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Conductance of Single Triangular Dehydrobenzo[12]annulene Derivative Bridged between Au Electrodes

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A triangular dehydrobenzo[12]annulene (DBA) molecule bridged between Au electrodes was investigated by scanning tunneling microscopy break junction technique. The conductance of the single DBA molecule was determined to be 2.5×10^{-5} G_0 ($G_0 = 2e^2/h$). Though the DBA has three anchor units which can bind to metal electrodes, the conductance measurement revealed that two of three anchor units per molecule are most likely to bind to the Au electrodes to form a single molecular junction.

Electron transport through a single molecule has received great attention for realization of molecular electronics.[1] Various single molecular junctions have been evaluated by means of scanning tunneling microscope (STM) and other techniques.[1] One experimental challenge in this field is to control the electronic properties of a single molecular junction by external field or stimuli. For example, the switching of a photochromic molecular junction from the conducting state to the insulating state was performed upon irradiation of visible light.[2] A single molecular device with three terminals is an alternative approach.[3] The general scheme of a single molecular device with three terminals is the molecule bridges between two metal electrodes, and at the same time its properties can be modulated by a third electrode. In order to fabricate single molecular devices with three terminals, it is important to investigate how a single molecular junction consisting of a molecule having three anchor units to a metal electrode would behave.

In the present study, we chose a planar triangular molecule, dehydrobenzo[12]annulene (DBA), as a molecule with three terminals. The DBA can be substituted with up to three anchor units at each corner of the triangle because of the synthetic versatility at the periphery, and thus various anchor units can be introduced to the DBA core.[4] Furthermore, high conductivity is expected for the molecular junction of DBA because DBA comprises planar phenylene–ethynylene conjugation.[5] Indeed, it is known that single oligo(phenylene–ethynylene) molecular junctions show high conductivity compared with those of other single molecular junctions of the same size (e.g., alkane dithiol).[6] Moreover, planarization of the π-conjugation pathway by fixing free rotation of the phenyl ring around the molecular axis in biphenyl derivatives enhances conductivity.[7,8] Thus, we believe that DBA derivatives could be a good candidate for single molecular devices with three terminals by incorporating appropriate anchor units. Herein we report conductance of DBA substituted with three amino groups as anchors determined by STM break junction technique.

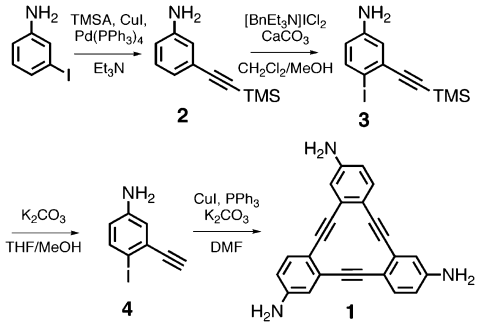

Figure 1. Synthesis of DBA **1**.

The synthetic route to **1** is shown in Figure 1. The reaction of commercially available *m*-iodoaniline with trimethylsilylacetylene (TMSA) in the presence of copper and palladium catalysts afforded ethynylated compound **2**. Iodination of **2** with the Kajigaeshi reagent[9] gave **3**. After removal of the TMS group of **3**, copper-catalyzed trimerization reaction afforded DBA **1** in 26% yield.[10] The structure of **1** was confirmed by X-ray analysis.[11,12]

The conductance measurements were performed with modified STM (Pico-SPM, Molecular Imaging Co.). Details of the experimental design used in this study have been previously reported by our group.[13,14] Briefly, the Au STM tip was repeatedly moved into and out of contact with a Au(111) substrate at a rate of 50 nm s^{-1} in the solution. The solution was tetraethyleneglycol dimethyl ether (tetraglyme) containing DBA **1** (1 mM). Conductance was measured during the breaking under an applied bias of 20 mV between the tip and substrate. The bias voltage was applied to the sample.

Figure 2 shows typical conductance traces and conductance histograms of the Au contacts in solution with and without DBA. In pure tetraglyme, neither plateaus nor peaks were observed both in the conductance traces and conductance histograms. In the presence of DBA, the conductance of the junction decreased in a stepwise fashion with each step occurring at an integer multiple ($1\times$, $2\times$, $3\times$) of 2–3×10^{-5} G_0. The corresponding conductance histogram showed a feature around 2–3×10^{-5} G_0. Neither plateau nor peaks were observed below 1×10^{-5} G_0 both in the conductance traces and conductance histograms. These experimental results revealed that the plateau in the conductance traces and peaks in the conductance histograms showing values of 2–3×10^{-5} G_0 can be ascribed to the single DBA molecule bridged between the Au electrodes. By measuring three individual samples, the conductance of the single Au/DBA/Au molecular junction is precisely determined to be $2.5\ (\pm 0.4) \times 10^{-5}$ G_0.

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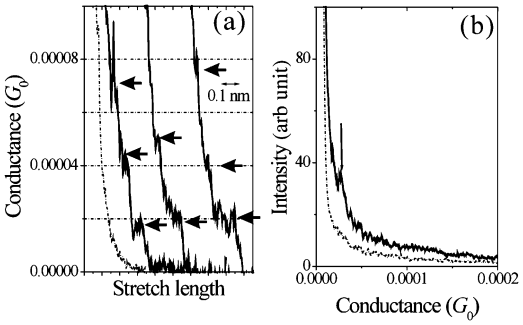

Figure 2. Typical conductance traces and conductance histogram of the Au nano contacts during contact breaking in ether solution containing DBA (1 mM). The conductance histograms were obtained from the 1000 traces. The bin size is 1×10^{-7} G_0. The dotted-line shows the result in the absence of molecules.

In general, there are two possible configurations for a single molecule with three terminals when bridged between two electrodes; two anchor units bind to one Au electrode and one anchor unit binds to another Au electrode (two Au–N and one Au–N) and one anchor unit binds to one Au electrode and one anchor unit binds to another Au electrode (one Au–N and Au–N). When the DBA is bridged between the Au electrodes with the two Au–N and one Au–N configurations, we foresee that its conductance would be two times larger than that with the one Au–N and Au–N configuration, reflecting the number of the conduction channels through oligo(phenylene–ethynylene) units. The combination of steps at 1× and 2× certain conductance value would be observed in the conductance trace for the junction with the two Au–N and one Au–N configurations. In the present study, the probability of appearance of steps at 1×, 2×, and 3× $(2.5 \times 10^{-5})G_0$ was 93 (±7)%, 79 (±7)%, 61 (±7)%, respectively, in the 555 conductance traces. The combination of steps at 1× and 2× $(2.5 \times 10^{-5})G_0$ were not preferentially observed, which does not agree with the expected behavior. Moreover, crystal structure of DBA revealed that the spatial arrangement of anchor units is unfavorable for adapting the double Au–N and single Au–N configuration (*meta*- and *para*-substitutions of the anchor units with respect to the C–C triple bond). Therefore, the DBA would bind to the Au electrodes through two of three anchor units.

Here we discuses the obtained conductance value of the single molecular junction of DBA based on the previously reported values in related compounds.[6,15] In the case of molecular junction of DBA, electrons would be transported through the oligo(phenylene–ethynylene) conjugation. Huber et al. reported that the conductance of the phenylene–ethynylene dithiol bridged between Au electrodes is 1×10^{-4} G_0.[6] The molecular size of the DBA is 1.1 nm (estimated by N–N distance), which is smaller than that of oligo(phenylene–ethynylene) molecule by 0.7 nm. The conductance of the single molecular junction of π-conjugated molecule decreases ten fold with an increase in the molecular size of 0.7 nm.[1] The oligo(phenylene–ethynylene) dithiol binds to the Au electrodes via strong Au–S bond, while the DBA binds to the Au electrode via rather weak Au–NH_2 bond. The conductance of the single molecular junction with the Au–NH_2 bond is about ten fold smaller than that with the Au–S bond.[15] Therefore, the conductance of the single DBA molecular junction is expected to be around 1×10^{-4} G_0. The obtained conductance value of 2.5×10^{-5} G_0 is smaller than the expected value, however, the order of these values are the same, showing the validity of the present experimental results. The difference between the two values is probably because of rough the estimation mentioned above and unfavorable *meta*- and *para*-substitutions of the anchor units with respect to the C–C triple bond.[16]

In conclusion, we have investigated a single planer triangular DBA molecule bridged between Au electrodes. The conductance of the single molecular junction of DBA was determined to be 2.5 (±0.4) $\times 10^{-5}$ G_0. The electron conducting behavior of the molecular junction suggested that two of three anchor units would be used to construct a single molecular junction, and another anchor unit would be free. The present results, the relationship between three terminal molecule and electronic conductivity, are very useful for designing novel three terminal molecular devices.

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12 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-777498. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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