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Communication

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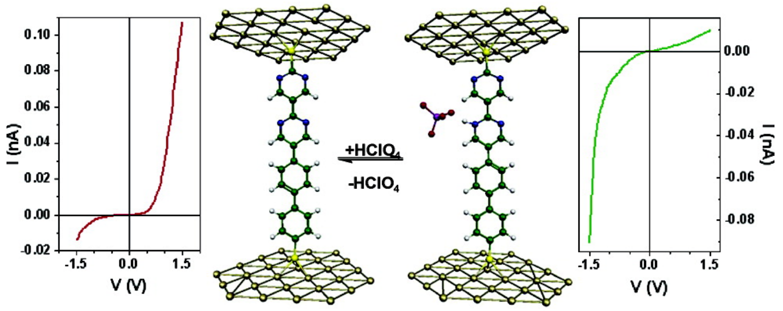

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Inversion of the Rectifying Effect in Diblock Molecular Diodes by Protonation

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Organic rectifiers or molecular diodes are asymmetric organic molecules in which the electrons flow through in one preferential direction.[1] In this paper, we report the effect of protonation on the rectifying behavior in newly designed and synthesized molecular diodes. In our previous publications, we have described the synthesis and characterization of a series of diode molecules.[2−4] These diode molecules are based on diblock oligomers with electron-rich dithiophene covalently connected with electron-deficient dithiazole. Scanning tunneling spectroscopy (STS) studies revealed a pronounced rectification effect in single molecular devices.[2−4] It was also demonstrated that we could control the charge transport direction by controlling the orientation of the diode molecules.[4] We attributed this to the dipole orientation of the thiophene−thiazole diblock molecule. Those results point out an approach to enhance the rectification effect by increasing the dipole moment of the molecules. With that in mind, we have designed and successfully synthesized a new diode molecule **1**, where a dipyrimidinyl moiety was connected with diphenyl groups (Figure 1). Scanning tunneling microscopy (STM) and STS studies revealed that the molecules not only have a more pronounced rectifying behavior but also exhibit a dramatic effect by protonation on the nitrogen atoms by strong acids, which can reversibly alter the rectifying direction completely. This is the first example where the effect of protonation on charge transport through a molecule was observed.

Detailed synthesis of molecule **1** is described in the Supporting Information. Various physical characterizations confirmed the structure of the molecule. To control the orientation of **1** onto the surface of the gold substrate and at the same time allow the connection of a second electrode on the opposite side of the molecule, we utilized two different thiol-protecting groups (cyanoethyl, CNE, and trimethylsilylethyl, TMSE).[4] The CNE group was cleaved in situ by sodium ethoxide (NaOEt) in ethanol to form free thiol, which was then co-assembled with dodecanethiol (DDT) in a 1:500 ratio on a Au(111) substrate (step a in Figure 1). Next, the TMSE group on the top of the molecule was cleaved with a solution of tetrabutylammonium fluoride (TBAF) in THF. The resulting thiol was derivatized with a suspension of gold nanoparticles (AuNP) to give the final assembly (step b in Figure 1).

The assembling processes were monitored with STM studies of the sample at different stages. The STM topography after the self-assembly process shows two main characteristics, a highly ordered structure of DDT and randomly distributed bright spots. The position, shape, and size of these spots were constant during consecutive scans, except for small variations in the intensity due to the stochastic behavior of single molecules inserted into the alkanethiol SAM.[5] The average sizes for the spots are approximately 2.5 nm. Finally, the bright spots were not observed in the images of control samples prepared under identical conditions described in Figure 1 without the addition of NaOEt. These observations indicate that the bright spots are the image of a single or a small group of diblock molecules bonded to the Au substrate.

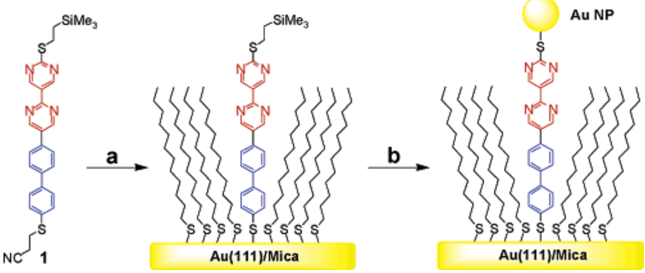

Figure 1. Preparation of the assembly (a) NaOEt, ethanol/THF, dodecanethiol, Au(111); (b) TBAF, THF, Au nanoparticles.

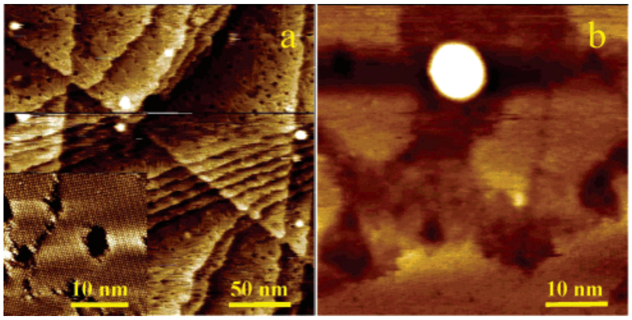

Figure 2. Constant−current STM topography of (a) dodecanethiol/**1** SAM on Au(111) after attachment of AuNP to the top termini of **1**. Inset: High-resolution image of the DDT SAM. (b). Image of a single AuNP. STM imaging conditions: $V_{\text{bias}} = +1.0$ V, $I_t = 1$ pA.

The cleavage of the TMSE protecting group, on the top of the molecule, was confirmed with grazing incidence FTIR spectroscopy with a SAM of molecules **1** on the gold substrate. The C−H symmetric deformation vibration from the $-$Si$-$CH$_3$ moiety was considerably reduced after the TMSE cleavage.[6] The free thiol was immediately treated with a solution of AuNPs to give the final assembly. Figure 2 shows the constant−current STM image of the Au surface of the sample after the assembly was completed. The apparent diameters of the AuNPs were in the range of 7−10 nm, depending on the STM tip and scan rate used. This value is much larger than the bright spots due to single molecules. STM images of control samples prepared under the same conditions without cleavage of the TMSE group or in the absence of inserted target molecules do not show images of AuNPs. The evidence presented above allows us to conclude that the consecutive deprotection and orientation of the molecules resulted in the formation of an assembly, as depicted in Figure 1. The current−voltage characteristics of the resulting unprotonated assembly were studied with STS. Figure 3a summarizes the averaged $I(V)$ data. The STS spectrum showed asymmetric charge-transport behavior. The $I(V)$ asym-

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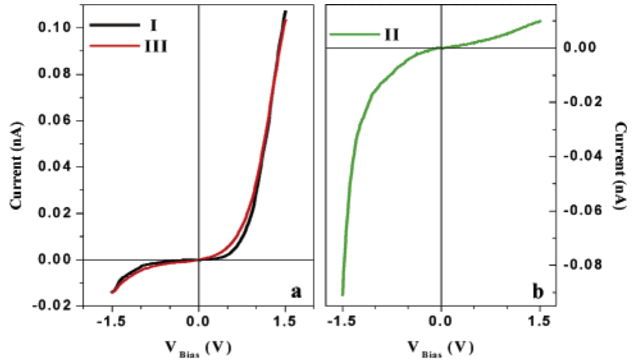

Figure 3. Averaged $I(V)$ curves measured over AuNPs at $V_{\text{bias}} = 1.5$ V for (a) assembly deprotonated, **I** sample before protonation, **III** sample after protonation−deprotonation ($I_t = 0.1$ nA) and (b) assembly protonated by ClO_4H ($I_t = 0.01$ nA).

metry was quantified by the rectification ratio (RR) defined as $I(+1.5\text{ V})/-I(-1.5\text{ V})$, whereas the reproducibility of the data acquired for different NPs on the SAM was evaluated from the RR range. The RR values for the unprotonated assembly range from 4.5 to 9 with an averaged RR around of 7.4. This value is larger than the previously reported RR of 5 for the dithiophene−dithiazole diblock oligomer in a similar assembly.[4] The increase in the RR can be explained by the stronger intrinsic polarization of the dipyrimidinyl−diphenyl in comparison with that of the dithiophene−dithiazole diblock. This difference is reflected in the theoretically calculated dipole moment for the compound **1** (6.3 debye) and dithiophene−dithiazole (1.6 debye).[4,6]

The most interesting result is the reversible change in the rectifying direction by protonation/deprotonation of the dipyrimidinyl block (Figure 3b). Perchloric acid in a methanol/THF mixture and NaOEt in methanol were used to protonate/deprotonate the nitrogen atom in the assembly, respectively. The reversibility of this process was followed by FTIR in a SAM of **1** and UV−visible spectroscopy in solution. The FTIR studies demonstrated the appearance and disappearance of the absorption band due to the ClO_4^- anion after the protonation and deprotonation.[6] In addition, the UV−vis spectra of **1** in a THF solution exhibited a 0.2 eV bathochromic shift and decreases in relative oscillator strength for the $\pi \rightarrow \pi^*$ absorption band after addition of perchloric acid. The energy absorption maxima recovered the original position with the treatment of NaOEt.[6,7] We can assume that, at least, monoprotonation of the dipyrimidinyl block occurred under the conditions used. In addition, a more pronounced rectifying effect was observed with the inverse of the RR (1/RR) in a range of 4−12, with an average around 9.2. Moreover, if we change the orientation of molecule in the assembly and let the dipyrimidine moieties remain embedded in the DDT SAM, the dipyrimidine is not accessible by protons. We observed that the sample has a reversed rectification direction from the unprotonated assembly **1**. However, the rectification direction is not affected by the treatment with strong acid solution.

These results and observations can be explained based on a crude model shown in Figure 4. The electron density of the diblock cooligomer is polarized and induces a permanent dipole moment in the molecule. When the molecule is connected to the electrodes, the surface dipole layer induces a shift of the vacuum level at the surface (VL) of the gold electrodes, which alters the Fermi level (E_F) alignment in the interface.[8] Although it is difficult to know exactly the position of E_F within the molecular energy gap, as a first approximation, we assumed a band lineup corresponding to the E_F at the middle of the gap between the HOMO and LUMO.[9] Thus, for the assembly with the unprotonated diode molecule, the dipole moment of the molecule will shift the local VL in the organic layer from that of the metal in ΔE_d. Assuming an elastic resonant tunneling mechanism for the charge transport, a smaller bias potential is needed to produce electron-tunneling current through the HOMO than through the LUMO ($E_- > E_+$).

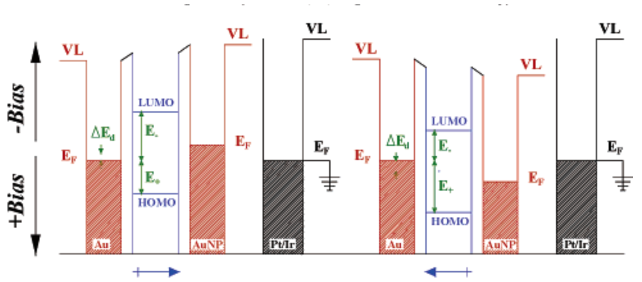

Figure 4. Energy diagram for the unprotonated (left) and protonated (right) assemblies, respectively. ΔE_d is the relative shift in the local VL at the interface due to the dipole layer. E_+ (E_-) represents the energy barrier needed to align the Fermi level with the molecular HOMO (LUMO) level.

When the molecule in the assembly is protonated, the positive charge centered on the nitrogen reverses the sign of the electronic density on each block, that is, the dipyrimidinyl became positively charged. Theoretical calculation for the molecule **1** in the absence of the anion revealed that the dipole moment also points in the opposite direction. The local VL of the organic layer decreases and lays the E_F of the gold substrate electrode closer to the LUMO. Now, the resonance tunneling through the LUMO becomes more accessible ($E_+ > E_-$). Thus, the protonation inverted the rectification direction in a reversible manner.[10]

In summary, a new molecular diode was synthesized and a pronounced rectifying effect observed. It was found that protonation on the nitrogen atoms of the diode molecule by strong acids affects the charge transport dramatically, which can reversibly alter the rectifying direction.

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Supporting Information Available: Experimental details for the synthesis of **1**, assembly preparation, theoretical calculation, STM, STS, FTIR, and UV−visible measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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