

Unimolecular Electronic Devices

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Abstract The first active electronic components used vacuum tubes with appropriately-shaped electrodes, then junctions of appropriately-doped Ge, Si, or GaAs semiconductors. Electronic components can now be made with appropriately-designed organic molecules. As the commercial drive to make ever-smaller and faster circuits approaches the 3-nm limit, these unimolecular organic devices may become more useful than doped semiconductors. Here we discuss the electrical contacts between metallic electrodes and organic molecular components, and survey representative organic wires composed of conducting groups and organic rectifiers composed of electron-donor and -acceptor groups, and the Aviram-Ratner proposal for unimolecular rectification. Molecular capacitors and amplifiers are discussed briefly. Molecular electronic devices are not only ultimately small (<3 nm in all directions) and fast, but their excited states may be able to decay by photons, avoiding the enormous heat dissipation endured by Si-based components that decay by phonons. An all-organic computer is an ultimate, but more distant, goal.

Keywords Aviram-Ratner theory · Cold gold evaporation · Electron-acceptor groups · Electron-donor groups · Langmuir-Blodgett film · Langmuir-Blodgett monolayer · Orbital-mediated tunneling · Rectifier · Scanning tunneling microscopy · Schottky barrier · Schottky-Mott theory · Self-assembled film · Self-assembled monolayer · Unimolecular amplifier · Unimolecular electronic devices

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1 Introduction

Molecules, acting either singly or in parallel as a monolayer array, can serve as electronic components. This ability has spawned the field of “Unimolecular Electronics” (UE) [1, 2], which, with some luck, could eventually lead to ultra-tiny and ultra-fast electronic circuitry with dimensions of 1–3 nm – a true nanotechnology. UE was inspired by organic crystalline metals [3, 4] and superconductors [4, 5] and organic conducting polymers [6–10], and it exploits the valence molecular orbitals of molecules, that is, molecular Highest Occupied Molecular Orbitals (HOMOs) and Lowest Unoccupied Molecular Orbitals (LUMOs) where electrons can be most easily influenced. UE differs from the robust area of molecule-based electronics, involving electrically-conducting crystals and polymers [1], in that UE focuses on nonpolymeric organic molecules, as will the present chapter [11, 12].

The push to make ever smaller and denser arrays of electronic devices may be inspired by technological feasibility, but it is driven by commercial considerations and by Moore’s empirical “law” [13]: ever since the 1960s, the minimum distance or “design rule” (DR) between components in integrated circuits has halved every 2 years, and therefore the speed of the digital circuits has doubled [13]. At present, 3-GHz computers use 65-nm DRs, 35-nm DRs are found in research, and the challenges of DRs < 22 nm are under discussion [14]. However, Moore’s “second law” suggests that the cost of higher integration increases exponentially. Going down to DR = 3 nm using inorganic materials and inorganic metal electrodes will be difficult and expensive [14].

This opens the door for UE, with its organic molecules as the circuit building blocks, with typical sizes of 2–3 nm. But there are challenges beyond the synthesis

of appropriate organic candidates. Even when carefully designed, organic molecules may be air-sensitive, and may lose their integrity above about 150 °C, while inorganic systems (or pure carbon nanotubes) may continue to perform as hot as 600 °C. Furthermore, the “molecule | metal” interface must be well understood in order to connect the molecular circuit to the macroscopic world.

UE provides an important potential advantage beyond small size. The excited states in Si-based electronics decay by phonons, and thus a huge heat dissipation problem faces nanoscale inorganic electronics at DR = 3 nm. In contrast, UE devices may be able to decay from their excited states by photon emission [15]. If the photon decay channel can be maximized, UE devices will have a great heat advantage over inorganic ones.

2 Contacts to Metal Electrodes

To extract useful results from a molecular electronic device, or just to measure its electronic characteristics, connections must be made to macroscopic probes. That is, metallic electrodes must interface to different ends of the molecule of interest. An experiment may interrogate a single molecule, or may measure a one-molecule-thick layer, i.e., a *monolayer*, of the molecules of interest, provided all the molecules are oriented in the same direction. In either case, several questions arise. What is the nature of the contact between metal and molecule(s)? What metal should be chosen, and what should be the form or shape of this electrode?

There are two ways to attach a single molecule or a monolayer of molecules to a metal electrode: *physisorption* (where the connection is maintained by noncovalent forces) and *chemisorption* (where the connection is maintained by coordinating or covalent bonds). Monolayer devices often begin with the physisorption of a monolayer onto one (the “bottom”) electrode. One could imagine deposition of vapor-phase molecules onto a metal electrode substrate, but such depositions usually yield poor, disordered packing and random orientations. Much better is the physisorption of an ordered *Langmuir* [or *Pockels-Langmuir* (PL)] *monolayer* formed by amphiphilic molecules floating at a water–air interface. The monolayer is laterally compressed until the molecules are close-packed. The *Langmuir-Blodgett* (LB) or vertical transfer method [16, 17] then lets the monolayer adhere to an electrode (or any solid surface) being gradually removed from (or inserted into) the water, while the *Langmuir-Schaefer* (LS) or quasi-horizontal transfer method [18] lays the electrode flat onto the interface so that the monolayer sticks to it.

Ordering of a PL film presents some restrictions on the chemical nature of the molecules. The molecules will typically need to be made amphiphilic by attaching either pendant nonpolar (e.g., alkyl) groups to yield a hydrophobic end, or pendant polar (e.g., carboxylic acid) or even ionic (e.g., carboxylate anion) groups to make a hydrophilic end, complicating the synthetic task. Further, the pendant groups may have a cross section that is not well matched with the size of the electroactive

portions of the molecule. As a consequence, it may not be possible for the monolayer to be tightly-packed at all depths. If the second (“top”) electrode is introduced by vapor deposition, stalactite- or stalagmite-like shards or filaments or whiskers of metal may partially penetrate the monolayer, yet dominate the electrical characteristics [19, 20]. Also, such a monolayer may not be laterally uniform, leading to poorly-reproducible measurements. Finally, physisorbed molecules can move easily after deposition, either as they seek a thermodynamic steady state on the surface, or in response to an applied electric field (a 2-V bias across a monolayer 2 nm thick makes a 1 GV/m field). That means that LB and LS films can reorient over days, weeks, or months, changing their properties.

A variety of chemisorption techniques can covalently bind molecules to specific metal surfaces [21]. Most commonly, thiols (H-S-R) or thioesters (like thioacetates, $\text{CH}_3\text{CO-S-R}$) coordinate to gold or mercury, serving as “alligator clips” (by analogy to the clips that connect macroscopic wires and terminals). In addition, carboxylates can bind to oxide-covered aluminum or silver, chlorosilanes to silicon oxide, amines to platinum, etc. The resulting films are called “*self-assembled monolayers*” (SAMs) because they form spontaneously when the molecules are allowed access to the surface [22, 23]. The binding of SAMs to metals often involves a homolytic bond scission in the ligand, and the formation of a covalent or partially ionic bond to the substrate. For example, the chemisorption of thiols to Au involves the bonding of $\text{R-S}\cdot$ to Au; the S-Au bond is fairly polar [24]. The thiol’s H could escape the substrate as H_2 or H_2O [24]. Because thiols easily oxidize to disulfides under ambient conditions, they are often supplied as protected thioacetates. In situ base-assisted cleavage of the thioacetate produces thiolate anion, which then coordinates to Au. The Au-S bond is normal to the Au plane, but the binding of alkanethiols to Au as thiolates involves a tilt angle (typically 30°) between the Au-S bond and the rest of the molecule. For aromatic thiols, the tilt angle is typically closer to the normal [24]. For thiolate-Au(111) SAMs in high vacuum, there is evidence that the Au surface reorganizes to control the SAM structural phases, and that a single Au atom coming out of the Au(111) surface plane may bond to the thiolate [25–27].

The advantages of SAMs are that they are sturdily anchored at a fixed distance from the metal substrate, may be more robust than Langmuir films, and can be convenient to prepare. A disadvantage is that uniform monolayer coverage, so easily achieved kinetically for LB films, is more difficult to obtain in SAMs. This is because SAMs are created by random attack on the electrode surface, in contrast to Langmuir films, which are transferred when they are close-packed.

3 Electrode Metal and Schottky Barriers

Most metals are covered by an oxide (impervious and insulating, or more often, as with Al, defect-ridden). In contrast, *gold* has no oxide, and has the advantage of making SAMs with thiols. However, Au atoms migrate somewhat after deposition to minimize total energy, and migrate even more under an electric field

(“electromigration”), so the surface may not be stable during measurement [28]. Further, an Au film freshly deposited on a substrate from Au vapor is hydrophilic, but after about 20 min of exposure to room air, becomes hydrophobic because of adventitious adsorbates from air. These impurities can be displaced later during SAM formation. *Palladium* and *platinum* are less susceptible to spontaneous migration than Au, and stable nanogaps of 0.5–2.1 nm can be formed [29]. *Magnesium* has a low work function, comparable to the electron affinities of some good organic one-electron acceptors; however, Mg oxidizes rapidly in O₂ to MgO, and dissolves as Mg(OH)₂ in the presence of H₂O; so if Mg is used, it needs a protective cover layer, e.g., of Ag. *Aluminum* also has a relatively low work function, and forms a protective but very disordered oxide Al₂O₃ layer in air.

The interface between a metal electrode and an organic molecule creates a set of interfacial dipoles as charges reorganize across the interface. These dipoles constitute a “Schottky barrier” to electron transport. The Schottky barrier [30] is formed because the chemical potential, or partial molar Gibbs free energy, or Fermi energy E_F , must become the same if one accosts two materials of different free energy, e.g., a metal and a semiconductor; it is conceptually related to the Schottky–Nordheim energy barrier to electron emission from a metal surface (where the local metal work function is reduced). Charge will flow toward the interface, and semiconductor valence and conduction bands will “bend” until the equilibrium in free energies is established. The charge clustering becomes a set of interfacial dipoles, and the Schottky barrier becomes a rectifying junction.

The Schottky–Mott theory predicts a current $I = (4 \pi e m k_B^2/h^3) T^2 \exp(-e \Delta/k_B T)[\exp(e n V/k_B T)-1]$, where e is the electronic charge, m is the effective mass of the carrier, k_B is Boltzmann’s constant, T is the absolute temperature, n is a “filling factor,” Δ is the Schottky barrier height (see Fig. 1), and V is the applied voltage [31]. In Schottky–Mott theory, Δ should be the difference between the Fermi level of the metal and the conduction band minimum (for an n-type semiconductor-to-metal interface) or the valence band maximum (for a p-type semiconductor-metal interface) [32, 33]. Certain experimentally observed variations of Δ were for decades ascribed to “pinning” of states, but can now be attributed to local inhomogeneities of the interface, so the Schottky–Mott theory is secure. The opposite of a Schottky barrier is an “ohmic contact,” where there is only an added electrical resistance at the junction, typically between two metals.

Inorganic Schottky barrier rectifiers are commercially available. Of course, for a monolayer, one cannot speak of band bending as in a bulk semiconductor, but the ideas of a barrier, and of dipoles across it, are valid.

To avoid having different-sized Schottky barriers at the two interfaces, the same metal (or metals with almost the same work functions) should be used for both electrodes. For example, the different work functions of Pt and Mg made studies of “glass | Pt | molecule | Mg | Ag” sandwiches hard to interpret [34]. In that case, Mg probably reacted with the end of the molecule containing the strong acceptor TCNQ to form a TCNQ-salt Schottky barrier that dominated the electrical asymmetry [34]. With a different molecule lacking TCNQ, the dominating Schottky barrier effect was eliminated [35, 36].

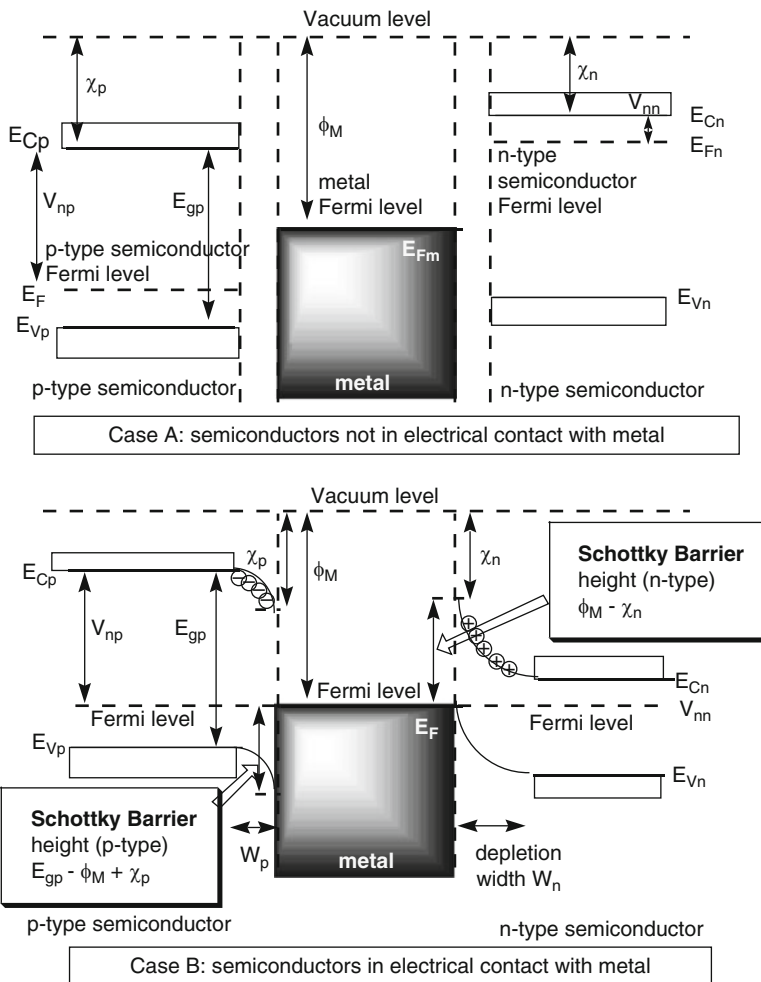


Fig. 1 Idealized energy band diagram and Schottky barrier between metal (*center*) an n-type semiconductor (*right*), and a p-type semiconductor (*left*), not in electrical contact (Case A) and after contact between metal and semiconductors (Case B) (adapted from [32]). Here ϕ_M is the work function of the metal, E_F is the common Fermi level, E_V is the top of the valence band, E_C is the bottom of the conduction band, χ is the electron affinity of the semiconductor, and E_{gp} is the energy gap inside the bulk semiconductor. The band bending is shown, as well as the Schottky barrier heights, and the charges in the “space charge region” responsible for the band bending. A set of corresponding image charges of opposite charge will exist within the metal: hence the Schottky dipole layer

4 Bottom Electrode Surface

A uniform monolayer surface depends upon it having been deposited on a flat electrode substrate. Impressive flatness can be achieved with the semi-metal graphite, a lamellar structure with weak van der Waals forces between the layers. A clean

and flat surface can be exposed by the “Scotch® tape technique”. A graphite sample is pressed between sticky tapes; when the tapes are separated, the graphite separates along the layers. The fresh surface that is exposed is atomically flat over large areas (e.g., 20×20 nm), except for steps and corrugations. Iteration of this process can eventually create a one-molecule-thick graphene layer [37].

For metals and crystals, cleavage can attempt similar feats, but the results are not as good. Metal surfaces formed by cleavage are usually not atomically flat. When an Au wire is flame-annealed in a hydrogen-air flame, the Au(111) face is formed preferentially, since it has a lower surface energy than the Au(100) or Au(110) faces, but these Au(111) faces resemble New Mexico “mesas”: the atomically flat region may be only 50×50 nm, and is surrounded by one- or two-atom steps leading down to the “plain,” and then on to the next mesa.

The Si wafer industry has achieved very flat Si surfaces by electropolishing: a root-mean-square (rms) roughness of 0.3 nm is customary, even for highly-doped degenerate Si. For a 100-nm Au layer deposited atop a 10-nm Ti adhesion layer atop an electropolished Si wafer, an rms roughness of 0.4 nm was measured by AFM [38].

5 Top Electrode

The second (or “top”) electrode used to interrogate a UE monolayer that has been deposited on the underlying (“bottom”) electrode can be, most simply, the *probe tip* of a scanning probe microscope, i.e., a Scanning Tunneling Microscope (STM) or a Conducting-Probe Atomic Force Microscope (CP-AFM), brought close to the monolayer surface. Voltage can be controlled easily and the resulting currents measured. Disadvantages include that the monolayer is sampled over only a very small portion of its expanse at a time, so that the measurement may not be representative.

The second metal electrode can also be a *macroscopic pad*, typically $0.25\text{--}1$ mm² in area, that can give measurements representative of a population of molecules. Disadvantages include the danger that the larger area sampled may include defects in the monolayer with electrical short circuits that perturb measurements. Also, construction of a second electrode pad is not trivial. Laying a preformed pad on a monolayer can disrupt the integrity of the monolayer. Letting a pad accumulate by sputtering is not feasible because the metal vapor is too hot and damages the monolayer. Deposition from evaporated low-melting metals (Mg, Ca, Al, or Pb) is possible, especially if the monolayer assembly is externally cryo-cooled to circumvent thermal damage [39, 40]. In our experience, half of the pads made in this way avoided electrical shorting [38, 41]. In contrast, higher-melting metals, such as Au, are not cooled quickly enough by the cryocooled substrate holder, so that Au atoms reach the monolayer hot, and every “Au | monolayer | Au” sandwich is shorted. Adding a low pressure of room-temperature Ar to the

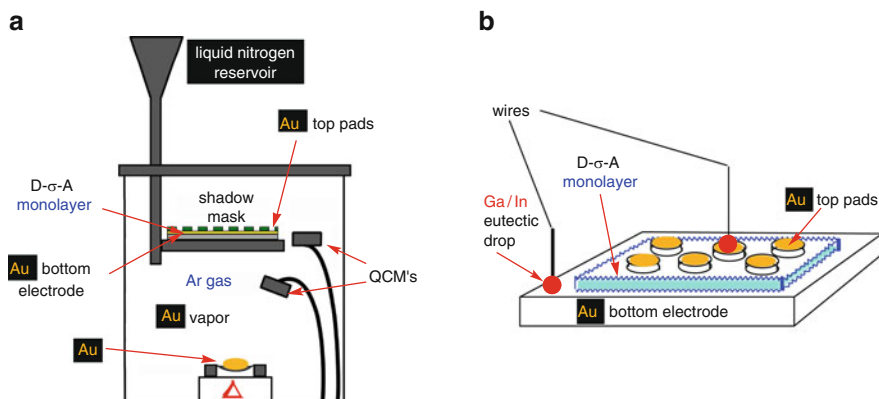
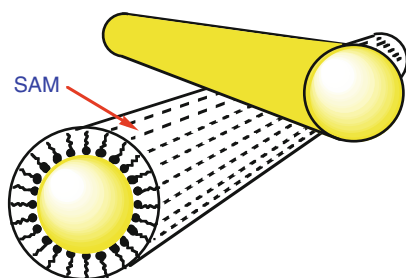


Fig. 2 (a) Edwards E308 evaporator. One quartz-crystal thickness monitor is pointed towards the Au source to monitor Au vapor deposition on chamber walls; the other monitors Au deposited through the shadow mask atop the organic layer. In the “cold Au” deposition, a small amount of Ar gas is added to the chamber to cool the Au atoms to room temperature before they physisorb atop the cryocooled organic monolayer. (b) Geometry of an “Au | monolayer | Au pad” sandwich, with electrical connections made using a Ga/In eutectic

Fig. 3 Geometry of the crossed-wire technique



evaporation chamber allows the hot Au atoms to be cooled by several collisions with Ar atoms, so that they arrive at the sample surface at room temperature, in what is called the “cold-gold” technique (Fig. 2a). The rms roughness of a cold-gold electrode was measured as 1 nm, twice rougher than the bottom Au electrode [38].

Preformed gold *nanoparticles* have been used as the top electrode for interrogating SAMs of dithiols diluted within an alkylthiol matrix. The alkyl tails of the alkylthiols do not coordinate to the nanoparticles, but a dithiol’s second SH group, sticking above the alkyl level, can bond to the nanoparticle, which is then contacted with an Au-coated AFM probe [42].

Another electrode geometry is the *crossed-wire* technique (Fig. 3). Here, the bottom electrode is a wire, coated cylindrically with a SAM of UE molecules. The second electrode is a second wire, oriented at right angles, and slowly brought into soft mechanical contact with the monolayer. Wires of 10 μm diameter would interrogate a patch of about 10^3 molecules [43–45].

6 Break Junctions

An alternative method to position two electrodes at nanometer distances apart is the *mechanically-controlled break junction* (MCBJ) technique. An ultra-thin, notched Au wire on a flexible substrate can be broken reliably by pushing on the Au with a piezoelectric piston, cracking the Au (Fig. 4). This produces a gap between the Au shards whose size can be finely varied to ± 1 Å by a piston or control rod [46, 47]. When UE molecules with thiol groups on both ends are present in a surrounding solution, the gap can be adjusted until the molecules can span it. A dilute solution means the number of spanning molecules will be small, and the least-common-multiple of current flow among many junctions indicates those spanned by a single molecule [47].

A break junction can also be created by passing a current (0.5–1.0 V) through an Au nanowire (<20 nm diameter) defined by electron-beam lithography and shadow evaporation. Such *electromigrated break junctions* (EMBJs) have yielded reproducible 1–3 nm gaps between electrodes [48–50].

Another type of break junction, the “in situ” or *STM break junction* (STM-BJ), involves pushing an STM tip through a SAM to make contact with the underlying electrode (Fig. 5). The probe tip is then quickly withdrawn, stretching a bridge of metal atoms until the bridge breaks. As the gap widens, SAM molecules can fill it, giving distinctive current flows, until the gap becomes too wide for molecules to

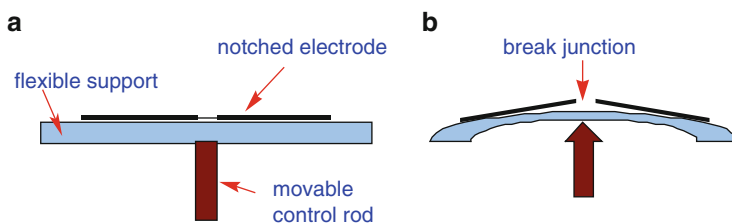


Fig. 4 Design of the Mechanically-Controlled Break Junction (MCBJ) technique

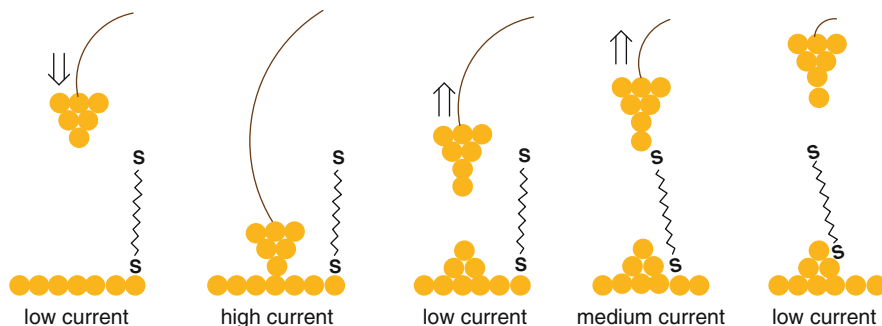


Fig. 5 Steps in the STM Break Junction (STM-BJ) technique

bridge, and the current ceases [51, 52]. Similar measurements can be made by varying the gap distance without actually making tip-to-electrode contact first [the $I(s)$ method] [53], while in the $I(t)$ method, the gap is held constant and current changes are monitored as bridging molecules spontaneously attach and detach [54]. The $I(t)$ method favors the formation of single-molecule bridges.

7 Molecular Resistors

Among the two-terminal devices that can be imagined for UE [capacitors, inductors, rectifiers, negative differential resistance (NDR) devices], the simplest is a molecular wire, that is, a molecule capable of conducting electricity: a nanoconductor or, equivalently, a nanoresistor. Even the most conductive of molecular wires has a minimum resistance.

The electrical resistance R of a device (in ohms, Ω) is given by Ohm's Law [55]: $R = V/I$, where V is the applied potential (in volts, V), and I is the resulting current (in amperes, A). Its reciprocal, the conductance, is given by $G \equiv 1/R = I/V$ (in siemens, $S = \Omega^{-1}$). This law is valid in macroscopic wires, where electron scattering off impurities and lattice defects dominates the conductivity. For nanoscopic objects like a molecular wire, the current I is determined by Landauer's formula [56], which incorporates the concept of a minimum resistance. That is, resistance is quantized, and even a perfectly conductive molecule retains a quantum of resistance, R_0 , due to contact resistance from its connections to the external circuit used to measure it [56, 57]. R_0 is calculated to have a value of $h/2e^2 = 12.906493 \text{ k}\Omega$ (much larger than a macroscopic wire because a molecule is so small). R_0 's reciprocal, the Landauer (or von Klitzing) constant G_0 , must then represent the maximum conductance possible through a molecule; $G_0 \equiv 1/R_0 = 2e^2/h = 7.74809 \times 10^{-5} \text{ S}$, or 77,481 nS. The maximum overall conductance of a molecular wire and its junctions to arbitrary metal electrodes is $(1/2) G_0$, assuming two carriers of opposite spin.

The resistance R of a macroscopic device is best measured by four probes: an electrical potential drives a fixed current I between the outermost two probes, and the potential drop V is measured across the inner two. After some geometrical corrections, V/I is the true resistance of the device, independent of the electrode contacts of the outer two probes. Such four-probe methods would be very desirable for nanoscopic devices (e.g., a medium-sized molecule of size $3 \times 3 \times 3 \text{ nm}$), but electron-beam lithography cannot yet reliably generate three or four electrodes 3 nm apart. Two-probe measurements of a wire are much easier to realize, although this can only give the sum of all resistances (instrument-to-first-electrode, first-electrode-to-molecule, molecule, molecule-to-second-electrode, and second-electrode-to-instrument). A four-probe experiment has been described on a one-dimensional wire of GaAlAs with a two-dimensional electron gas providing the probes, showing a resistance-free conductance when the outer contacts are bypassed [57, 58].

The *IV* measurements on molecules and monolayers have been carried out almost exclusively using direct current (DC); frequency-dependent alternating current (AC) impedance measurements have rarely been performed, even though a rich spectroscopy may reveal itself, if the *IV* measurements were followed as a function of frequency ν .

8 Molecular Wires

An early measurement of current through a molecule was the report in 1995 of the resistance of a single C_{60} molecule, **1** (Fig. 6), deposited on an Au substrate and located and measured by an STM probe [59]. The conductivity was a respectable 18 nS. Most molecules studied as wires are more linear, with a coordinating atom at one or both ends.

For example, 1,4-benzenedithiol (**2**) was suspended between the two shards of an MCBJ to create a molecular wire consisting of a single benzene ring [47]. The conductance of this aromatic molecule was 45 nS [47]. When measured by the STM-BJ technique, a larger value of 833 nS was obtained [60]. When 1,4-xylenedithiol (**3**) was also measured by the STM-BJ technique, a smaller value, compared to **2**, of 47 nS was obtained [60]. Finding a smaller conductance when insulating methylene (CH_2) groups separate the aromatic ring from the metal electrodes is consistent with the intuitively sensible idea that the more polarizable and delocalized electrons of π systems should be better conductors than σ -bond frameworks.

This idea is borne out by additional experiments. Alkanethiols should be poor conductors (although better than no wire at all). An octanethiol (**4**) SAM, interrogated by CP-AFM, gave a miniscule conductivity of ca. 0.1 pS [42]. The advantage of having a chemisorption contact, rather than a physisorption one, is shown by the results with octanedithiol **5**, distinguished in a matrix of **4** by its contact to an Au nanoparticle. Here, the conductance jumped to 1.1 nS – a remarkable increase, although still well below that of conjugated systems [42]. Measurement with the $I(t)$ STM single-molecule technique gave a comparable value [54]. When measured by the STM-BJ technique, **5** gave a larger conductance value of 20 nS [51]. In that study, **5** was compared with dithiols of difference length: hexanedithiol was more conductive (95 nS) while decanedithiol was less so (1.6 nS), consistent with the idea that saturated chains are relatively insulating.

The inconvenient finding that different techniques can give quite different conductances for the same molecule is compounded by the inconvenience that measurements of the same molecule with the same technique may give results, clustering around two or three different values, representing up to three different “conductance groups” or conductance maxima. For example, **5** also gives conductances around 3.8 nS [61]. These results can be interpreted as reflecting the strength of the S–Au attachment. The low-conductance value occurs when

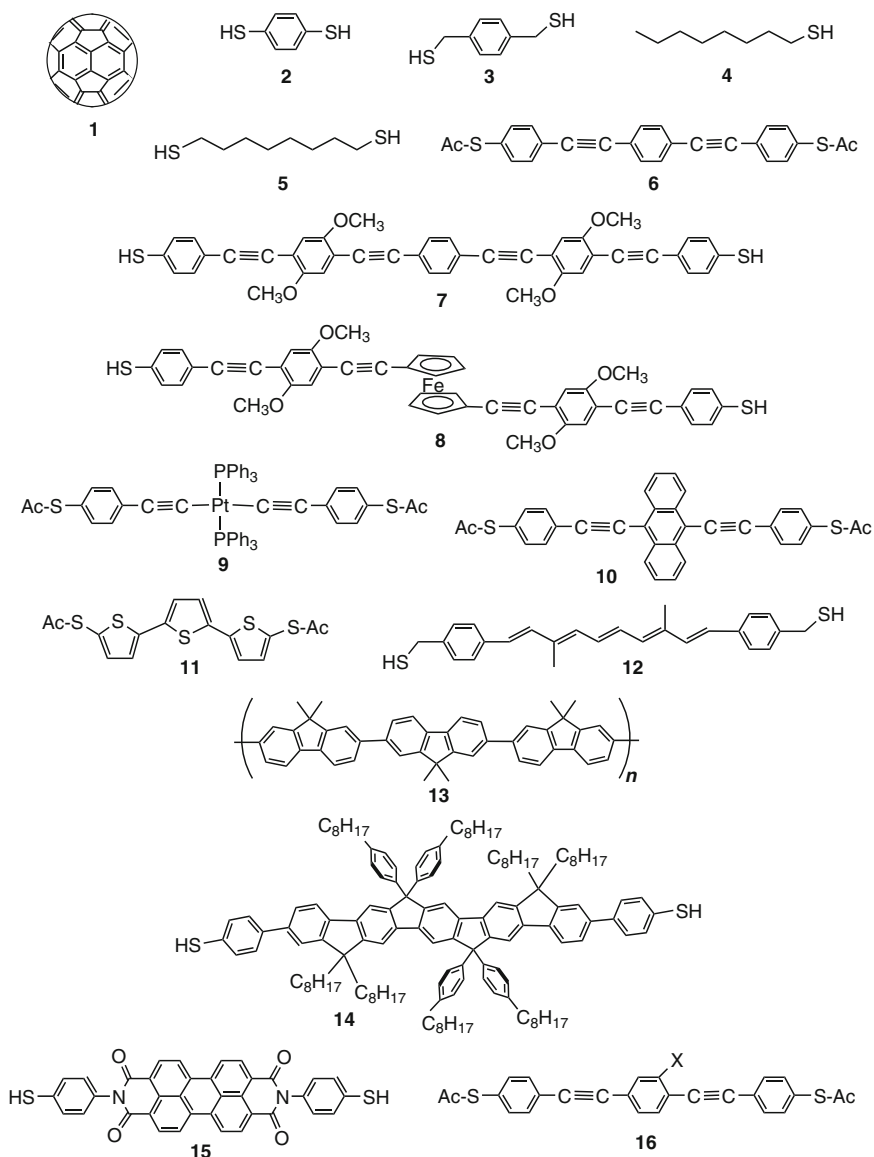


Fig. 6 Representative molecular wires

each end of the molecule connects to a single gold atom. When one end is more highly coordinated to Au – e.g., at a defect on a rough surface, or attached to the side, rather than the end of an STM tip – the medium-conductance value is obtained. Multiple Au coordinations at both ends give the high-conductance value [61, 62].

Longer unsaturated “oligophenylethynyl” (OPE) wires have been made by alternating benzene rings with ethynyl ($\text{C}\equiv\text{C}$ triple bond) groups. For example, **6** has a conductance of 13 nS, measured by STM-BJ [63]. In an EMBJ geometry, the longer OPE **7** gives two orders of magnitude lower conductance than the analog with a ferrocene core, **8** [64]. In this comparison, the swiveling flexibility of the ferrocene may allow it to make better contact with the two break-junction electrodes, improving the conductance. The insulating platinum atom at the center of **9** lowers its MCBJ conductance by three orders of magnitude, compared to **10** [65, 66].

Thiophene chains also make serviceable wires. The terthiophene **11**, measured by MCBJ, gives two conductance maxima, at 10 nS and 80 nS [67]. Even simple polyene chains can be wires: the carotenoid derivative **12** has a conductance of 2 nS, measured by STM-BJ [68].

Dimethylfluorene polymers **13** were made by polymerization of a dibromotrimer on the Au(111) surface, leaving a debrominated radical at each end. A single end can be picked up by an STM tip, and, as the tip is raised, the conductance falls, as each fluorene unit lifts off the surface [69]. The conductance begins at about 10 nS, and drops roughly two orders of magnitude each time a unit is added to the wire. The monomer units are not in the same plane, and hence are not fully conjugated, contributing to the poor conductance. This experiment cannot be duplicated in solution, because the polymer would not be soluble, but the similar, decorated fluorenoid **14** has been studied with the STM-BJ method and has a conductance of 1 nS [70].

The dimer, trimer, and tetramer of **14** were also studied, and the conductance was found to be independent of temperature, but inversely dependent on oligomer length for **14** and the dimer [70]. Conversely, the conductance of the trimer and tetramer were thermally activated, but without a wire-length dependence. Thus, the longer trimer could be made more conductive than the dimer by raising the temperature. The rationale is that the shorter wire passes electrons by tunneling, while the longer oligomers are too long for tunneling, and must transport electrons by incoherent charge-hopping. The transition between transport mechanisms appears to take place at a length of around 6 nm. Similar studies have been reported on highly-substituted oligothiophenes [71] and amino-terminated OPEs [72].

The conductance of the perylenebisimide (PBI) **15** was measured by the STM-BJ technique as 1 nS [73]. Note that the thiophenol handles are not conjugated to the central core, contributing to the small value. Electron transport was temperature-independent, indicating a tunneling mechanism. However, when a gate electrode reduced the core to its radical anion, the conductance became thermally activated, indicating that electron transport then follows a hopping mechanism into and out of the core.

The conductance of the OPE nitro-**16** ($\text{X} = \text{NO}_2$) was monitored by the STM-BJ method, as the nitro group was reduced to NO and NH_2 , and then protonated to NH_3 . The resulting data gave an inverse linear Hammett plot with the meta- σ substituent parameter, indicating that substituent electron release into the aromatic core increases conductance [63].

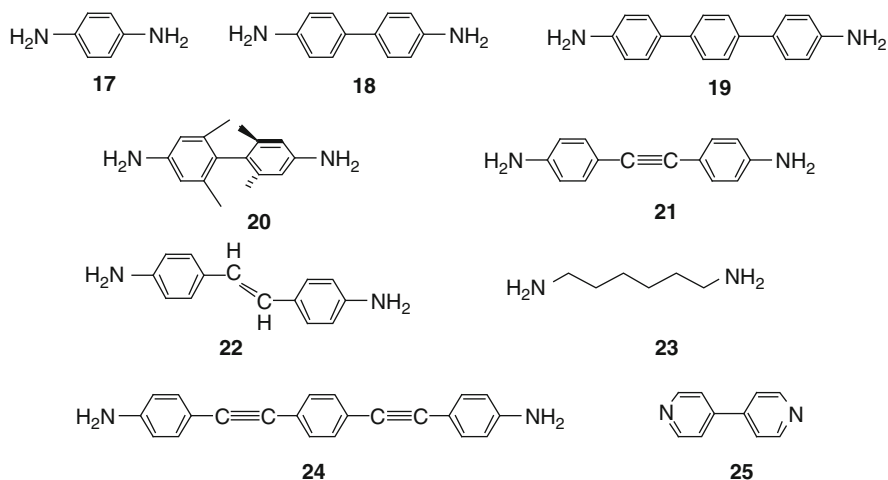


Fig. 7 Representative molecular wires with nitrogen connectors

Several molecules have also been studied with nitrogen rather than sulfur “alligator clips” to gold (Fig. 7). Using the MCBJ technique, **17** showed a healthy 496 nS of conductance; the effect of lengthening the wire can be seen in the biphenyl analog **18** (90 nS) and the terphenyl analog **19** (14 nS). The hindered biphenyl **20** has nearly orthogonal benzene rings; loss of conjugation lowers its conductance to 6 nS [74].

The prototypical OPE **21** has a conductance of 62 nS by the STM-BJ technique; the analog with an ethene bridge, **22**, has a similar value (77 nS). By way of comparison, the saturated **23** has a lower conductance of 9 nS [75]. Another STM-BJ study of six OPEs included **21** (43 nS) and **24** (10 nS), an analog of **6**. As the OPE wire length increased, the conductance diminished [72]. The STM-BJ technique was also used to examine bipyridine, **25**. Here the alligator clip nitrogens are part of the aromatic bridge, and the conductance is large, at 770 nS [51].

9 Schottky and Asymmetric Rectifiers

A rectifier, or diode, passes electrical current in one direction (the forward bias direction), but blocks it in the other direction (reverse bias). For a molecule between two electrodes in a “metal | molecule | metal” sandwich, there are three distinct processes that can give rise to such an asymmetrical conduction.

The first process is due to Schottky barriers [30], which are electrical dipole moments that form at the “metal | molecule” interfaces, as discussed above [34, 40]. The second process arises if the electrically-active portion of the molecule is placed asymmetrically within the “metal | molecule | metal” sandwich. This geometry is common, because a long alkyl “tail” is often needed to make the molecule amphiphilic so that it will form well-ordered Langmuir-Blodgett monolayers [76–78].

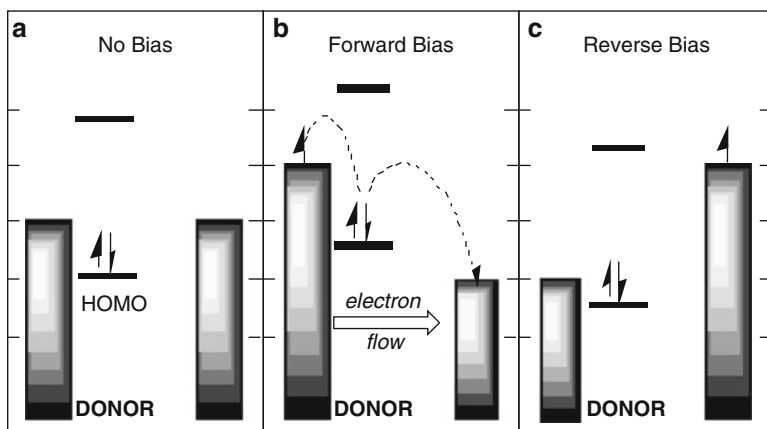


Fig. 8 Rectification via HOMO

To understand how an asymmetric geometry leads to rectification, consider the electroactive group(s) in the molecule that serve as “way-stations” for the flowing electrons. A donor group, with high-energy electrons in the molecule’s HOMO, may relinquish an electron to a low-potential electrode. Conversely, an acceptor group, with a low-energy vacancy in the molecule’s LUMO, may be willing to take on an electron from a high-potential electrode.

Figure 8 shows asymmetric rectification via HOMO. In Fig. 8a, the electrodes have no bias, and the HOMO orbital of a donor group is fairly high in energy. Forward bias, shown in Fig. 8b, consists of the proximal electrode being raised in potential and the distal electrode lowered. The energy of the molecule’s orbitals reflects the altered potential; since the HOMO is nearer to the high-potential side, its energy is raised. When the HOMO energy is intermediate between the two electrodes, electrons can flow from left to right with a decrease in energy. But in Fig. 8c, when the same amount of bias is applied in the reverse direction, the HOMO is lowered by being closer to the low-potential electrode, so that no downhill pathway is available for reverse electron flow.

Similarly, Fig. 9 shows asymmetric rectification via LUMO. Here, an acceptor supplies a low-lying but vacant orbital, as in Fig. 9a. When the proximal electrode has high potential, the LUMO energy rises high enough to avoid providing a pathway for current flow, as in Fig. 9b. But when the near electrode has low potential, as in Fig. 9c, the LUMO energy lowers enough to be intermediate in energy between the two electrodes, and electrons can flow downhill from right to left.

10 The Aviram-Ratner Proposal for Unimolecular Rectification

UE began with Aviram and Ratner’s 1973 proposal for a molecular rectifier; this is the third rectification process [79]. An Aviram-Ratner rectifier has donor and acceptor groups in one molecule, separated by an insulating bridge of sigma

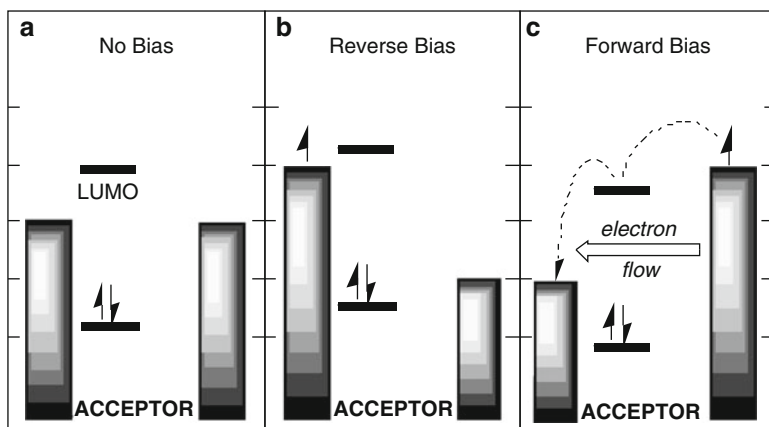


Fig. 9 Rectification via LUMO

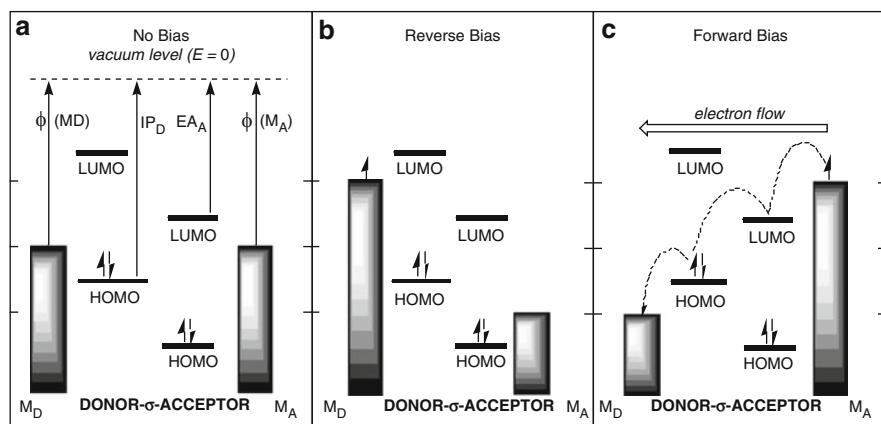


Fig. 10 Aviram-Ratner rectification via HOMO and LUMO. (a) A D-σ-A molecule is sandwiched between two metal electrodes. M_D is the electrode proximal to the donor, M_A is the electrode proximal to the acceptor, ϕ is the electrode metal work function, IP_D is the ionization potential of the donor, EA_A is the electron affinity of the acceptor. (b) No pathway for current exists when a voltage is applied in the reverse bias direction. (c) Under a comparable voltage to (b) but in the forward bias direction, rectification results from electrons flowing from M_A to LUMO to HOMO to M_D .

bonds. Figure 10 shows how the rectification arises. Under no bias, as in Fig. 10a, the electrode potentials are the same. Under reverse bias, as in Fig. 10b, the M_D potential is raised and the M_A potential is lowered: no direct pathway exists for electron flow from M_D to M_A . Under forward bias, as in Fig. 10c, the M_D potential is lowered and the M_A potential is raised, so there is now a direct downhill pathway for electrons to flow from M_A to the acceptor's LUMO to the donor's HOMO to M_D . This may be considered true unimolecular rectification, and has been the impetus for much work, including the focus of our labs.

If M_D takes a donor HOMO electron while M_A gives an electron to the acceptor LUMO, the molecule's ground state $D^0-\sigma-A^0$ will transform into the electronic excited state $D^+-\sigma-A^-$. This highly-polar zwitterionic state will decay back to the less-polar ground state $D^0-\sigma-A^0$ by inelastic tunneling through the molecule, completing the passage of an electron from M_A to M_D [79]. This decay can be enhanced by intramolecular charge transfer (ICT) or intervalence transfer (IVT) mixing of the donor and acceptor states, which would be indicated by the existence of an extra ICT or IVT absorption band. If the D and A moieties are too far apart to communicate, then $D^+-\sigma-A^-$ will not decay, and no rectification will occur. On the other hand, if D and A are too close, they will form a single, mixed ground state, so that electron flow is the same in both directions, and no rectification will occur. The right length for σ is probably between two and six atoms.

The Aviram-Ratner D- σ -A molecule is analogous to a “pn” junction rectifier: the electron-rich donor region D would be similar to the electron-rich semiconducting “n” region, while the electron-poor A region would be similar to a semiconductor’s “p” region [79]. However, note that under forward bias the preferred direction of Aviram-Ratner electron flow is from A to D, while in a pn junction rectifier the preferred direction is from n to p.

It is worth noting that a metal | D- σ -A | metal assembly may yield a combination of Schottky, asymmetric, and Aviram-Ratner effects. Pure unimolecular rectifiers are rare [78]. As an example of the possible complexities involved, consider how far from the center of the D- σ -A molecule the D and A groups reside. We can use the factor ρ to represent the fractional distance across the electrode-electrode gap for each group. In Fig. 11, we assume that the center of the donor is 40% of the distance from M_D to M_A (i.e., $\rho_D = 0.4$) while the center of the acceptor is 60% of the distance ($\rho_A = 0.6$). We show the bias in Fig. 11 by assuming M_D is at ground and the potential of M_A varies as follows: Fig. 11a, -2 V; Fig. 11b, -1 V; Fig. 11c, no bias; Fig. 11d, $+1$ V; Fig. 11e, $+2$ V. Under no bias (Fig. 11c), we arbitrarily choose a donor HOMO level of -0.5 eV and an acceptor LUMO level of $+0.5$ eV. But the MO energy levels change under the influence of an electric field: the closer to the biased electrode, the stronger the influence. We model this by changing each MO by an amount = bias $\times \rho$.

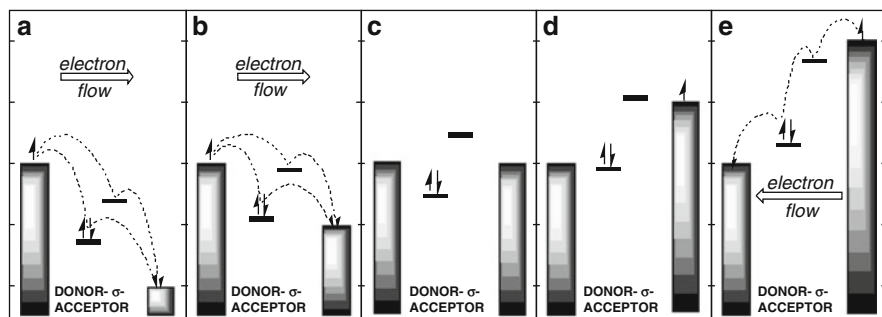


Fig. 11 Aviram-Ratner rectification with centered donor and acceptor groups

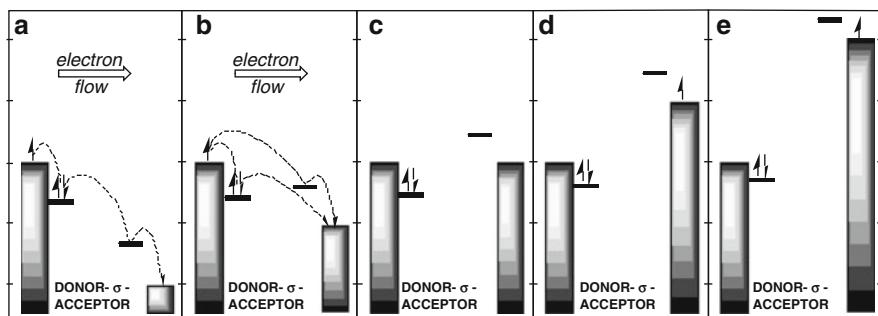


Fig. 12 Aviram-Ratner rectification with edge-positioned donor and acceptor groups

Under +1 V of forward bias (Fig. 11d), there is no pathway for current flow. At +2 V, however, the orbitals have adjusted to give a downhill path from M_A to acceptor to donor to M_D , and Aviram-Ratner current flows. On the reverse bias side, however, two pathways exist for current flow at -1 V (Fig. 11b) as well as -2 V (Fig. 11a). These pathways (Fig. 11a, b) are asymmetric rectification via HOMO and via LUMO, and they are in the anti-Aviram-Ratner direction, i.e., from donor to acceptor. This could allow for anti-Aviram-Ratner rectification under moderate biases. Note, however, that the electrons in Fig. 11a, b must tunnel over longer distances than those in Fig. 11e, because there is only one “way-station,” instead of two. The Aviram-Ratner current flow under the higher bias of Fig. 11e could therefore be much more intense than the reverse flow of Fig. 11b or 11a.

Now consider a case where the donor and acceptor are at the far ends of the D- σ -A molecule: let $\rho_D = 0.1$ and $\rho_A = 0.9$ (Fig. 12). The energy levels under no bias (Fig. 12c) are the same as in Fig. 11(c). Now, under “forward” bias (Fig. 12d) of even +2 V (Fig. 12e) there is no current flow, because the raising LUMO stays higher in energy than M_A , and the HOMO stays lower than M_D . At -1 V of bias (Fig. 12b) there are two anti-Aviram-Ratner asymmetric pathways that should, however, be slow because of long tunneling distances. At -2 V of bias (Fig. 12a), the acceptor LUMO has assumed a lower energy than the donor HOMO. Now there is a direct electron pathway from donor to acceptor via two way stations: this might be considered a reverse-Aviram-Ratner rectification.

While the arrangement in Fig. 12 may not be realistic, because of the extreme length of σ bridge required, it highlights the complexity of factors involved in designing a good Aviram-Ratner rectifier. Having the donor and acceptor groups near the center of the D- σ -A molecule, with a small HOMO-LUMO gap, should improve the chances of accomplishing Aviram-Ratner unimolecular rectification.

11 Donors and Acceptors; HOMOs and LUMOs

Building a successful D- σ -A molecule requires knowledge of the appropriate HOMO and LUMO energies and the work function energies of the electrodes. A donor’s ionization potential IP_D corresponds to its HOMO energy, and an

acceptor's electron affinity EA_A corresponds to its LUMO energy. Usually, good electron donors (with low IP_D) are poor electron acceptors, while good acceptors (with large EA_A) are poor donors. An electrode's zero-bias energy is represented by its metal's work-function ϕ . The work function is related to the metal's Fermi level E_F , and is moderately dependent (0.1–0.3 eV) on the Miller indices of the exposed crystallographic face of the metal.

These relationships are represented graphically in Fig. 13, which also shows some representative donor and acceptor structures. In practice, the range of IP_D and

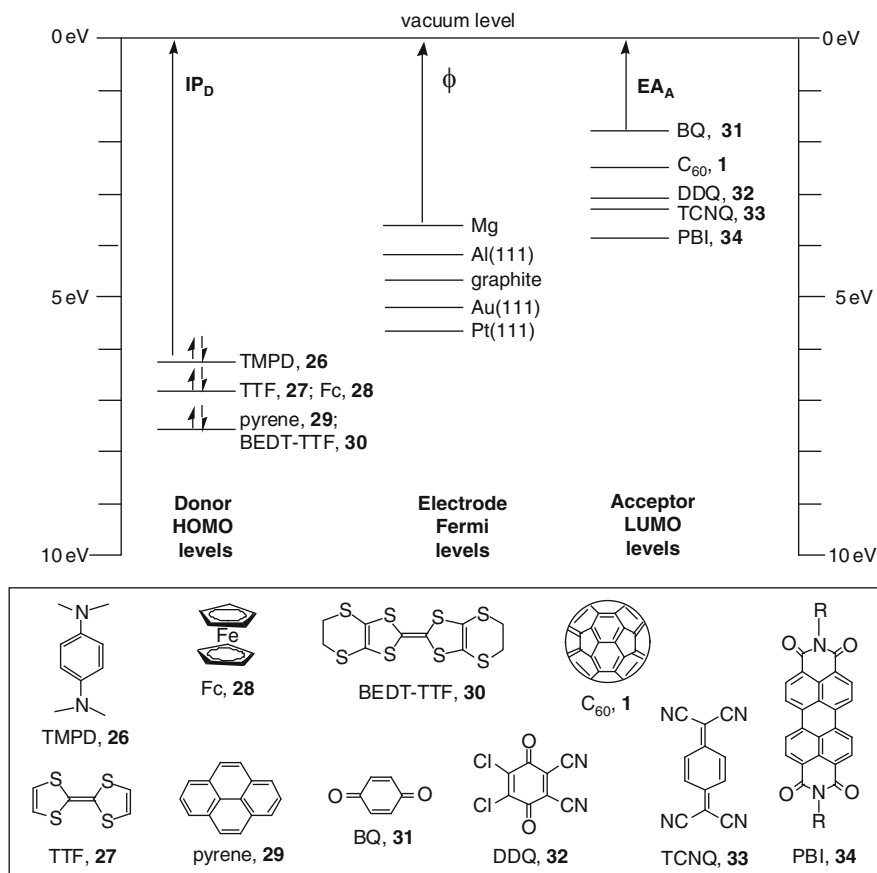


Fig. 13 Representative donor, electrode, and acceptor energy levels. First gas-phase ionization potentials IP_D of five donors: *N,N,N',N'*-tetramethylphenylenediamine (TMPD, **26**) = 6.25 eV [80]; tetrathiafulvalene (TTF, **27**) = 6.83 eV [81]; ferrocene (Fc, **28**) = 6.72 eV [82]; pyrene (**29**) = 7.55 eV [83]; bisethylenedithio-tetrathiafulvalene (BEDT-TTF, **30**) = 7.6 eV [84]. Bulk work functions ϕ of four metals and one semimetal: Mg = 3.66 eV [85]; Al(111) = 4.24 eV [86]; graphite = 4.3 eV [87]; Au(111) = 5.31 eV [88]; and Pt(111) = 5.7 eV [89]. Gas-phase electron affinities EA_A of five acceptors: para-benzoquinone (BQ, **31**) = 1.9 eV [90]; buckminsterfullerene (C₆₀, **1**) = 2.6 to 2.8 eV [91]; 2,3-chloro-5,6-dicyano-para-benzoquinone (DDQ, **32**) = 3.13 eV [92]; 7,7,8,8-tetracyanoquinodimethane (TCNQ, **33**) = 2.8 eV [93] corrected to 3.33 eV [94]; perylenetetracarboxylic bisimide (PBI, **34**) = 3.9 eV [95]

EA_A is limited because the molecules, as well as their cations or anions, must be stable in ambient air or solvent: donors that are too powerful as reducers, and acceptors that are too powerful as oxidizers, will not persist until their rectification is measured. Further, the donor's HOMO must not be so high, or its LUMO so low, that spontaneous electron transfer occurs to convert the molecule into a zwitterion.

12 Molecular Rectifiers

Aviram and Ratner's originally proposed D- σ -A molecule (or "Gedankenmolekül"), **35** (Fig. 14), included the excellent donor TTF (**27**) and the excellent acceptor TCNQ (**33**), separated by a rigid bicyclooctane bridge [79]. This molecule was never made (and would likely not have made a good monolayer), but it was the impetus for the synthesis of many new candidate rectifiers.

The fundamental figure of merit for rectification, the *rectification ratio*, RR , is defined as the current at a positive bias V divided by the absolute value of the current at the corresponding negative bias $-V$: $RR \equiv I(V)/|I(-V)|$. Commercial doped Si, Ge, or GaAs pn junction rectifiers have RR between 10 and 100.

Beginning in 1986, Samble developed techniques for studying the electrical properties of LB multilayers and (harder to work with) monolayers, by sandwiching them between a high-work-function noble metal (Ag or Pt) on one side, and, to minimize damage, the low-work-function metal Mg on the other [34, 40]. In 1990, Ashwell, Samble, and co-workers reported rectification from the zwitterionic molecule $C_{16}H_{33}$ - γ Q-3CNQ, **36a** (Figs. 15 and 16) between Pt and Mg electrodes [35]. This molecule has a couple of peculiarities. First, because the donor and

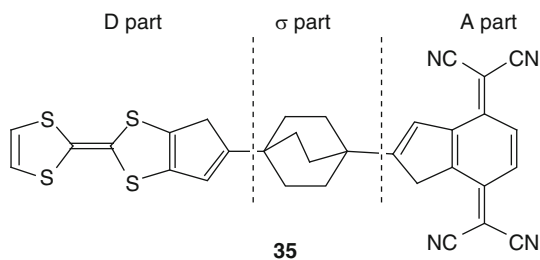


Fig. 14 Aviram-Ratner proposed D- σ -A molecule for unimolecular rectification

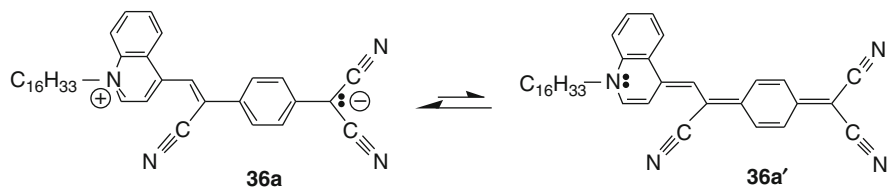


Fig. 15 First confirmed unimolecular rectifier

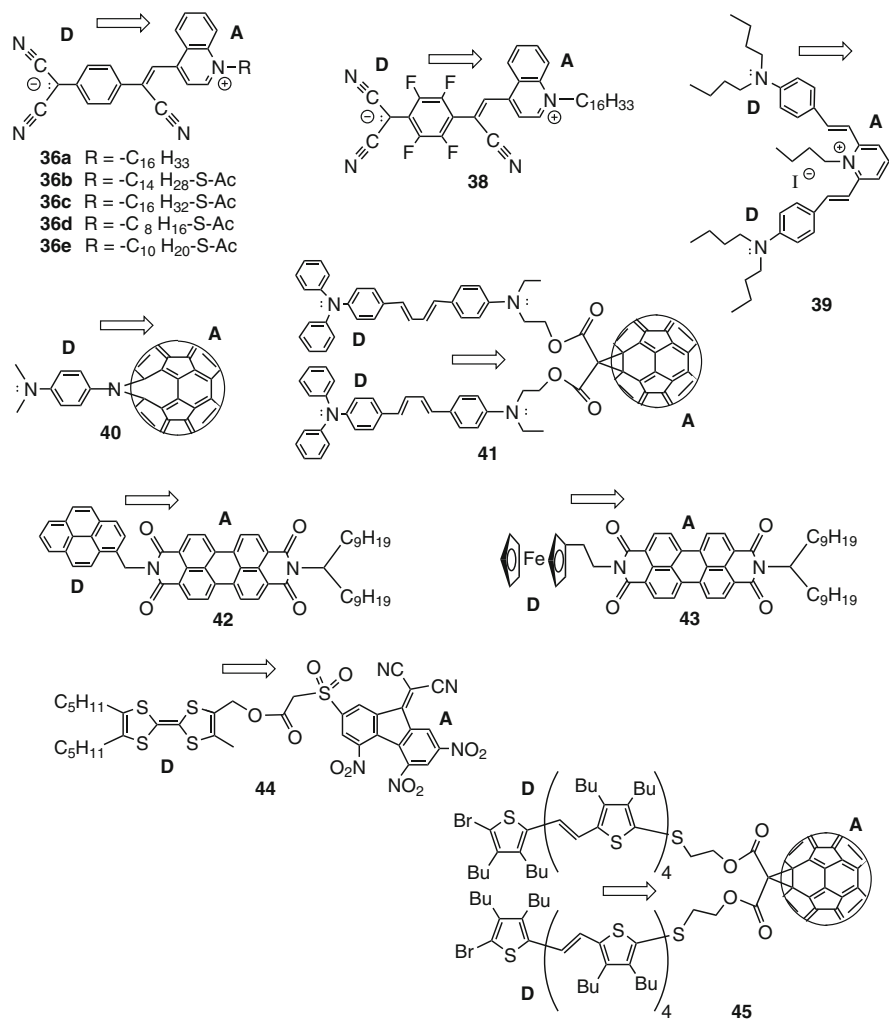


Fig. 16 Eleven unimolecular rectifiers studied at the University of Alabama as monolayers between Au electrodes (except for **36d** and **36e**: see text). The *arrows* indicate the experimentally observed direction favored electron transfer; however the direction is reversed for **36d** and **36e** (see text)

acceptor are connected by a C=C bridge, it is formally a zwitterionic $\text{D}^+-\pi-\text{A}^-$ molecule. However, due to an angle twist between D and A, the C=C bridge is not conjugating, so the bridge functions as a σ bridge. Second, the molecule is ionic, with a dipole moment of 43 D [39]. The 3CNQ portion is clearly related to the strong acceptor TCNQ (**33**), but it has grabbed an electron and become the anionic, donor part of the molecule. The acceptor is a quinolinium cation. It is possible to write an apparent resonance form, **36a'** (Fig. 15), in which there is an anilinoïd

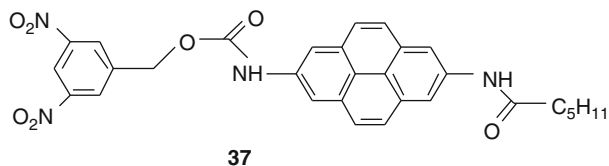


Fig. 17 Multilayer rectifier

donor and a quinoid 3CNQ acceptor, but this actually represents an *excited state* with a different (planar) geometry and a much smaller dipole moment of ~ 6 D [96]. An IVT band between the D^+ and A^- ends of the molecule was observed at 535 nm [97]. In 1993, the incorporation of insulating layers between the molecule and the electrodes excluded “molecule | electrode Schottky barriers” as major contributors to the rectification [36]. In 2002, it was reported that at 8 K, a monolayer film of **36a** reversed its rectification direction [98].

Among the early potential rectifiers studied, one of us (Mattern) designed the D- σ -A molecule **37** (Fig. 17), whose multilayer conductivity was measured by the Sables group [99]. Multilayers gave striking rectification, with $RR = 130$. Current flow was in the anti-Aviram-Ratner direction, however, and having an assembly of multilayers rather than a monolayer complicated the interpretation of the results [99].

Between 1982 and 1997, one of us (Metzger) studied many D- σ -A molecules as potential rectifiers, but could not measure their IV properties reliably [11, 12, 100]. Due to difficulties in interpreting how electron transport occurs between adjacent layers in a multilayer, Metzger decided to focus on monolayers, and to avoid difficulties with asymmetric Schottky barriers, decided to use the same metal on both sides of the monolayer (first Al for **36a**, later Au).

In the initial University of Alabama studies on **36a**, utilizing oxide-covered Al electrodes [39, 101, 102], the monolayer had a dramatically asymmetric current, with a rectification ration of 26 at 1.5 V, and a current flow of about 0.3 electrons/s/molecule [39]. RR s and current varied from pad to pad, because these were two-probe measurements, with all electrical resistances (wire to paste to electrode to monolayer) in series. Further, as high potentials were repeatedly scanned, the IV curves became less asymmetric, with RR s gradually decreasing: the monolayers appeared to be losing their asymmetric Langmuir film orientation. A minority of monolayers of **36a** rectified in the reverse direction [102]. With the change to oxide-free Au electrodes, the asymmetry persisted, with RR s as high as 27, and the current per molecule increased dramatically to as high as 9×10^4 electrons/s (Fig. 18a) [38, 41]. Figure 19 shows the current I and $\log I$ vs V for **36a** [38]. As before, however, the RR decreased upon repeated scanning. In some cells, the current increased until breakdown occurred at 5.0 V, i.e., the cells suffered dielectric breakdown only at a field close to 2 GV/m [38].

Since 1997, 11 of the molecules studied at the University of Alabama, including **36a**, have exhibited rectification as monolayers between Au electrodes [19, 38, 41, 97, 103–109]. The structures are shown in Fig. 16. With the exceptions of **40** and

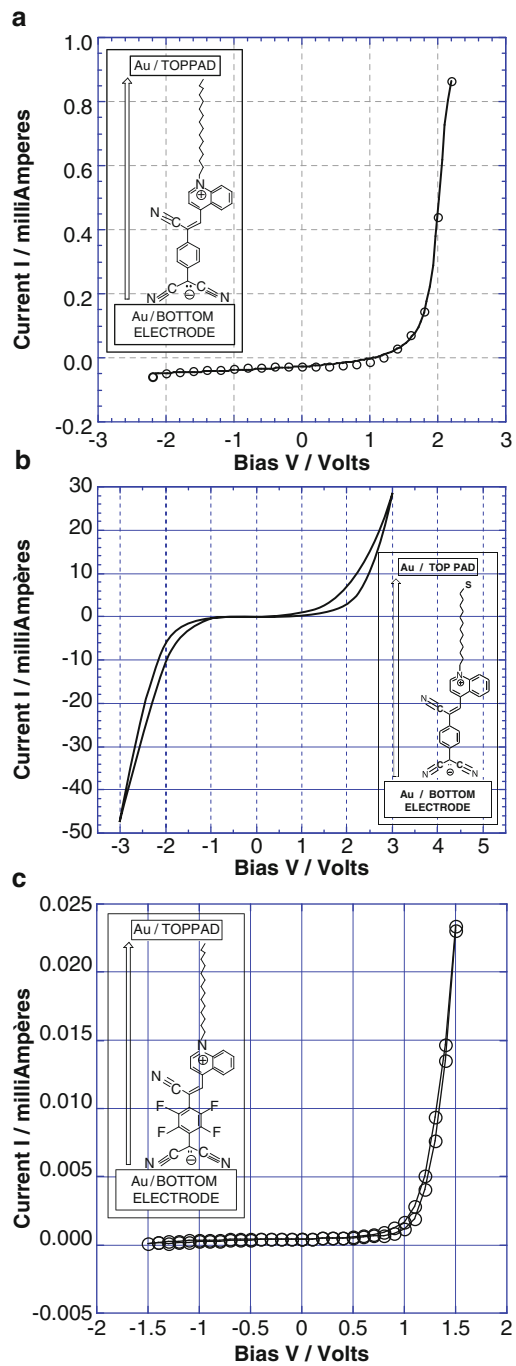


Fig. 18 (continued)

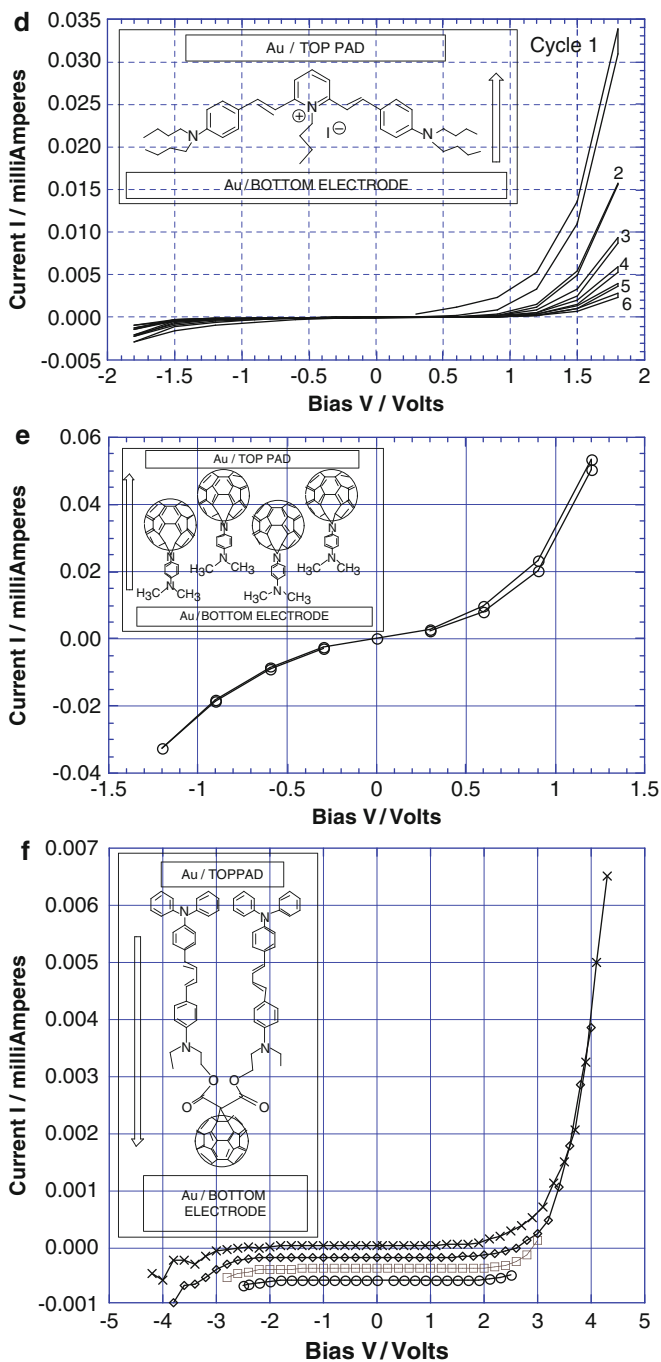


Fig. 18 (continued)

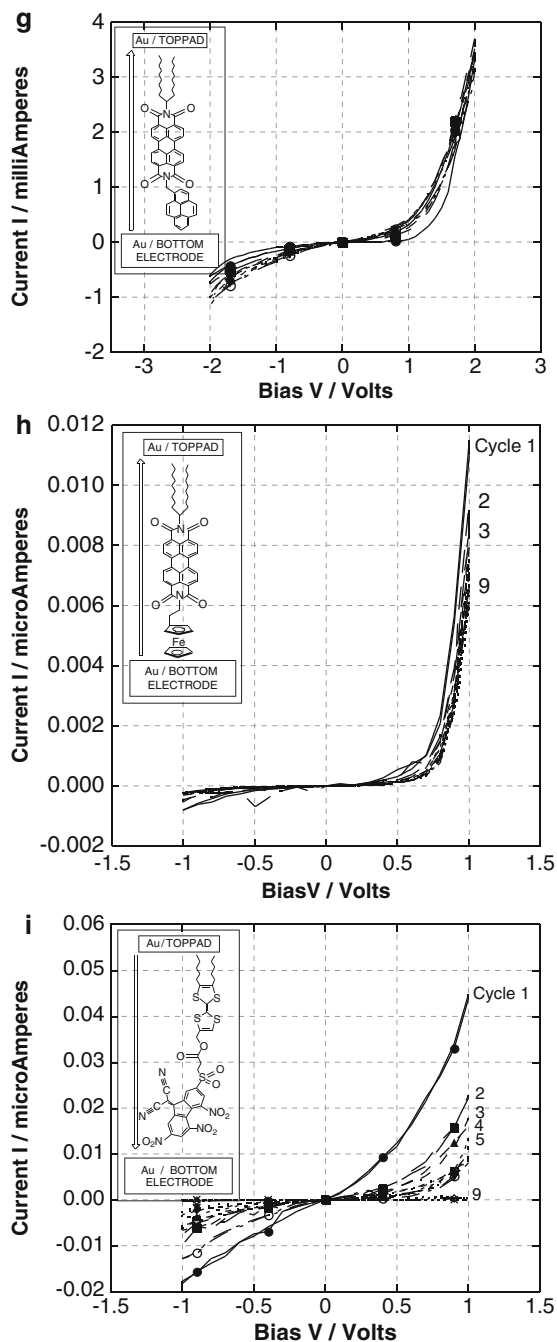


Fig. 18 The rectification of MOM (Metal | Organic | Metal) sandwiches consisting of three elements: (1) a macroscopic bottom Au or Al electrode, (2) an 0.3 mm² top Al or "cold Au" electrode pad, and, between them: (3) (a) an LB monolayer of **36a** [38]; (b) an LB monolayer

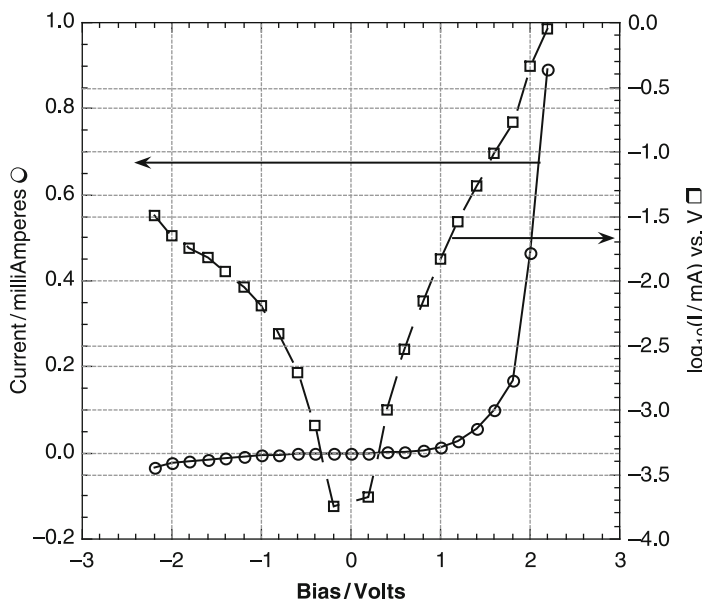


Fig. 19 I/V curve (squares) and $\log_{10}I$ vs V (circles) for first IV cycle for **36a** [38]

41, all have pendant alkyl groups for assisting their organization as monolayers. In each case, the bottom Au electrode was evaporated onto glass, quartz, or very flat Si substrates, and the transfer of monolayers was routine. (The contact angle of a drop of water on a monolayer of **36** transferred to a gold surface was 92° , consistent with its C_{16} tail being in the air of the LB trough, as expected [110].) Depositing the second metal electrode atop the delicate monolayer required institution of the “cold gold” technique (Fig. 2a) [38, 41, 111].

Characteristic IV curves at room temperature are shown in Fig. 18, and some of the results are summarized in Table 1. These results have been reviewed often [11, 12]. Efforts were made to identify the molecular mechanisms for the rectification, and to buttress them by theoretical calculations [39, 76, 106, 112]. Not all compounds tested rectified, because of their chemical structure and/or monolayer structure. The direction of larger electron flow (“forward direction”) is shown by arrows in Fig. 16; it is noteworthy that in all cases the direction is from the electron donor D to the electron acceptor A, that is, in the anti-Aviram-Ratner direction.

Fig. 18 (continued) of **36b** [103]; (c) an LB monolayer of **38** [104]; (d) an LB monolayer of **39** [104]; (e) an LB monolayer of **40** [19]; (f) an LS monolayer of **41** [105] (the repeated scans are offset for clarity); (g) an LB monolayer of **42** [106]; (h) an LS monolayer of **43** [106]; (i) an LB monolayer of **44** [107]

Table 1 Summary data for 11 unimolecular rectifiers studied at the University of Alabama

#	Type	IVT (nm)	LB or LS	RR	Survives cycling	AR or anti-AR	Ref.
36a	D ⁺ - π -A ⁻	530	LB	2–27	No	anti-AR	[38]
36b	D ⁺ - π -A ⁻	530	LS	5	Yes	anti-AR	[103]
36c	D ⁺ - π -A ⁻	530	LS	5	Yes	anti-AR	[103]
38	D ⁺ - π -A ⁻	504	LB	3–64	No	anti-AR	[97]
39	D ⁺ I ⁻	480	LB	8–60	No	anti-AR	[104]
40	D- σ -A	720	LB	2	No	anti-AR	[19]
41	D- σ -A	—	LS	10	Yes	anti-AR	[105]
42	D- σ -A	—	LB	2–5	No	anti-AR	[106]
43	D- σ -A	595	LB	30	Yes	anti-AR	[106]
44	D- σ -A	1,220	LB	13	No	anti-AR	[107]
45	D- σ -A	—	LS	6–60	Yes	anti-AR at low V, AR at high V	[108]

All compounds were measured at room temperature in air between Au electrodes inside a Faraday cage. IVT = maximum of the optical InterValence Transfer or intramolecular charge transfer band. RR Rectification Ratio. “Survives cycling” means RR does not decrease with cycling of IV measurements. “AR or anti-AR” indicates whether electron flow is from A to D (AR) or from D to A (anti-AR)

For the rectifiers listed in Table 1, the current was found to decay with successive measurements of the same junction for **36a**, **38**, **39**, **40**, **42**, and **44** between Au electrodes (where the monolayers were not sufficiently rigid, there probably was room in the “Au | monolayer | Au” sandwich for molecular reorientation under applied bias) (see Fig. 18d, g, and i for examples). In contrast, the current did not decay at all in subsequent cycles for **36b** (Fig. 18b) or **36c**, where the molecules were chemisorbed onto the Au electrode with an S anchor, or for **41** (Fig. 18f), **43**, or **45** (where the monolayer was sufficiently rigid and closely packed to resist reorientation).

The unwelcome gradual decreases in the electrical conductivity and in the RR of an LB monolayer of **36a**, from an initial value of 27 [38, 39] to close to 1 upon repeated cycling, was seen in about half the rectifiers studied in Table 1. This prompted us to try combining the LB and SAM techniques, by using variants of **36a** with thioacetyl anchors at the end of their C₁₄ (**36b**) or C₁₆ (**36c**) alkyl tails. LB films should put these tails in the air, where the deposited top Au pads should strongly coordinate to the sulfur groups. LS films would directly coordinate to the bottom electrode laid on top of it. In either case, the Au–S bond should stabilize the monolayer and prevent reorientation [103, 109]. The thioacetate analog with a C₁₁ tail did not make a satisfactorily-ordered LB film [109], but **36b** and **36c** (Fig. 20) made LB films, rectified, and survived cycling without loss of RR [103].

For most of the molecules, the electron flow is from D to A, which is supported by the “anti-Avram-Ratner mechanism” of Fig. 11a. However, there may be yet another possibility, shown in Fig. 21: implicit in the analyses of Figs. 9–11 has been the Avram and Ratner assumption [79] that “auto-ionization” is a less efficient competing process. If the electric field induces intramolecular ionization first by sufficiently altering the orbital energies, then the direction of electron flow may occur in the anti-AR direction (Fig. 21)!

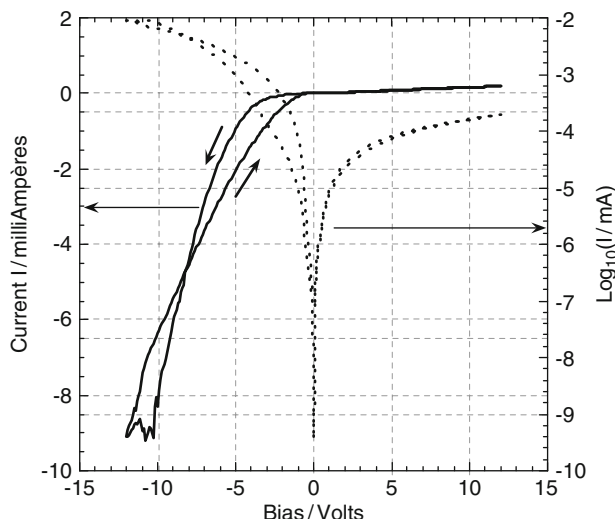


Fig. 20 I/V curve and $\text{Log}_{10}I$ vs V (first cycle) for an LB upstroke film of **36c** [103]

The issue of whether the ground state of **36a** is zwitterionic (**36a**) or quinoid (**36a'**) has received renewed attention, and was recently reviewed [113]. The length of the alkyl tail R, the solvation, and the packing mode within a monolayer are important. For the very short tail $R = \text{CH}_3$, theory at the semiempirical AM1 and PM3 level, with solvation corrections, predicts that the molecule is largely ionic, with dipole moments increasing upon “solvation” in acetonitrile [112]. For the long tail $R = \text{C}_{16}\text{H}_{33}$, in experiments, in a monolayer, in a multilayer, and also in dichloromethane solution, the zwitterionic form **36a** is the ground state [39, 110]. It is important to note that in monolayers and multilayers the chromophore in **36a** is tilted about 45° from the normal to the film, thus stabilizing the zwitterionic state **36a** (rather than **36a'**) through favorable intermolecular electrostatic interactions. If the tail is intermediate in length, as in **36d** ($R = \text{C}_8\text{H}_{16}$) and **36e** ($R = \text{C}_{10}\text{H}_{20}$), the chromophore is no longer tilted, but aligned, the quinonoid form (similar to **36a'**) is now the ground state, and the rectification direction is *opposite* to the arrow direction given in Fig. 16 [114].

The four fluorines present in **38** should have made its 3CNQF_4 group a much poorer donor than the 3CNQ in **36a**; however, **38** also rectified, with electron flow in the same D to A direction as in **36a** (Fig. 18c) [97].

The butylpyridinium iodide **39** transfers to hydrophilic substrates as a Z-type LB multilayer [104]. The initial RR (for a monolayer) is as high as 60; rectification shows a decrease upon successive cycles (Fig. 18d). The favored direction of electron flow is from iodide to pyridinium, i.e., in the direction of “back-charge-transfer.” The rectification may be attributed to an interionic electron transfer, or to an intramolecular electron transfer [104].

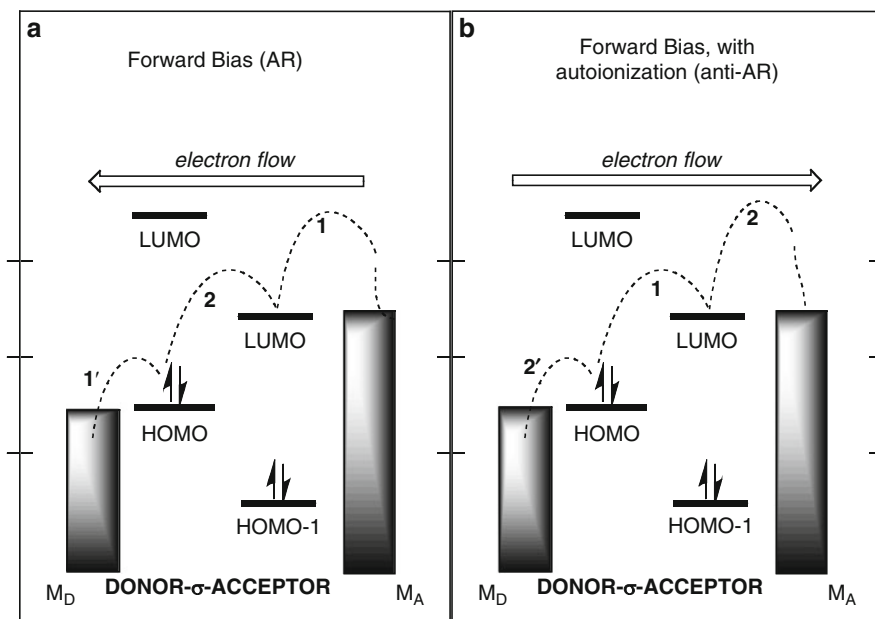


Fig. 21 (a) Rectification in the AR sense: electron transfers occur first between electrode M_D and the HOMO of the D- σ -A molecule (1'), and between the LUMO and M_A (1), thus establishing the zwitterionic excited state $D^+-\sigma-A^-$, which then (2) relaxes back into the neutral state. (b) Rectification in the anti-AR sense if "auto-ionization" occurs first (1), forming the excited state $D^+-\sigma-A^-$ by an interaction of the intense electric field and the molecule, followed by transfers to and from the electrodes (2) and (2'), resulting in the electron passing from M_D to M_A . The molecular energy levels, which in reality must perform shift dramatically during the electron transfer process, are drawn here for simplicity as if the molecule were still isolated in the "gas phase"

Dimethylaminophenylazafullerene, **40**, consists of the weak electron donor dimethylaniline bonded to the moderate electron acceptor N-capped- C_{60} , with an IVT peak at 720 nm [19]. The Langmuir film is very rigid, i.e., the slope of the isotherm is relatively large. However, the molecular area is $50 \text{ \AA}^2$ at the LB film transfer pressure, whereas the true molecular area of C_{60} is close to $100 \text{ \AA}^2$. Therefore it is thought that **40** transfers onto Au in a staggered arrangement, as shown in the insert of Fig. 18e. Angle-resolved N1s XPS spectra confirm that the two N atoms are closer to the bottom Au electrode than is the C_{60} cage [19]. Molecule **40** is a moderate rectifier with $RR \approx 2$. It can also exhibit a tremendous, *spurious* apparent rectification ratio as high as 20,000. This is probably an example of partial penetration ("electromigration") of Au, forming stalagmites that create an electrical short [19].

The bis(triphenylamine)-substituted fullerene **41** makes a dense and stiff monolayer that transfers onto an Au substrate by LS but not by LB [105]. It rectifies with $RR = 10$ (Fig. 18f) and the RR does not decrease at all upon successive cycling [105].

Compounds **42** and **43** are based on the PBI acceptor, made soluble by a C₁₉ “swallowtail” attached to one imide nitrogen. The donor is attached through the other imide nitrogen. In **42**, the moderate donor pyrene is separated from the PBI by a C₁ σ bridge that holds the donor and acceptor close to perpendicular, with limited motion possible. Nonetheless, **42** has a persistent, small *RR* (Fig. 18g) [106]. In **43**, the good donor ferrocene is separated from the PBI by a more flexible C₂ σ bridge. It has an IVT band that peaks at 595 nm and forms a rectifier with a persistent *RR* between 25 and 35 (Fig. 18h) [106].

Compound **44** has a TTF donor group and a fluorene group made into a good acceptor by electron-withdrawing nitro, cyano, and sulfone groups. It has an IVT band maximum at 1,220 nm. It rectifies (Fig. 18i), but the *RR*s decrease to unity after ~nine cycles of measurement [107]. Similar results were reported by Bryce’s group for a closely-related molecule [115]. In that case, the direction of electron flow depended on the LB film substrate, and the rectification direction was reversed when X and Z LB films were compared. These differ by film deposition occurring on an upstroke or downstroke of the substrate through the film, and therefore should produce films with the opposite molecular orientations, consistent with the rectification reversal.

Compound **45** incorporates a fullerene acceptor and two substituted polythiophene-ethenyl tails; it rectifies as an LS monolayer. Interestingly, it rectifies in one direction for smaller biases between 0 and ± 2.0 V, but in the reverse direction at higher biases, perhaps indicating a change in conduction mechanism, as discussed above. It also rectifies between Al and Pb electrodes at 4.2 K (Fig. 22a) [108].

Compound **45** was analyzed by *inelastic electron tunneling spectroscopy* (IETS) using a home-built instrument [108]. In IETS, a low-frequency (~ 100 Hz) AC source and a low-bias DC voltage are applied together to a thin film at low temperatures (4.2–100 K). The second derivative of the current as a function of the voltage, measured using second harmonic detection, reveals peaks that correspond to intramolecular vibrations [116]. This verifies that the current is traveling through the molecule. In addition, an elastic component measured at slightly higher bias can reveal “orbital-mediated tunneling” [117, 118], an enhanced current due to resonance between the Fermi level of an electrode and an accessible molecular orbital of the molecule [108]. The IETS spectrum of **45** at 4.2 K shows the expected intramolecular vibrations (Fig. 22b), and a wide-scan IETS spectrum shows the signature of rectification: an asymmetric signal (higher intensity at positive bias) occurs at the same potential as the enhanced current due to rectification (Fig. 22c): this is orbital-mediated tunneling, and is a *definitive proof that the rectification is due to through-bond tunneling, not through-space tunneling* [108].

Bryce, Petty, and co-workers studied **46** (Fig. 23), containing a TTF donor and a TCNQ acceptor like the original Aviram-Ratner Gedankenmolekül **35**. Although **46** gave strong Langmuir films, the TCNQ group lies flat on the water surface rather than end-on, and rectification could not be observed [119].

Weber, Mayor, and co-workers created the D- π -A compound **47**, where four fluorine atoms serve to make an acceptor end. The π link is a combination of ethyne

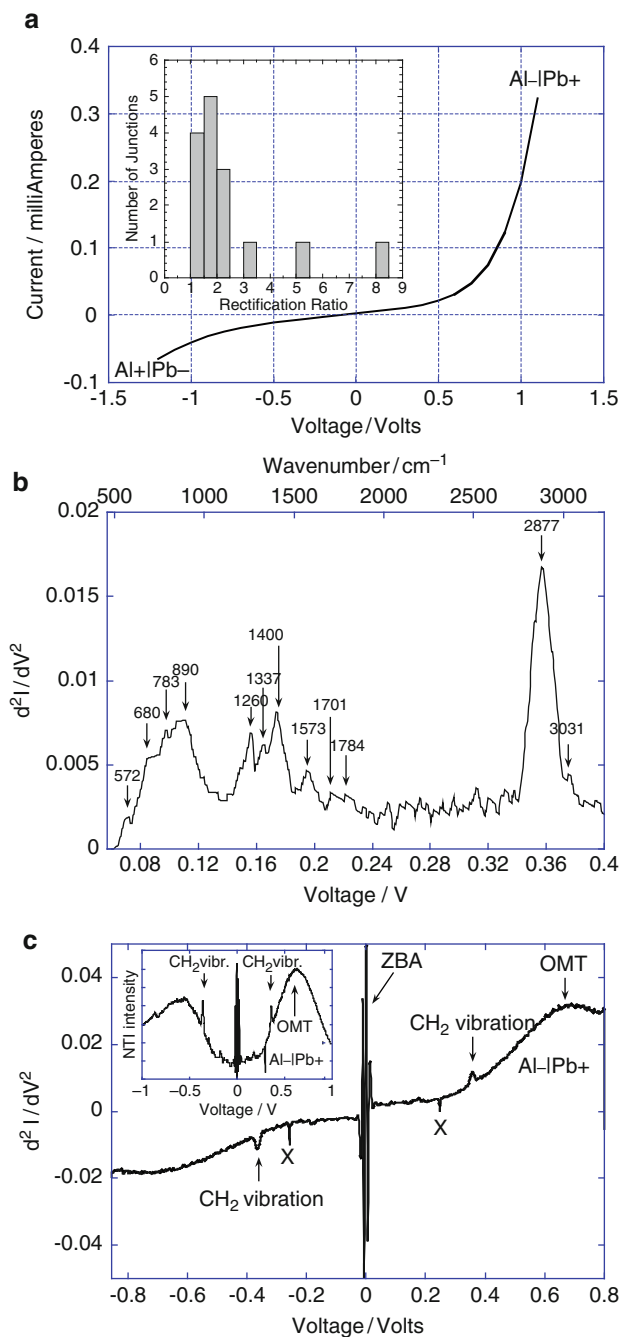
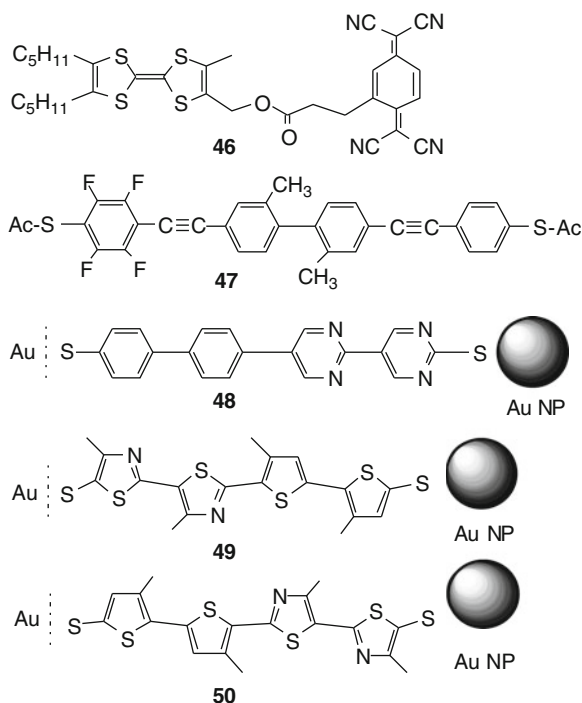


Fig. 22 (a) Rectification at 4.2 K due to an LS monolayer of **45** between Al and Pb electrodes: the onset is at 0.65 V. (b) IETS of **45** at 4.2 K: the most prominent peaks are the CH₂ vibrations

Fig. 23 More donor-acceptor molecules

and aromatic groups, with conjugation broken by a hindered biphenyl at the center. Thioacetates at both ends allow the molecule to attach suspended between an Au MCBJ. Rectification was seen, with *RR*s scattered between 2 and 10 [120].

Yu et al. prepared **48**, bound to an Au(111) surface by a thiol on the biphenyl end, then deprotected on the bipyrimidine end to expose a thiol to bind an Au nanoparticle. Rectification was measured by scanning tunneling spectroscopy (STS), and it could be reversed by the addition of acid, which protonated the pyrimidine rings, converting them from donor to acceptor [121]. Yu's group has also inverted the attachment of a rectifier, as shown with **49** and **50**, and confirmed that the rectification direction reversed [122]. This was recently verified by STM-BJ measurements [123].

Fig. 22 (continued) at 0.36 V ($2,877\text{ cm}^{-1}$) due to the butyl groups of **45**. (c) Inelastic and elastic tunneling spectrum (wide voltage scan, -0.85 to $+0.8$ V) of an LS monolayer of **45** between Al and Pb electrodes at 4.2 K. The central peaks are artifacts (zero-bias anomalies due to metal phonons); the peaks marked "X" are artifacts; the peaks at ± 0.36 V are the prominent CH_2 vibrations [see (b)]; the broad peak centered at $+0.65$ V, marked OMT, is orbital-mediated tunneling, an elastic current at 0.65 V [same as the onset in (a)] in resonance with the LUMO [108]

Ashwell and co-workers studied several zwitterionic systems (Fig. 24) by STS, starting with **36a** [124]; for **36a**, and for several other zwitterionic systems [21, 125, 126], the addition of acid stopped the rectification, while addition of base restored it. Ashwell and co-workers saw a reversal of the direction of rectification

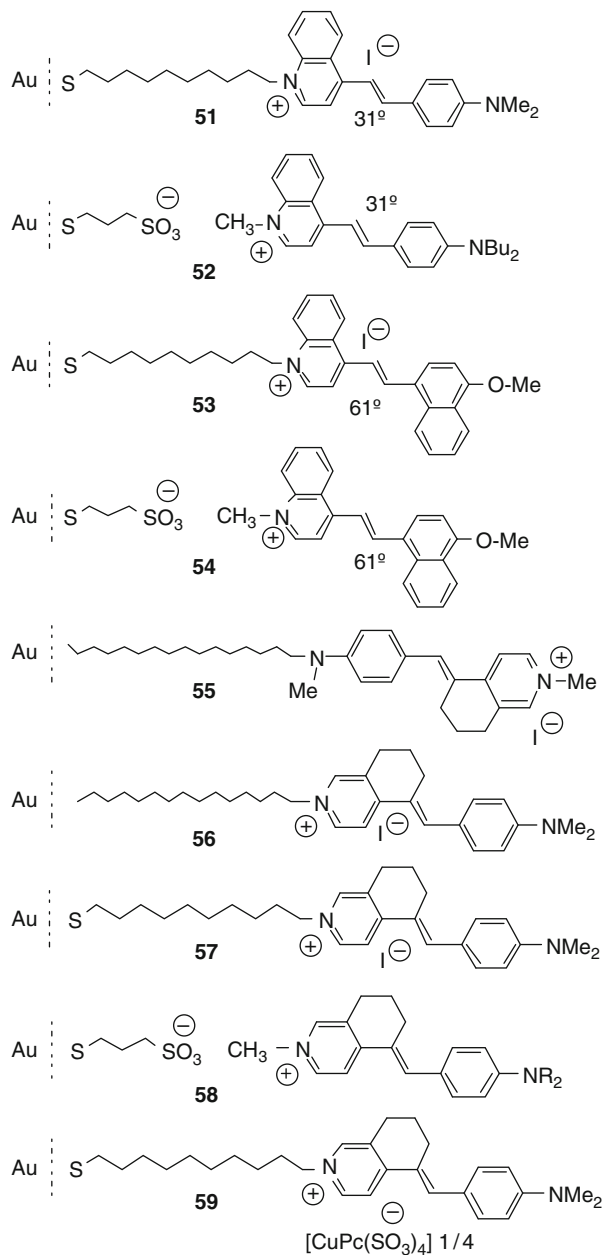


Fig. 24 Some Ashwell rectifiers

Fig. 25 STS curves (normalized I/V plots of LB monolayers of isomers **55** (*crosses*) and **56** (*dots*), deposited on an Au film over HOPG (highly oriented pyrolytic graphite), and scanned with a Pt/Ir nanotip. The films exhibit rectification in opposite quadrants of the plot, where the polarity is defined by the sign of the substrate electrode. Electron flow at forward bias in each case is from the acceptor to the donor [127]

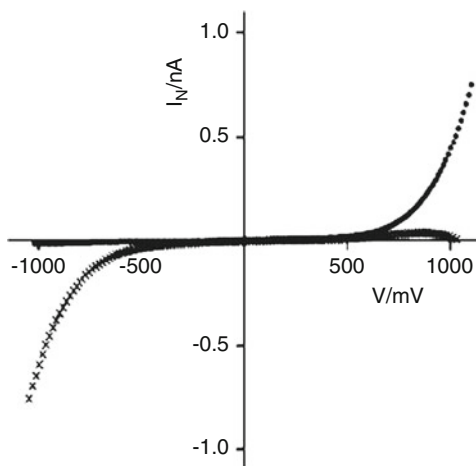
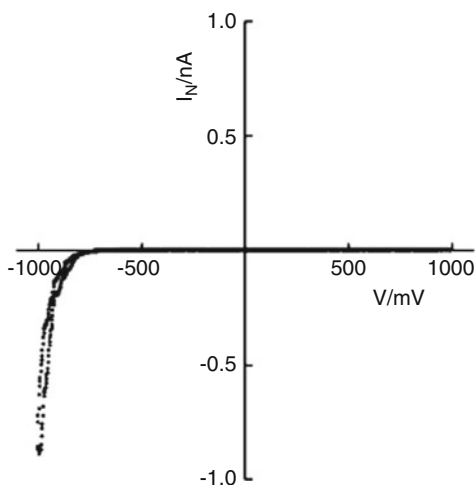


Fig. 26 I/V plot by STS for SAM monolayer of **59** on Au (set-point current of 0.8 nA at 40 mV). The higher current in the third quadrant corresponds to electron flow from the Au-coated substrate to the contacting tip (acceptor to donor) [129]



with **55** vs **56** (Fig. 25): the D- π -A chromophore is oriented in mutually opposite directions [127].

Ashwell's pyridinium and quinolinium D- π -A rectifiers, like **51**, **53**, **55**, **56**, and **57**, have good RRs (Fig. 25), but the RR can be raised by an order of magnitude with a new attachment technique. First, a short thiol ending in a sulfate anion forms a SAM on gold. This creates a lawn of sulfate anions. Then a cationic rectifier forms ionic-bond attachments to the anionic lawn, making a second SAM of the rectifier molecules, as in **52**, **54**, and **58**, which gave an RR of 450 [128]. A surprising further advance comes from using a bulky phthalocyanine counteranion **59** which yielded a remarkable RR of 3,000 (Fig. 26) [129]. It is not known how much ionic motion contributes to rectification in these molecules (or in **39**).

Gayathri and Patnaik found rectification in a C₆₀ dialkoxybenzene dyad by STM, with the RR as high as 158 [130].

13 Capacitors

In macroscopic circuits, a capacitor consists of two conductor plates, close to each other, but not in contact, that respond to a voltage by accumulating, rather than passing, charge. In the nanoscopic world, then, we might think of a nanocapacitor as a way of collecting, and later providing, charge to a circuit. But while a macroscopic plate can tolerate the accumulation of billions of electrons (or holes), a molecular-sized device will be limited to a handful of charges confined in its nano-sized volume.

A quantum limit called the “Coulomb blockade” [131] involves the capacitance (C , typically 1 fF) of a two-dimensional confined region, or quantum dot. If an electron is confined to such a dot, then adding another electron will cost a “charging energy” of e^2/C . If $(e^2/2C) < k_B T$, a Coulomb blockade occurs, and no more charges can be added until a threshold voltage $V_{CB} = k_B T/e$ is reached. This causes a flat region of no current increase in the I/V curve from $V = 0$ to $V = V_{CB}$ (at 300 K, $V_{CB} = 0.026$ volts). When $V > V_{CB}$, the original charge can move off the quantum dot, and a finite current can be observed; the maximum capacitance of the dot has been exceeded. Coulomb blockade behavior has been observed in single molecules such as **60**, where the complexed cobalt ion plays the role of the quantum dot (Fig. 27) [49].

A single electron avoids the problem of forcing multiple charges into close proximity: Shkrob and Schlueter have calculated that the cavity of one conformation of calix[4]cyclohexanol, a cyclic tetramer of 2-methylcyclohexanol, represents a deep electron trap. Essentially, the electron would be “solvated” by four hydroxy groups in a tetrahedral arrangement. Such a molecule could serve as a nanocapacitor for a unit charge [132].

Bocian, Lindsey and co-workers studied sandwich complex nanocapacitors comprised of porphyrin and phthalocyanine ligands separated by lanthanide metals [133]. A triple-decker sandwich of phthalocyanine-Eu-phthalocyanine-Eu-porphyrin, with two phenylethynyl linker wires from the porphyrin, potentially has up to nine accessible oxidation states (-4 to $+4$). SAMs of monomers, dimers, trimers, and oligomers of this sandwich, anchored at one or both ends by thioacetyl groups, gave charge densities up to 10^{-10} mol cm^{-2} , electron-transfer rates up to 10^5 electrons s^{-1} , and charge-dissipation half-lives in the 10–50 s range.

On a larger scale, it is possible to store charge in gold nanoparticles. Chen described 1.8 nm diameter nanoparticles coated with a layer of alkylthiols,

Fig. 27 Quantum-dot molecule **60** involved in Coulomb blockade between electromigrated Au electrodes [49]

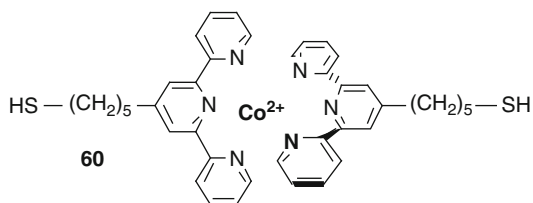
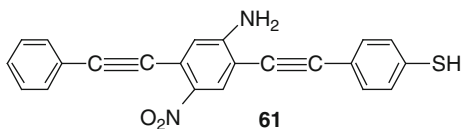


Fig. 28 About 5,000 molecules of **61**, covalently attached to Au, exhibit NDR at 60 K, but not at 300 K [136]



including occasional dithiols that allow the nanoparticles to form a SAM on Au. The dielectric nature of the alkyl coating allows the nanoparticles to exhibit a molecular capacitance of the order of attofarads [134].

Finally, Eklund's group has described double-walled nanotubes (DWNT), with ca. 0.7 nm inner diameter and 1.4 nm outer diameter, that can form a three-layer cylindrical capacitor with a shell of bromine anions forming the outer electrode. Holes segregate on the outer nanotube, and saturation bromine doping creates 1 hole per 26 carbon atoms in the DWNT [135].

14 NDR Devices

A monolayer of about 5,000 molecules of **61** (Fig. 28) in a “nanopore,” attached to Au on one side and topped by a Ti electrode on the other, provided rectification (due to the dissimilar metal electrodes) but also NDR within a definite range of applied bias, i.e., increasing voltage was associated with a decrease in current, so (dI/dV) is negative. NDR was dramatic at 60 K, but vanished at room temperature [136]. NDR is also observed in inorganic two-terminal Esaki tunnel diodes [137], which do have a limited commercial application: signal amplification is possible within such two-terminal devices, because in the output circuit a finite negative resistance R_T from the tunnel diode may be matched in series by an equal but opposite positive load resistance R_L . In the output circuit the equation for power amplification contains the circuit resistance in the denominator: if this resistance $R_T + R_L = 0$, then infinite gain is seen. However, efforts to commercialize the organic NDR effect failed, because the devices proved to be unreliable.

15 Field-Effect Transistors/Gates

Field-effect transistors (FETs) have dominated the semiconductor industry, largely displacing the earlier bipolar junction transistor (BJT) because of its negligible gate current and convenience in the design of integrated circuits. Figure 29 sketches how an FET works.

In Fig. 29 the crucial elements are the p-doped Si layer, which can be replaced by any thin semiconducting layer, and the very thin insulator below the gate electrode. FET behavior was observed for polymeric LB films three decades ago [138], and by

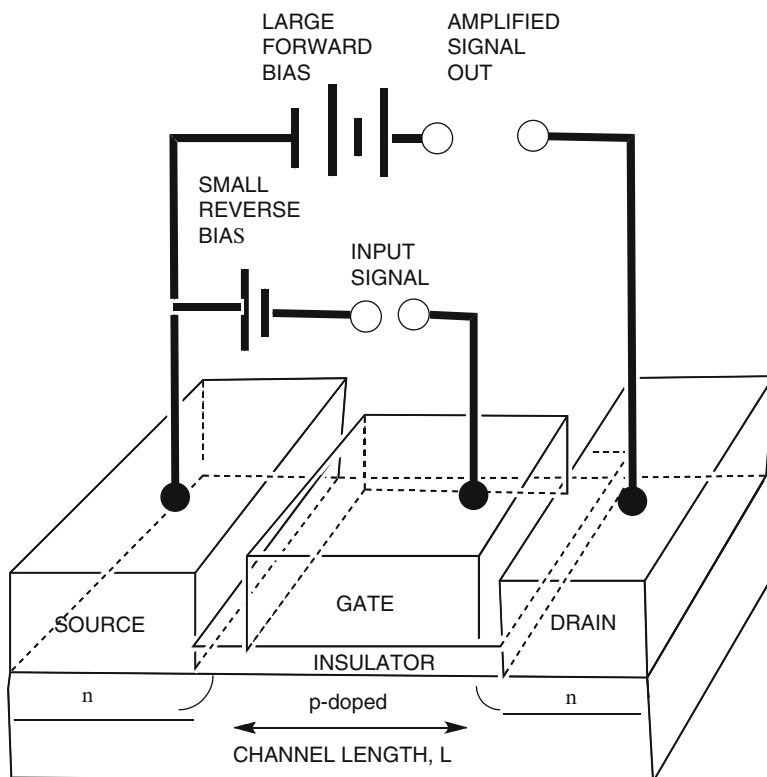


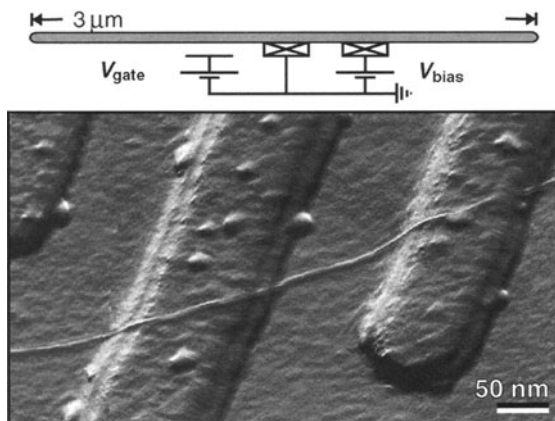
Fig. 29 N-channel complementary oxide FET: a large external forward bias applied between the metallic source and metallic drain electrodes allows electrons to flow from the n-doped region below the source, across the p-doped region, to the n-doped region below the metallic drain electrode. The p-doped region (the “channel,” of length L) is covered by a very thin oxide (10–50 nm thick), which provides electrical insulation from the metallic gate electrode. A back bias voltage applied to the gate electrode controls the thickness of the channel by an electric field effect: this field controls the amount of current that can go from source to drain. A small input signal applied to the gate-to-source leg is then amplified into a large output signal between source and drain, drawing power from the external DC bias

low-temperature STM for a single-walled carbon nanotube curled over parallel Au lines, with the STM acting as a gate electrode (Fig. 30) [139].

Lee and Reed have modified the MCBJ measurements for 1,4-benzenedithiol (2), and have used the Si electrode substrate as a gate electrode to find that the conductivity through the benzenedithiolate bonded to two Au shards showed evidence of FET behavior [140]. However, these results are controversial (van der Zant HSJ, 2010, private communication).

Using an EMBJ between two Au electrodes, the organometallic equivalent of a no-gain single-electron transistor (SET) was realized at 0.1 K with an

Fig. 30 STM micrograph of a single-walled carbon nanotube curled atop Au electrodes [139]



organometallic Co(II) complex using two electromigrated Au electrodes covalently bonded to molecule **60** [49]. Once again, this SET is a Coulomb blockade device with no possibility of power gain: the term SET is, alas, a misnomer.

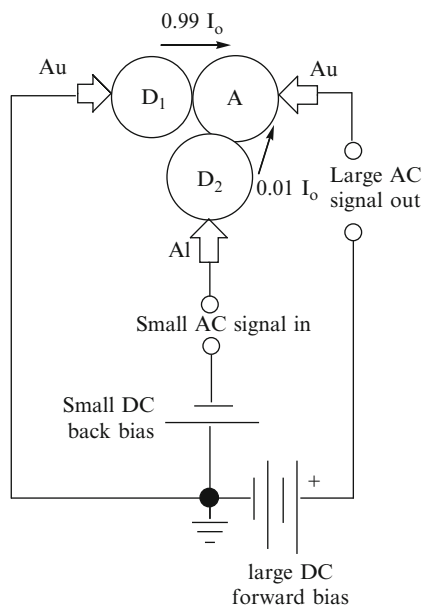
Conductivity differences were seen in a bistable [3]catenane closed-loop molecule, with a naphthalene group as one “station,” and tetrathiafulvalene as the second “station,” “decorated” by a tetracationic catenane salt that could travel on the catenane, like a “train” between two stations, making a nano-switch [141].

16 Future Unimolecular Amplifiers

A three-sided molecule, designed to control the current pathway within it by judicious choice of three moieties with different electron affinities and/or ionization potentials, when covalently bonded to three metal electrodes 3 nm apart, could be the unimolecular equivalent of a BJT.

Many suitable molecules can be designed, with end-groups chosen for SAM formation with dissimilar metal electrodes. For instance, two Au and one Al electrode could be used. The molecule D_1D_2A would have two $-SH$ terminations to bond to Au, and one $-COOH$ end group (on D_2) to bond to Al. The electron path between the two Au electrodes would traverse a donor moiety D_1 with low IP_D and an acceptor moiety A, while the path from the Al electrode to the second Au electrode would traverse a weaker donor moiety D_2 (with larger IP_D) and the common acceptor moiety A. The larger electron current would flow between the two Au electrodes, because the intra-molecular electron mobility would be larger $D_1 \rightarrow A$, while the smaller electron current would flow $D_2 \rightarrow A$. The smaller

Fig. 31 Proposed unimolecular amplifier D_1D_2A , in a circuit analogous to a grounded-emitter junction transistor, grounded-source FET, or grounded-cathode triode circuit. The arrows show the direction of preferred electron flow. The two Au and one Al electrode tips must be about 3 nm apart



current path would be either under zero bias or slightly back-biased, and carry the input signal; the larger current, under forward bias, would carry the amplified output signal (Fig. 31). Whether the Al electrode would function as a gate electrode, affecting conductivity by an electric field, or as a drain electrode, affecting conductivity by an electric potential, is not yet clear. Metal-molecule interface issues would be important, just as in two-electrode resistors or rectifiers. The details of how the electron current from D_1 to A would be significantly larger than the current from D_2 to A must still be worked out.

At present making the first unimolecular amplifier is mainly hampered by the experimental difficulty in placing three electrodes 3 nm apart from each other. As discussed above, MCBJs and EMBJs have yielded reproducible 1–3 nm gaps between two electrodes; the third “gate” electrode can be an STM tip or a CP-AFM tip or an oxide-covered Al electrode.

17 Future Organic Interconnects

Once a sufficient set of resistors, capacitors, rectifiers, and amplifiers have been demonstrated with conventional metal electrodes, one can initiate a new project, of assembling all-organic polymeric electrodes to replace the inorganic metals. This would lead to the all-organic computer! The controlled electrochemical growth of conducting oligomer filaments has already been demonstrated [142]. Alas, single-

walled carbon nanotubes are not yet fully chemically processable. For that we may need defect-free, differently end-derivatized SWCNT, e.g., A_n -SWCNT- B_m , with n polar or formally charged groups A and m polar or oppositely charged groups B , such that the nanotubes can be chemically separated by chromatography by charge, dipole moment, and conductivity: if this can be achieved, then the A_n -SWCNT- B_m would become ideal connectors in UE.

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