Electronics using hybrid-molecular and mono-molecular devices

C. Joachim*, J. K. Gimzewski† & A. Aviram‡

* *Centre d'Elaboration de Matériaux et d'Etudes Structurales–Centre National de la Recherche Scientifique, 29 rue J. Marvig, 31055 Toulouse Cedex, France*
† *IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland*
‡ *IBM Research, T. J. Watson Research Center, Route 134, Yorktown Heights, New York 10598, USA*

The semiconductor industry has seen a remarkable miniaturization trend, driven by many scientific and technological innovations. But if this trend is to continue, and provide ever faster and cheaper computers, the size of microelectronic circuit components will soon need to reach the scale of atoms or molecules—a goal that will require conceptually new device structures. The idea that a few molecules, or even a single molecule, could be embedded between electrodes and perform the basic functions of digital electronics—rectification, amplification and storage—was first put forward in the mid-1970s. The concept is now realized for individual components, but the economic fabrication of complete circuits at the molecular level remains challenging because of the difficulty of connecting molecules to one another. A possible solution to this problem is 'mono-molecular' electronics, in which a single molecule will integrate the elementary functions and interconnections required for computation.

Aviram and Ratner[1] suggested that a single molecule with a donor–spacer–acceptor (d–s–a) structure (see **1** in Fig. 1c) would behave as a diode when placed between two electrodes: electrons can easily flow from the cathode to the acceptor, and electrons from the donor are then transferred to the anode. The working principle of this device is analogous to that underlying the "valve" effect introduced by Schockley 60 years ago[2], but involves manipulating the electronic wavefunction of the metallic electrodes extending through the d–s–a molecule, rather than the carrier density in a semiconductor material. Such hybrid molecular electronic (HME) devices, comprising molecules embedded between several electrodes, thus differ radically from bulk-material-based molecular electronic technologies found in applications such as dye lasers, light-emitting diodes, liquid-crystal displays, and soft plastic transistors. However, the design of functional devices and machines based on the molecular electronics concept poses the challenge of integrating the functions required for advanced processing, particularly computing, within the same molecule in a mono-molecular electronics (MME) approach.

Owing to the lack of suitable technologies for establishing electrical contact between individual molecules, experimental investigations of the fundamental processes involved in electron transfer through molecules have long focused on gas-phase and liquid-phase systems. Although these approaches cannot result in working nanoscale devices[3], they have established that a simple shift in the energy of a molecular orbital—induced, for example, by a photo-isomerization—can fine-tune the intramolecular electron transfer rate through an individual molecular bond connecting two redox centres. Experimental studies involving averaging over many isolated molecules have, for example, demonstrated long-range through-bond electron transfer processes in molecule **2** (Fig. 1a)[4,5], intramolecular light-induced conformation changes in molecule **3** (Fig. 1b)[6], and intramolecular interference effects in molecule **4** (Fig. 1b)[7].

Electrical addressing of molecules

Langmuir–Blodgett (LB) and self-assembly fabrication techniques[8] can be used on many molecules to form organized molecular monolayers on suitable substrates. This allowed Mann and Kuhn to investigate long-range tunnelling through alkane chains in ordered LB monolayers[9]. Similarly, sandwiching molecule **5** (Fig. 1c) between differing metallic electrodes allowed the first (albeit somewhat ambiguous) observation of rectification effects in a molecular monolayer[10], confirmed by subsequent work[11] using molecule **6** (Fig. 1c) sandwiched between electrodes made from the same material.

The scanning tunnelling microscope (STM) enables controlled two-terminal measurements, and its development has thus allowed new experimental approaches for demonstrating and probing electron transport through individual molecules[12]. Examples include the electrical single-atom switch realized using a Xe atom[13] at cryogenic temperatures and the first experimental determination of the electrical contact point of a single C_{60} molecule (ref. 14). The resistance of $R = 55\,\mathrm{M\Omega}$ obtained in the C_{60} experiment corresponds to an electronic transparency (ease of transmission) of $T = 2.3 \times 10^{-4}$, with T being approximately proportional to the square of the inter-electrode electronic coupling introduced by the molecule compared to the corresponding vacuum gap. Ohmic dissipation in the electrodes is one way to evaluate T from the macroscopically measurable quantity R, as $T = h/2e^2\, R^{-1}$. However, owing to R being the resistance of the metal–C_{60}–metal tunnel junction, rather than that of the C_{60} molecule, it cannot be used to define molecular conductivity.

STM measurements on C_{60} have revealed linear current–voltage (I–V) characteristics at low applied bias voltages[14], indicating that the system behaves similarly to a metal–vacuum–metal tunnel junction at low bias voltage. However, 'squeezing' a C_{60} molecule by applying a small force in the nanonewton range with a metallic STM tip results in a shift of the molecular orbital levels[14]. This mechanically induced shift provides a means to modulate tunnelling through a single C_{60} molecule, even in a nonresonant tunnelling regime, and to change its resistance up to a limiting value approaching the quantum of resistance, $h/2e^2$ ($\sim 12.9\,\mathrm{k\Omega}$) (ref. 14). The phenomenon, mechanically modulated virtual-resonant tunnelling (VRT), has also been used to design an electromechanical amplifier (Fig. 2a), by making use of the ability to mechanically reduce molecular level degeneracy[15]. Specific to highly degenerate systems, the electomechanical amplifier is the tunnelling equivalent, on the nanometre scale, of the Schockley "valve" effect[2].

A variety of other techniques, such as experiments based on Coulomb blockade[16], nanopore[17], break junction[18,19], electro-deposition[20] and nanolithography[21,22], have been used to determine