ANALYTICAL CHALLENGES in
In the late 1990s, molecular electronics emerged rapidly and spectacularly as an area of research that encompasses several paradigms in which electrons are transported through molecules (1, 2). An often-stated motivation for pursuing these devices is to extend Moore’s law of the exponential growth in microelectronic device density. The state of the art in silicon technology is a minimum feature size of 65 nm. If the trend toward miniaturization continues, eventually devices will have to be fabricated on the molecular scale of a few nanometers. This article will address the promise of molecular electronic devices and some of the problems with characterizing electronic components with molecular dimensions.

An early and widely publicized molecular electronic component was a bistable rotaxane molecule with 2 configurations that, in principle, could act as a single-molecule, 1-bit memory cell (3, 4). The molecule was switched between two metastable configurations by an applied electrical pulse. If such a device could be mass-produced in microelectronic circuits, it would represent an increase in device density of 2–3 orders of magnitude. In addition to the fabrication challenges associated with the further extension of Moore’s law, the physical properties of silicon become a limitation as feature size decreases. For example, insufficient tunneling barriers and capacitance associated with very thin silicon oxide films (<10 nm) can significantly degrade device performance.

Although small size is indeed a potentially valuable feature of molecular electronics, the incorporation of molecules into electronic circuits has other equally important advantages. The function of the device must also be considered. Do molecules have distinct electronic behavior compared with metals and semiconductors? Yes, certainly. And might they be used to augment silicon technology? In an analytical context, could molecules be incorporated as chemical or biological sensors, perhaps directly integrated with conventional support electronics? Can molecules replace certain conventional microelectronic components to provide better performance or lower cost? For example, nearly all random-access memory in today’s computers is based on DRAM (dynamic random-access memory), which stores charge in a parallel-plate capacitor. DRAM becomes leaky and “forgetful” as the device is made smaller and the memory more dense, with a typical persistence of <100 ms. Might a chemical change in a molecular memory provide a less forgetful DRAM, which would require fewer refresh cycles and therefore less power (5, 6)?

Photolithography is another aspect often overlooked but exceedingly important for the practical realization of any electronic device,
molecular or not. The exquisite photolithography methods developed during the ~40-year existence of the microelectronics industry provide massively parallel fabrication techniques for producing low-cost components containing millions of electronic devices. If molecular electronics is to augment or replace existing silicon devices, the cost benefits of massively parallel fabrication must continue, at least in most foreseeable applications. Existing silicon-based devices will probably be enhanced with molecular components in hybrid devices, which maintain massively parallel fabrication. A notable exception to the need for parallel fabrication is analytical sensors, in which only a few active devices may be necessary for a given application. Although the term “molecular electronics” emerged fairly recently, the concepts and phenomena related to electron transport (ET) are much older. ET in donor–bridge–acceptor complexes dates from at least the 1960s, and activated ET between two molecules or between an electrode and a molecule is the fundamental basis of electrochemistry (7–9). ET in films of redox polymers by a series of steps between redox centers has been studied in dry and solvent-wetted films (10, 11). Conducting polymers and electronic devices that use organic thin films have been known for decades; they include light-emitting diodes, thin-film transistors, and photovoltaic cells (12–17). These examples are definitely molecular and involve ET through and between molecules, so what is new about “molecular electronics”?

The innovation is generally considered to have begun with a theoretical paper by Aviram and Ratner (18). They proposed that, with suitable alignment of energy levels in a molecule suspended between two metallic contacts, electrons would flow preferentially in one direction (19). If the proposed rectifier could be realized, a useful function could result from a single molecule, provided it could be properly oriented and kept in electronic contact with two conductors. Molecular electronics as a contemporary term does not have a rigorous definition, and the lines separating it from existing areas of chemistry and physics are often blurred. Nevertheless, it is usually distinguished from organic electronics on the basis of the size or thickness of the active electronic component.

Several experimental approaches for investigating ET through molecules are shown in Figure 1. In each of the structures, one or more molecules are positioned between two conductors; the method of bonding and the orientation depend on the fabrication technique. These paradigms can be categorized into two types: those containing only one molecule (or a few) and those with $10^3$–$10^{12}$ molecules in parallel. The experiments themselves are quite different for these two classes.

**Single-molecule paradigms**

Single-molecule experiments are often based on scanning probe techniques, including scanning tunneling microscopy (STM; Figure 1a) and conducting probe atomic force microscopy (20–23). Conceptually similar experiments are based on “break junctions” in which a molecule bridges across two nanostructured metal contacts with a gap that can be controlled mechanically or by electron-beam lithography (24, 25; Figure 1b). Several exquisite experiments have been reported on the electronic structure of single molecules as modulated by attachment to the conducting contacts (26, 27).
For example, STM has been used to image the electron density of single molecules of copper phthalocyanine bridging two gold atoms, thus permitting direct investigation of the electronic structure of the molecule as a function of the dimensions of the gap between gold atoms (27). Single-molecule paradigms for molecular electronics have the advantage of reducing the complexity of the chemical system down to one molecule. The molecule will have minimal interaction with its surroundings, and less possibility will exist of inhomogeneous broadening caused by a variety of molecular conformations or environments. A disadvantage is sampling error because it is experimentally difficult to study a large number of single molecules in order to get good statistics. Tao et al. have used a break-junction geometry based on repeated insertion and retraction of a gold scanning tunneling microscope tip onto a gold surface in a dilute solution of the molecules of interest (24). Thousands of measurements of resistance or current–voltage behavior can be obtained, and variations in contact and conformation can be averaged out.

One can appreciate the exceedingly difficult challenge of characterizing the structure of a single-molecule device. The electronic properties of a single molecule suspended between two metal contacts depend not only on its structure but also on the geometry and bonding of the molecule to the contacts. Furthermore, the atoms of the contact (usually a metal) may have several different arrangements near the molecule; and these arrangements may affect electronic behavior. Very few types of spectroscopy have single-molecule sensitivity, and those that do provide limited structural detail.

An exception is inelastic tunneling spectroscopy (IETS), in which the current–voltage curve for a single molecule is modulated by interactions with the vibrational modes of the molecule. IETS is sufficiently sensitive, and it is based on ET through the molecule, the very phenomenon of interest to molecular electronics (28, 29). In addition, the molecule may be “buried” in a device structure that might not permit access by scanning probe microscopy (SPM) or photons. The need for very low temperature is a limitation, because $kT$ must be small enough to prevent serious broadening of vibrational spectral features. For example, $kT$ in liquid helium (4 K) corresponds to $\sim 3 \text{ cm}^{-1}$, whereas $kT$ in liquid N$_2$ (78 K) is 54 cm$^{-1}$, so vibrational features observed in liquid N$_2$ are generally too broad to be useful. Although IETS shows promise for structural analysis of single-molecule devices (at least at low temperatures), one could argue that characterization of such devices has been a serious impediment to progress in molecular electronics.

**Many-molecule paradigms**

Figures 1c and 1d illustrate two paradigms for investigating ET with an array of molecules oriented (ideally) in parallel. Nanopore and nanowire arrangements made of gold/thiol self-assembled monolayers between metallic wires with nanoscale diameters have been exploited (30, 31). Crossbar junctions of metallic or carbon nanotube wires and approaches that use mercury drops have generally larger junction areas and many more molecules in parallel (32–36). What distinguishes the molecular junctions in Figures 1c and 1d from existing organic electronic devices with molecular films $>$100-Å thick is the thin molecular layer, often only 1 molecule thick ($\sim 10–25$ Å). In addition, the molecules are generally oriented such that electrons must move through an ensemble of
molecules in parallel with (ideally) identical orientations. The phenomena that control ET over short distances may be fundamentally different from those that control ET in thick and/or disordered molecular films. Tunneling and other quantum effects may dominate device performance, resulting in distinct physical behavior and possibly new applications.

Our line of investigating molecular electronics involves the many-molecule approach, in which \(10^{11}\) molecules are bonded to a conducting carbon substrate, and a top contact of metal or metal oxide is applied (Figure 2; 36–45). The core of the device is an oriented layer of molecules covalently bonded to the carbon substrate and a conducting top contact, which may also interact covalently with the molecular layer. Two important analytical questions come to mind. How can we verify that the real structure actually corresponds to that shown in Figure 2? And, if we suspect that the molecular structure changes in response to a voltage applied across the molecular layer, can we characterize such changes with an independent analytical probe? For example, if a bistable molecular switch, such as a rotaxane (4), involves a bias-driven change in structure or conformation, can we confirm such a change with spectroscopy? These questions may have different analytical solutions, because characterization of a static junction may be destructive, whereas observation of a dynamic junction under bias must be nondestructive.

### Techniques for molecular electronic devices

Characterization techniques for single-molecule devices are quite limited and generally involve SPM methods. For larger devices, many surface analytical probes can be applied to typical molecular junctions (Figures 1c, 1d, and 2). These probe techniques include X-ray photoelectron spectroscopy (XPS; 46–49); secondary ion MS (SIMS; 50, 51); FTIR (52) and Raman spectroscopies (37, 48, 53); and STM and atomic force microscopy (Table 1). Because the substrate and molecular layer of a molecular junction are often the same as those used for modified electrodes and surface science, the literature on the characterization of “exposed” molecular layers is extensive. In addition to the verification of the monolayer and substrate structure and orientation, other considerations are important to molecular electronics. Are the molecules oriented properly with respect to the surface? Do pinholes, which might lead to a short circuit between the top contact and substrate, exist? How is the work function of the substrate modified by the molecular layer? What is the degree of electronic coupling between the molecule and substrate?

Once the top contact is applied, usually by vapor deposition, the analytical problems become more challenging. SIMS, XPS, and SPM have very shallow sampling depths and are unlikely to penetrate the commonly used >50 Å-thick top contacts. SIMS and XPS depth profiling are useful destructive probes of successive metal/molecule/substrate layers and have sufficient sensitivity to provide composition and structural information down to the monolayer level. Many investigators have used IR spectroscopy to probe the structure of the molecular layer and any changes in structure during metal deposition (46, 54, 55). In some cases, the molecular layer is damaged or destroyed by deposition of reactive metals such as titanium (47).

An example of XPS and Raman characterization of a molecular junction is the deposition of copper and titanium onto nitroazobenzene (NAB) bonded to pyrolyzed photoresist film (PPF), a form of graphitic carbon that resembles glassy carbon (48, 56). Raman spectra of the NAB/PPF surface before and after copper deposition are shown in Figure 3. The copper film attenuates the Raman spectrum ~50%, so the spectra shown are normalized to the 1140 cm\(^{-1}\).
intensity, and the broad PPF bands at ~1360 and 1600 cm$^{-1}$ have been subtracted. Copper deposition results in a decrease in the 1340 cm$^{-1}$ intensity due to the NO$_2$ stretch and an increase in the 1400/1450 intensity ratio.

In addition, XPS of a nominal 10-Å copper film on NAB shows a copper–nitrogen bond and partial loss of the N1s band characteristic of the NO$_2$ group (406 eV). Combined with other evidence, the results indicate a carbon/NAB/copper molecular junction with partial reduction of the NAB centers and formation of covalent copper–nitrogen bonds (57). Similar XPS analysis of PPF/fluorene/copper junctions revealed no copper–carbon bonds, nor any detectable oxygen within the junction (37). The electronic behavior of several PPF/molecule/copper molecular junctions is shown in Figure 4 (38). The pronounced variation of the current–voltage curves for biphenyl, fluorene, and nitro-biphenyl junctions indicates that ET through the junction is dependent on molecular structure and is not dominated by artifacts such as metal filaments or high resistance at the PPF/molecule or molecule/copper interface.

Live monitoring of a working molecular junction with spectroscopy requires that at least one of the contacts be transparent to the probe particles and that the analysis be nondestructive. This analytical target is sometimes referred to as the “buried interface” and is prominent in the semiconductor industry. Top contacts ~100 Å thick are generally sufficiently transparent to permit Raman, UV–vis, and FTIR analysis during molecular junction operation (37, 39).

Figure 5 is an example of live monitoring of a PPF/NAB/TiO$_x$/gold junction. The TiO$_x$/gold top contact is ~60% transparent in the 500–600-nm wavelength range used for Raman spectroscopy. The titanium occurs in mainly the +3 and +4 oxidation states, determined with XPS depth profiling (49). Changes in absolute and relative peak intensities during voltage excursions unequivocally establish that structural changes occur in the junction under bias; such changes were shown to correspond to reduction and oxidation of the NAB (37, 39, 53). As shown in Figure 5, a negatively biased PPF surface causes a loss of the nitro group features in the original spectrum (~1340 and ~1108 cm$^{-1}$), and these changes are irreversible.

The 1400/1450 intensity ratio also changes with bias, but these effects are at least partially reversible. In addition to providing firm evidence for structural rearrangement inside a ~70-Å junction, the live Raman experiment led to an understanding of the rectification observed with TiO$_x$/NAB junctions. Reduction of the NAB for negative bias creates an anionic NAB layer that resists ET when the PPF is negative. Although Raman spectroscopy is quite informative in the NAB case, it does require a strong Raman scatterer, as provided by resonance enhancement of NAB with 514.5 nm light. FTIR and UV–vis absorption spectroscopy should also be informative and possibly more general, provided they can be applied successfully to the buried interface.

**Molecular electronic sensors**

Although a majority of the proposed molecular electronics applications are for the microelectronics realm, definite possibilities exist for analytical sensors. Many readers are probably famil-
Chemical and ion-sensitive field-effect transistors (CHEMFETs and ISFETs) are silicon-based FETs with gate electrodes modified to be sensitive to chemicals or ions (58). A different electronic–chemical hybrid device contains a polymer whose conductivity varies with exposure to gases or components in a solution (59, 60). CHEMFETs and conducting polymers are precedents for molecular electronic sensors with a direct interface between an electronic signal and a chemically specific binding event or interaction. Such an interface has existed in electroanalysis for approximately a century, but electrochemistry requires solvent, mobile ions, and often a redox reaction. If molecules that are sensitive to chemical and biological analytes can be integrated into electronic circuits and microelectronic devices, the interaction between an electronic signal and a chemical event can be made more direct.

For example, consider a monolayer of 2,2'-bipyridyl molecules positioned between 2 conductors. The two pyridine rings would not be expected to be coplanar, and the electronic interaction between them would be weak. The observed conductance through the bipyridyl layer would be expected to resemble the biphenyl curve of Figure 3 and be controlled by tunneling through the molecular layer. However, if a transition-metal ion known to complex bipyridyl were present, the pyridine rings would be expected to become coplanar upon complexation, and the conductance of the junction might increase significantly. Although the value of direct integration of chemically sensitive molecules with microelectronic devices is still the subject of speculation, it may have substantial analytical applications. An obvious point is that molecules are much more sensitive to the presence of chemical or biological analytes than are silicon or related semiconductors.

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FIGURE 4. Current–voltage curves for PPF/molecule/copper junctions, each with an area of $4.5 \times 10^{-4}$ cm$^2$. Curves were independent of scan rate and repeatable for thousands of scans. Each curve is an average of four junctions; the standard deviations are much smaller than the differences between the responses for different molecular structures. The voltage axis is PPF relative to gold. (Adapted from Ref. 38.)

FIGURE 5. In situ Raman spectra of a PPF/NAB/TiO$_x$/gold junction at various applied voltages (PPF relative to gold). The spectra were acquired for 20 s each, from top to bottom (37, 53).
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References