two partial waves may interfere constructively or destructively, yielding to a modification of the conductance. This can be compared with an optical analogue: the Fabry-Perot interferometer.

Hence, the understanding of MME devices is so far very poor. The design rules are not evident. Detailed theoretical studies which attempts to simulate electronic functions with MME devices for certain examples can be found in Ref. [65] – [66]. Presumably, one has to think in a modular way. Once the electronic function of a molecular unit is understood, it has to be connected to another unit by a well defined node which suppresses the mutual interaction. The search for such decoupling building blocks is therefore very important.

If HME devices are connected together and the anorganic part is sufficiently large such that phase coherence and charging of the electrode can be neglected (i.e. it serves as a *reservoir*), the interaction between the modules can be neglected and the conventional circuit rules apply.

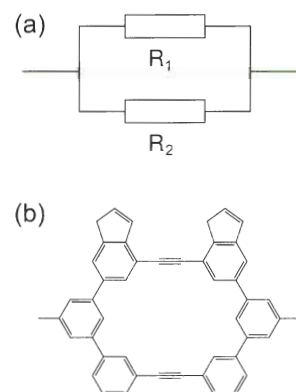
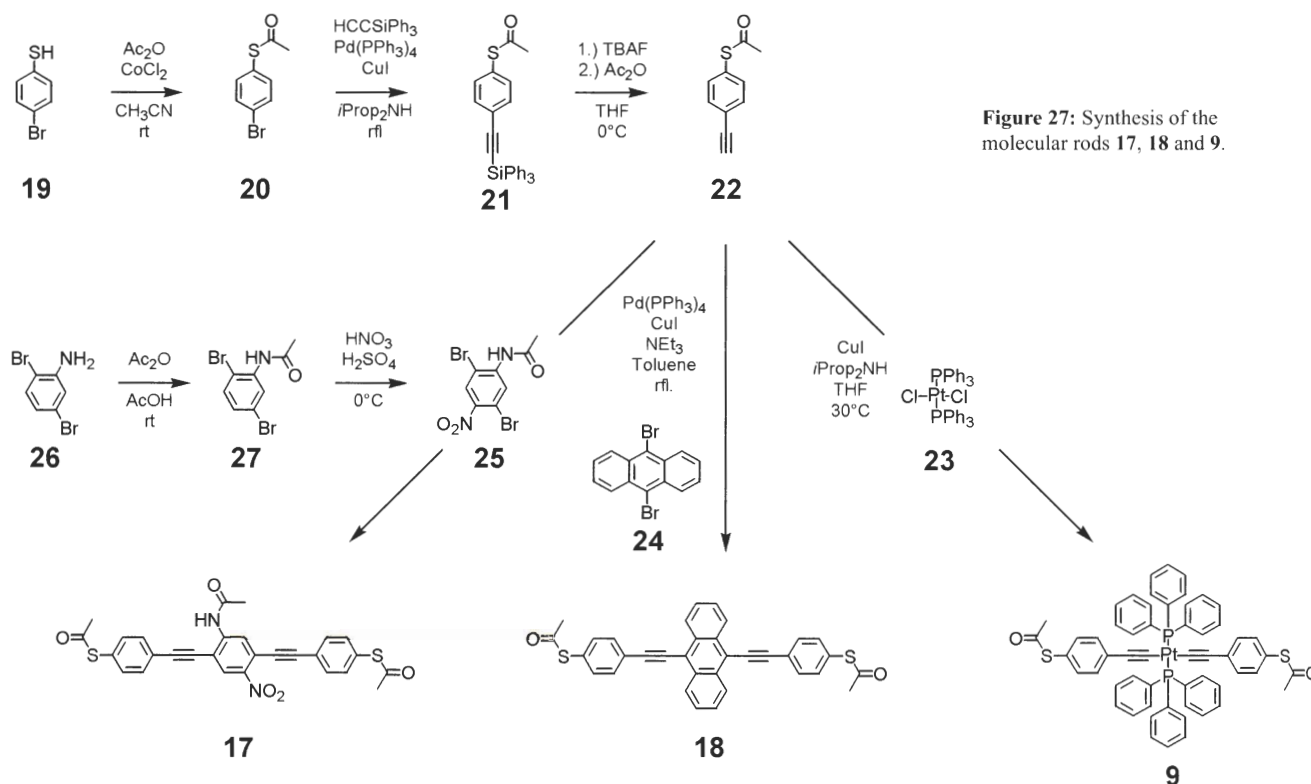


Figure 26:

(a) If two resistors are in parallel connection, the overall conductance G results as $G = G_1 + G_2$.

(b) Sketch of a MME device with two different branches. The molecular unit in the upper branch is strongly interacting with the lower branch. Thus, no G_1 or G_2 can be reasonably assigned to each branch.



6 Fabrication

The fabrication of molecular devices depends strongly on the individual type of device and a general description is hardly possible. However, both crucial steps of device fabrication, the synthesis of the molecular components and their integration will be discussed here using specific examples.

6.1 Chemical Synthesis

The routes towards the molecules employed in the electronic functions described above are based on elementary and advanced synthetic strategies and methods of organic, inorganic, metalorganic and supramolecular chemistry. A successful synthesis is often carried out over many steps. After each step, the reaction products need to be separated and analyzed in order to verify and characterize the molecular structure. The separation of the desired compound from unwanted by-products is frequently performed through selected distillation, crystallization, and chromatographic techniques. The analyses involves e. g. NMR spectroscopy, mass spectroscopy, elemental analysis, X-ray analysis as well as optical spectroscopy. In this section, synthetic aspects will be discussed with the help of four molecules, which are part of the devices already discussed.

In Section 4.4, the electric currents through three molecular rods were discussed extensively. Here we focus on the chemical synthesis that made these rods available. Every synthesis starts with the definition of the target compound. In this particular case, the synthetic targets were designed molecules, only made to be investigated in a MCB. Prior to their synthesis was a designing and development step in which the chemist tries to optimize a multitude of different aspects. Due to the limitations of this section only two key points are mentioned. The target structure must meet numerous physical requirements (stiff, rod like structure, anchor groups, symmetry options, conductivity, solubility etc.). And at least as important, the target structure must be achievable by chemical synthesis (in a reasonable effort by a reasonable number of synthetic steps, starting materials available, etc.). Often the careful balance of many aspects leads to the final choice of synthetic targets.

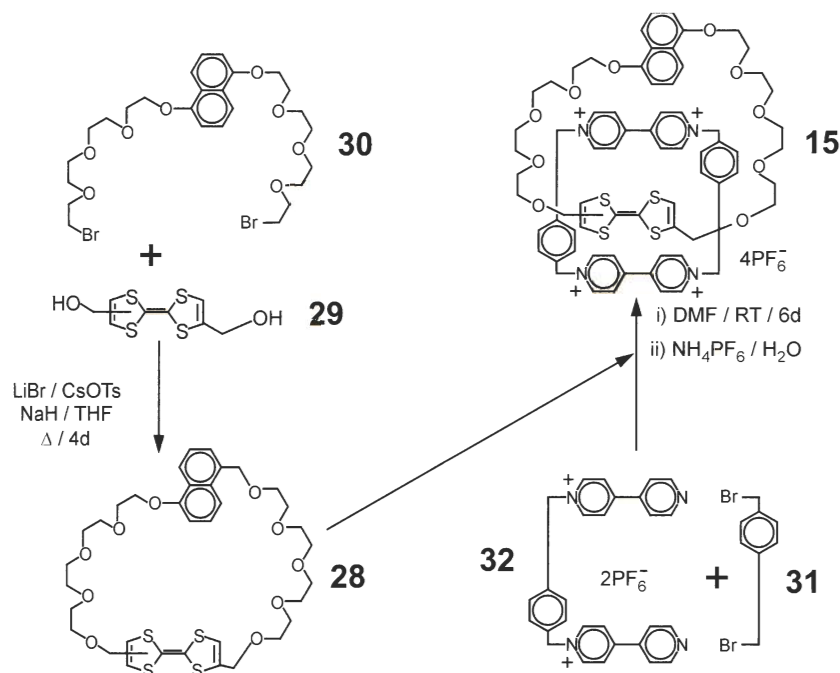


Figure 28: Synthesis of the catenane 15 [56].

The synthesis of the organic rods **17** and **18** and of the metalorganic rod **9** is displayed in Figure 27. It is striking that all three rods have a common intermediate, the phenylacetylene **22** with an acetyl protected thiol function in *para*-position. Often synthetic pathways are chosen, so that intermediates may lead to several target structures with interesting properties. The synthesis of the intermediate **22** starts with the acetyl protection of commercial *para*-bromothiophenol **19** to yield in its acetyl-protected form **20**. In a palladium(0) and copper(I) catalyzed *Sonogashira* acetylene coupling with triphenylsilylacetylene, the bromine on the aromatic core was substituted to yield in the desired *para*-thiophenylacetylene in its twice-protected form **21**. Treatment of **21** with fluoride anions deprotected both, the silyl protection group of the acetylene and the acetyl protection group on the sulfur. As the latter was required for the further steps, the crude reaction mixture was subsequently treated with acetylanhydride to reprotect the thiol to give the desired intermediate **22**. In a copper(I) catalyzed reaction with *trans*-bis(triphenylphosphine)dichloro platinum the organometallic target compound, the rod-like platinum complex **9** was synthesized. The symmetric organic rod **18** was again synthesized in a *Sonogashira* coupling as **21** above, with similar catalysts but with variations in solvents, bases and temperature. The challenge of organic synthesis is often not to find the right synthetic pathway, but to find the right conditions for a desired product. The acetylene functions of **22** replaced the bromines of commercial 9,10-dibromoanthracene **24** to yield in the symmetric organic rod **18**. To synthesize the asymmetric rod **17** the required dibromo-benzene **25** with an acetyl-protected amino group and a nitro group had to be synthesized in two steps. Commercial 2,5-dibromoaniline **26** was first acetyl-protected with acetylanhydride in acetic acid to its acetyl protected form **27**. To introduce the nitro group, **27** was treated with a 1/1 mixture of nitric acid and sulfuric acid at 0°C to yield the desired intermediate **25**. Similar coupling conditions as for the symmetric rod applied to **22** and **25** gave the asymmetric rod **17** as the desired target compound. All three molecular rods were synthesized with acetyl-protected terminal thiol functions, as these protection group turned out to be ideal for their immobilization between the Au electrodes of a mechanically controlled break junction (MCB). This protection group is removed spontaneously on Au surfaces but has the advantage of reducing the kinetic of SAM formation on the Au surface [61]. All target compounds

and intermediates during the course of the synthesis were fully analyzed by classical chemical methods, like ^1H - and ^{13}C -NMR spectroscopy, mass spectroscopy and elemental analysis.

The second synthetic example demonstrates how supramolecular structures arise. Supramolecular chemistry describes the interaction between molecules beyond covalent bonds, which is a rather recent discipline in chemistry. It evolved in the 1970s of the last century and for their pioneering work in the field, Cram, Pedersen, and Lehn received the Nobel prize for Chemistry in 1987. A typical example of a supramolecular structure is Stoddard's catenane, discussed in the sections 3.3 and 4.2. Both ring molecules of the catenane are interlocked and not fixed by a covalent bond. But how does one interlock two molecules? From the very beginning, the two rings are carefully designed by Stoddard to interlock each other. The synthesis of the catenane is displayed in Figure 28. First the cycle **28** containing a redox active tetrathiofulvalene (TTF) unit is closed. Therefore a building block consisting of a TTF with two benzylic alcohols **29** reacts with a polyether with two terminal alkylbromines **30** as leaving groups. In a nucleophilic substitution reaction the deprotonated alcohol functions of **29** replaced the bromines of **30**. This reaction was carried out in sufficiently dilute conditions to favor the formation of the cycle **28** rather than chain-like polymers. The formation of the second ring was based on a nucleophilic substitution reaction too. The bromines of 1,4-di(bromomethyl)benzene **31** were replaced by the terminal nitrogen atoms of the 1,4-di(bipyridinium)benzene $(\text{PF}_6)_2$ salt **32** to yield the second ring. The trick necessary to get the catenane, is to make this second ring closure reaction in the presence of the first ring **28** under appropriate reaction conditions. Due to supramolecular interactions, the precursor **32** is preorganized in the ring **28** and hence, substantial amounts of the second ringclosure reaction resulted in the desired catenane **15**. Such supramolecular structures are purified and analyzed with the same established chemical methods as mentioned above. The structure of catenane **15**, for example could even be analyzed by X-ray diffraction.

6.2 Integration Processes

The integration of the basic logic and memory function within the MME concept is, indeed, performed by chemical synthesis. All synthesized molecules would be able to perform the designated functions. The remaining task is to interconnect them among each other and to the outside world. This task is similar to the tasks required for fabricating HME devices. The steps of this fabrication are similar to the standard micro- and nanoelectronic processes (see Part II). For circuit fabrication deep in the (few) nanometer regime, bottom-up techniques based on self-assembly and self-organization steps will gain importance. The additional challenge is to integrate a – typically monomolecular – *organic* film or *organic* molecules into the entire device. This fact imposes several severe limitations on the selection of the process steps and process parameters because of the low temperature budget of the organic molecules, their sensitivity to oxygen at elevated temperatures, and their mechanical softness. The process strategy requires all high-temperature process steps to be performed prior to the deposition of the organic film. An example of a fabrication strategy which, in principle, is suitable for mass-production has been sketched in Section 4.2. A sequence of pictures of the cross-bar Pt/molecule/Ti system is shown in Figure 29 for a wide range of magnification factors. As mentioned above, an interpretation of the observed characteristic is not yet possible.

7 Summary and Outlook

This chapter presents the potential of carefully designed molecular structures to act as specific electronic components. They may be the core of very small devices, which may be fabricated by means of self assembly.

In the past, important preparatory work came from the chemistry of molecules in solution. Oligomers as molecular conductors and molecular switches have been investigated spectroscopically and by electrochemistry in solution. Some correlations between molecular structure and physical properties were elaborated.

In more recent years, the immobilisation of molecules on metallic electrodes allowed experiments, where a steady-state current flows through the molecules. Molecular films, sandwiched in between metallic electrodes, were shown to act as diodes, con-

figurable switches (memories), transistors and negative differential resistance devices. Single molecule junctions have been investigated with STM techniques on surfaces and by means of the mechanically controlled break junction technique. It was demonstrated that the electronic properties of the device depend strongly on the choice of appropriate molecules, which opens up an infinite space of possible variations and design possibilities. The properties of the junction, however, also strongly depend on the electrode material, its shape and the chemical bonds between the molecule and the leads. The challenge is to understand these complex systems and to convert this increasing knowledge into useful devices. To reach this goal, also theoretical advances in these interesting systems are required.

Reproducibility and stability still remains a challenge in molecular electronics. The molecule itself is often pretty stable and might not be the reason for short lifetimes. It is rather the metallic electrodes that provide instability because the movement of few metal atoms may strongly affect the conductance properties of the whole device. While single molecule devices are a very interesting tool for basic research, they do not seem to be suitable for technological applications. The lifetime, in particular when a voltage is applied and a current is flowing, is insufficient. A molecular film device, representing a larger ensemble, might be more suitable and might be integrated soon into existing circuitry. Nevertheless, a good reproducibility requires the absence of defects and high stability of the electrodes and the molecular film. A great effort is necessary to better engineer the electrodes.

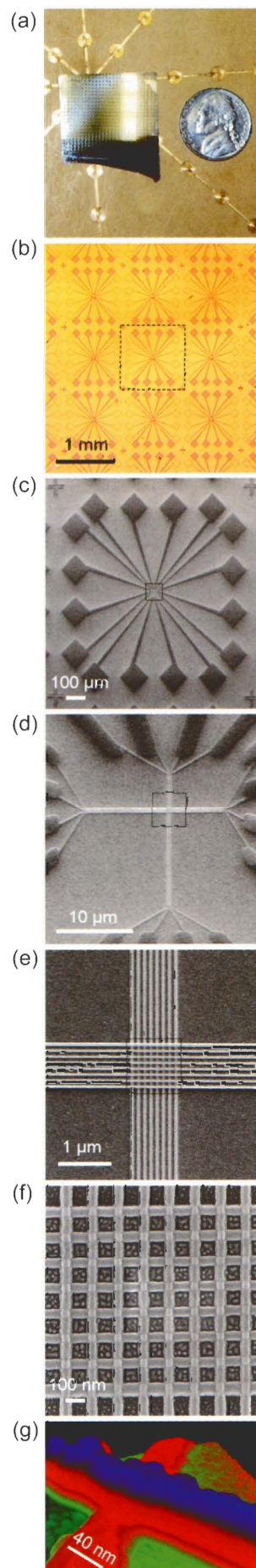
The key problem of molecular electronics, however, remains the interface to the molecules and thereby their integration and addressability. To overcome this problem great efforts are still required. The implementation of molecular electronics into traditional silicon architectures requires a 100% yield on a chip. This might not be achievable when self-assembly is used. New, fault-tolerant architectures are probably needed. A promising approach to cope with huge but imperfect computer systems is the Teramac project of Agilent Technologies [62], as outlined in Section 4.2.

In conclusion, while the ongoing miniaturisation in electronic circuits continues, the use of molecules in electronic circuits seems to be likely. Despite the many challenges to be met, the concept of molecular electronics shows an outstanding potential for the long-term future of the information technology because of the ultimate density of logic and memory functions, their low fabrication costs, their low power consumption, and the huge number of opportunities different by the plethora of possible molecules.

Acknowledgements

The authors are grateful for discussions with Ari Aviram, Detlef Beckmann, Jean-Philippe Bourgoin, Luisa De Cola, Michelle Di Leo, Mark Elbing, Ferdinand Evers, Harald Fuchs, Carsten von Hänisch, Jim Heath, Matthias Hettler, Christian Joachim, Jean-Pierre Launay, Jean-Marie Lehn, Hilbert von Löhneysen, Mark Ratner, Mark Reed, Joachim Reichert, Mario Ruben, Günter Schmid, Christian Schönenberger, Ulrich Simon, Christophe Stroh, Daniel Vanmaekelbergh, Florian Weigend, Wolfgang Wenzel, René Williams, Stanley Williams, Olaf Wollersheim, Sophia Yaliraki. Thanks are due to Stephan Kronholz, Björn Lüssem, Lars Müller-Meskamp (FZ Jülich) for corrections.

Figure 29: Cross-bar array of reconfigurable switch junctions fabricated at Hewlett-Packard laboratories. An outline of the fabrication process is given in Sec. 4.2. The photos show an increasing magnification from (a) to (g). (a), (b) optical micrographs, (c) – (f) SEM micrographs, (g) AFM micrograph. Courtesy of Yong Chen at Hewlett-Packard Laboratories, Palo Alto.



References

- [1] J. M. Tour, *Acc. Chem. Res.* **33**, 791 (2000).
- [2] A. Aviram and M. R. Ratner, *Chem. Phys. Lett.* **29**, 277 (1974).
- [3] A. Aviram and M. R. Ratner, *Ann. N. Y. Acad. of Sci.*, **852** (1998).
- [4] A. Aviram, M. R. Ratner and V. Mujica, *Ann. N. Y. Acad. of Sci.*, **960** (2002).
- [5] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **408**, 541 (2000).
- [6] M. A. Reed and J. M. Tour, *Scientific American* **282** (2000) 86.
- [7] W. B. Davis, W. A. Svec, M. A. Ratner, M. R. Wasielewski, *Nature* **396**, 60 (1998).
- [8] J.M. Tour, *Chem. Rev.* **96**, 573 (1996).
- [9] K. Müllen and G. Wegner, *Electronic Materials: The Oligomer Approach*, Wiley-VCH, 1998.
- [10] R. Kuhn, *Angew. Chem.* **50**, 703 (1937).
- [11] W. Kern, M. Seibel, H.-O. Wirth, *Makromol. Chem.* **29**, 164 (1959).
- [12] W. Steinkopf, R. Leistmann, K.-H. Hofmann, *Lieb. Ann. Chem.* **546**, 180 (1941).
- [13] G. Drefahl, G. Plötner, *Chem. Ber.* **94**, 907 (1961).
- [14] G. Drefahl, G. Plötner, *Chem. Ber.* **91**, 1274 (1958).
- [15] Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price Jr, A. M. Rawlett, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **292**, 2303 (2001).
- [16] M. Uno, P.H. Dixneuf, *Angew. Chem.*, **110**, 1822 (1998); *Angew. Chem. Int. Ed. Engl.* **37**, 1714 (1998); H. Fink, N.J. Long, A.J. Martin, G. Opromolla, A.J.P. White, D. J. Williams, P. Zanello, *Organometallics* **16**, 2646 (1997).
- [17] M. Mayor, J.-M. Lehn, K.M. Fromm, D. Fenske, *Angew. Chem.*, **109**, 2468 (1997); *Angew. Chem. Int. Ed. Engl.*, **36**, 2370 (1997); M. Mayor, J.-M. Lehn, *J. Am. Chem. Soc.* **121**, 11231 (1999).
- [18] M. Mayor, C. von Hänisch, H. B. Weber, J. Reichert, D. Beckmann, *Angew. Chem. Int. Ed.* **41**, 1183 (2002).
- [19] P. F. H. Schwab, M. D. Levin, J. Michl, *Chem. Rev.* **99**, 1863 (1999).
- [20] A. S. Martin, J. R. Sambles, G. J. Ashwell, *Phys. Rev. Lett.* **70**, 218 (1993); C. M. Fischer, M. Burghard, S. Roth, K. von Klitzing, *Appl. Phys. Lett.* **66**, 3331 (1995); R. M. Metzger, *Acc. Chem. Res.* **32**, 950 (1999).
- [21] T. Xu, I. R. Peterson, M. V. Lakshmikantham, R. M. Metzger, *Angew. Chem. Int. Ed.* **40**, 1749 (2001).
- [22] D. R. Stewart et al., *Nano Letters* (2004), **4**, 133–136
- [23] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **286**, 1550 (1999).
- [24] R. Sessoli, D. Gatteschi, A. Caneschi, and M. Novak, *Nature* **365**, 141 (1993).
- [25] B. L. Feringa, *Molecular Switches*, Wiley-VCH, 2001.
- [26] M. Irie, *Mol. Cryst. Liq. Cryst.* **227**, 263 (1993).
- [27] V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem. Int. Ed.* **39**, 3349 (2000).
- [28] M. Asakawa, P. R. Ashton, V. Balzani, A. Credi, C. Hamers, G. Mattersteig, M. Montalti, A. N. Shipway, N. Spencer, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White, D. J. Williams, *Angew. Chem. Int. Ed.* **37**, 333 (1998).
- [29] C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **289**, 1172 (2000).
- [30] L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **271**, 1705 (1996).
- [31] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **278**, 252 (1997).
- [32] C. Kegueris, J. P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga, C. Joachim, *Phys. Rev. B* **59**, 12505 (1999).
- [33] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. v. Löhneysen, *Phys. Rev. Lett.* **88**, 176804 (2002).
- [34] J. K. Gimzewski, E. Stoll, R. B. Schlittler, *Surf. Sci.* **181**, 267 (1987).
- [35] D. L. Allara, T. D. Dunbar, P. S. Weiss, L. A. Bumm, M. T. Cygan, J. M. Tour, W. A. Reinert, Y. Yao, M. Ko-zaki, and L. Jones, *Ann. N. Y. Acad. of Sci.* **852**, 349 (1998).
- [36] P. S. Weiss, L. A. Bumm, T. D. Dunbar, T. P. Burgin, J. M. Tour, and D. L. Allara, *Ann. N. Y. Acad. of Sci.* **852**, 145 (1998).

- [37] J. Chen, M. A. Reed, C. L. Asplund, A. M. Cassell, M. L. Myrick, A. M. Rawlett, J. M. Tour, and P. G. Van Patten, *Appl. Phys. Lett.* **75**, 624 (1999).
- [38] J. K. Stroschio, D. M. Eigler, *Science*, **254**, 1319 (1991).
- [39] R. S. Becker, J. A. Golovenchko, B. S. Schwarzenruber, *Nature*, **325**, 419 (1987).
- [40] G. Dujardin, R. E. Walkup, P. Avouris, *Science*, **255**, 1232 (1992).
- [41] A. A. Gewirth, B. K. Niece, *Chem. Rev.* **97**, 1129 (1997).
- [42] C. Joachim, J. Gimzewski, *Chem. Phys. Lett.* **265**, 353 (1997).
- [43] E. Scheer, N. Agrait, J. C. Cuevas, A. L. Yeyati, B. Ludolph, A. M. Rodero, G. R. Bollinger, J. M. van Ruitenbeek, C. Urbina, *Nature* **394**, 154 (1998).
- [44] H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs, H. v. Löhneysen, *Chem. Phys.* **281**, 113 (2002).
- [45] H. Park, A. K. L. Lim, A. P. Alivisatos, J. Park, P. L. McEuen, *Appl. Phys. Lett.* **75**, 301 (1999).
- [46] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, D. C. Ralph, *Nature* **417**, 722 (2002).
- [47] H. Park, J. Park, A.K.L. Lim, E.H. Anderson, A.P. Alivisatos, P.L. McEuen, *Nature* **407**, 57 (2000).
- [48] W. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* **417**, 725 (2002).
- [49] C. M. Fischer, M. Burghard, S. Roth, K. von Klitzing, *Appl. Phys. Lett.* **66**, 3331 (1995).
- [50] R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, G. J. Ashwell, *J. Am. Chem. Soc.* **119**, 10455 (1997).
- [51] R. M. Metzger, B. Chen, D. Vuillaume, M. V. Lakshmikantham, U. Höpfner, T. Kawai, J. W. Baldwin, X. Wu, H. Tachibana, H. Sakurai, M. P. Cava, *Thin Solid Films* **327**, 326 (1998).
- [52] O. Kwon, M. L. McKee, and R. M. Metzger, *Chem. Phys. Lett.* **313**, 321 (1999).
- [53] C. Zhou, M. R. Deshpande, M. A. Reed, L. Jones II, and J. M. Tour, *Appl. Phys. Lett.* **71**, 611 (1997).
- [54] J. Chen, W. Wang, M. A. Reed, A. M. Rawlett, D. W. Price, J. M. Tour, *Appl. Phys. Lett.* **77**, 1224 (2000).
- [55] J. M. Seminario, A. G. Zacarias, J. M. Tour, *J. Am. Chem. Soc.* **122**, 3015 (2000).
- [56] C. P. Collier, E. W. Wong, M. Belohradsky, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, J. R. Heath, *Science* **285**, 391 (1999).
- [57] S. N. Yaliraki, M. Kamp, M. Ratner, *J. Am. Chem. Soc.* **121**, 3428 (1999).
- [58] R. Landauer, *IBM J. Res. Dev.* **1**, 223 (1957).
- [59] A. Nitzman, *Ann. Rev. Phys. Chem.* **52**, 681 (2001).
- [60] S. Datta, *Electronic transport in mesoscopic systems*, Cambridge University Press, 1995.
- [61] J. M. Tour, L.R. Jones II, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh, S. V. Atre, *J. Am. Chem. Soc.* **117**, 9529 (1995).
- [62] J. Heath, P. Kuekes, G. Snider, S. Williams, *Science* **280**, 1716 (1998).
- [63] Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart, and J. R. Heath, *Chem. Phys. Chem* **3**, 519 (2002).
- [64] P. J. Kuekes, R. S. Williams, J. R. Heath, Patent No. US 6,314,019 B1, Nov. 6, 2001; P. J. Kuekes, R. S. Williams, Patent No. US 6,256,767 B1; see also: <http://www.nanotechweb.org/articles/news/1/9/8/1>
- [65] J. C. Ellenbogen and J. C. Love, *Proc. IEEE*, 386, March 2000.
- [66] S. Ami and C. Joachim, *Phys. Rev. B* **65**, 155419 (2002).
- [67] J. Heurich, J. Cuevas, J. C. Wenzel, G. Schön, *Phys. Rev. Lett.* **88**, 256803 (2002).