Molecular Electronics: Observation of Molecular Rectification

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The term molecular electronics evokes varied images, everything from circuits consisting of single molecules to off-the-shelf biosensors (*1*). However, truly molecular artificial devices do not yet exist, despite the existence proof provided by biology that a single molecule (DNA) can code a retrievable unit of protein sequence information in about 3 nm^3 (*2*). In some cases, the connection between molecular and macroscopic properties is clear. For example, the properties of a thin-film optical device made from organic chromophores may, with certain assumptions, be understood from the properties of the active chromophores themselves. In contrast, one can only draw analogies between macroscopic electronic properties, such as conduction or rectification, and the chemical physics of single molecules.

Bulk electrical properties map less directly from the molecular domain. Consider doped polyacetylene, which has a bulk conductivity limited not by carrier mobility in a molecule but by interchain hopping. In this case, macroscopic conductivity measurements do not directly probe single molecule properties. More fundamentally, the definition of the conductivity of a single molecule is ambiguous. Injecting carriers into a molecule may cause profound structural changes, and the carrier motion is not governed by macroscopic current-voltage relations. Nevertheless, under special circumstances molecules might behave in a manner analogous to that of familiar macroscopic devices and materials. Martin *et al.* (*3*) claim to see just this kind of analogy in current rectification through monolayer and multilayer organic films.

In 1974, Aviram and Ratner (*4*) described an analogy in the current versus voltage response of conventional rectifiers and bridged, organic donor-acceptor molecules. In their picture, an asymmetric molecule, one side containing an electron donor and the other side an electron acceptor, can operate as a nanometer-scale rectifier when "coupled" to electrodes. More specifically, the current flowing through the molecule should have the essential characteristics of the electronic device known as a rectifier, a device that allows current to flow when a voltage is applied with one polarity but not with the opposite one. The asymmetry of the Aviram-Ratner class of molecules is essential for the rectification properties, in analogy with the asymmetry of the np junction of conventional solid-state rectifiers or diodes.

One may view rectification in the Aviram-Ratner picture as proceeding in three electron transfer steps (Fig. 1A). An electron transfers from a cathode (nominally a bulk metal) to the lowest unoccupied electronic orbital on the molecule localized on the acceptor species to create DBA$^-$. A molecular orbital localized on the donor site transfers an electron to the anode (once again a bulk metal), creating D$^+$BA$^-$. This step requires that the Fermi level of the metal be lower or equal to the orbital energy of the donor. Finally, the electron transfers from the reduced acceptor to the oxidized donor, regenerating the DBA species. The intramolecular electron transfer reaction D$^+$BA$^-$ → DBA is facilitated by a weak bridge-mediated electronic coupling between the donor and acceptor units. If the coupling is too strong, the asymmetry is broken, and bidirectional electron transfer should become possible. We present this scenario for heuristic reasons. Generally speaking, the order presented here does not necessarily reflect the time sequence of actual electron transfer steps. Furthermore, full localization of the tunneling electron on the donor or acceptor species is not essential. Experimental studies of the electron transfer mechanism would be informative.

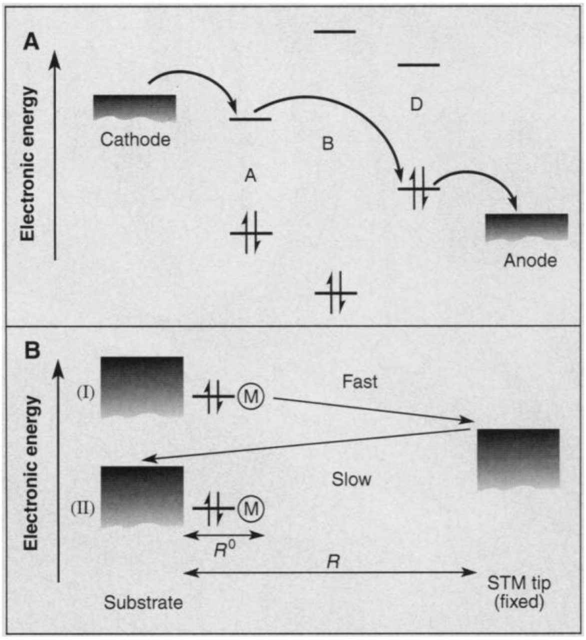

Fig. 1. Molecular one-way street. (**A**) The Aviram-Ratner "molecular rectifier," sandwiched between two electrodes, consists of electron donor (D), bridge (B), and acceptor (A) species. The orbital energies of the frontier molecular orbitals are shown. When a voltage of one polarity (as shown) is applied, electrons can flow between electrodes, but when the polarity is reversed, only unfavored long-range electrode to electrode tunneling is allowed. (**B**) When the substrate Fermi energy is high (I), current flows from cathode to anode by hopping through molecule M. However, when the substrate Fermi energy is low (II), only inefficient long-range tunneling from cathode to anode is allowed. Here the asymmetry is not intrinsic to the molecule, but rather to the device structure and applied voltages.

The requirements on the position of the Fermi levels of the electrodes connected to the molecule provide a means for control of the current flow in this device. With an adjustment of the bias potential between the two electrodes, it is possible to change the relative energies of the electrodes. Alternatively, one could tune each electrode independently with respect to a common voltage, namely ground. Clearly, the bias potential can have an effect on the molecule's intrinsic electronic properties as well. The electric field is on the order of 10^6 V/cm for a 1-V bias potential across a 100 Å molecule. This is relatively weak compared with the internal fields of the molecule, typically 10^8 V/cm.

In this situation, the picture in Fig. 1A is expected to be appropriate on a qualitative level. The case shown in this figure corresponds to current flow (that is, the diode is forward biased). If, however, the Fermi level on the right side were raised, it would no longer be possible for the donor molecule to inject electrons into the metal by means of its ground state, although it still could inject from an excited state configuration of the donor orbitals. It is not likely however that the donor-acceptor transfer will result in an excited state of the donor system. Hence, the current flow is shut off. Of course, if the Fermi level on the right is high enough, electron transfer from the metal to the donor excited states is possible. This step could be followed by tunneling of the electron to the excited state of the acceptor and injection into the metal on the left; hence, reverse current flows (this voltage would correspond to a breakdown voltage for the diode).

The Aviram-Ratner proposal takes advantage of the asymmetry in the frontier (highest occupied and lowest unoccupied) orbitals of linked donor-acceptor molecules. Other kinds of asymmetry can likely be used to produce rectification of current. Even a single

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molecular orbital can produce rectification when the molecule is chemisorbed to one of the electrodes (Fig. 1B).

Pomerantz and co-workers (*5*) recently reported a scanning tunneling microscope (STM) experiment closely related to the orbital energetics shown in Fig. 1B. Rectification (up to a factor of 60) was seen at a graphite electrode derivatized with a Cu phthalocyanine derivative (CuTAP) when probed with a Pt/Ir STM tip. Furthermore, these workers find that the onset of large current flow occurs at a bias voltage of –1.2 V, which corresponds very well to the binding energy (about 1.3 eV below the Fermi level) of the highest occupied molecular orbital (HOMO) of CuTAP, which they measured using photoelectron spectroscopy. Pomerantz *et al.* found that two other adsorbates that did not have appropriately positioned energy levels were shown not to rectify current flow. A third and unusual piece of data they present is a constant current scan of the surface at a fixed applied bias (the distance of the STM tip from the surface is changed to maintain a fixed current at a fixed bias potential), which provides a map of the spatial extent of the electronic orbitals normal to the surface. When the bias potential is near –1.0 V, these data show quite clearly very large distances and variations in distances for the electronic orbitals accessed by the tip.

The scenario for the rectification in this case (*5*) does not result from the built-in asymmetry of the molecule as in the Aviram-Ratner model. A plausible scenario for the rectification is asymmetry in the width of the tunneling barrier with applied potential. The electron tunneling between electrodes occurs over distance R when the bias voltage is positive, and over the reduced distance $R - R^0$, with R^0 the extent of CuTAP normal to the electrode, when the bias voltage is sufficiently negative that the HOMO is above the Fermi level of the tip. The CuTAP species essentially increases the spatial extent of the electrode.

The recent report by Martin *et al.* (*3*) exploits molecular asymmetry. In this study, the DBA molecule (Fig. 2) is demonstrated to provide an asymmetric current-voltage profile. They construct a metal–Langmuir-Blodgett (LB) film–metal sandwich junction. When the LB film consists of a few monolayers of insulating molecules, the current-voltage traces are symmetric. When the DBA molecule is included in an otherwise insulating LB film, however, the current-voltage curve becomes asymmetric and is enhanced over that of the insulator. The magnitude of the asymmetry appears to be of the order 3 or 4 to 1 at a 0.5-V bias. These workers verified that the DBA molecule provides the rectification by an experiment in which metal ions complex the LB film, deactivating the electron transfer reactions. This work shows that the molecule, not the molecule-electrode junction, is responsible for the asymmetry (*6*).

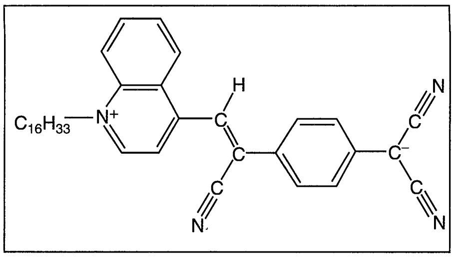

Fig. 2. Portrait of a diode. The molecular structure of the Martin *et al.* molecular rectifier (*3*).

One of the goals of molecular electronics is to mimic macroscopic electronic functions and devices with molecules. For this reason, the observation of molecular rectification is an important early step. This accomplishment demonstrates the potential of single molecules as electronic components. For example, a molecular transistor is a next evolutionary step, as was the case with solid-state devices. Yet, application of these molecular devices is far from being realized; many practical concerns have been raised (*7*). How will benign connections between molecular devices be made to produce two- or three-dimensional arrays? How will degradation problems be skirted? How will devices be synchronized? A particularly daunting challenge in molecular electronics is the development of strategies that utilize many molecular devices per macroscopic interface. The impressive information storage density in DNA is somewhat deceptive in this regard because macromolecules at least an order of magnitude larger than the information units read and process the information. Except perhaps in the sensor area, it is disappointing if each molecular device requires a conventional micrometer electrode or wire to drive it.

Even if it is possible to tackle these tasks, and numerous breakthroughs will be required, it is not clear that molecular electronics will ever compete directly with more conventional solid-state devices. Certainly silicon and GaAs technologies have not yet reached their limits for miniaturization (device structures may very well attain resolutions of less than 100 nm and perhaps 10 nm). It may well be that the new thinking and perspectives arising from molecular electronics, particularly with respect to single molecule chemical physics, will have the dominant impact on more conventional electronic technologies.

The relation between molecular and conventional electronics technology is uncertain. Yet, in addition to the observation of molecular rectification, there are some other promising recent developments. The synthesis of oligomeric precursors of conducting polymers (*8*) suggests that we may soon be able to study the transport of charge carriers through single molecules. Other applications for molecule-based devices could be in the area of high-density memory storage or holographic memory devices. An ability to design (*9*) and construct molecules with prescribed electron transfer rates is essential for many of the imagined ultrasmall memory devices, like the molecular shift register (*10*). A recent breakthrough in synthetic methods for the construction and covalent linking of electron transfer–active porphyrins (*11*) essentially eliminates one key bottleneck in the construction of proposed molecular memory devices like the shift register. In related work, Burrows *et al.* recently assembled donor-acceptor LB films between electrodes to build an electron transfer shift register memory prototype with nanometer-scale spacing between the information storage bins (*12*).

Although molecular devices are not likely to supplant conventional solid-state devices, fascinating analogies between the electronic properties of single molecules and the electronics of bulk materials are just beginning to emerge. It seems clear that the kind of technology that will arise from molecular electronics research will find significant applications in chemical and biochemical sensing as well. In addition to mimicking conventional electronic elements, molecular devices could become important in new types of computing architectures that are not based on binary systems or are strongly nonlinear, such as neural network or cellular automata architectures. It is perhaps equally useful to use molecular electronics to understand how macroscopic electronic properties emerge from the dynamics of carrier motion in molecules, clusters, and assemblies of these units.

References and Notes

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13. We thank A. Aviram, J. J. Hopfield, J. N. Onuchic, M. Pomerantz, and M. A. Ratner for helpful comments. We acknowledge the support of the National Science Foundation and the U.S. Department of Energy.