

Unambiguous One-Molecule Conductance Measurements under Ambient Conditions

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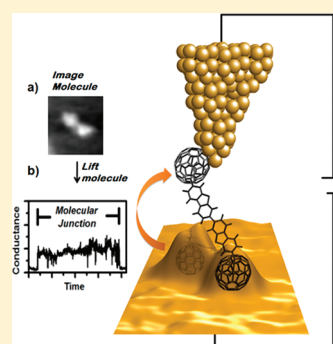
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 Supporting Information

ABSTRACT: One of the challenging goals of molecular electronics is to wire exactly one molecule between two electrodes. This is generally nontrivial under ambient conditions. We describe a new and straightforward protocol for unambiguously isolating a single organic molecule on a metal surface and wiring it inside a nanojunction under ambient conditions. Our strategy employs C₆₀ terminal groups which act as molecular beacons allowing molecules to be visualized and individually targeted on a gold surface using an scanning tunneling microscope. After isolating one molecule, we then use the C₆₀ groups as alligator clips to wire it between the tip and surface. Once wired, we can monitor how the conductance of a purely one molecule junction evolves with time, stretch the molecule in the junction, observing characteristic current plateaus upon elongation, and also perform direct *I*–*V* spectroscopy. By characterizing and controlling the junction, we can draw stronger conclusions about the observed variation in molecular conductance than was previously possible.

KEYWORDS: Single molecule conductance, molecular electronics, STM, break junction, nanoelectronics, fullerene



The highly attractive concept of integrating individual molecules into electronic devices is drawn from ideas that molecules can behave as functional components in everyday devices.¹ Such electrical components could include transistors,² amplifiers,³ and switches.⁴ To achieve this engineering feat electron transport across individual molecules must be understood in great detail, and for this, single molecules must be wired between two electrodes. Even now, however, those methods which have been developed to measure single molecule conductance at room temperature cannot directly determine the number of molecules contained in individual molecular junctions. It is accepted that these methods can result in an uncontrolled number of molecules bridging the two electrodes,⁵ which is both inefficient and undesirable. The most abundant method is the in situ molecular break junction (BJ) technique, skillfully demonstrated by N. J. Tao and collaborators, in which the tip of a scanning tunneling microscope (STM) is driven in and out of contact with a substrate immersed in a solution of molecules.^{6,7} The method relies on the probability that a low number of molecules is found bridging the metal gap. The absolute number is not, however, a parameter which can be extracted directly from individual experiments. Closely related are the methods of Haiss et al. which form junctions from molecules adsorbed on a gold surface in a random manner without forming a metallic contact.^{8,9} Cui et al. developed a different approach using a conducting atomic

force microscope to contact gold nanoparticles capping alkane-dithiol molecules embedded in a matrix of alkanethiols.¹⁰ Importantly, these methods do not require cryogenic temperatures or ultrahigh vacuum conditions to be carried out successfully, and this has led to their widespread use. A common factor among these methods is that they attempt to define the conductance of a single molecule by carrying out a statistical analysis of many individual junctions. Problematically, however, there is no consensus on the best type of statistical approach to adopt.^{11–13} This can lead to data being interpreted differently by different groups, making the comparison of results for the same compound difficult.

It has also become apparent that wires with common anchoring groups, such as thiols^{14,15} or pyridines,^{16,17} do not yield a unique molecular conductance, even within the same measurement.^{5,18} The origin of the multiple conductance values, derived from histogram peaks with noninteger relationships, often remains speculative. The common assertion is that they arise from different coordination modes of the anchor group to the metal,^{12,18} although it cannot be ruled out that they also involve multiple molecule junctions.¹⁹ As a result of the variability in the number of molecules and their mode of anchoring, analyzing

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junction conductance alone cannot reveal the presence of just one molecule. This severely limits the potential for performing reliable direct electrical experiments on single molecule junctions. As a consequence of this, the field of molecular electronics requires a straightforward approach to wire precisely one molecule inside an electrical junction. This approach should also be applicable to a range of compounds.

Surface imaging using an STM allows precise positioning of the tip of the STM above individual molecules, which ensures that spectroscopic features can be reliably attributed to just a single molecule.^{20,21} Confining a molecule to a surface and measuring its spectroscopic properties while maintaining a tunnel gap has been carried out on many different compounds, from porphyrins²² to proteins.²³ Our demand, however, is to wire a molecule by contacting both of its termini. Controlled contact to a single molecule adsorbed on a surface was first performed by pressing the tip of an STM onto a single C₆₀ molecule.²⁴ Recently, the charge flow across two stacked C₆₀ molecules has even been measured.²⁵ Experiments such as this normally require low temperatures in order to prevent diffusion of the molecules across the surface. In a few cases controlled lifting of a molecule has been achieved. Such experiments have been achieved with a single polyfluorene chain,²⁶ and a perylenetetracarboxylic dianhydride (PTCDA) molecule²⁷ and octanethiol.²⁸ Cryogenic temperatures were employed under ultrahigh vacuum conditions to reduce molecular motions and, in the case of PTCDA, prevent oxidation of the surface allowing the molecule to bind to the electrodes. In the polyfluorene experiment it was noted that bonding to the tip was achieved through a radical located at the end of the chain, and this radical would not exist under ambient conditions. These experiments are therefore specific examples and contain no guidelines on how they can be applied to other molecules or be attainable under ambient conditions.

We have addressed the issue of wiring just one molecule under ambient conditions by designing an experiment which allows visualization of discrete molecules using a room temperature STM operated in air. Visualization allows us to target precisely one molecule before wiring the molecule and measuring electron transport. The images we take directly before measurements give us the explicit information necessary to prove that only one molecule can be wired in the junction. To achieve this level of control we have utilized a C₆₀ capped bifluorene molecular wire (described as a fullerene-dumbbell). The C₆₀ groups provide the clear visual signature for the molecule while also serving as effective anchoring groups. We incorporated a fluorene spacer due to their excellent wire properties,²⁹ while the central nine carbon atom possesses the potential to have functional groups added at a later date. We draw attention to the fact that, other than fluorene, many chemical groups can be incorporated between the C₆₀ termini³⁰ giving a wide scope for this method. Indeed, we have successfully wired a phenyl dumbbell (molecule 2) and the results are shown in Figures 10–12 in the Supporting Information. Employing C₆₀ as an anchoring group for molecular wires has recently been suggested with preliminary studies carried out using the standard break junction technique.³¹ The electrical properties of free C₆₀ have also been widely studied, showing various interesting phenomena.^{32–34}

To form the samples we use a solution casting procedure. Molecule 1 (Figure 1c) was deposited from a highly dilute solution, between 1 and 10 nM in mesitylene, to give a very low coverage on a Au(111) surface (Figure 1a). We used gold STM tips to image and contact the molecules.

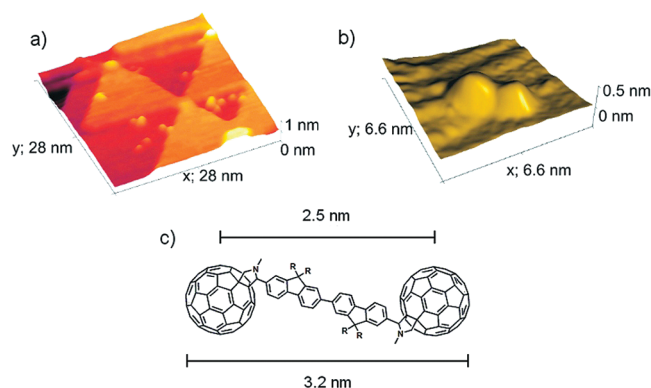


Figure 1. (a) STM image of a low coverage of molecule 1 (C₆₀–Fl₂–C₆₀) on Au(111) under ambient conditions. Image taken at $U_{\text{bias}} = 0.4$ V and $I_{\text{set}} = 0.14$ nA. The molecules appear as two closely spaced spheres, and the gold surface displays characteristic monatomic high terraces (0.24 nm in height). (b) High-resolution STM image of molecule 1 adsorbed over a step edge. $U_{\text{bias}} = 0.4$ V and $I_{\text{set}} = 0.2$ nA. (c) Chemical structure of molecule 1 ($R = \text{C}_6\text{H}_{13}$). The C₆₀ groups can rotate with respect to one another, leading to subtle changes in C₆₀ separation. The center to center distance of the C₆₀ spheres is shown, as well as the maximum distance between the extreme edges of the molecule, when oriented trans to each other. (See panels a and b of Figure SI 8 in the Supporting Information for structural representations of cis and trans orientations.)

As shown in Figure 1a and, with higher resolution, in Figure 1b, molecule 1 appears as two closely spaced spheres on the surface. We have measured the distance between the centers of the two spheres for 14 isolated molecules and found the mean value to be 2.2 (± 0.3) nm, corresponding well with the predicted C₆₀ separation (Figure 1c). In contrast to our observations of pristine C₆₀ we find that the dumbbell molecules do not diffuse significantly across the surface. The immobility is key in allowing us to image molecules clearly and target an individual isolated molecule.

After an isolated molecule is selected, which is shown in Figure 2a, our procedure to lift the molecule is as follows. The tip was placed directly above the molecule and approached slightly to arrive at a set point conductance of $G_{\text{set}} = 8 \times 10^{-6} G_0$ using a bias of 0.4 V (we also tested bias voltages of 0.1 and 1.0 V—see Figures SI 2 and 3 in the Supporting Information). G_{set} was chosen to be as low as possible while still placing the tip close enough to allow bridge formation. At this value of G_{set} we estimate a separation of 1.8 nm between tip and surface (see Supporting Information). This places the tip approximately 1 nm above a C₆₀. Subsequently the feedback loop was switched off and the conductance (G) versus time recorded for a period of 2 s, after which it is reengaged. We repeated this for a total of 60 s. During this period the conductance jumped between G_{set} and higher levels, and an example of this is presented in Figure 2d (see also Figures SI 2 and 3 in the Supporting Information for further examples at different bias voltages). The jumps up in conductance can be attributed to the anchoring of the molecule between the tip and the surface through both its C₆₀ (anchoring) groups.³⁵ Hence, by placing the tip above the molecule at the correct distance, we induce one of the C₆₀ groups to jump between the surface and the tip, as depicted in Figure 2b. During the whole 60 s of measuring, we observed around 200 individual attachment events occurring with a rate of ca. 3 per second. We do not resolve events occurring on time scales quicker than

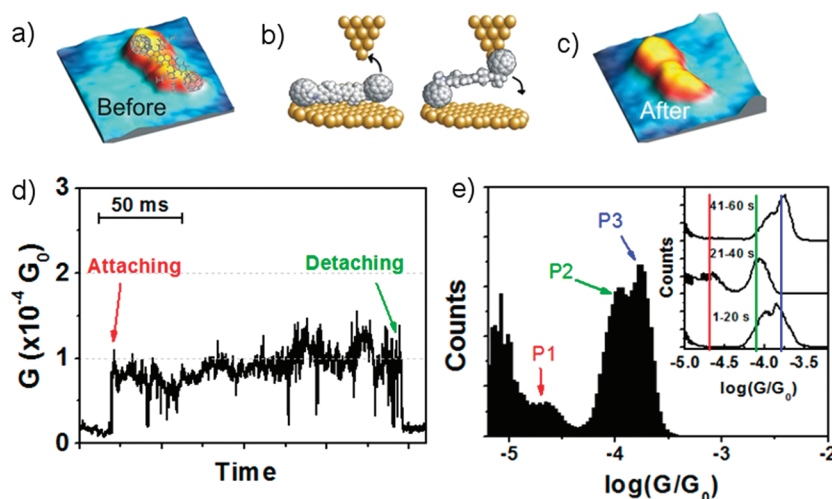


Figure 2. (a) 4×4 nm STM image of a single molecule of $C_{60}-Fl_2-C_{60}$ taken at $U_{bias} = 1.0$ V and $I_{set} = 0.5$ nA before disabling the feedback loop and recording the conductance. A sketch of the molecule has been overlaid. (b) Schematic view of the molecule attaching to the tip and the surface. (c) STM image recorded after 60 s of recording the conductance with the tip above the molecule with identical conditions as in (a) and from the same starting coordinates. (d) Example conductance trace recorded with the tip positioned above the molecule and the feedback loop disabled. The set junction conductance (G_{set}) at the beginning of the measurement was $8 \times 10^{-6} G_0$, $U_{bias} = 0.4$ V. (e) Total histogram of the data recorded after disabling the feedback for 60 s. Three peaks can be seen and are labeled P1, P2, and P3. The inset shows how the groups varied over the 60 s. In the 1–20 and 41–60 s periods P2 and P3 are seen, while in the 21–40 s period P1 and P2 are visible, but not P3.

0.25 ms. Also, we noticed that, while the molecule was bridging, the conductance could switch between different discrete values (Figure SI 4 in the Supporting Information). After our measurement was complete, G_{set} was reduced and the area reimaged showing the molecule to be fully on the surface (Figure 2c). Increasing the tip sample distance, by reducing G_{set} , prevents the molecule from bridging, allowing its position to be determined, and this image shows little change in the orientation of the molecule on the surface. Also, when placing the tip over a molecule free area no jumps were observed (see Figure SI 5).

Current jumps have also been observed on low coverage dithiol modified gold surfaces and attributed to the spontaneous attachment or detachment of molecules.^{9,35} In these experiments, however, the absolute number of molecules inside the junction is not determined and many molecules could, potentially, be bound to both electrodes, with just one or a few molecules contributing to the signal.³⁶ The key to our experiment is that we identify before hand that there is only one molecule beneath the tip.

When we plotted all the individual traces in the form of a histogram we noticed that certain conductance values appeared more frequently than others (Figure 2e). There are four different histogram peaks, the lowest is centered at the value of G_{set} and unrelated to the conductance of the molecule. The three other peaks (labeled P1, P2, and P3 in Figure 2e) relate to the most likely conductance values when the molecule bridges. We show the data in intervals of 20 s in the insert to Figure 2e which shows the progression of the histogram conductance peaks throughout the whole measurement. We have listed the peak values we find during each interval in Table 1.

The different conductance values as seen in Figure 2e and Figure SI 4 in the Supporting Information could arise from internal conformational changes of the single molecule, or changes to the binding of C_{60} at the metal/molecule interface,³⁷ but we can rule out the presence of more than one molecule in the junction. It is known that C_{60} can bind to gold through different

Table 1. Conductance Histogram Peak Positions for the Data Presented in the Inset of Figure 2e^a

	time interval		
	1–20 s	21–40 s	41–60 s
peak 1		$2.0 \times 10^{-5} G_0$	
peak 2	$9.9 \times 10^{-5} G_0$	$9.9 \times 10^{-5} G_0$	$1.1 \times 10^{-4} G_0$
peak 3	$1.4 \times 10^{-4} G_0$		$1.7 \times 10^{-4} G_0$

^a Peak positions have been determined from linear histogram representations of the data. We have labeled the peaks as 1, 2, or 3 based on their contribution to the peaks in the overall histogram.

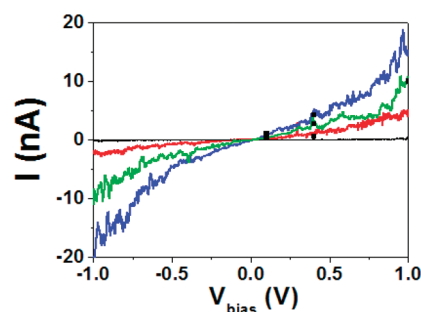


Figure 3. I – V curves for one molecule junctions of molecule 1. The curves were recorded with a starting bias voltage of 0.4 V and current of 0.1 nA. The positions of the histogram peaks from Figure 2, plus other voltages, are overlaid for comparison (black squares).

parts of its cage structure, and at 7 K in ultrahigh vacuum two geometries prevail; adsorption via a hexagonal ring and via a 6:6 double bond^{38,39} (the formal double bond adjoining two hexagonal rings). It has been suggested that the amount of charge transfer between a gold surface and C_{60} depends quite strongly on the

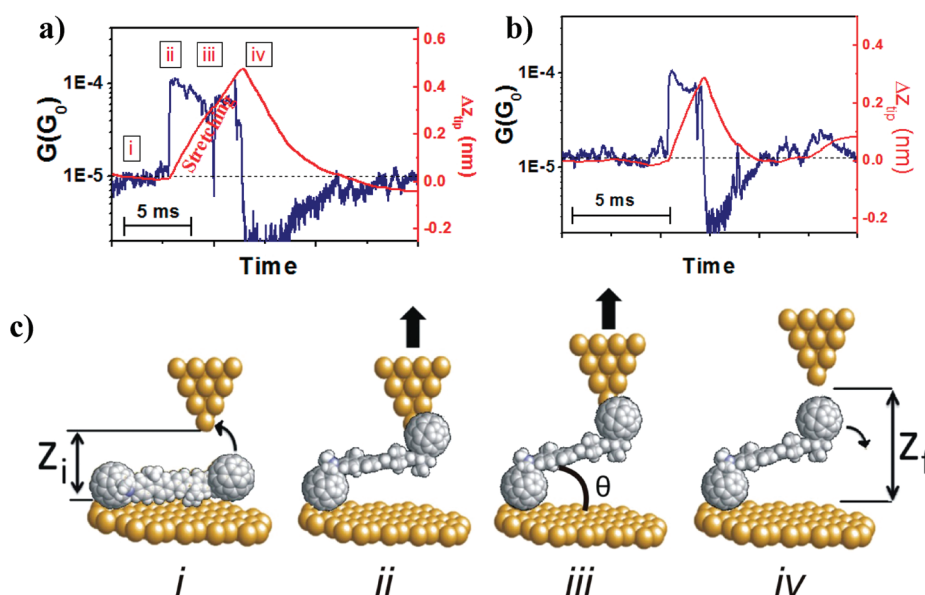


Figure 4. (a) and (b) Example $I(t)$ traces (solid blue lines) with feedback enabled. $G_{\text{set}} = 1 \times 10^{-5} G_0$, $U_{\text{bias}} = 0.4$ V. The red lines show the vertical piezo movement corresponding to the changes in tunnel current. The dashed black line shows the position of G_{set} . The speed of retraction was in the range of 60–100 nm s⁻¹. The red numbers indicate the different stages of the experiment, as depicted in part c. (i) = molecule resting on surface, (ii) = molecule jumps to the tip, (iii) = molecule is stretched inside the junction, (iv) = the molecular junction cleaves. Following the cleavage the tip returns to its original position with the gap conductance following an exponential behavior. (c) A schematic representation showing the proposed stages of attachment and detachment of the molecule inside the metal junction. The picture is drawn to approximate scale to give an idea of the angles and distances involved, $z_i \approx 1.8$ nm, $z_f \approx 2.3$ nm and $\theta = 45^\circ$ as an approximate minimum.

adsorption geometry.³⁸ This causes a change in the position of the LUMO relative to the metal Fermi level, and affects the electronic coupling strength of the molecule to the electrodes.

We have directly measured I – V curves on the single molecule junction. We carried out the measurement on the same molecule as in Figure 2. While many curves showed the molecule attaching and detaching throughout the scan, some showed the molecule attached for the whole duration (50 ms). Examples of these are shown in Figure 3 where the I – V curves indicate nonresonant transport. We found only a slight increase in the conductance at voltages approaching ± 1 V, with a maximum of approximately $2 \times 10^{-4} G_0$.

While the molecule is wired, we can further check the mechanical stability of the molecular junction by carrying out a stretching experiment, schematically illustrated in Figure 4c. Stretching the molecule is easily achieved by keeping the feedback control switched on during the measurement. This causes the tip to retract linearly following a jump up in the conductance. We set the response time much slower than that used for imaging in order to follow the current as the tip moves. The conductance plateaus we observed upon stretching showed the molecule was stably attached over a distance of several angstroms. Ultimately, the molecular junction breaks, and this is highlighted by the abrupt drop in conductance. Two representative conductance versus time curves are shown in Figures 4a–b. The amount of retraction was 4.6 Å in (a) and 2.7 Å in (b). Following the breaking of the junction, and drop in conductance, the tip returns to its original position. The measured barrier height during the reproach was consistently close to 1 eV, which is in the range of that which we find on a clean substrate in air.

To obtain the amount by which the molecule is lifted upon extension of the junction, we have estimated the tip to surface distance (see Supporting Information). After stretching we obtain a final separation for the gold electrodes, z_f of 2.3 nm

(using the example in Figure 4a), which, as expected, is less than the total length of the molecule. The molecule may actually anchor at the apex or at any point higher up the tip it can reach. Consequently the resulting molecular tilt angle, immediately before the junction cleaves, is at least of the order of 45° from the surface.

We have also carried out conductance measurements employing the molecular-BJ method of Xu et al.⁶ We used a different gold substrate than that used for the measurements presented thus far, with a higher coverage of molecules, a prerequisite for this type of experiment. Specifically, we immersed the gold surface in a solution of approximately 1 μM concentration for several minutes. These conditions expose the gold to many more molecules than the 1 nM drop which was applied to produce the low coverage samples. Individual conductance–distance traces showed very clear plateaus over several nanometers (Figure 5 inset), in agreement with the molecular length. However, even after removing traces showing just tunneling, the histogram built from the 20% of remaining traces showed a much broader peak than the histogram we present in Figure 2e. Some of the plateaus actually varied by less than a factor of 2 along their entire length, which suggests that upon elongation of certain junctions the binding of C_{60} to gold remains strong and stable. However, as the broad peak shows, we see a large junction to junction variation over 2 orders of magnitude in conductance.

The large variation in conductance plateaus recorded using the break junction method could arise from several sources. The large number of molecules required for this method to be successful increases the probability of measuring multiple molecules wired in parallel.^{6,19} If this is the case, then each junction can contain a different number of molecules, leading to different conductance plateau heights. Another consequence of having many fullerene containing molecules present on the surface is

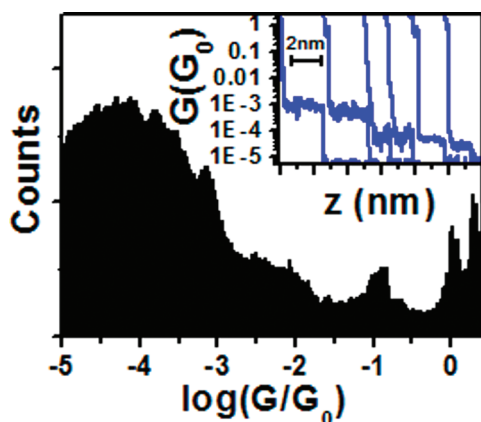


Figure 5. Conductance histogram built from 686 individual break-junction traces, recorded on a high coverage of C_{60} - Fl_2 - C_{60} on Au(111), which showed a conductance higher than $1 \times 10^{-5} G_0$ at a separation greater than 1 nm. This form of filtering removes background tunneling only. The stretching rate was 40 nm s^{-1} . The histogram is much broader than the histogram in Figure 2e, showing the larger spread in conductance values that are produced by this method. The inset to the figure displays representative $I(z)$ traces.

that electronic interactions can exist between wired and surrounding unwired molecules. It has been shown by several studies that the local electronic structure of individual C_{60} molecules changes depending upon whether they are located within a cluster, at the edge, or isolated.⁴⁰ Hence, even though unwired molecules are not expected to contribute to electron transport across the junction,¹⁰ they may perturb those which are wired in an appreciable way. Finally, as we have already suggested, different contact modes of C_{60} likely affect the molecular conductance, and the nature of break junctions is to create many subtly different atomic configurations of the gold electrodes after each metal junction is broken. Due to this, the coordination environment for the C_{60} groups is likely to change significantly during the break junction method, contrary to the stationary tip method in which at least one of the electrodes is an atomically flat surface. Surface roughness has been proposed as a strongly contributing factor to molecular conductance.¹³

This comparison with the BJ method highlights the advantages of using our controlled one molecule lifting experiment. In particular, by determining that only one molecule is attached, the variability of the conductance we have seen can be unambiguously attributed to arising just from a single molecule. We can rule out the presence of more than one molecule in the junction. Moreover, we actually see a reduction in the junction to junction conductance variation, and hence a dramatic increase in the precision of defining the conductance of a *one*-molecule junction. The most likely reason for this reduction is that the molecule is forced to explore fewer junction configurations.

The key advantage of studying C_{60} -dumbbell molecules is that the C_{60} groups behave both as “molecular beacons” and “alligator clips”. Furthermore, a wide variety of different chemical groups can be probed, with single molecule precision. We also emphasize that the principle of targeting one molecule in this way is actually very general and could be applied to other compounds not necessarily containing C_{60} groups. The only prerequisites are that the molecule should be immobile enough at room temperature to be imaged, and hence its position known, and, second, possess a reliable way of attaching at both ends to the electrodes.

This method, however, will not be applicable to small molecules which rapidly diffuse across the surface at low coverage and at room temperature, rendering them impossible to image.

In conclusion, single molecule experiments carried out using the STM are increasing the ability to control and investigate matter at a fundamental level.^{41,42} So far, however, ambient condition methods to wire molecules inside nanojunctions have lacked the sophistication of being able to resolve individual molecules and ensure that only one is wired. Here we have demonstrated that it is necessary to image and target one molecule in order to provide the necessary support to prove the junction we formed contained just one molecule. The large spread in conductance plateaus observed in our break junction studies of molecule 1 gives no clear indication of what the conductance of a *one*-molecule junction is. Also, the ease in substituting the chemical group at the center of the dumbbell is highly advantageous. Combined with the experimental single molecule precision, the versatility of the C_{60} -dumbbell system will provide a straightforward approach to explore the role of chemical structure in relation to electron transport in *one*-molecule electrical junctions.

■ ASSOCIATED CONTENT

S Supporting Information. Materials and methods, tip-sample calibration, control experiments, further examples of the technique on different molecules, and drawings of the different conformations of the molecule. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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