Four Examples of Unimolecular Electrical Rectifiers

by Robert M. Metzger

Molecular electronics or unimolecular electronics (UE), defined narrowly, is the study of electrical phenomena on a molecular scale,[1,2] while molecule-based electronics, defined more widely, studies the electronic properties of molecules in crystals and polymers.[1] UE aims to produce molecular electronic devices (wires, resistors, capacitors, rectifiers, amplifiers, etc.) at the 1-2 nm scale, hopefully in time to meet the needs of integrated circuits, whose inexorable march to smaller and faster devices[3] may encounter fundamental difficulties at small design lengths (<15 nm) for inorganic components. UE was launched 30 years ago by a proposal for unimolecular rectifiers.[4] UE has seen much recent progress.[5] Some bumps in the road to UE may have been encountered.[6] This article reviews our progress in electrical rectifiers, achieved either in single molecules, or in monolayers of molecules studied in parallel.

UE was advanced by measuring the electrical conductivity of single molecules, of Langmuir-Blodgett (LB) monolayers of molecules,[7,8] or of self-assembled monolayers (SAMs).[9] A single molecule can be touched by a scanning tunneling microscopy (STM) tip, by a conducting-tip atomic force microscopy (AFM) tip, or between two Au tips, or else a monolayer of molecules may be measured in parallel by making electrical contacts to sandwiches of organic monolayers placed between inorganic metal pads (1 μm^2 to 1 cm^2). The metal | organic | metal sandwiches must be prepared and measured without destroying the organic layer.

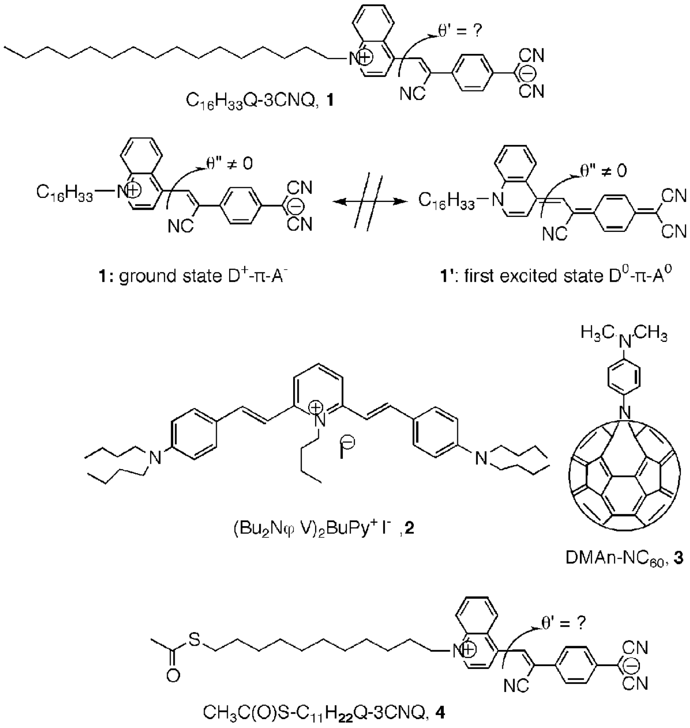

*Fig. 1. The first confirmed molecular rectifier, $C_{16}H_{33}$Q-3CNQ, **1**.[14-18] An important non-zero twist angle θ´ must exist in **1** (for which no crystal structure is available): its first excited state is **1´**. Three more unimolecular rectifiers: **2**,[21] **3**,[22] and **4**, a thioacetyl-terminated version of 1.[23]*

S, A, and U rectifiers and two competing assembly techniques (LB, self-assembly)

There are three distinct processes, S, A, and U, for asymmetrical electrical conduction, *i.e.*, rectification in metal | organic | metal sandwiches,[2,10] Schottky, or S rectifiers have Schottky barriers[11] at the metal | organic interfaces.[10] A rectifiers have the chromophore (*i.e.*, the part of the molecule whose molecular orbital must be accessed during conduction) asymmetrically placed between the metal electrodes, *e.g.*, because of a long alkyl tail.[10] U, or unimolecular rectifiers,[4] have asymmetric IV curves, because the current involves electron transfers between the metals and molecular orbitals, whose significant probability amplitudes are asymmetrically placed within the chromophore.[10] An ordered monolayer of organic molecules between two inorganic metal electrodes may show some combination of these three effects.[10]

The rectification ratio (*RR*) is the ratio of the current *I* at some positive bias *V*, divided by the absolute value of the current at the corresponding negative bias –*V*

$$RR(V) = I(V)\ /\ |\ I(-V)\ | \qquad [1]$$

Molecules can be placed on a metal electrode by physisorption or by chemisorption. Physisorption includes the random deposition from a vapor onto a solid, and also the transfer of an ordered monolayer (Pockels-Langmuir monolayer) from the air-water interface to a solid substrate, forming an LB monolayer or, if the transfer is repeated, an LB multilayer. For LB multilayers, the percent coverage of the surface at transfer is measured directly (good), but an LB film may slowly reorient toward a thermodynamic equilibrium, and adventitious adsorbates are covered by the physisorbed LB film (bad). Chemisorption includes the formation of a covalent bond of thiols or other chalcogenides to gold and similar metals, or of chlorosilanes to hydroxyl-covered silicon surfaces: these are SAMs. In chemisorption, the reaction displaces from the surface any previous adsorbates, and forms a permanent bond of molecule to the surface (good), but full coverage of the surface is not guaranteed, further chemical reactions may

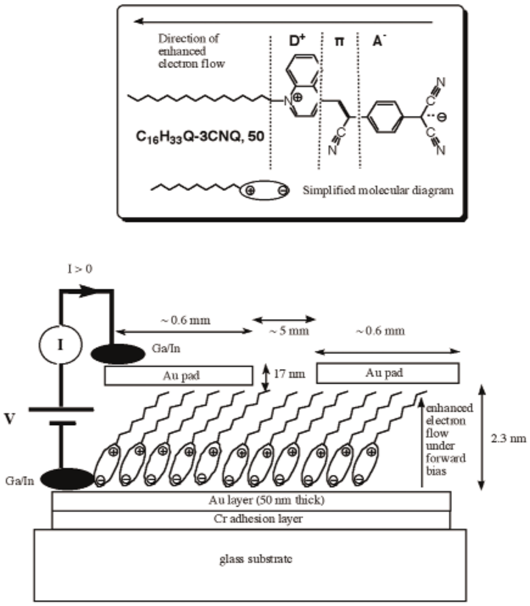

*FIG. 2. Molecular structure and geometry of LB monolayer of $C_{16}H_{33}$Q-3CNQ, **1** sandwiched between Au electrodes, with an arrow showing the direction of enhanced electron flow under positive, or forward bias. The substrate was glass, 50 × 50 × 0.4 mm, covered either by a Cr adhesion layer, or by a hydrophobic xylene covering, followed by an evaporated Au film, 50 mm × 50 mm × 50 nm, then the LB monolayer or multilayer, then by 48 cylindrical Au pads, 17 nm thick and with an area of 0.283 mm^2 each.*[18]

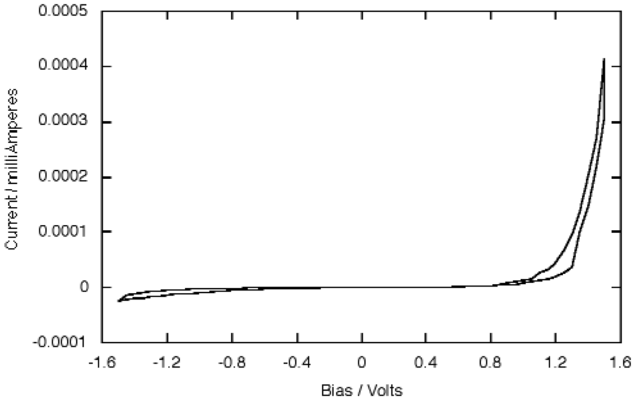

*FIG. 3. Plot of the dc current I vs. the dc applied voltage V (I-V plot) through a single monolayer of $C_{16}H_{33}$Q-3CNQ, **1** sandwiched between Al electrodes (top Al pad area 4.5 mm^2, thickness 100 nm), using Ga/In eutectic and Au wires. The dc voltage is swept at a rate of 10 mV s^{-1}.*[14]

occur, and surface dipoles are formed during chemisorption (bad). The work on rectifiers described below has been performed largely with LB films, but a fusion of both techniques is under development.

Hexadecylquinolinium tricyanoquinodimethanide, $C_{16}H_{33}$Q-3CNQ, 1

Ashwell *et al.* found that Mg vapor and thin Mg films would damage the LB films least, and studied molecular rectification by γ-hexadecylquinolinium tricyanoquinodimethanide, $C_{16}H_{33}$Q-3CNQ, 1 (Fig. 1).[12] Molecule **1** is one of the zwitterionic molecules synthesized by Ashwell *et al.* for nonlinear optics. The rectification measured for LB monolayers and multilayers of **1** sandwiched between a Pt electrode on one side and a Mg electrode on the other (with an overcoat of Ag)[12] was confirmed, when insulating LB layers of tricosenoic acid, added between the electroactive layers of **1** and the electrodes, did not destroy the rectification.[13]

We definitively confirmed unimolecular rectification by studying **1**, using the same metallic electrode on both sides on an LB monolayer or multilayer (at first Al,[14-16] and then Au[17-18]) by concentrating on metal | LB monolayer | metal sandwiches, and by a thorough chemical and spectroscopic characterization.[19,20] The synthesis of **1** was improved.[14] The molecular ground-state static electric dipole moment is 43 ± 8 debye.[14] The absorption spectrum in solution shows a narrow, strongly hypsochromic band, peaked between 600 and 900 nm: this is an intervalence transfer (IVT), or intramolecular charge-transfer band:[14] it fluoresces in the near IR.[14] The excited-state dipole moment is 3-9 debye.[19] The molecule is zwitterionic in the ground state (D^{+}-π-A^{-}), and less dissociated (D^{0}-π-A^{0}) in the first excited state (**1**´). The twist angle θ´ in structure **1** must be non-zero for steric reasons. The vis-UV spectrum of LB multilayers of **1** on quartz exhibits an intense IVT peak at 570 nm.[14] Molecule **1** forms a Pockels-Langmuir monolayer at the air-water interface,[14] and transfers on the upstroke only, with transfer ratios around 100% (Z-type transfer), onto hydrophilic glass, quartz, or aluminum[14] or fresh hydrophilic Au.[15,16] The LB monolayer thickness of **1** is 2.3 nm.[14,19] For a calculated molecular length of 3.3 nm (with an all-trans geometry for the $C_{16}H_{33}$ tail), the tilt angle of the molecule to the surface is 46° from the surface normal.[14,19] The X-ray photoelectron spectroscopy (XPS) spectrum of one monolayer of **1** on Au shows two N (1s) peaks, one at 401.7 eV (attributable to the quinolinium N), and one at 399.4 eV (attributable to the three CN groups).[19]

LB monolayers and multilayers of **1** were sandwiched between macroscopic Al electrodes,[14] and between Au electrodes.[17,18] First, a bottom electrode (either Al,[14] or an adhesion layer of Cr followed by Au[17,18]) is evaporated onto a glass, quartz, or Si substrate; second, the LB monolayer or multilayer of **1** is transferred above it; third, the sample is dried for 2 days; fourth, the second electrode is deposited through a shadow mask[14] or a contact mask,[17,18] to make 30-48 pads per substrate (area of 0.283 mm^2 each[18]). During the evaporation of the top electrode, a copper plate holding the sample is cooled by a liquid nitrogen bath; this suffices for Al[14] but not for Au top electrodes. For Au deposition, one adds 10^{-3} Torr of Ar gas to the evaporation chamber, and protects the substrate from direct thermal radiance from the heated Au source.[18] This cold gold deposition forces the Au atoms to undergo multiple scattering by Ar atoms before they reach the substrate.[17,18] Fifth, a metal wire (Au or Cu) bearing a droplet of either Ag paste or Ga/In eutectic, is gently put above the bottom electrode and sequentially also on one of the pads of the top electrode, and electrical measurements are made. The final metal-LB film-metal geometry is shown in Fig. 2 for Au electrodes.[17,18] The Al layers and the Ga/In eutectic drop are covered by oxide, while Au is oxide-free.

When a monolayer of **1** is placed between Al electrodes (with their inevitable patchy and defect-ridden covering of oxide), then a dramatically asymmetric current is seen (Fig. 3): *RR* = 26 at 1.5 V[14] Assuming a molecular area of 50 Å^2, the total current at 1.5 V corresponds to 0.33 electrons molecule^{-1} s^{-1}.[14] This same asymmetry is seen also for multilayers of **1**, for a sample covered by Mg pads topped by Al pads,[14] for monolayers and multilayers of **1** on graphite studied by STM,[14] and even for a solution of **1** in dimethyl sulfoxide placed in the STM cell.[14] *RR* varies somewhat from pad to pad, as does the total current, in part because these are all two-probe measurements, with all electrical resistances (Al, Ga/In, or Ag paste, wires, etc.) in series. A thorough review of all data suggested that any molecule which exhibits $RR(V) < 2$ at maximum bias V is not a rectifier;[15] some samples of **1** studied between Al electrodes have enhanced currents, albeit smaller, under negative bias instead of positive bias.[15] As high potentials are scanned repeatedly, the current-voltage (*IV*) curves show progressively less asymmetry; the *RR* decreases gradually with measurement, *i.e.*, with repeated cycling of the bias across the monolayer. Putting 1.5 V across a monolayer of thickness 2.3 nm creates a very large electrical field of 0.65 GV m^{-1}; under such fields, zwitterionic molecules in the monolayer may turn end-over-end. The more liquid-like the monolayer, the easier this process would be. No temperature dependence ($105\ K < T < 390\ K$) of the rectification onset of **1** between Al electrodes was found.[16]

With Au electrodes the current through the pads increased dramatically, as expected (for Au, all surface atoms are oxide-free; for Al, only the defect sites with no oxide covering conduct readily) but the asymmetry persisted: the same asymmetric conduction through the molecules could be measured using Au or Al electrodes.[17,18]

The best rectification ratio at 2.2 V for Au electrodes was *RR* = 27.53; the highest current was 9.04 × 104 electrons $\text{molecule}^{-1}\ s^{-1}$. Figure 4 shows how *RR* decreases from cycle 1 to cycle 6. The rectification by a one-molecule-thick layer of **1** is an established fact.

One plausible mechanism for rectification by **1** is a minor change in the Aviram-Ratner proposal[4]

$$M_1 + D^+\text{-}\pi\text{-}A^- + M_2 \rightarrow M_1 + D^0\text{-}\pi\text{-}A^0 + M_2 \qquad [2]$$

$$M_1 + D^0\text{-}\pi\text{-}A^0 + M_2 \rightarrow M_1^- + D^+\text{-}\pi\text{-}A^- + M_2^+ \qquad [3]$$

where the first step is the electric field-driven excitation from ground to excited state, followed by electron transfers across the two molecule | metal interfaces.[14]

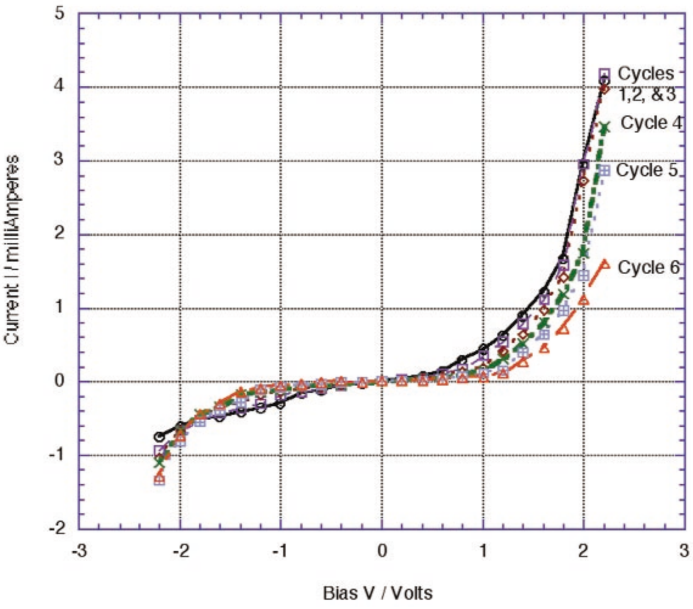

FIG. 4. I-V plot for a cell Au|monolayer of $C_{16}H_{33}$*Q-3CNQ,* **1***|Au, showing the decrease in rectification ratio. At 2.2 V in the first cycle,* $R = 538\ \Omega$*,* $I = 4.09$ *mA =* 4.5×10^4 *electrons* $\text{molecule}^{-1}\ s^{-1}$*, and RR = 5.39. Cycle 1: circles ○; cycle 2: squares □; cycle 3: diamonds ◇; cycle 4: x's X; cycle 5: squares with crosses ⊕; cycle 6: triangles Δ.*[18]

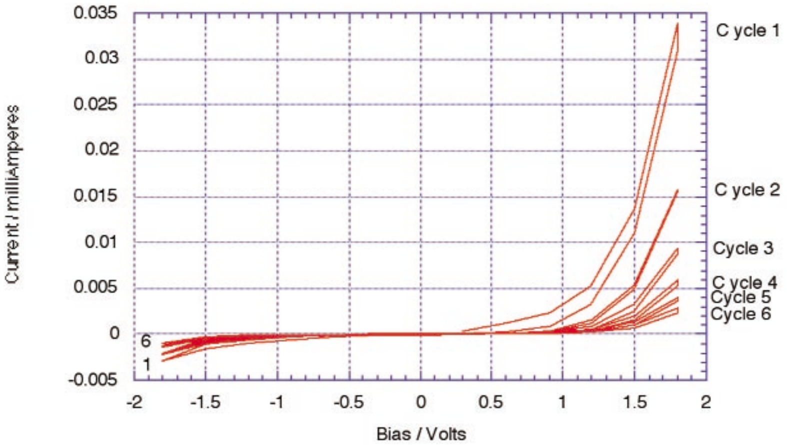

FIG. 5. I-V plots for $(Bu_2N\varphi V)_2BuPy^+I^-$*,* **2** *measured in a Au | LB monolayer of* **2***|Au cell, for six successive cycles of measurement. The rectification ratios are RR = 12, 7, 5, 4, 3, 3, for cycles 1 through 6, respectively.*[21]

2,6-di[dibutylamino phenylvinyl]-1-butylpyridinium iodide, $(Bu_2N\varphi V)_2BuPy^+I^-$, 2

Recently, two more molecules were studied, **2** [21] and dimethylanilinoaza[C_{60}]fullerene, DMAn-NC_{60}, **3** [22]: both are unimolecular rectifiers.

$(Bu_2N\varphi V)_2BuPy^+I^-$, **2** forms a Pockels-Langmuir film at the air-water interface, and transfers to hydrophilic substrates as a Z-type multilayer. The monolayer thickness was estimated as 0.7 nm by spectroscopic ellipsometry, 1.3 nm by X-ray diffraction, and 1.15 nm by surface plasmon resonance (at $\lambda = 532$ nm) or 1.18 nm (at $\lambda = 632.8$ nm).[21] The films exhibit an absorption maximum at 490 nm (which is slightly hypsochromic in solution), attributable to iodide-to-pyridinium back-charge-transfer.[21] The rectification is shown in Fig. 5: here also, there is a decrease of rectification in successive cycles. Some cells have initial rectification ratios as high as 60. The direction of enhanced electron flow is from the bottom Au electrode toward the top Au pad (as in Fig. 2). Therefore, the favored direction of electron flow is from the gegenion to the pyridinium ion, *i.e.*, in the direction

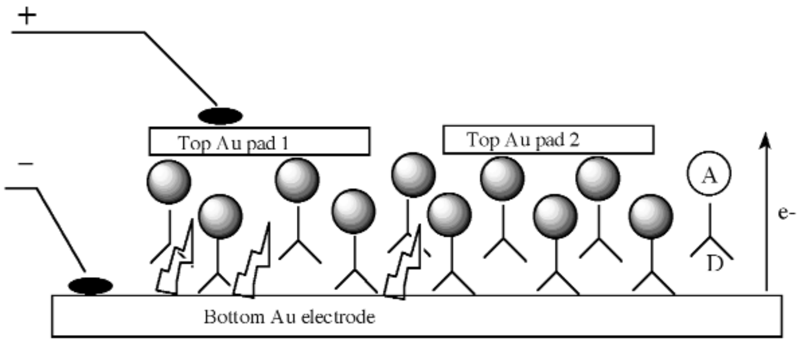

*Fig. 6. Schematic of LB monolayer of DMAn-NC$_{60}$, **3** on Au, including top Au pads and Au stalagmites. The direction of preferred electron flow under forward bias is also shown, as an arrow, from the bottom Au electrode to top Au electrode pads.*[22]

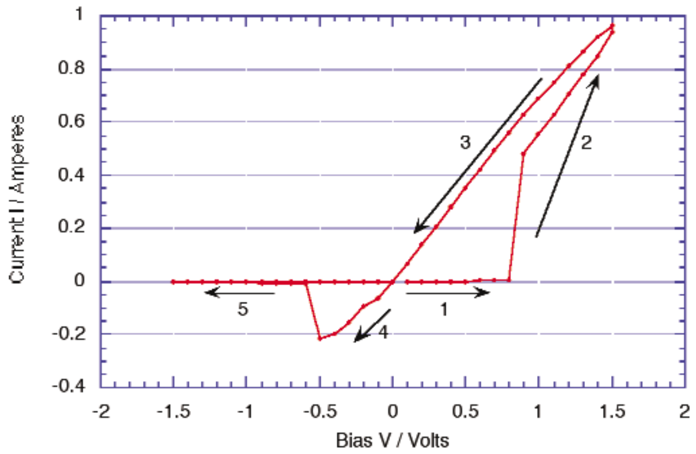

*Fig. 7. I-V plots for DMAn-NC$_{60}$, **3** measured in a Au | LB monolayer of **3** | Au cell, with numbers indicating the measuring sequence.*[22]

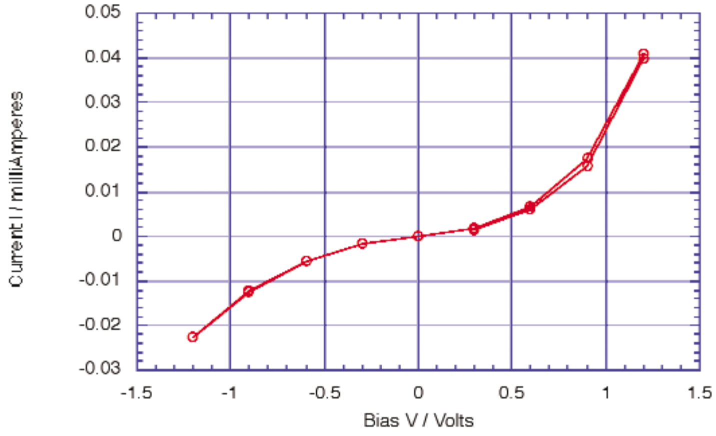

*Fig. 8. I-V plots for DMAn-NC$_{60}$, **3** measured in a Au | LB monolayer of **3** | Au cell, in which the current stays small: this should be the current due to **3** and not to the Au filaments.*[22]

of back-charge-transfer, and the rectification in $(Bu_2N\varphi V)_2BuPy^+I^-$, **2** can be attributed to an interionic electron transfer, rather than to an intramolecular electron transfer, although a transfer from the two amines to the pyridinium ion could not be excluded.[21]

Dimethylanilino-aza[C$_{60}$]fullerene, DMAn-NC$_{60}$, 3

The azafullerene DMAn-NC$_{60}$, **3** consists of a weak electron donor (dimethylaniline) bonded to a moderate electron acceptor (N-capped C$_{60}$). It has an IVT peak at 720 nm.[22] The Pockels-Langmuir film is very rigid, *i.e.*, the slope of the pressure-area isotherm is large. However, the molecular areas are only 70 Å^2 at extrapolated zero pressure, and 50 Å^2 at the LB film transfer pressure of 22 mN m^{-1},[22] whereas the true molecular area of C$_{60}$ is close to 100 Å^2. Therefore, molecules **3** transferred onto Au on the upstroke, may be somewhat staggered, as shown in Fig. 6, with the more hydrophilic dimethylamino group closer to the bottom Au electrode. The film thickness is 2.2 nm.[22] The monolayer is covered with 17 nm thick Au pads, deposited by the cold gold technique. The dimethylamino groups in the LB film are probably not as close-packed as the azafullerenes. Angle-resolved N (1s) XPS spectra show that the N atoms are closer to the bottom Au electrode, than is the C$_{60}$ cage.[22]

The I-V plot shown in Fig. 7 is an unwelcome surprise.[22] The cell now supports 1 A of current across it! (per molecule, that would be an absurdly large 5×10^{11} electrons molecule^{-1} s^{-1}). Moreover, the high current between 1.5 and –0.5 V in the return path (3 and 4 in Fig. 7) is Ohmic. This asymmetry decreases upon cycling.[22] Probably, metallic Au filaments formed within the monolayer, without piercing the fullerene ends of the monolayer, and are progressively destroyed by cycling the voltage. These Au stalagmites are shown in Fig. 6 as jagged arrows or thunderbolts. Some other cells show smaller currents, which are marginally rectifying in the forward direction, with $RR \approx 2$ (Fig. 8).[22]

Thioacetyl-undecylquinolinium tricyanoquinodimethanide, 4

A modification of **1**, equipped with a thiocetyl ending, to enable it to bond covalently to Au, yet be assemblable as Langmuir film at the air–water interface, was synthesized molecule **4**. The plan was to bond it to Au by combined LB and self-assembly techniques, to prevent the rotation of the molecule during measurement, and thus eliminate the decay of the rectification signal.[23] The results were disappointing: the pressure-area isotherm was not sufficiently vertical at the transfer pressure, and disordered LB monolayers of **4** ensued. By STM of a monolayer of **4** on Au, asymmetric currents of either polarity were seen, as the molecule adhered to Au either by thiolate bonds, created in **4** by losing the acetyl group (as acetate), or by the dicyanomethylene ending of **4**.[23] Sandwiches Au | monolayer of **4** | Au were only moderately rectifying.[23] A version of **4** with a longer alkyl chain is under study.

Conclusion

Our work on unimolecular rectification may suggest many new ideas for molecular devices to power the ultimate computers of the future. ■

Acknowledgments

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About the Author

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