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Molecular Diodes Based on Conjugated Diblock Co-oligomers

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Controlling, predicting, and understanding the flow of charge through single molecule and molecular assembly is the central theme in the area of molecular electronics. Since the 1970s when Aviram and Ratner (AR) proposed that individual molecules of the type donor−spacer−acceptor (D−s−A) between two electrodes would behave as molecular rectifiers under an electrical voltage bias,[1,2] molecules and nanostructured materials that act as electrical wires,[3] transistors,[4] diodes,[5,6] and switching[7] components have been identified. In AR's original molecular design, the nonconjugated component (electronically insulating spacer) between donor and acceptor plays the role of tunneling barrier. In the past few years, the design of the majority of rectifying molecules is based on the AR model.[5] Here we show a different molecular system that exhibits a pronounced rectifying effect. It is based upon simple diblock conjugated molecules incorporating two different conjugated blocks with opposite electronic demands, an idea analogous to semiconductor p−n junction.

The designed molecule consists of an electron-rich bithiophene segment and an electron-poor bithiazole segment; they are efficient hole- and electron-transporting agents, respectively. Scheme 1 outlines the synthetic approach to the molecule, diblock disulfide molecule, along with that of a structurally similar reference compound **7** without the diblock structure.[6d] A disulfide was introduced at the thiophene end so that the diblock molecule can be assembled into monolayers on a conductive gold surface for physical studies.[8] Previous studies have established that disulfide compounds are equally effective in forming self-assembled monolayers (SAMs) directly on gold surfaces.[9] The symmetric "monoblock" compound was synthesized for a meaningful comparison of the electrical properties with those of the diblock oligomer **4**.

The monolayers assembled from pure disulfide **4** were investigated with optical ellipsometry and scanning tunneling microscopy (STM). Ellipsometry provides a macroscopic film thickness of 16.0 ± 0.5 Å, compared to a theoretical end-to-end distance of 18.6 Å based on the fully optimized geometry of conjugated thiol derived from **4** performed at the HF/6-31G* level of theory. This result indicates that the molecules adopt an average tilt angle of ∼30° from the surface normal, as schematically shown in Figure 1. Grazing angle IR studies indicated a slightly large tilt angle value (∼36°).[10] The current−voltage (*I*−*V*) characteristics of the monolayers of the diblock molecule were investigated by scanning tunneling spectroscopy (STS) (Nanoscope III, Digital Instruments). After a stable STM scan was obtained, the feedback loop for the STM control was briefly interrupted. The Pt/Ir STM tip (grounded to zero potential) was then held at a constant position above the film, the tip−sample separation being determined by the impedance used, which typically ranged from 60 to 300 GΩ in these experiments. High impedance was used throughout the STM experiment to avoid large fluctuations in tip movement and prevent mechanical damage to the sample surface. The voltage was then ramped from positive to negative bias while the current tunneling through both the air gap and the molecule was recorded.

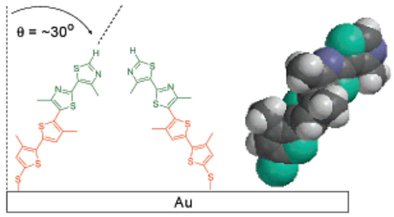
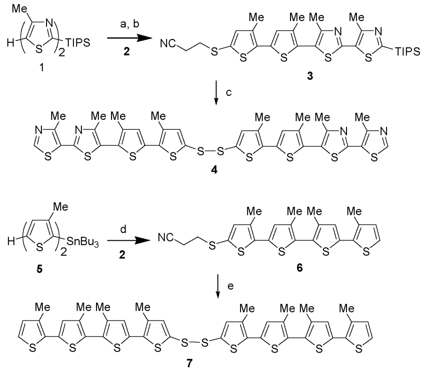
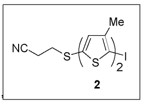


Figure 1. Schematic drawing to illustrate plausible orientation of conjugated diblock molecules covalently attached to a gold surface through the terminal thiolate group resulting from cleavage of disulfide linkage. A geometry-optimized (HF/6-31G*) structure of the thiol-terminated diblock oligomer **4** (computed in a vacuum) depicts nonplanar conformations between adjacent aromatic rings.

Scheme 1 [a]





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[a] (a) *n*-BuLi, THF, -78 °C, then Bu_3SnCl;
(b) Compound **2**, 2.5 mol% $Pd_2(dba)_3$, 20 mol% PPh_3, 50 mol% Cu_2O, DMF, 115 °C;
(c) TBAF (1.5 equiv), THF, rt.
(d) Compound **2**, 2.5 mol% $Pd(PPh_3)_2Cl_2$, 5 mol% PPh_3, toluene, 115 °C;
(e) NaOEt (3 equiv), THF-EtOH, rt.

First, to probe the rectifying effect due to single molecules, molecules **4** were inserted into the SAM of the alkanethiol host.[3] The bright spots in the inset of Figure 2a represent the constant-current STM image of molecules **4** inserted into preassembled monolayers of decanethiol. The bright spots all over the monolayers of decanethiol are very uniform in size (∼2 nm diameter) and constant-current height (∼5−6 Å from background).[11] STS studies were performed on top of both the bright spots and the surrounding decanethiol molecules. The *I*−*V* characteristics determined for single molecules of **4** is depicted in Figure 2a. Pronounced *I*−*V* asymmetry is observed for these single molecules, with turn-on voltage at around +1.0 V, whereas the corresponding tunnel current at −1.0 V remains at a low value. In contrast, the decanethiol background showed a near-perfect symmetric *I*−*V* curve, and the

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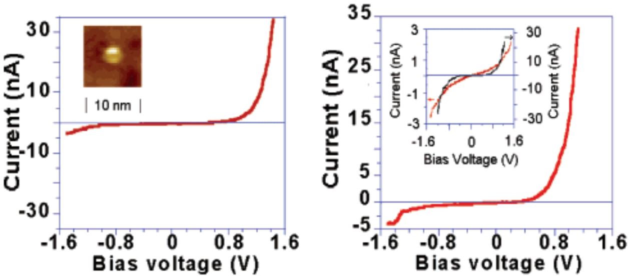

Figure 2. (a) Current−voltage ($I-V$) characteristics of isolated molecules of diblock oligomer **4** inserted into pre-assembled monolayers of 1-decanethiol on Au/mica (setpoint conditions: +1000 mV and 2 pA). (Inset) Constant-current STM image of the mixed monolayers on Au/mica. Same tunneling conditions were used to acquire the image. The bright spots (∼5 Å higher than background) correspond to molecules derived from **4**. (b) $I-V$ characteristics of pure monolayers of diblock oligomer **4** on Au surface (setpoint conditions: +600 mV and 2 pA). (Inset) $I-V$ characteristics of pure monolayers of reference oligomer **7** with bipolar turn-on voltage ∼±0.8 V (black curve) and decanethiol monolayers (red curve) (setpoint conditions: +600 mV and 2 pA).

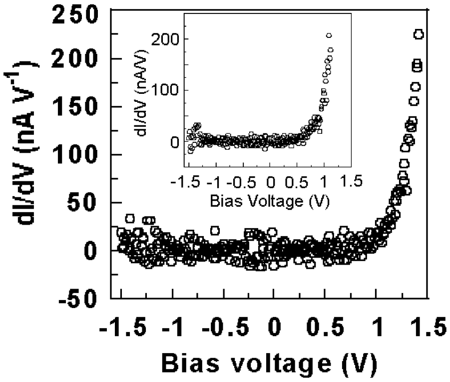

Figure 3. Differential conductance (dI/dV) versus voltage relationship for the $I-V$ data shown in Figure 2a (isolated molecule **4**). Inset: dI/dV versus voltage plot of the $I-V$ data shown in Figure 2b.

current is more than an order of magnitude smaller than that of diblock molecule **4** (inset of Figure 2b). The differential conductance curve (obtained from data in Figure 2a) is shown in Figure 3. A turn-on voltage of ∼1.0 V on the positive side can also be deduced.

A large current−voltage ($I-V$) asymmetry was also consistently observed in the SAM of pure compound **4** (Figure 2b). The threshold voltage for significant current increase on the positive sample bias was about +0.75 V, a measure of the tunneling barrier for electron injection from the STM tip to the LUMO of the molecule. The difference in turn-on voltage between that observed here (+0.75 V) and that found for mixed monolayers of **4** (+1.0 V) is due to difference in tunneling resistance (bias of 600 mV for data shown in Figure 2b and +1000 mV for Figure 2a). To illustrate the asymmetry in conductivity on both positive and negative biases, the differential conductance (dI/dV) versus voltage relationship was considered and is shown in Figure 3 (inset). The large asymmetry in conductance is evident with threshold turn-on voltage of ∼+0.8 V.

To confirm that the $I-V$ asymmetry was not due to work function difference between the gold substrate and the Pt/Ir tip or to artifacts caused by poorly controlled tip−sample interaction, monolayers of a reference oligomer **7** were prepared and studied accordingly by STS under the same conditions as for compound **4**. The $I-V$ curves obtained for monolayers of **7** exhibited nearly perfect symmetric behavior over a fairly large bias range (inset in Figure 2b). This is clear evidence that the rectifying effect observed in monolayers of disulfide **4** is due to the intrinsic diblock nature of the molecule, and possible contribution to $I-V$ asymmetry due to charge transfer at the gold−sulfur interface[12] can be ruled out. The mechanism of rectifying effect can be ascribed to the asymmetric charge polarization. It is clear that the direction of easy electron flow is from the tip to the thiazole and then to the thiophene block because the thiophene block is the electron donor and the thiazole block is the electron acceptor. In the excited state, the thiazole block would bear a negative charge and the thiophene block, a positive charge, and the electron flow would be from the thiazole to the thiophene block.

In conclusion, an organic p−n junction molecule capable of self-assembling on a gold surface has been synthesized, and monolayers have been prepared and studied by STM and STS. It is unequivocally demonstrated that diblock molecule **4** acts as a molecular rectifier, as shown by the large $I-V$ asymmetry in both pure monolayers and as single molecules inserted in an insulating environment. Control experiments using a reference compound further reinforce this conclusion. The simplicity of the diblock architecture and the versatility in the structural variation make this system unique and valuable in future designs of molecular-scale electronic components.

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Supporting Information Available: Monolayer preparation and synthetic procedures for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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