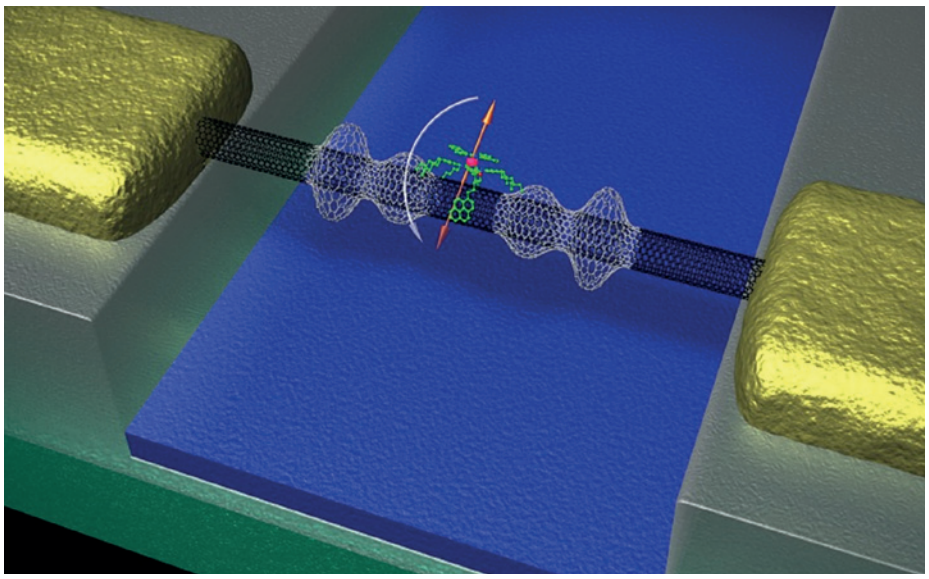
Visions for a molecular future

Leading researchers in molecular electronics discuss the motivation behind their work and what they consider to be the grand challenges for the field.

Molecular electronics has been around for more than 40 years, but scientists have only recently really begun to explore the properties and opportunities of single molecules. This collection of 12 features from researchers from a variety of backgrounds provides an overview of the different directions the field is going in.



The phonon modes of a carbon nanotube set between two electrodes can control the spin states of a molecule. Image reproduced with permission from C. Grupe/KIT.

To me molecular electronics is at the heart of nanoscience, because it hinges on the fundamental idea that novel devices can be created by using ingredients so small that new properties emerge. Molecules bring in their intrinsically quantum mechanical nature and hence molecular devices can exhibit characteristics that, even at ambient temperature, cannot be achieved otherwise. In fact, by making functional molecules, such as switches, synthetic chemists add a unique ingredient of variability and structural control that cannot be achieved with equivalent solid-state devices. For molecular electronics to be a future technology, basic research will be crucial. Here, we should concentrate our efforts not only on conductance properties, but especially on device stability. We need to find new paradigms on how to couple molecules to electrodes, possibly using multiple anchors, or experiment with nanosized objects as intermediates between electrodes and molecules. Single-molecule experiments will remain important from a fundamental standpoint, but I am convinced that future devices will be multi-molecular.

Once we take the step towards making robust devices, a great set of opportunities could open up with the exciting possibility of manipulating quantum interference effects, harnessing the thermoelectric properties of molecular systems for the efficient conversion of heat to electricity, or playing with electron spin for memory devices based on molecular spintronics. In the shorter term, the most likely devices will be electrical sensors based on molecules with unique recognition properties, either for physical stimuli or for other molecules. But most importantly, the success of molecular electronics depends on the continued willingness of chemists, physicists, surface scientists and engineers to work together. And if we can combine their skill and knowledge, we will be in a great position to move molecular electronics from a nanoscience to a nanotechnology.

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As the field of molecular electronics evolved from hypothesis into experimental realization one often heard the claims that here comes the solution 'beyond silicon' and that organic molecules are going to be used in electronics. Indeed, organic molecules have found a place in electronics as organic light-emitting diodes and in molecule-based photovoltaics, but the practical use of a single-molecule as a 'molecular transistor' remains elusive. Why has this challenge not been met? In part, it is at a dead end because most attempts have aimed at replacing the silicon in the 'silicon way', that is, to build solid state-like devices with single organic molecules.

As the field has matured and we better appreciate where the problems lie, it is clear we need to focus our efforts elsewhere. Here I recommend research efforts be concentrated in two directions. The first should be to study the properties of molecules at a fundamental level and would be analogous to the long tradition of molecular spectroscopy, which has provided a deeper understanding of molecular structure, dynamics and reactivity. The second should be to explore new paradigms for electronic, optoelectronic and logic devices in which full advantage is taken of the quantum properties of molecules. To this end, the new field of molecular spintronics exploits the electron spin in organic molecules, which is often a 'good quantum number' and hence a degree of freedom that maintains coherence for a long time, even at room temperature. Initial results using a monolayer of chiral molecules as an efficient spin filter are already promising. Such quantum properties are extremely difficult

to realize in solid-state devices, especially at room temperature; therefore, molecules promise to offer something fundamentally different from silicon-based technology.

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At two recent conferences on molecular electronics, held in the past 12 months, there were feelings that the field would by now be a mature technology that would soon result in applications, when in fact it is not. I like to compare the current status of molecular electronics with what happened to microelectronics: the concept of the transistor had already been well established when finally the complementary metal–oxide–semiconductor technology arrived with its disruptive power. In between, plenty of unexpected new physics had been developed and inspired solid-state physicists to look far beyond mere applications in electronic devices. I see molecular electronics being in a similar exploratory phase. The proposition to use molecules as functional building blocks can be considered rather old by now, with experimental molecular electronics starting over 15 years ago. After having put a lot of effort into the fabrication of electronic devices and gaining basic understanding of the electronic conduction mechanisms, researchers are now starting to look beyond electric-charge transport and focus on molecular-transport properties, for example, thermoelectric and spin transport. Although interfacing molecules with metallic leads has proven to be a major challenge, molecular electronics remains a fascinating playground for scientists for exploring new fundamental concepts and it will hopefully stay in this 'hunter-gatherer' phase for many more years. Meanwhile, the first technological achievements may come from the development of molecule–semiconductor hybrid structures, and perhaps from molecular spintronics.

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Driven by recent breakthroughs in experiment and theory, single-molecule junctions are emerging as novel ensemble platforms for understanding electronic structure and function at interfaces, in and out of equilibrium, and in heterogeneous environments. New and exciting phenomena such as thermoelectric effects, mechanical switching, quantum interference and spin filtering have all been reported at the single-molecule level. Our intuition connecting these phenomena to junction structure and chemical composition is still incomplete but improving and on a strong trajectory. Many junctions of increased complexity could be explored going forward. Here I point to three questions that should lead to new instrumentation and inspire synthesis and theory efforts in the near term. First, could time-resolved or near-field *in situ* electron and photon microscopies be brought to bear to better resolve junction structures? Although force measurements are evolving our picture of local junction geometries and their fluctuations, many atomic-scale structural and dynamic details are unknown. Second, could molecular junctions be used to probe photophysics at the single-molecule level? Directing visible light into junctions would allow controlled studies of vibrational modes, photocurrent, exciton generation and transport, and charge separation, processes central to solar-energy conversion devices. Third, could junctions be gated electrochemically, reliably and reversibly? Three-probe measurements in solution, although challenging, could allow efficient fine-tuning of energy-level alignment, and enable study of chemical reactions at the single-molecule scale. These questions will inevitably drive the development of new theoretical approaches, particularly for tackling van der Waals dispersion interactions, charged and neutral excitation energies at complex interfaces in and out of equilibrium, electron–phonon interactions, electron correlation and spin states, and coupled electron–ion dynamics. Single-molecule junctions are becoming increasingly less elusive and exclusive, and revealing themselves as a general tool for exploring fundamental questions across sciences.

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Over the past two decades, molecular electronics has evolved from a rapidly growing research field motivated by a rich spectrum of intriguing observations coupled with promises of technological breakthroughs, into a more sober phase of careful experimentation alongside increasingly reliable theoretical and computational methodologies. Still motivated by technological goals, molecular electronics continues to focus on fabrication, stability, characterization, functionality and control of molecular electronic devices. These issues, translated into fundamental science, pose exciting theoretical and experimental challenges that go beyond electronic transport. Other transport phenomena investigated at the single-molecule level are now entering the stage. These include: heat generation and heat conduction, the interplay between electrical and mechanical properties, spin selectivity, and the coupling of molecules with external electromagnetic and magnetic fields. In this regard, molecular plasmonics is a fast developing field that explores the consequences of the interaction between molecules and their local electromagnetic environment as affected by the proximity of small metal and semiconductor structures. Intensive studies of the interaction of nanosized metallic objects with light have indicated that enhanced optical effects between metal particles are often dominated by electromagnetic 'hot spots', sometimes to the level that makes it possible to observe the response of a single molecule. Molecular junctions, by their intrinsic nature, are often such hot spots, located in the same spatial region that determines the junction's conduction properties. Hence, there is a strong coupling between the electromagnetic radiation and electron transport at the single-molecule level and we can expect molecular plasmonics to offer an important input in our understanding of this cross-correlated and far-from-equilibrium process.

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Single-molecule junctions are important tools for studying quantum mechanical systems that are driven out of equilibrium. A macroscopic bias across a molecular junction leads to the steady-state motion of electrons and the irreversible dissipation of energy into many electronic and vibrational degrees of freedom. In this situation, the distribution of electrons as a function of energy and the populations of vibrational modes near the junction can be dramatically different from those in thermal equilibrium. It is extremely difficult, however, to examine these non-thermal distributions experimentally. Recent and ongoing studies of molecular electronic junctions can combine

traditional electronic transport with other techniques (for example, noise measurements; optical spectroscopies of vibrational modes; thermopower; mechanical measurements of binding forces), broadening molecular electronic investigations beyond ordinary current–voltage characteristics. These studies can access microscopic information about the flow of energy, the origins of dissipation, the fate of quantum coherence, and the relative importance of electron–electron and electron–vibrational interactions. These issues are of basic scientific interest, and at the same time can have real ramifications for nanoelectronics applications as the semiconductor industry approaches the few-nanometre scale. Single-molecule junctions are proving to be excellent model systems for these studies, because one molecule has enough degrees of freedom to show nontrivial physics, while still amenable to realistic calculations. Although single-molecule devices are never going to displace the metal–oxide–semiconductor field-effect transistor in consumer electronics, these structures can give us an experimental window into non-equilibrium processes that are largely inaccessible at the macroscale, but of major fundamental importance.

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Advances in the field of molecular electronics over the past decade both in experimental techniques and first-principle calculation methods have made it possible to obtain reproducible results from different laboratories. Charge-transport behaviour, for instance, can now be reliably controlled by tuning the molecular structure or by applying an external field, and detailed chemical and structural details of single-molecule junctions are available through inelastic electron tunnelling and surface-enhanced Raman spectroscopies.

However, in my opinion, the success of molecular electronics as a field should be measured on the broader impact it will have on other fields, and this is still yet to come. I believe that a better characterization of charge transport versus charge transfer in molecules will profoundly change our understanding of chemical reactivity, especially in oxidation and reduction reactions. Most molecular systems studied so far involve short

A cover of *Scientific American* celebrates molecular electronics, following the pioneering investigations of the late 90s. Image courtesy of *Scientific American*, a division of *Nature America*.

molecules with molecular energy levels aligned far away from the electrode Fermi levels. Moving the molecular energy levels close to the Fermi levels will in general lead to a strong coupling between the electronic and nuclear degrees of freedom. Progress in this direction will be useful to understand charge-transfer phenomena in biologically important molecules, such as DNA and proteins, as well. Another field that will benefit from a fundamental understanding of molecular properties at a single-molecule level is analytical chemistry for which single-molecule detection is the ultimate limit. Finally, studying the electronic, optical, mechanical, thermal and quantum properties of molecules will be important in materials science, eventually leading to unexpected applications that are different from today's silicon electronics.

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Contacting a single molecule in a device is not an easy task, and to do so reproducibly is an even more difficult one. Nevertheless, tremendous progress in this sense has recently been made and nowadays reproducible measurements from different laboratories are possible. These studies show that in single-molecule electronics one has to live with a certain degree of variability: statistical approaches to measure conductance and other molecular properties are essential, especially at room temperature. (A similar conclusion has long been established in biophysical research as well, for instance on the activity of single proteins.) Today, the main challenge for molecular electronics is to find ways to reduce variability even further or, alternatively, to exploit molecular functionalities that are largely insensitive to the details of the contacts. This approach would imply a shift of focus from the molecule–metal junction to the molecule itself. The unique properties of molecules, including large energy-level spacing, and the endless possibilities offered by chemical synthesis suggest the possibility of room-temperature operation, although converting these properties into electronic functionalities remains a tremendous challenge. Although it is tempting to use molecular electronics to mimic concepts that form the basis of silicon devices, we need to explore and be more open to alternative, yet unknown, routes. I cannot predict the outcome of this search but one thing is clear: quantum effects will be crucial in this game, and many surprises are in store from this front.

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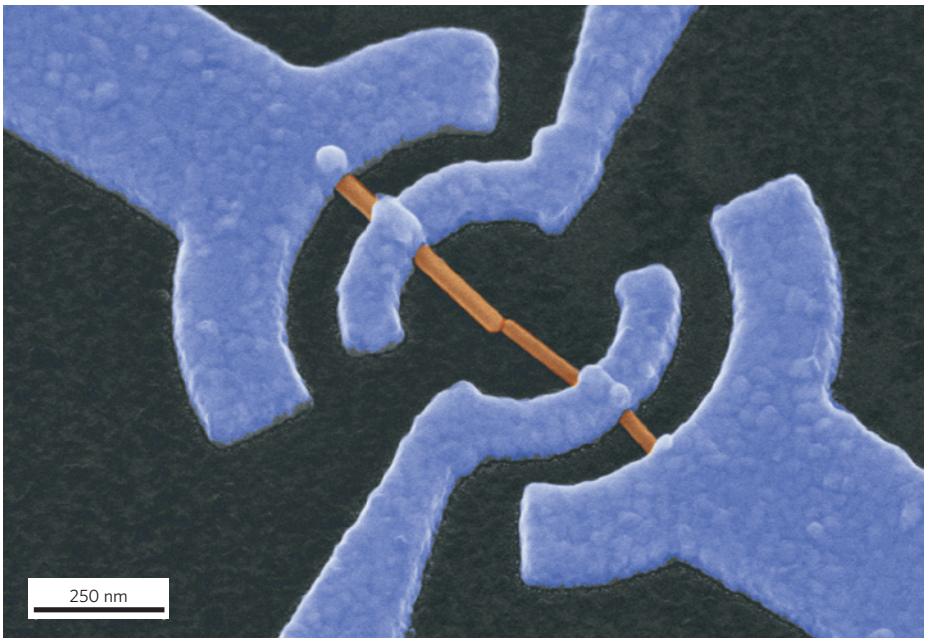
Molecular electronics offers, in principle, the unique opportunity to control the electronic functions of a molecular junction by design; synthetic chemistry enables the assembly of tailor-made structures with reasonably accurate predictions of their intrinsic electronic characteristics and associated charge-transport properties. That synthetic chemistry would play a central role in molecular electronics has been clear from the outset, but huge technological challenges regarding the integration of molecules in electronic devices have prevented a full exploitation of its potential. The dimensional advantage of molecules in miniaturized devices is usually lost considering the large size of the entire junction set-up and further limitations arise from the energy-level misalignment or the need for specific functionalization at the electrode/molecule interface. An impelling challenge of molecular electronics therefore is to optimize these interfaces. Carbon-based electrodes seem a particularly promising approach, because having molecules and electrodes of the same material (carbon



A molecule occupies the gap between two gold nanorods that are contacted to external electrodes to enable electrical measurements over the gap. Image courtesy of Antje Rey, IBM Research-Zurich and ETH Zurich.

atoms) considerably reduces the electronic interfacial mismatch of the junction. At the same time, protecting the charge-transport channel within a molecule from the surroundings can minimize sample-to-sample fluctuations, arising from structural variations of the nearby electrodes. To this end, cage macromolecular structures or supramolecular aggregates may represent a promising synthetic avenue. Furthermore, due to their minute size, molecules are usually contacted by only two electrodes. However, gated approaches that take advantage of molecular structures that alter their shape, electronic property, spin state and so on in response to an electric field can expand the range of tunability that molecules may offer. But before any integration of functional structures in practical electronic devices can occur, 'few-molecule' junctions will need to be extensively validated through a fine control of intermolecular interactions.

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Although the first concepts proposing to use molecular components in electronic devices were evoked as early as the 1960s, the development of molecular electronics only started during the past two decades with the explosion of the nanosciences and the availability of manipulation techniques at the lower nanometre scale. Whereas at the beginning, miniaturization and cost reduction were the main driving forces, benchmarking with conventional, semiconducting electronics revealed that molecular electronics would only 'grow up' if it looked beyond the border of conventional electronics, in a realm where the singular properties of molecules (for example, monodispersity, atomic precision, self-assembly ability, functionality and intrinsic quantum behaviour) can be pivotal. The central challenge is to achieve precise control at a multiscale level of the interface between molecules and (metallic) electrodes within device environments. Here, a better understanding of the molecule–electrode hybridization process and electron-injection dynamics is necessary to set the stage for the synthetic design of the electronic properties of the molecular and interface components. If the ongoing concerted efforts of synthetic chemists, experimental physicists, computational theorists and industrial partners fructify, candidates for novel applications and devices with impact beyond conventional electronics will emerge. The particular case of organic light-emitting diodes has exemplarily showcased what the full upstream development chain from cutting-edge basic research to high-end consumer products can look like. By following a similar path, and profiting from the emergence of new materials, such as graphene and other carbon nanomaterials, even more fascinating developments (for example, quantum computation, all-carbon photovoltaics, portable biosensing) can be expected from molecular electronics in the near and medium future.

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Since the 1970s, the visionary concept of electronic circuits and systems consisting of active molecular-scale components has been an enticing prospect for a revolutionary successor to solid-state computing systems. Throughout the past few decades, concerns that continued scaling of silicon metal–oxide–semiconductor field-effect transistor technology would eventually stagnate due to seemingly insurmountable issues, such as lithography limitations, dopant statistics, oxide thickness and short channel effects, have regularly arisen. Starting in the 1990s, experimental realizations of molecular-scale devices made the dream of molecular devices a reality, and recorded spectacular results. However, the microelectronics industry has not been idle, and one after another the past concerns about device scaling have been systematically overcome. What has become apparent is that the true limitation of integrated electronic systems is power dissipation, whose origin lies in the basic physics of field-effect transistor devices, regardless of structure, material, or technology. The exciting aspect of molecular devices is that many of the inherent transport phenomena that exist today in molecular transistors are similar to a number of advanced solid-state device proposals put forth to overcome the power dissipation limitation, but with the key advantage that molecular device functions can be controlled by chemical synthesis to degrees that are difficult to achieve by solid-state technology at present. Additionally, an important lesson learned over the past few decades is that an isolated device is a necessary, but not sufficient, condition for a successor electronic technology. (One of the most important device inventions of the twentieth century was not just the transistor, but the monolithic copper wire.) Integration capability is central to realizing future computing systems, and is a fundamental challenge to molecular

devices. Hopefully, this technical limitation will be overcome with enough focus, innovation and resources.

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Molecular junctions are a formidable test bed for investigating structure–function correlations in charge-transport phenomena at the nanometre scale. Various aspects of electron–electron and electron–phonon interactions are currently being explored including spin-mediated charge transport, molecular ferroelectricity, and light-coupled interactions in metal–molecule–metal junctions.

Making electronic devices that use molecules as the active element, however, requires atomic-scale precision fabrication and long-term stability. Also, the complexity of such systems still limits our predictive understanding of charge and energy transport at the interface of hybrid organic–inorganic systems. Despite these difficulties, it is striking to notice that organic electronic devices are nowadays finding their way into consumer electronics. At the industrial level, molecular fabrication processes are progressing fast and reaching an unprecedented accuracy.

Remarkably, we haven't yet really made the most out of the molecules' potential and specificity. Molecules are not simply quantum dots that can be fabricated at a large scale; they can undergo conformational changes and interact with neighbouring molecules. These aspects however do not easily translate into conventional electronics paradigms and the intrinsic functionality of molecules have been barely explored so far. But exploiting molecular properties may result in alternative ways to process information. Here, hybrid devices integrating molecular functionalities for massively parallel *in vivo* information processing together with more conventional electronic circuits for signal post-processing could open fascinating perspectives, for instance in the development of neuroprosthetic devices. It is time to put molecules to work, so they can do what they do best.

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