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Covalently Bonded Organic Monolayers on a Carbon Substrate: A New Paradigm for Molecular Electronics

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ABSTRACT

We report herein the fabrication of a molecular junction in which a thin (8–15 Å) layer of oriented organic molecules is positioned between two electronic conductors. The molecular layer becomes a component in an electronic circuit and exhibits properties that depend strongly on molecular structure. Bonding between the carbon substrate and the molecular layer is covalent and conjugated, and thus differs fundamentally from that of the widely studied self-assembled monolayers of alkane thiols on metal surfaces. The chemisorbed molecular layer is densely packed and stable and does not contain the tunneling barrier imposed by a sulfur atom. The current/voltage behavior of methyl-phenyl, *n*-butyl phenyl, *tert*-butyl phenyl, and stilbene monolayers between pyrolytic carbon and mercury indicates a negligible pinhole density and shows weak dependence on temperature. The action of a nitroazobenzene molecular junction as a bistable switch is demonstrated, and switching behavior persisted for many on–off cycles and over a period of at least 14 h. Carbon-based molecular junctions represent a new paradigm for molecular electronics, which shows promising electronic behavior and is amenable to low cost, benchtop processing.

1. Introduction. The rapid development of the area of “molecular electronics” has been stimulated by the attraction of incorporating a molecule into an electronic circuit.[1−5] One motivation for these developments is the potentially high information density available when circuit features are decreased to the size of one or a few molecules. Another motivation has been the wide range of transfer functions conceivable with molecules as compared to traditional semiconductors.

Electronic properties of molecules may vary over a wide range from insulators to conductors, and molecules may in principle function as memory devices, chemical sensors, photosensors, etc. Major hurdles in the development of molecular electronics include the practical problems of positioning single molecules or single layers of molecules in a microcircuit, and in making electrical contact between traditional circuit components such as gold, aluminum, silicon, etc., and the molecule of interest. The most common approach to address these hurdles involves the gold/thiol system, in which a self-assembled monolayer (SAM) is formed spontaneously on a gold surface immersed in a solution of an organic thiol.[6−9] Au/thiol chemistry has been exploited to form molecular junctions between gold clusters, gold break junctions, and vapor deposited metals. An alternative approach involves Langmuir−Blodgett films positioned between metal and metal oxide contacts.[10,11]

Metal/thiol and Langmuir−Blodgett structures have demonstrated very interesting properties about molecules as components in electronic circuits, including Coulomb staircases,[12−14] Schottky barriers,[8,15] rectification,[9,16] charge storage,[17] and staircase current/voltage curves.[18] However, the sulfur atom in the Au/thiol junction creates a rather large tunneling barrier (∼2 eV) and pinholes in SAMs generally restrict the molecular junction to very small areas (30 × 50 nm). Recent innovations with the Au/thiol SAM paradigm involve larger areas with Hg or Ag contacts, but so far have been limited to alkane thiols.[6,7]

2. Experimental Approach. Modified carbon surfaces prepared with diazonium chemistry, which features a strong, conjugated C−C bond and a low density of defects and pinholes,[19−22] provide an alternative to these approaches. Not only is such a linkage very stable, it also provides a conjugated molecular orbital between the substrate and molecular monolayer.

The molecular junction shown in Figure 1 was made by reduction of 1.0 mM stilbene diazonium salt in acetonitrile (containing 0.1 M tetrabutylammonium tetrafluoborate) on pyrolyzed photoresist film (PPF).[22−24] As shown elsewhere, the PPF film may be patterned lithographically and is flat on a molecular scale, with root-mean-square (rms) roughness of less than 0.5 nm.[24] PPF is a disordered, graphitic material similar to glassy carbon,[25] and the phenyl rings inside the PPF in Figure 1 are shown to indicate the existence of a conjugated C−C bond between the monolayer and the PPF substrate.[19]

A molecular junction was prepared by lowering a 1 mm diameter mercury drop suspended from a wire lead onto the top of the stilbene monolayer. The drop was pressed onto

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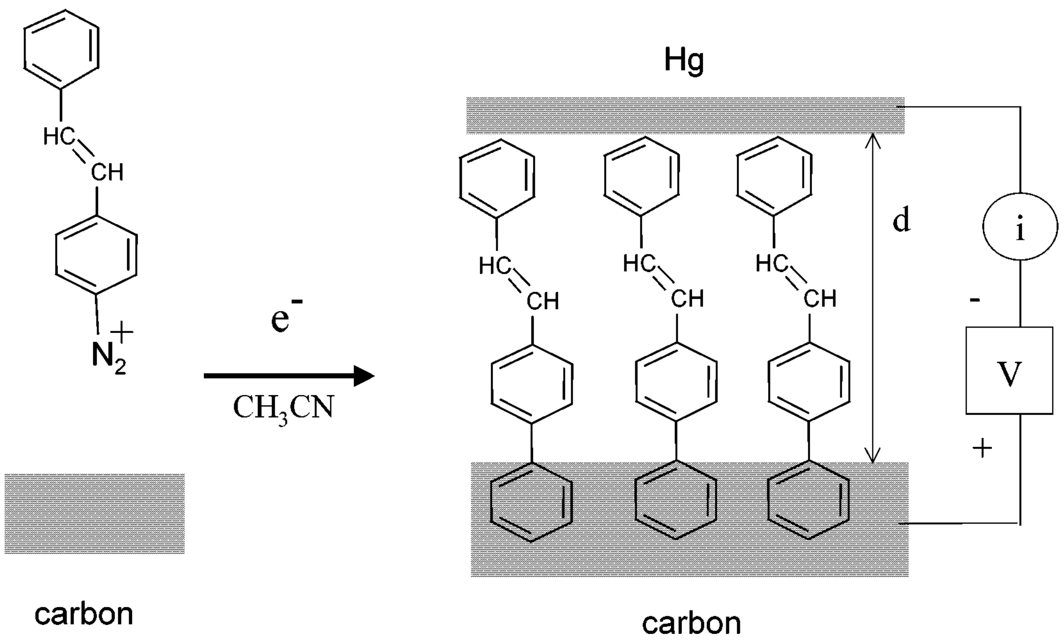

Figure 1. Schematic structure of a Hg/stilbene/PPF molecular junction, with the shaded phenyl rings representing a portion of the disordered graphitic framework. The distance "d" indicates the thickness of the monolayer from the PPF surface to the van der Waal radius of the terminal hydrogen atom. A positive voltage in *I*/*V* curves corresponds to PPF positive relative to Hg. Monolayer is bonded to carbon by electrochemical reduction of a diazonium salt in acetonitrile, as shown.

the monolayer for a vertical distance of 300 μm after initial contact, and the resulting contact area was approximately 0.8 mm^2 (determined with an optical magnifier). Although monolayers prepared by diazonium reduction have been shown to have very low pinhole density,[23,26] the high surface tension of Hg should reduce the possibility of short circuits if any pinholes are present. The observed resistance drifted upward for several hours after contact, but stabilized within 3 h if heated to 50 °C. With the exception of the nitroazobenzene (NAB) film, all molecular junctions reported herein were pretreated with such an "annealing" period.

3. Results. The current/voltage behavior of the Hg/stilbene/PPF molecular junction is shown in Figure 2 for several temperatures, with an inset showing a magnified view of the region near the origin. Positive potentials correspond to a positive bias on the PPF relative to the Hg. For small voltage excursions (±50 mV), the *I*/*V* (current/voltage) characteristic is linear, with an observed resistance of 511 ± 370 Ω. The observed resistance values summarized in Table 1 are averages of several samples and junctions on each sample, and no data points were rejected. For example, 12 stilbene junctions on 3 samples yielded the following resistance values for voltage excursions of less than 50 mV (all in ohms): 830, 76, 873, 528, 711, 87, 131, 174, 971, 564, 1024, 163. The *I*/*V* response becomes nonlinear for voltage excursions greater than ±50 mV. Weak rectification was observed for all four molecules examined, with the current at +500 mV about four times that at −500 mV. The current at 500 mV increases with temperature by a factor of 1.9 between 20 °C and 70 °C for stilbene, and similar factors were observed at other potentials. A plot of ln (*i*) at +500 mV vs 1/*T* was linear over the limited temperature range examined, with a slope corresponding to an activation barrier of 0.11 eV.

The *I*/*V* curves were strongly dependent on the structure of the monolayer, as shown in Figure 3 and detailed in Table 1. Several important observations about Figure 3 and Table 1 deserve special note. First, the junctions are very thin (7.6−13.4 Å based on the calculated lengths of spacer molecules) and there is apparently little contribution to the current from pinholes. Second, the strong thickness dependence for the three alkyl phenyl monolayers implies that tunneling is a major electron transfer mechanism. This conclusion is supported by the weak temperature dependence observed for stilbene. Third, the junction can support fairly high current densities (2 A/cm^2 for the Me-phenyl case) at low applied potential (~0.2 V). Larger current densities are possible, but 2 A/cm^2 corresponds to ~10^5 e^-/s/molecule. Fourth, conjugation greatly increases junction conductivity, with stilbene having more than 50 times the conductance of *n*-butyl phenyl, even though stilbene is a longer molecule. Finally, the junctions are stable for at least several days, including numerous voltage excursions and temperature excursions between −20 °C and +70 °C. In a few instances, an Hg/*n*-C_4H_9 phenyl/PPF junction was cycled between ±0.5 V at 1 kHz overnight, with little change in the observed *I*/*V* curve.

Figure 4 shows the action of a molecular junction as an active electronic device, in this case a ~47 Å thick multilayer of nitroazobenzene (NAB) in series with a 110 KΩ resistor. The NAB layer was formed electrochemically from the corresponding NAB diazonium salt,[20] as shown in Figure 1, and the NAB is covalently bonded to the carbon substrate. NAB is prone to multilayer formation, and the layer thickness was estimated by its effect on electron transfer to a redox system.[22] The initial junction resistance is high (~20 MΩ) and remains so for small positive or negative potentials. As the potential is scanned to −1.5 V, a dramatic decrease in film resistance occurs, from ~10 MΩ to <10 KΩ (after

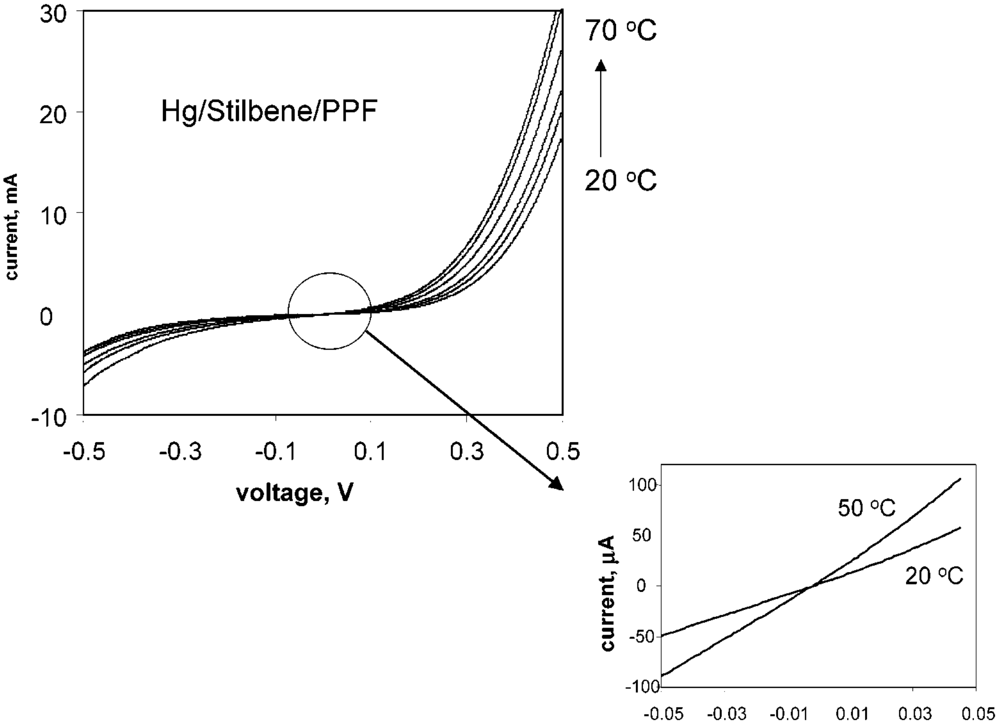

Figure 2. Current/voltage curves (scanned at 0.1 V/s) for the stilbene junction shown in Figure 1. Geometric contact area is approximately 0.8 mm^2, and I/V curves were obtained at 20, 30, 40, 50, 60, and 70 °C. Inset shows magnified view of the region near the origin.

Table 1: Observed Resistance for Hg−Monolayer−PPF Junctions

monolayer	calculated thickness, Å[a]	observed junction resistance, Ω[b]
CH_3-phenyl	7.6	53 ± 11 ($N = 10$)
tert-butyl phenyl	8.8	210 ± 160 ($N = 6$)
n-butyl phenyl	11.2	31 K ± 21 K ($N = 14$)
stilbene	13.4	511 ± 360 ($N = 12$)

[a] Calculated with "Spartan" software; includes 1.2 Å for van der Waal radius of hydrogen. [b] Mean ± standard deviation for N junctions on 2−4 samples, for ±50 mV potential range.

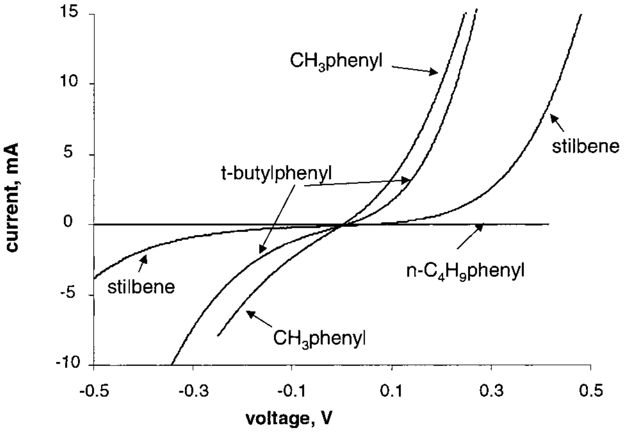

Figure 3. I/V curves for four molecular junctions with different structures. Contact area ~0.8 mm^2, scan rate 0.1 V/s, 20 °C. All junctions were annealed at 50 °C for at least 30 min.

correction for the 110 K resistor, which was included to avoid overcurrent damage). This low resistance state persists for hours, unless the potential is swept positive to > +2 V. As shown in Figure 4, positive potentials switch the junction back to its high resistance state. The NAB layer is acting as a bistable switch, which switches "on" for V < −1.5 V and "off" for V > +2 V. This switching behavior was repeated many times over a period of at least 14 h, but was "frozen out" at low temperature (< −60 °C). The action of the NAB layer as a bistable switch is apparently caused by a conformational change or redox process resulting from injection of electrons into the molecular film. Conductance switching by a redox process has been reported for a nitroaniline containing monolayer on Au[9] and by conformational changes in a phenyl ethynyl monolayer using STM.[27]

As a platform for investigating and fabricating molecular electronic junctions, the carbon-based approach introduced here has several potentially important features. First, the C−C bond between monolayer and substrate is strong and stable, and the junctions appear to be quite stable over time and temperature excursions. Second, the junctions function over a wide temperature range, at least −60 °C to +70 °C. Third, the C−C bond is nonpolar and conjugated, which should reduce the barrier toward electron transfer from the carbon substrate into the monolayer. Fourth, the irreversible deposition of monolayer molecules from diazonium precursors yields a low pinhole density, since pinholes would induce "patching" during film formation by electroreduction of diazonium reagent. Fifth, the PPF substrate may be patterned by conventional photolithography using commercially available materials to result in potentially complex circuits combining different types of molecular junctions. Sixth, the entire process of substrate preparation, monolayer deposition, and junction formation involves benchtop chemistry, with only the pyrolysis requiring prolonged heating (~8 h). After

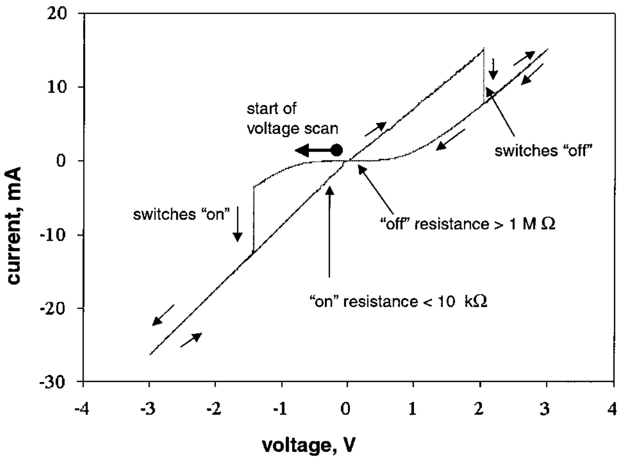

Figure 4. *I*/*V* curve for a nitroazobenzene junction (~47 Å thick), contact area ~0.8 mm^2. Arrows indicate scan direction. A 110 KΩ resistor was in series with the junction to prevent overcurrent damage.

pyrolysis, subsequent chemical steps are performed at room temperature. Seventh, unlike conventional semiconductors, the substrate, monolayer, and top contact are noncrystalline and apparently tolerant of defects. The ~10^{11} parallel molecules of the present ~0.8 mm^2 junction reduces to ~10^6 molecules in a 1 μm^2 junction, which might occur in a lithographically fabricated microcircuit. Finally, the range of possible monolayer structures is extensive, since only an aromatic amine is required to provide a route to the diazonium reagent. These advantages are tempered somewhat by the toxicity and poor mechanical stability of mercury, but preliminary experimental results with a silver top contact indicate that it will be possible to eliminate Hg from the junction. In addition, the rather poorly defined electronic properties of PPF make theoretical modeling of carbon-based junctions more difficult than that for metals.

Although their characteristics are only beginning to be defined, the carbon-based molecular junctions described herein show significant promise as a versatile, robust platform for investigating electronic properties of molecules as circuit components. Current efforts toward determining junction electron transfer mechanisms include examining conductivity over a wide temperature range, systematic variation of molecular length and structure, and examining alternatives to mercury for the top contact. We expect the behavior of carbon-based molecular junctions to differ significantly from those based on Au/Thiol or Langmuir−Blodgett monolayers due to the conjugation between the carbon substrate and the monolayer and the resulting strong electronic coupling.

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