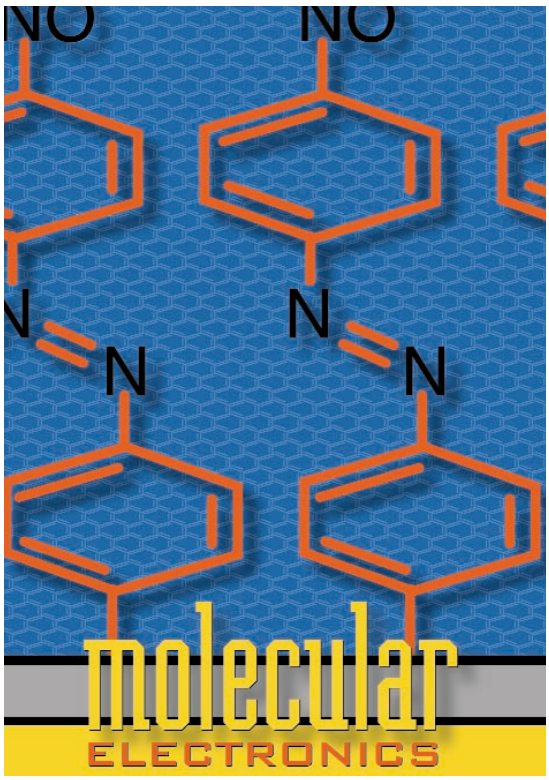
Molecular Electronics

by Richard McCreery

Molecular electronics has emerged as an area with both enormous promise and enormous challenges. The idea of using molecules as components in electronic circuits dates back at least to a 1974 article by Aviram and Ratner entitled, "Molecular Rectifiers" [*Chem. Phys. Lett.*, **29**, 277, (1974)]. Although this seminal paper introduced the concept of exploiting electron transfer in molecules to perform useful electronic functions, the idea was not realized in practice until the mid-1990s. Since then, a host of microelectronic functions has been proposed or observed in single molecules or molecular assemblies, including memory, rectification, switching, chemical sensing, and negative differential resistance (NDR). Several examples of molecular electronics are described in the accompanying articles, although the articles necessarily represent only a subset of recent activity.



The major promise of molecular electronics stems in part from three general aspects of conventional microelectronics: size, function, and massively parallel fabrication. In principle, a molecular circuit component may be as small as a single molecule, or approximately 2-3 orders of magnitude smaller than the current state of the art (~1300 Å) for silicon structures. Single molecule devices have been realized in practice, and represent a theoretical data density 10^4 to 10^6 times that possible today. Furthermore, molecules are electronically more complex than traditional semiconductors, with numerous energy gaps and variations in conjunction and conformation. So a molecule should be able to function in a wide variety of applications beyond those currently available with conventional semiconductors. For example, molecules may be chemically or biologically sensitive, or may exhibit "memory" with more persistence or fewer components than current semiconductor or magnetic memory. In order to exploit the small size and enhanced functionality of molecules in electronic circuits, methods of massively parallel fabrication must be retained or replaced. Self-assembly and scanning probe techniques have been demonstrated for fabrication of Au/thiol, Langmuir-Blodgett, and carbon nanotube structures, and some progress has been made toward scaling these techniques up to commercially interesting applications.

If one takes an optimistic view of molecular electronics, there is support for the idea of a paradigm shift of a scale as large as that from vacuum tubes to transistors that occurred in the 1950s and 1960s. While it is premature to predict that molecular devices can (or should) replace silicon, there is real promise for significantly augmenting silicon with hybrid circuits, which combine molecular properties with existing silicon and metal oxide semiconductors. However, a radical shift in experimental paradigm is usually accompanied by some "teething difficulty" due to previously unexplored concepts and phenomena. It is not yet clear how molecules "should" behave in electronic circuits, and the "rules" are only beginning to be worked out. On a few occasions reported in the literature to date, it was not clear which observations were "molecular" and which were artifacts of the measurement or fabrication technique. Inevitably, these false starts have resulted in reinterpretation of initial observations, but many of the basic questions about molecular conductivity and electronic function are now beginning to be answered reliably.

While viewing molecular electronics in general terms, it is useful to consider how the area is defined. What constitutes "molecular" electronics, as opposed to traditional semiconductor or metallic electronics, or conventional applications of molecular materials as insulators, dielectric materials, or thin film structures? Although a generally accepted definition of molecular electronics has yet to emerge, a few characteristics are clear. First, electron transport should depend strongly on molecular structure and possibly molecular orientation. A corollary is that small changes in structure, such as a dihedral angle between two aromatic rings, should have a large effect on conductivity. Second, electron transport is usually strongly dependent on distance, since tunneling is often an important transport mechanism. Third, molecular circuit components may have unusual temperature dependence, different from that of metals. Since molecular conformation should significantly affect conductivity, temperature dependent molecular motion should also affect electron transport. Fourth, many molecular electronic events should be observable with structurally specific spectroscopy. For example, a change in molecular structure accompanying a change in conductance should be amenable to spectroscopic monitoring. These characteristics are not intended to be comprehensive or exclusive, and most apply to related phenomena in other areas. However, they may be useful for considering whether a given electronic observation is "molecular", in that it is a characteristic of particular molecular structures acting to control electron transport and conductivity.

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The Electrochemical Society and *Interface* are particularly appropriate for reports and discussions on molecular electronics, given the diverse backgrounds of ECS members. Molecular electronics bridges the "dry" world of semiconductor concepts and engineering with the "wet" world of electrochemistry and electron transport in molecules. The accompanying four articles incorporate many concepts and techniques familiar to both the wet and dry camps, applied to several current examples of molecular electronics. First, Stuart Lindsay describes scanning probe microscopy observation of conductivity in single molecules, and examines the effects of molecular length and structure on electron transport. Second, Werner Kuhr outlines the integration of redox storage chemistry with commercial fabrication and engineering to yield high-density molecular memory. Third, Robert Metzger brings the search for a molecular rectifier up to date, in the context of molecular junctions containing single layers of oriented molecules. Finally, I describe the properties of molecular junctions made on a graphitic carbon substrate. Although these examples cover only a portion of the broad area of molecular electronics, they should provide a useful overview of both the promise and challenges inherent in this emerging field. ■