Functional molecules in electronic circuits

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Molecular electronics is a fascinating field of research contributing to both fundamental science and future technological achievements. A promising starting point for molecular devices is to mimic existing electronic functions to investigate the potential of molecules to enrich and complement existing electronic strategies. Molecules designed and synthesized to be integrated into electronic circuits and to perform an electronic function are presented in this article. The focus is set in particular on rectification and switching based on molecular devices, since the control over these two parameters enables the assembly of memory units, likely the most interesting and economic application of molecular based electronics. Both historical and contemporary solutions to molecular rectification are discussed, although not exhaustively. Several examples of integrated molecular switches that respond to light are presented. Molecular switches responding to an electrochemical signal are also discussed. Finally, supramolecular and molecular systems with intuitive application potential as memory units due to their hysteretic switching are highlighted. Although a particularly attractive feature of molecular electronics is its close cooperation with neighbouring disciplines, this article is written from the point of view of a chemist. Although the focus here is largely on molecular considerations, innovative contributions from physics, electro engineering, nanotechnology and other scientific disciplines are equally important. However, the ability of the chemist to correlate function with structure, to design and to provide tailor-made functional molecules is central to molecular electronics.

Introduction and motivation

Molecular electronics is currently a very active research area and the number of research groups from different disciplines of science contributing to this field is steadily increasing.[1–5] What is the reason for this recent interest? Is it only the availability of suitable tools for investigation at the nanometre range or is the interest based on the perspective of potential future applications? At first glance, the concept to profit from molecules as functional units has numerous very appealing advantages. Molecules are probably the smallest units still capable of providing a rich structural variety. Thus the development of an integration platform for molecules should in principle enable an enormous variety of different functions through the design of its molecular structure. Furthermore, an outstanding functional density has been predicted as a consequence of the minute size of molecules.[6–8] Fig. 1 depicts the reduction in size of amplification devices used in electronic circuits over the last century, and the further size reduction potential of molecules. Currently, integrated circuits can be produced with a resolution greater than 100 nm. Hence, molecular electronics could be considered as the ultimate target to follow for the ongoing miniaturization trend in electronic circuitry.

Silicon based electronic circuits demonstrate that only a very limited number of electronic functions is required in order to assemble highly functional devices. The potential for high integration density using molecules should, however, not be stressed in view of the limited number of massive parallel contacting concepts, poor reliability prospects, and the anticipated heat management challenges.[10–12] Furthermore, the minute size of molecules is more of a scientific challenge than an advantage, which must be overcome to enable their integration. Such size restrictions further limit the potential of molecules, since, for example, the number of contacts to a molecular structure will be restricted to two.[1] Then what is the motivation to integrate molecules?

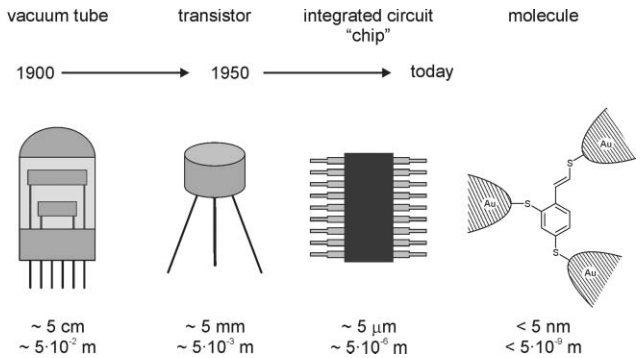

Fig. 1 Miniaturization of amplification devices used in electronic circuits over the last century. From left to the right starting with the vacuum tube over the transistor to current integrated circuits. The last picture on the right side displays a hypothetical single molecule quantum interference transistor for which, based on calculations, interesting transport features have been predicted.[9] However, contacting a minute object like a single molecule with three independent electrodes remains an unsolved experimental challenge.

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Nicolas Weibel (right) was born in Sélestat (France) in 1977. After graduating in 2000 from the European Chemistry, Polymers and Materials Engineering School (ECPM) in Strasbourg (France), he undertook a PhD at the University Louis Pasteur of Strasbourg under the supervision of Dr Loïc Charbonnière and Dr Raymond Ziessel, where he synthesized and studied new luminescent lanthanide complexes for biological material labelling and time-resolved imaging. In 2005, he obtained his PhD degree and moved to the University of Basel (Switzerland) to join the group of Professor Marcel Mayor. His current post-doctoral research activities are focused on molecular electronics, in particular on the design and synthesis of electrochemically addressable molecular switches. His PhD was awarded by the French Chemical Society (SFC) in 2006.

Sergio Grunder (left) was born in Luzern (Switzerland) in 1980. He studied chemistry at the University of Basel, obtaining his BSc in 2005. In the advanced courses, he focused on organic synthesis, graduating in 2006. He then started his PhD in the group of Professor Marcel Mayor in Basel, working on the design and synthesis of functional molecules for electronic circuits, in particular molecular switches.

Marcel Mayor (middle) was born in Zürich (Switzerland) in 1965. He studied chemistry at the University of Berne (Switzerland) where he received his PhD in 1995 supervised by Professor Rolf Scheffold and Professor Lorenz Walder. After working together with Professor Jean-Marie Lehn in the Laboratoire de Chimie Supramoléculaire of the University Louis Pasteur in Strasbourg as a SNF post-doctoral fellow and at the Collège de France in Paris (France) as Maître de Conférences invité, he founded his own research group in the Institute for Nanotechnology of the Forschungszentrum Karlsruhe GmbH (Germany) in 1998. After defending his habilitation at the University Louis Pasteur in Strasbourg in 2002, he became Professor of Chemistry at the University of Basel in 2005. In 2004 he obtained, together with Frank Hennrich, Ralph Krupke and Heiko Weber, the Erwin Schrödinger Award for the common research on "Molecules for Future Nanoelectronics". His current research interests are molecular electronics, nanoscale architectures, functional materials and hybrid materials.

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The electronic miniaturization trend described and predicted in the mid sixties by Intel co-founder Gordon Moore is solely the consequence of costly silicon wafers consisting of numerous copies of integrated circuits, entitled 'chips". A large number of chips on each wafer allows division of production costs by the number of units produced. The miniaturization known as Moore's law is only driven by the prospect to reduce the price per unit.[13,14] The true motivation of molecular electronics is not to further reduce the size of each functional unit, but rather to provide specific solutions for electronic functions based on molecules of lower cost, since molecular integration assemblies may be of comparable size or even larger. In this respect, a particularly interesting aspect is the cost development of semiconductor production plants, often referred to as Moore's second law.[14,15] The even more striking exponential increase in the cost of semiconductor production will most likely stop the miniaturization trend before the physical limits are reached.

The physical size of molecules has already been addressed as a disadvantage, which restricts the number of contacting electrodes to no more than two. To investigate the correlation between their structural features and electronic transport properties, complex physical setups such as mechanically controlled break junctions (MCBs),[16–19] scanning probe based molecular junctions,[20–22] crossed wire junctions[23,24] and other investigations are required.[24–27] Furthermore, the restricted number of electrodes limits the electronic functions in a circuit which might be substituted by molecular devices. Amplification of an electronic signal requires subunits that are connected to at least three electrodes such as tubes or transistors.[2,6] There currently exists no apparent concept of how this basic function of electronic circuits will be realized using molecules. As amplification is required in almost every logic circuit, there is a rather low substitution potential for molecular devices in this area of electronics. However, there are particular applications for which molecule based solutions might be very appealing and hence, molecular devices might supplement CMOS circuits in the future, resulting in hybrid CMOS-molecular electronic circuits.[3] For example the production of memory cells using CMOS technology is laborious and expensive, since numerous production steps are required to arrange several transistors to store one bit of information. A molecular device which displays hysteretic switching between two metastable states could also act as a memory cell.[28,29] Furthermore, it is likely that the cost of its production and integration will be competitive with the current expenses of CMOS strategies. However, whether or not

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its reliability and stability will also be competitive remains to be investigated following the identification, design, synthesis and integration of suitable devices.

To integrate and address molecular devices in a hybrid CMOS-molecular electronic circuit, the large difference in sizes between molecules and CMOS electrodes needs to be overcome. The most appealing concept is the crossbar structure, consisting of two series of parallel electrodes between which a molecular film is sandwiched.[8,28,30–32] As shown in Fig. 2, the top electrodes are perpendicular to the bottom electrodes, defining a small area of the sandwiched molecular film, which consists of numerous molecules at each intersection, addressable by applying an electric current at the corresponding junction between the top and bottom electrodes. In the ideal case, the junction would consist of a molecular monolayer comprising metastable molecular structures whose states may be defined (written) and altered by strong current pulses. The read-out of the state of the junction is accomplished by applying lower voltages, which do not alter the state of the junction. Such crossbar architectures might provide the required reliability since each junction consists of numerous molecules in parallel feeding the hope for robust molecular memory cells.[28] As illustrated in Fig. 2, leaking currents through neighbouring closed junctions might result in false answers. To overcome this drawback, rectification within the molecular film is of particular importance.[33,34] Unidirectional current transport through the film, *e.g.* only from the top to the bottom electrode, guarantees the exclusive inspection of the junction under investigation. Furthermore, although amplification of the signal remains a challenge, complementation of the switching device with rectification enables the assembly of basic logic circuits.[28] Hence, an ideal molecular memory cell displays not only voltage induced hysteretic switching but also unidirectional current transport through the molecular film.

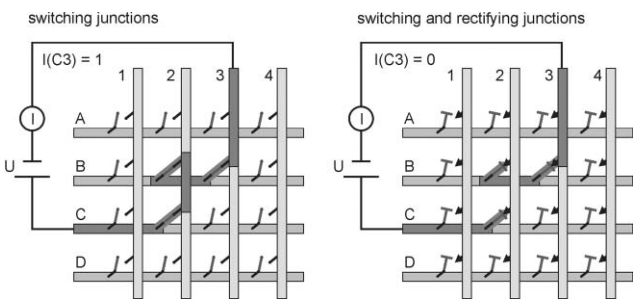

Fig. 2 Crossbar architecture for the integration of molecular devices as potential memory cells. While switching junctions (left side) might lead to wrong read-outs due to leaking currents through neighbouring closed junctions, the combination of a switching and rectifying junction (right side) inhibits such leaking currents.

Other particularly interesting applications of molecular devices integrated into electronic circuits are sensors and antennas.[1,27] Molecules display highly selective interactions with external stimuli such as chemical compounds or electromagnetic radiation. While the minute size of integrated molecules will not be able to overcome the thermodynamics of binding and occasionally encountered concepts of single molecule sensors consisting of an immobilized single molecule as host to detect a single analyte molecule as guest remain questionable, it might allow an unprecedented large surface area for the analyte combined with an immediate coupling of the binding event to the electronic signal. The principle of photosynthesis profits from light as an energy source and is based on the interaction between the electromagnetic wave and molecular structures. The study of such interactions on a single molecule level will be very challenging given the discrete and minute number of electrons. However, differences in electronic transport properties due to light-triggered photoreactions are already under investigation, and help to further elucidate molecular switching mechanisms.[35–37]

In view of the intrinsic application potential of hybrid molecular–electronic devices, the growing interest in integration strategies for molecules in general and in electronic transport investigations through molecular structures in particular is not surprising. Future solutions based on integrated molecules require significant contributions from very different and classically separated scientific disciplines ranging from synthetic chemistry through experimental physics to electronic engineering and circuit design. However, the focus of this perspective article is set on the contribution of synthetic chemistry to the field while equally important contributions from other areas of applied science like, *e.g.,* experimental physics or electronic engineering are mentioned at most.

Within this article, investigations towards both basic electronic functions required for molecular memory devices, namely rectification and hysteretic switching, are discussed. While the reported single molecule investigations are rather focused towards fundamental comprehension of the correlation between molecular structure and the physical properties of the resulting junction, devices based on small assemblies of supramolecular systems have already reached an impressive level of complexity and are geared towards electronic applications. To investigate molecular switching mechanisms and to unravel the potential and the limits of molecular systems, optical or electrochemical triggers are of fundamental interest, however, there remain difficulties to realize these stimuli inside a CMOS based integrated circuit. With a few recently reported examples, this perspective article displays the promising potential of molecular systems as functional units in electronic circuits, without neglecting the remaining challenges and potential drawbacks of the molecular approach. The field of molecular electronics, still in its infancy, is currently exploring the potential but also the limits of this concept.

Basic electronic functions transferred to a molecular level

The most fundamental electronic function is charge transport, classically realized by wires and conductors between subunits. Molecular wires have been suggested and investigated as interconnectors on the nanometre scale. Saturated alkanes turn out to be poor conductors, but very useful models for both theoretical and experimental investigations.[21,22,38–42] To improve electronic communication over larger distances, delocalized π-systems with smaller HOMO–LUMO gaps are more promising.[1] Increased electron mobilities, in the range of classical semiconductors, have been observed for delocalized π-systems.[7,19,20,39,43] Arranged with increasing complexity in terms of electronic functions, the next basic electronic feature is rectification. Diode-like systems that

allow the electric current to pass more easily in one direction than the other. Followed by bistable switching devices providing two different transparencies for the electronic current, which can be altered by a stimulus. As already pointed out in the introduction, lagged switching systems resulting in hysteretic behaviour are of particular interest. Even though numerous other electronic devices based on molecules like insulators[44] or transistors[45,46] showing either Coulomb blockade[47] or the Kondo effect[47,48] have been proposed and investigated; this article will exclusively focus on molecular rectifiers and switches comprising light-triggered, redox active and hysteretic elements.

Molecule based rectifying systems

The concept of a rectifier based on the use of a single organic molecule was first discussed by Aviram and Ratner.[49] They designed the molecular rectifier **1**, consisting of a donor π-system (D) and an acceptor π-system (A) separated by a σ-bonded (methylene) tunnelling bridge (Fig. 3).

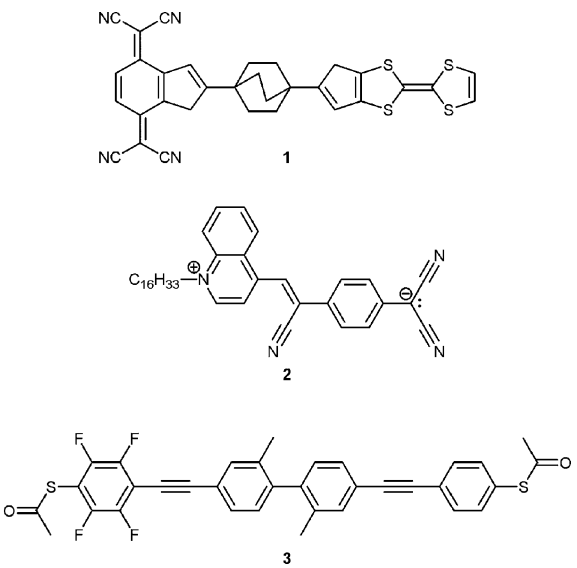

Fig. 3 Hypothetic molecular rectifier **1** consisting of a tetracyanoquinodimethane (TCNQ) moiety as acceptor and a tetrathiafulvalene (TTF) as donor linked by a rigid triple methylene σ-electron system as tunnel junction.[49] Zwitterionic molecule **2** displaying rectification assembled as Langmuir-Blodgett monolayer between two electrodes.[50] Rectifying molecular rod **3** consisting of electron rich and electron poor subunits separated by a twist in the backbone of the molecule.[51]

To ensure correct functioning of the device, the donor and acceptor units need to be electronically separated from one another; if not, the two units interact and one single donor level is predicted. In a Gedankenexperiment, the molecule was addressed with metallic electrodes on each side to form a metal–molecule–metal junction. Electric current is predicted to pass at lower voltage from the acceptor to the donor rather than in the other direction. The response of such a molecule to an applied field was calculated and rectification was predicted.

These promising predictions solely based on semi-quantitative calculations encouraged and fuelled the search for both suitable molecular systems and experimental integration setups.

As already discussed in the introduction, rectification is of particular interest for the modular assembly of molecular devices. Since the principle of a molecular electronic device was proposed by Aviram and Ratner in 1974,[49] several molecular diodes have been realised.

Metal-D–σ–A-metal molecular devices have been assembled with molecular films between two parallel planar electrodes, profiting from the self-assembly properties of amphiphilic molecules in Langmuir–Blodgett (LB) films at the water–air interface.[50] Metzger investigated the zwitterionic molecule **2**, carrying a positive charge on a quinolinium part and a negative charge on a dicyanomethylene moiety. In a LB film between two aluminium electrodes, **2** displayed rectification ratios up to 26 : 1. While the devices displayed very limited stability features, it was the first conceptual example of molecular based electronic rectification. Even though its dipole moment and LB film-forming properties were the selection criteria for the design of **2**, the observed rectification is rather explained by the asymmetric proximity of the π-chromophore to one electrode.[52]

Rectification was also observed in self-assembled monolayers (SAMs) of diblock oligomers, consisting of an electron-rich oligothiophene and an electron-deficient oligothiazole subunit.[53]

Different molecule–electrode contacts on both ends of a molecular rod also provide asymmetric current voltage curves (I–Vs),[19,54] as reported by Kushmerick *et al.* investigating oligophenylene-ethynylene (OPE) derivatives with various anchor groups. While all investigated molecules have a sulfur anchor group in common, the second anchor group was either a pyridine or a nitro function. Immobilized between two gold electrodes, asymmetric I–Vs were observed.

Only 33 years after the proposal of Aviram and Ratner, the investigation of a prototype single molecule diode has been reported. A terminally sulfur functionalized molecular rod (**3**) with two weakly coupled π-systems with mutually shifted energy levels was synthesized by Elbing *et al.*[51] Single molecules were immobilized between the two electrodes of a MCB and electronic transport was investigated. In transport experiments, the donor and acceptor properties are less important, since the accepting–donating process is taken over by the reservoirs. But if a single molecular rod is fixed between two electrodes, the D–A system implies a broken symmetry in the electronic transport, which is comparable with the principle of a semiconductor diode. On a single molecule level in a MCB, the recorded I–Vs displayed a weak diode-like behaviour with a rectification ratio of about 1 : 5 at $U = \pm 1.5$ V.

Molecular switches

As already mentioned in the introduction, a particularly appealing molecule based functional device would be a bistable system that can be toggled between two distinct states on request, providing a molecular switch. On the nanometre scale, molecular switches are the most relevant elements to be developed, studied and integrated into electronic circuits.[2] Mainly light-triggered switches and redox active systems have been reported recently as molecular systems comprising switchable electronic transport properties. While in light-triggered systems a reversible photoreaction provides two different molecular structures with different transport properties, systems based on redox chromophores provide transport

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differences due to variations of the electronic population of their frontier orbitals. Prominent candidates in each category will be described and discussed, such as photochromic dithienylethenes and systems based on redox chromophores like viologens, anthraquinone and tetrathiafulvalene.

Light-triggered molecular switches

Light turns out to be an attractive physical stimulus as it can be easily addressed in various media with short response times.[55] Photochromic systems displaying light-induced reversible transformation (*e.g.* an isomerization) accompanied by spectral changes in absorption are particularly appealing.[56,57] The most prominent photoswitches are dithienylethene derivatives, which have been investigated in detail by Irie.[58] Their absorption properties, together with their stability features, make them ideal subunits for materials displaying light-triggered alteration of physical properties. In solution, either the open-ring isomer (**4o**) or the closed-ring isomer (**4c**) can be enriched upon irradiation with a suitable wavelength (Fig. 4). Typically, **4o** requires UV light to be converted into **4c**, the open-state being enriched again by exposing **4c** to visible light.

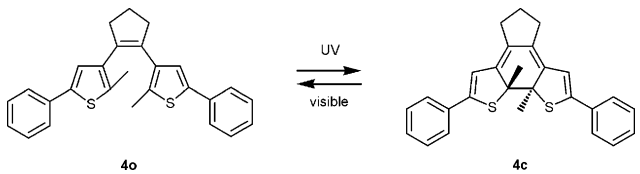

Fig. 4 Principle of reversible photoswitching between the open-ring (**4o**) and the closed-ring (**4c**) isomers of a dithienylethene in solution.

The two isomers offer different absorption spectra, that of the closed form extends towards longer wavelengths up to the visible region, suggesting the delocalization of π-electrons over the entire structure in **4c**. In **4o**, delocalization of π-electrons is restricted to each half of the molecule and electronic communication through the unsaturated bond of the middle ring is interrupted. The structural subunit with two optically addressable isomers, which considerably differ in the delocalization of their π-systems and hence in the electrical communication between both sides of the molecule, provides ideal features for a photoswitch in an electronic circuit. Functionalized with suitable anchor groups and immobilized between two electrodes in a junction, **4c** would then correspond to the ON state while the less conducting form **4o** would be referred to as the OFF state. Dithienylethenes are of particular interest due to the thermal irreversibility of their ring-opening reaction. Such photochromic switches can usually undergo a large number of colouration–decolouration cycles without loss of their spectral features due to side reactions or decomposition. With thermal stability and fatigue resistance, two critical technical requirements for optoelectronic devices are already fulfilled.[58] To inhibit the *cis* to *trans* photoisomerization side reactions, the ethene moiety is often part of a cyclopentene ring. Furthermore, such a five-membered ring substructure helps to increase both, the cyclization quantum yield and the absorption maximum shift. The aryl groups are also often bound to a perfluorocyclopentene unit, allowing the compound to reach superior photochromic performances (fatigue resistance, spectral splitting of the isomers).[58] But are these promising properties of the dissolved molecule conserved immobilized in a macroscopic surrounding? Several studies have been reported recently to contribute to this fundamental issue for the integration of molecular switches in electronic circuits, which will be discussed in the following section (Fig. 5).

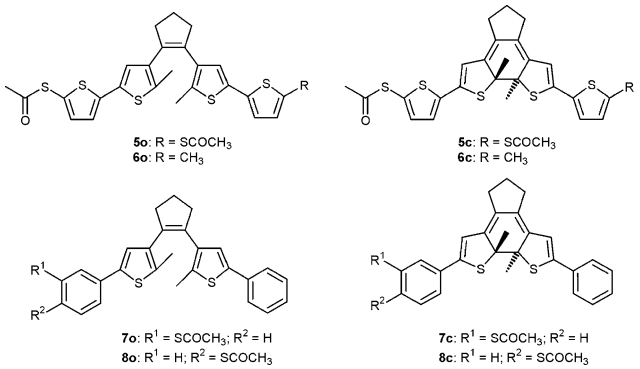

Fig. 5 Diarylethene derivatives **5–8** have been synthesized to investigate the electronic coupling between the switching subunit and gold electrodes.[59,61] Due to the thiophene-based spacer, derivatives **5** and **6** display enhanced coupling resulting in quenching of the excited state and inhibiting the light-triggered ring-closing reaction.[61]

The deprotected derivative of **5** was self-assembled on gold and investigated by combining transport and optical spectroscopy in a MCB.[59] The central switching unit is functionalized with a thiophene ring bearing an acetyl-protected sulfur group at each end, ideally suited for the immobilization of the molecule between both gold electrodes of a MCB.[19,59] The metal–molecule–metal junction was formed with the molecule in its closed state **5c** and then illuminated with visible light while monitoring the resistance as a function of time. After a short time, a sharp increase in resistance from the MΩ regime to the GΩ range was observed and attributed to the switching of the immobilized molecule from the closed form **5c** to the open form **5o**. The reverse isomerization to the closed form **5c**, which occurs with a high quantum yield in solution, failed upon exposure of the junction to UV light. Theoretical investigations of the switching process revealed quenching of the open form excited state by the Fermi level of the gold electrode as a possible explanation of the inhibition of the closing reaction.

This unexpected irreversibility of the switching process of immobilized **5** in the former MCB setup motivated the use of a model system mimicking molecule–gold electrode interactions, allowing the fast screening of properties of functional molecules grafted on gold surfaces. Monolayer-protected gold nanoparticles have been functionalized with dithienylcyclopentene derivatives **6–8** comprising aromatic linkers of varying electronic communication to their anchor groups.[61] In particular, a thiophene ring in **6** and a *meta*- or *para*-substituted benzene ring in **7** and **8**, respectively, were used as linkers to tailor the extent of coupling to the electrode.[60] The acetyl-protected derivatives **6–8** displayed reversible photochromic behaviour in solution. Immobilized on gold particles, successful ring-opening reactions have been observed for all three derivatives, while exclusively in the case of **6o**, the ring-closing reaction upon irradiation with UV light failed. These findings are consistent with the interpretation of the unidirectional switching behaviour of **5** immobilized between two gold electrodes in a junction.[59]

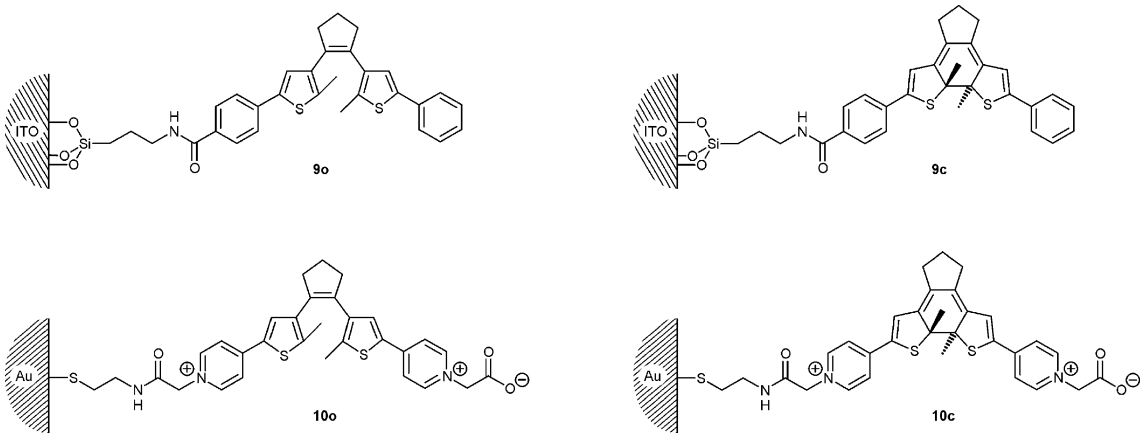

Fig. 6 Examples of diarylethene derivatives immobilized on electrode surfaces to enable electrochemical read-out of their states. While **9** is immobilized on a transparent semiconductor electrode,[63] **10** is immobilized on a gold electrode.[64]

The reversible switching of SAMs of **7** on Au(111) was also studied by a scanning tunnelling microscopy (STM) experiment.[62] As the difference in molecular length between the open and closed forms is very small (0.1 nm), the two different STM apparent heights were attributed to two different conductive states of a single molecule. Thus, reversible switching from an OFF state (**7o** as low-contrast spots) to an ON state (**7c** as bright spots) was achieved upon irradiation with the corresponding wavelength. Statistics were used to unequivocally separate light-induced switching from stochastic switching from Au–S bond fluctuations or tip-induced conformational modifications. Obviously, the switching behaviour depends crucially on the nature, the length and the position of the spacer linking the switching unit to the anchor group, leading to either uni- (**5** and **6**) or bi-directional (**7** and **8**) switching. These results do not only display how subtle changes in the molecular structure can have a large effect on the electronic transport properties, but also motivate the detailed investigation of various linkers in order to correlate properly molecular structures and switching properties, and to permit the development of photoswitches combining full reversibility and high photochromic performances.

Aside from switching applications, diarylethene derivatives have been investigated as information storage devices (Fig. 6). Particular dithienylcyclopentene derivatives combine photochromism and electrochromism, thus their isomerization reactions can also be triggered electrochemically.[65,66] For example, the dithienylethene **9o** was immobilized on an indium-tin oxide (ITO) electrode and was switched either photochemically or electrochemically between both isomers.[63] Interestingly, a non-destructive electrochemical read-out of the state of the monolayer (either open or closed) was exploited to perform a read–write–erase sequence that was repeated several times. Obviously, these molecular devices can be grafted on a non-metallic conductive surface without loss of functionality. Also, cysteamine-modified gold electrodes have already been functionalized with the dithienylethene derivative **10o** comprising carboxymethyl-pyridinium end-groups.[64] The corresponding electroactive and photoisomerizable monolayer was exploited as a read–write–erase information processing unit as well as a set–reset flip-flop memory element. Read-out signal amplification was accomplished by a secondary electrocatalytic process. The read-out of the state has been achieved in both examples (**9** and **10**) electrochemically.

Photochromic dithienylethenes are not only exciting in the investigation of fundamental switching and information storage concepts, they are also appealing for numerous other devices like, *e.g.*, chiroptic applications,[67] photoregulation in metal catalysis[68] and photodelivery applications.[69] However, their integration as molecular switching units in future hybrid molecular CMOS devices seems rather unlikely. In particular, systems operated by light raise numerous issues like nature, size and integration of the light source into the circuit, control over the illuminated area and the number of illuminated molecules.

Electrochemically-triggered molecular switches

In a molecule integrated in an electronic circuit, the current is assumed to pass through one of both frontier orbitals (HOMO or LUMO) through the molecular structure. A strong effect of the electron population of these orbitals, which can be tuned electrochemically, on the passing current is thus expected and has already been displayed in conductance experiments.

Schiffrin *et al.*[70] investigated transport properties through molecules with redox centres that were used to link metal nanoparticles to the substrate in a STM experiment. As displayed in Fig. 7, the investigated molecule **11** ($n = 6$) consisted of a dialkyl pyridinium as a redox centre, also referred to as viologen, with two terminal sulfur anchor groups at both ends of the alkyl chains. The molecules were assembled on a gold surface and gold nanoclusters were placed on top of the sulfur functionalized molecules. The STM tip was positioned on top of a nanoparticle to measure the tunnelling current through the substrate–molecule–nanoparticle–STM tip junction. Scanning tunnelling spectroscopy (STS) enabled monitoring of the tunnel current through the junction, while the redox state of the viologen subunits in the linking molecules was controlled electrochemically without affecting the bias between the STM and the substrate. Increased conductivity was observed for reduced viologen linkers $V^{\bullet+}$ compared to their dicationic state V^{2+} by these measurements.

In 2003, a straightforward technique used to measure the conductivity of single molecules as a function of their redox

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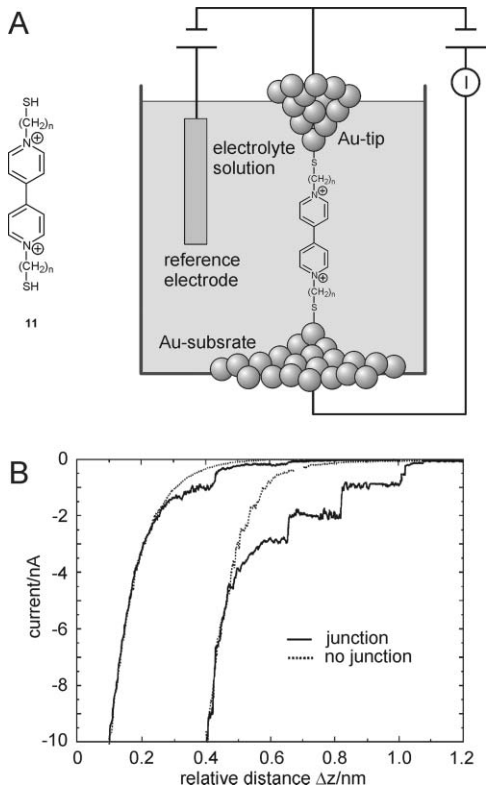

Fig. 7 Viologen derivative **11** ($n = 6$) has been investigated in several electrochemical STM setups like the sketched single molecule junctions (A)[71–73] or Au–nanoparticle covered junctions.[70] (B) displays typical pulling traces for **11** ($n = 6$) during the electrochemical STM experiment reported in ref. 72. Statistical analysis of the current plateaus of a large number of measurements suggested the formation of junctions consisting of a discrete number of molecules as the origin of the effect.[72] Reprinted with permission from ref. 72.

state was reported by the same group.[71] Viologen derivatives with terminal sulfur functionalized alkyl spacers were assembled in a low coverage phase on a gold(111) substrate. Upon dipping an STM tip into the assembly, the spontaneous formation of stable molecular junctions between the substrate and the STM tip was observed. Subsequently, the current was measured and plotted as a function of the distance between the tip and the substrate. For a considerable amount of such pulling traces, reproducible plateaus have been observed exclusively for distances below the length of the stretched linking molecule (~2.5 nm), which have been interpreted as results from a concrete number of molecules linking the substrate and the tip. In similarity to the nanoparticle junction experiment, an increased conductivity was observed for the linking viologen derivative in its reduced form.

A more comprehensive investigation of viologen derivatives as electrochemical potential dependent structures to gain information about the relationship between molecular and electronic structure in macroscale and nanoscale molecular assemblies has been reported by Wandlowski and coworkers. In particular, self-assembly and redox properties of viologen derivatives on gold electrodes have been reported.[72,73] Three different types of addlayers were found, low coverage (disordered), striped, and high coverage monolayers, depending on the assembly conditions. Electron-transport properties were explored by *in situ* STM experiments. Again substrate–molecule–STM tip junctions were formed and analyzed statistically. The redox state dependent transport currents through single molecule junctions revealed a sigmoidal potential dependence, which was attributed to the electronic structure change.[72] Variation of the length of the alkyl chains (**11** ($n = 5,6,7,8$)) separating the viologen subunit in the junction from the substrate and the tip, revealed a surprising low tunnelling decay constant for the molecular system.[73]

The difference in electronic transport properties through viologen functionalized junctions is based on the electronic population of the redox chromophore, which is separated from the electrodes by rather insulating alkyl spacers. For redox chromophores comprising conjugated linkers to the electrodes, additional new effects are expected. In analogy to the optically addressed diarylethene derivatives, the conjugation through a redox chromophore may be addressed electrochemically. Hummelen and coworkers suggest the integration of anthraquinone subunits as displayed in Fig. 8.[74] While the reduced hydroquinone form of **12** should provide a fully conjugated pathway for the tunnelling current, the oxidized anthraquinone form divides the π-system in two.

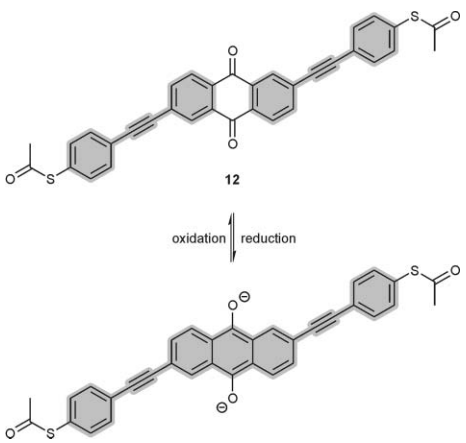

Fig. 8 Anthraquinone based molecular rod **12** proposed as potential electrochemically addressable molecular switch.[74] The extent of expected π-delocalization in the oxidised (top) and reduced (bottom) form of **12** is indicated by a grey background.

The molecular rod **12** consists of the central electrochemical active moiety as a conjugation divider and is functionalized with terminal acetyl-protected sulfur anchor groups. Cyclic voltammetry (CV) investigations displayed a two-step reversible redox process with a semiquinone intermediate upon reduction to the hydroquinone dianion. Considerable differences are reported for the absorption spectra of the fully conjugated reduced state and the oxidized state already pointing at the differences of delocalization of the chromophore's π-system. Molecular orbital calculations have further supported the proposed switch, but transport investigations through an immobilized molecule in an electrochemically addressable junction have, to the best of our knowledge, not been reported yet.

Also based on the idea of addressing the π-conjugation through a chromophore electrochemically, Nielsen and coworkers suggest the extended TTF derivative **13** (Fig. 9).[75] The proposed and synthesized molecule **13** is an OPE derivative with two sulfur groups on each end enabling the immobilization between noble metal electrodes. The central moiety bears an electrochemically

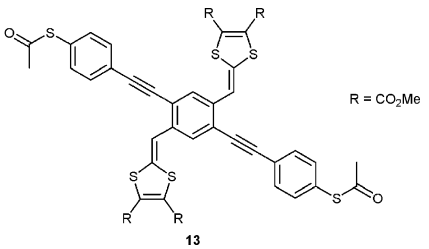

Fig. 9 Electrochemically triggered switch **13** comprising an extended TTF derivative as a redox active central unit.[75]

addressable extended TTF subunit. The conjugation of the molecule is supposed to be interrupted by oxidation, and considerable changes in electron transport are expected. CV measurements and computational calculations support the proposed switching mechanism. However, immobilization between two electrodes and physical measurements have not been reported yet to the best of our knowledge.

Voltage-triggered hysteretic molecular switches

While an immediate switching event upon reduction or oxidation is observed or expected for the above described electrochemically triggered molecular switches, hysteretic switching properties are required to enable data storage with such devices. Hysteresis, in general, describes the behaviour of a system that does not respond instantly to an applied force but rather displays a delayed reaction. By plotting the applied force against the state of the system, loop-like graphs are obtained. For applied forces within the region of the hysteretic loop, the system is bistable and remembers its latest state.

Furthermore, read-out becomes feasible within the force regime of the loop without altering the state, an ideal situation for logic applications or memory cells as already elaborated in the introduction.

To achieve hysteretic switching in molecular devices, Stoddart and coworkers combined electrochemical triggered systems with supramolecular rearrangement reactions. These most advanced and sophisticated hysteretic molecular switches are based on interlocked supermolecules like catenanes or rotaxanes.[76] While catenanes consist of two interlocked cyclic molecules, rotaxanes are assembled from a molecular axis surrounded by a cyclic system. For both supermolecules, the intended switching mechanism is based on Coulomb interactions between the mechanically interlocked molecules, which can be altered by electrochemical charging. The differences in conductivity solely depend on the spatial arrangement of the components, as during the read-out process both states have the same redox state. However, temporal charging of subunits is assumed to alter the spatial arrangement. The considerable stability of the supermolecules in two different spatial arrangements is the origin of the bistability and the hysteretic switching.[77] The modular synthesis of these rotaxanes and catenanes allows these supermolecules to be tailored for different electrode materials and integration setups. Thus, both supermolecules have been tailored and developed for several integration setups and have been investigated in detail.[78–80] For example, the rotaxane **14** displayed in Fig. 10 was able to store information integrated in a crossbar architecture.[28] Recent improvements of these rotaxane based memory cells even enabled the fabrication of a 160-kilobit memory unit with a lateral density of 10^{11} bits per square centimetre.[34]

The underlying switching mechanism has been investigated in detail and is discussed briefly with the rotaxane **14** as an example. The axis of rotaxane **14** provides two coordination sites for the $CBQT^{4+}$ ring system, namely a TTF and a dioxynaphthalene (DNP) site resulting in the two translational conformers displayed in Fig. 10 A. In the ground state co-conformer **14(GSCC)**, the $CBQT^{4+}$ ring encircles the TTF site and in the meta-stable co-conformer **14(MSCC)**, the ring encircles the DNP site. Temporal electrochemical charging of the TTF subunit allows control of the equilibrium of two different translational conformers. As the $CBQT^{4+}$ ring is able to slip from one coordination site to the other, oxidation of the TTF subunit results in electrostatic repulsion and the $CBQT^{4+}$ ring moves to the DNP site. After reducing the TTF unit back to its initial state, the $CBQT^{4+}$ ring remains at the DNP site for a while providing the required hysteretic features. In the solution phase, these types of molecular-mechanical switches have been investigated extensively.[78–80] To explore solid state applications at a fundamental level, suitably functionalized rotaxanes were immobilized within a solid state polymer and an electrochemical cell was used to enable electrochemical triggering.[77] The polymer environment slows down mass transport and mechanical motion, but the overall mechanism remains the same. Thermodynamic properties of the switch were quantified through time and temperature dependant cyclovoltammetry. By CV, the MSCC and the GSCC are readily distinguishable due to the considerable lower oxidation potential of the bare TTF in the MSCC (200 mV less positive).[77] The [2]rotaxane **14** was further investigated in the solid-state in a molecular switch tunnel junction (MSTJ).[28] In a crossbar architecture, a Langmuir–Blodgett film of **14** was sandwiched between a polySi bottom electrode and a Ti/Al top electrode (Fig. 10 B). The resulting MSTJ displayed two distinguishable signals for the low voltage (0.1 V) tunnel current depending on the prior applied voltage. Fig. 10 C displays the hysteresis window opened by the bistability of the MSTJ. Switching cycles upon applying voltage pulses (±2 V) are displayed in Fig. 10 D. In analogy to the behaviour of comparable rotaxanes in solution, the observed bistability is expected to emerge from a rearrangement of some of the immobilized supermolecules upon temporal charging of subunits by the voltage pulse. According to ground state equilibrium thermodynamics and switching kinetics of bistable [2]rotaxanes in solution, polymer gels and molecular electronic devices, the low-conductance (switch-open) state is related to the MSCC–GSCC ratio at equilibrium while the high-conductance state (switch-closed) probably corresponds to the immobilized MSCC.[81]

Another very interesting example of hysteretic switching behaviour was reported recently with molecule **15**, consisting of a terminal sulfur-functionalized OPE rod comprising a bipyridyl-dinitro central unit (Fig. 11). SAMs of **15** were investigated using three different techniques (STM, crossed-wire tunnel junction and magnetic bead junction).[82] I–V measurements revealed a unipolar voltage-triggered conductance switching. While sweeping the bias voltage, the molecule suddenly switches from a low conductance state to a high conductance state, which is maintained until the applied bias approaches 0 V. This reversible process allows the system to be cycled many times between both discrete states.

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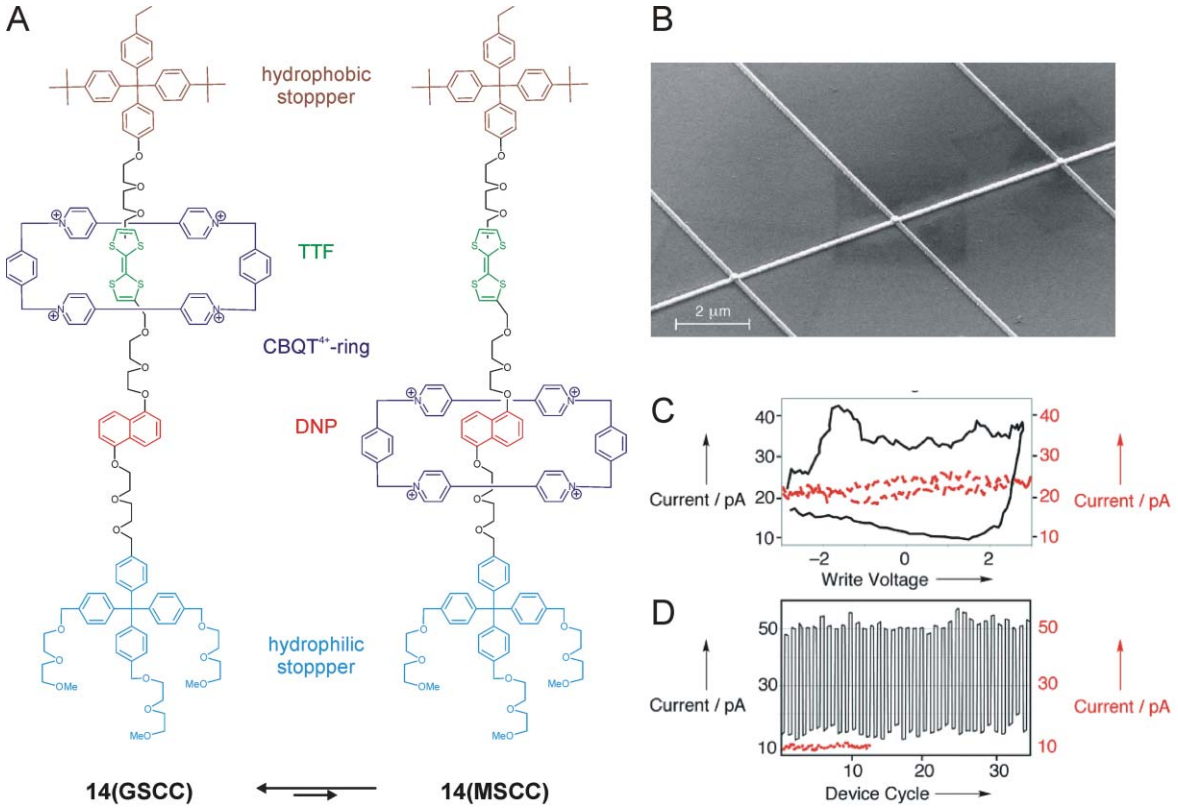

Fig. 10 (A) Rotaxane **14** providing two binding sites for its $CBQT^{4+}$ ring resulting in two co-conformers, namely the thermodynamically favoured ground state co-conformer **14(GSCC)** and the meta-stable co-conformer **14(MSCC)**.[81] (B) MSTJ consisting of two crossed electrodes sandwiching an LB-film of **14**. (C) Hysteresis loop of the tunnel current through the MSTJ as function of the prior applied switching voltage. (D) Repetitive switching of the MSTJ between both states.[28] Reprinted with permission from ref. 28.

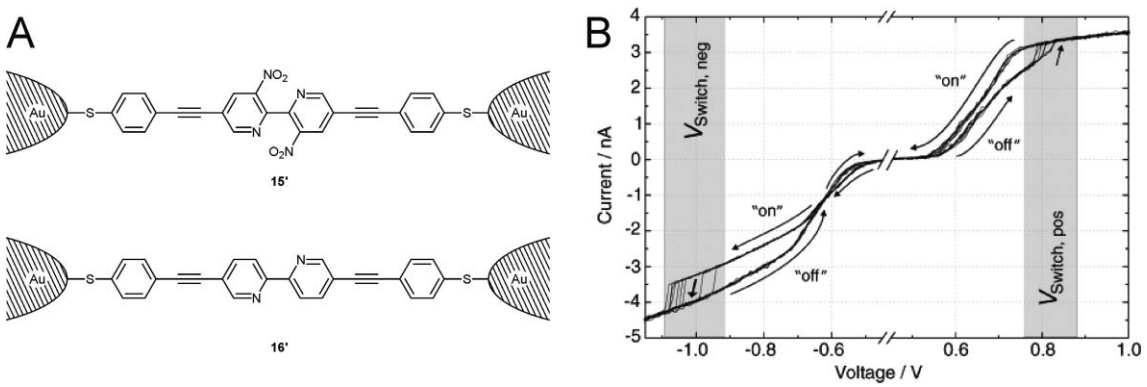

Fig. 11 (A) Sketch of the immobilized molecules **15** and **16** in a MCB. (B) Repeatedly recorded I–V curves of **15** immobilized in a MCB displaying hysteretic switching cycles. The system switches from the OFF state to the ON state when the applied voltage exceeds a certain positive threshold ($V_{\text{Switch, pos}}$). The molecule is reset to the initial OFF state below $V_{\text{Switch, neg}}$.[29] Reprinted with permission from ref. 29.

Even though the measuring technique influences the threshold voltage, it is reproducible within each setup. Furthermore, the voltage-induced switching behaviour is an intrinsic feature of the molecule which depends neither on neighbouring molecules nor on the technique used. Voltage-triggered conductance switching was clearly differentiated from random statistical switching (stochastic switching) originating from molecular motion or Au–S bond fluctuations.

The intrinsic molecular functionality of **15** was further investigated on single molecules in contact with two symmetric gold leads in a MCB setup.[29] A hysteretic switching behaviour was revealed by I–V measurements (Fig. 11), in contrast to the reference molecule **16** lacking the nitro groups, which only exhibits monotonic traces. The origin of the conductance switching is currently under investigation. Conformational change, electrostatic charging and tilting have been hypothesized as the origins of the observed behaviour so far. The reversible and controllable voltage-triggered switching ability of **15** has already been used as single molecule memory element by reading and erasing bits by simple voltage pulses. Even though the switching mechanism of the system is not

yet fully understood, it is a beautiful example of a rather simple molecular structure comprising promising electronic features. Further inspection of the origin of its switching will hopefully enable the improvement of the electronic properties by rational design of the molecular structure.

Conclusions

As has been illustrated with several examples, beautiful synthetic chemistry has been developed to contribute considerably to the progression of molecular electronics, and basic electronic functions such as rectification or switching have been demonstrated on the molecular level with various systems. However, the design and assembly of molecule based electronic devices is a strongly interdisciplinary challenge, with the chemists' contribution as a fundamental one, namely the design and synthesis of the functional unit itself—the molecular device. While the ability of the chemist to provide tailor-made molecules is a crucial requirement, their interaction and communication skills with colleagues from neighbouring disciplines will be equally important for the further successful development of molecular electronics.

Further improvements of the integrated molecular structures enable us to go beyond proof of principle devices and perfection of their performance and fatigue properties will provide promising functional building blocks to complement existing electronic circuits. Apart from the developments of molecular structures, considerable contributions are expected from the development of the interface between molecules and electrodes. While for numerous fundamental studies the already well explored interface between molecules and gold electrodes has been used, semiconductor electrodes are much more appealing from an application view-point. A further challenge in the area of nanotechnology is to overcome the size gap between molecules and electrodes and to develop concepts for the massive parallel integration of molecular devices.

All together, the integration of molecular devices into electronic circuits as a strongly interdisciplinary enterprise has recently made impressive developments. Enriching participating disciplines, molecular electronics equally profits from and contributes to synthetic chemistry and beautiful molecular structures have been developed and synthesized. Currently, the potential, as well as the limits of the molecule based approach to electronic functions, is being explored.

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