Cross-plane Conductance through a Graphene/Molecular Monolayer/Au Sandwich

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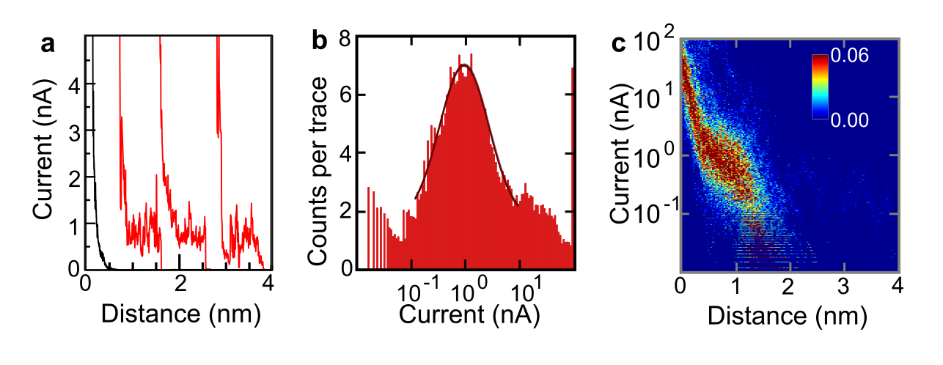
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# **Experimental Supplementary Information**

## Analysis of BPDT at Single Molecule and Film Level

During I (s) experiments, Pico View was controlled using the software developed by Inkpen et al [1]. Data analysis was carried out by the sorting algorithms developed by Lemmer et al [2]. For I (s) experiments, BDPT/Au (111) samples were obtained as following: Au (111) single crystal (99.999% purity, polished with roughness <0.01 μm and orientation accuracy <0.1°, MaTecK GmbH, Germany) was firstly annealed by H2 flame and then, immersed in 100 μM BPDT ethanoic solution for 30 s. Then, the sample was removed from solution, rinsed with ethanol and dried under a stream of N2. Prior molecular adsorption, the Au (111) substrates were H2 flame annealed for 2 min and I (s) experiments were carry out on the same conditions used later for the BPDT samples (shown in **Figure S1**).



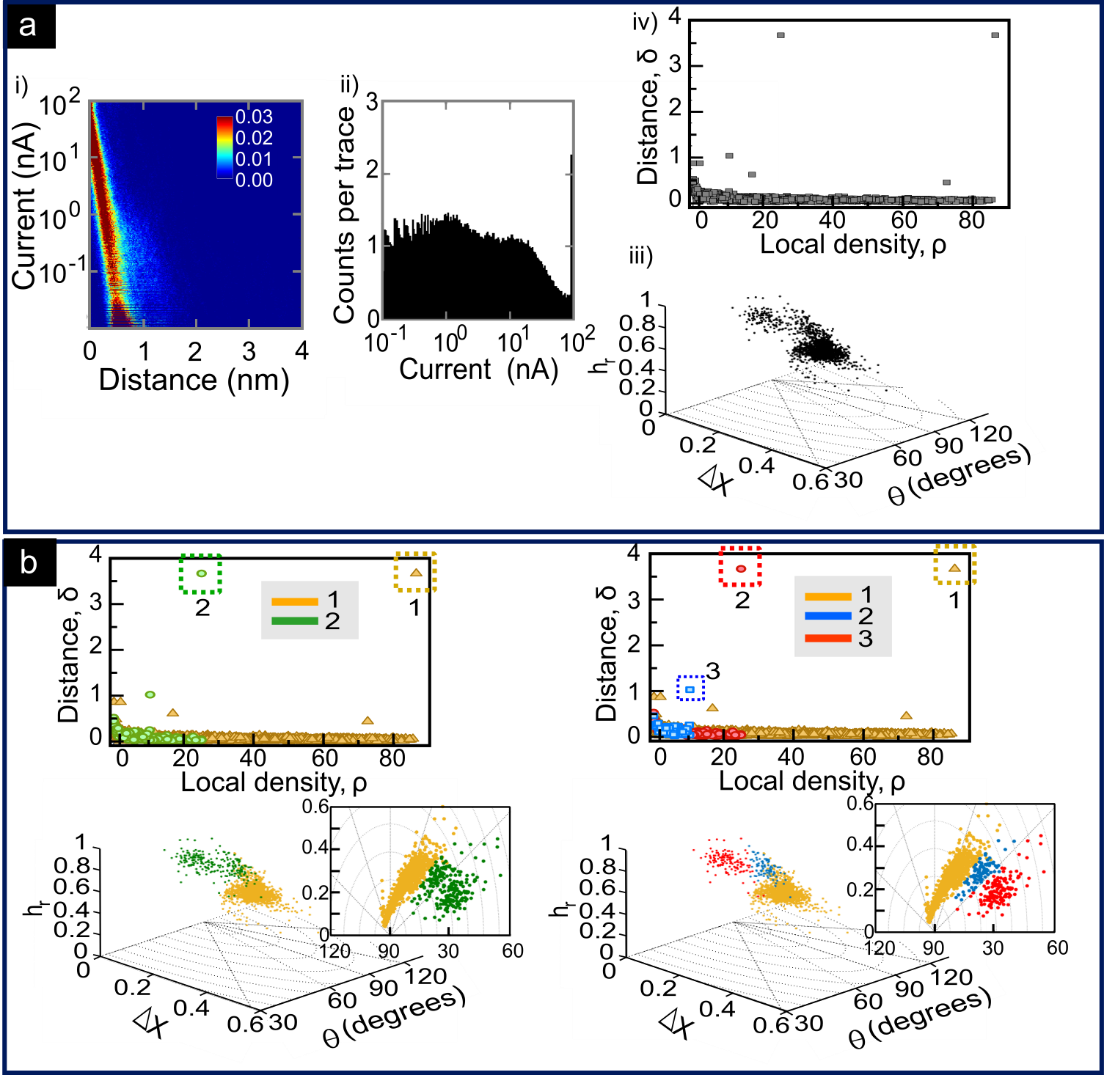
*Figure S1. BPDT molecular conductance data from STM measurements. (a) Typical I (s) traces correspond to the Au-Au (black) and the Au/BPDT/Au junctions (red). They were shifted horizontally for clarity. (b) Current plateaus histogram compiled from traces similar as the ones showing in (a). The peak histogram is centred at 0.91 nA, as noted by the black curve (Gaussian fit, R2 = 0.94). (c) 2D histogram showing all analysed traces. I (s) traces were acquired at I0 and Vbias were 32.5 nA and 0.5 V. Color map indicates the number of count per data points in each trace (2000).*

### I (s) Traces Sorting Methodology

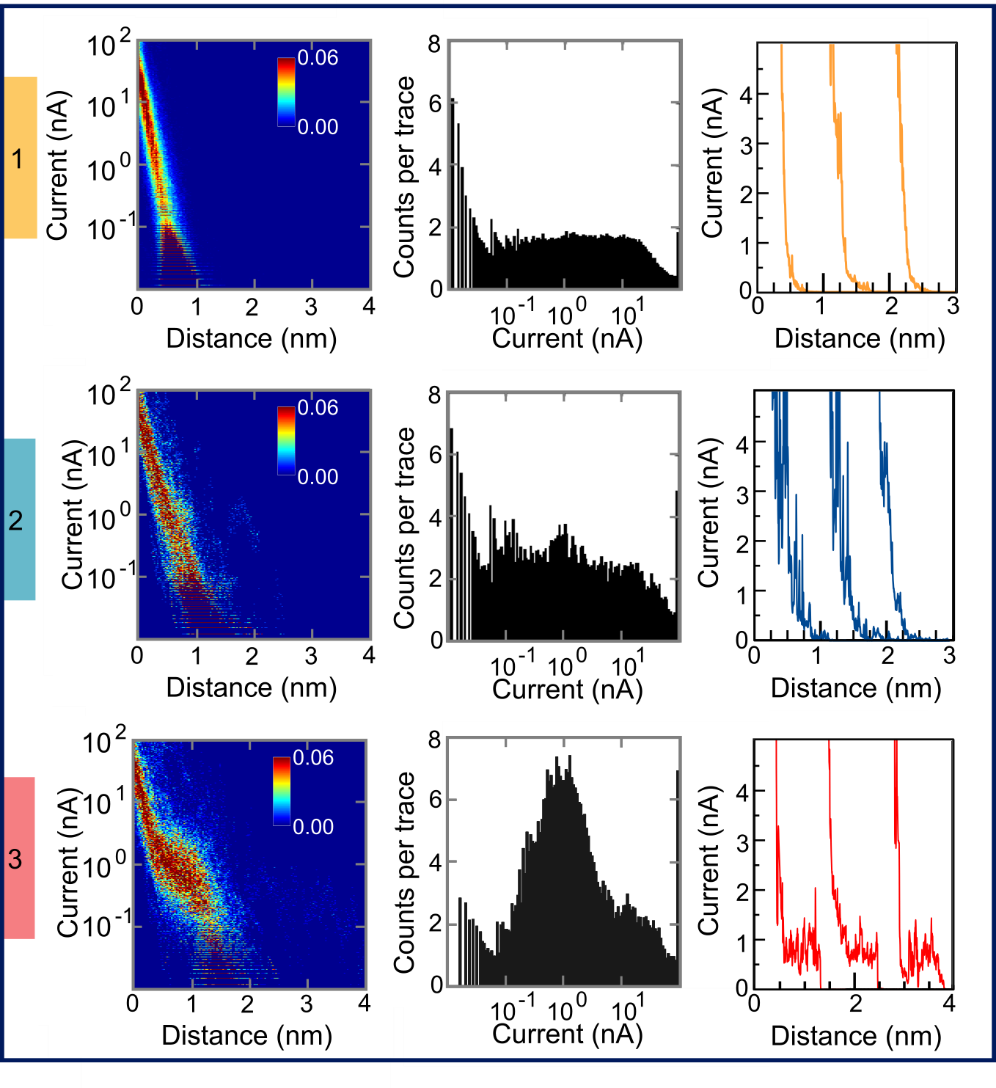
The formation of single molecular conductance junction is a stochastic process; this implies that in a regular experiment just a few I (s) traces will show single conductance events. In order to obtain the molecular conductance, we need to extract the I (s) containing molecular events from the rest of the traces no counting single events. To this end, here we use the recently unsupervised method developed by Lemmer [2]. Briefly, the method implies the following steps:

* Experimental I (s) traces are vectorised.
* A reference vector R is defined. This one is a noise-free exponentially decaying current–distance trace, which is similar to the experimental data without molecular binding events (I0\*exp (β\*s); I0 = current set point and β = exponential decay factor). Starting with the all experimental I (s) traces (Fig. S2 (a)), different reference vectors were tested until find the one, which gives better separation between parameters. In this step, two parameters were used: the data range to be consider (ranging from 0 to 8 nm) and the exponential decay factor (β). The best reference vector was found in the range of 0.08-1.2 nm with I0 = 32.5 nA and β = 10 nm-1.
* Three vector properties in relation to the data sets (X) and R are determinate: the length of the difference vector ΔX=|X−R|; the angle θ between X and R and the reduced Hamming distance hr between vectors.
* ΔX, θ and hr are represented in a 3D-cylinder plot (**Figure S2 (a)**) and ‘fast search and find of density peaks’ algorithm is used to determinate the number of cluster, i.e. group of I (s) traces with similar properties (**Figure S2 (b)**) [3]. The algorithm has its basis in the assumptions that cluster centres are surrounded by neighbours with lower local density and that they are at a relatively large distance from any points with a higher local density. For each data point, two quantities are computed: its local density (ρ) and its distance (δ) from points of higher density (Figure S2 (b), top). These two quantities are plotted giving the ‘decision graph’ (Figure S2 (b) top). The data points with high ρ and relatively high δ are the cluster centres. After the cluster centres have been found, each remaining point is assigned to the same cluster as its nearest neighbour of higher density.

We start the cluster assignment by selecting the two point with highest δ, which were labelled 1 and 2. After selected them as cluster centre the data point were plotted in a cylinder plot as is shown in Figure S2 (b) left. The clustering process effectively found 2 clusters. However a close inspection on cluster 2, revels that this one is actually composed by two clusters. In order to improve the cluster’ sorting, a third point in the decision plot was taken (Figure S2 (b) right panel). Now, the three clusters are effectively sorted, as it clears from comparison of cylinder plots in Figure S2 (b). After the above sorting process, three groups of traces were found. Group 1 and 2 contain plain and noisy exponential decay traces, respectively, while cluster 3, traces with plateaus (see **Figure S3**).



*Figure S2. Sorting process of I (s) traces. (a) Log 2D current–distance (i) and 1D current (ii) histograms of all I (s) traces recorded in the experiment. Bottom-right panel shows the 3D-cylinder plot resulting after vectorising the traces (iii). Top-right panel the decision graph used later for clustering the traces. (b) Clustering based on density. Right panel shows the decision graph after select the point 1 and 2 as cluster centres (top) and the resulting data clusters plotted in a 3D and 2D cylinder plot (bottom, left and right, respectively). Panel right shows the same but after point 1, 2 and 3 were selected as cluster centre. By comparison of 2D cylinder plots, is evident that 3 clusters are needed to describe the data.*



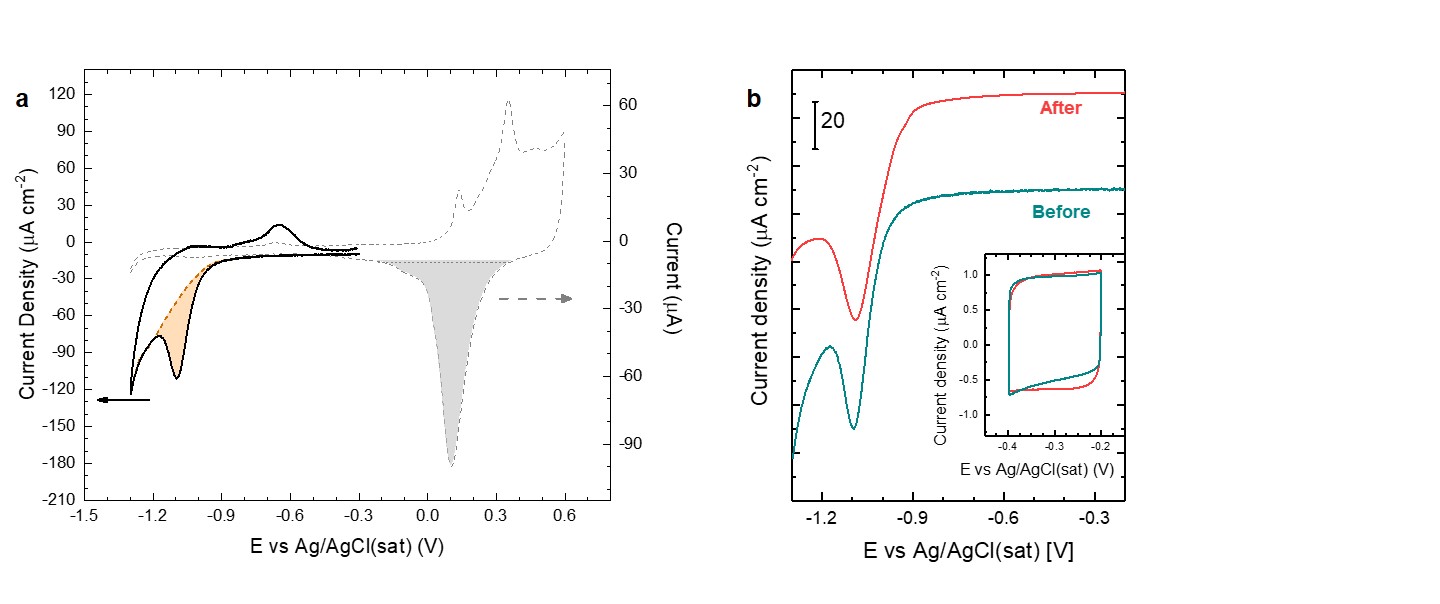
*Figure S3. Statistical analysis of each cluster found in b. From left to right: Log 2D current–distance histograms, 1D current histograms, representative I (s) traces of the cluster Data analysis corresponding to I (s) traces recorded using I0= 32.5 nA and Vbias = 0.5 V.*

### CV Characterisation of BPDT Film

The charge density (q) involved in the reductive peak desorption was obtained by integration of the reduction peak (orange shadowed area in **Figure S4**). The real electrode area was determined through the gold oxide reduction peak after complete electrodesorption of the thiol (grey shadowed area in Figure S4).

Reductive electrodesorption curves for thiolated-SAMs on Au (111) are characterised for a sharp cathodic peak associate to RS-Au + e- → RS- (RS: thiolated analyte). For BPDT-covered Au (111) surface, desorption takes place at current peak located at −1.09 ± 0.01 V and involves a charge density of 62 ± 2 μC cm-2. These values were obtained from five independent samples.

In order to characterise the effect to SAM on gold caused by the removal of photoresist, electrodesorption curves were taken before and after the photoresist is removed. As it shown in Figure S4 (b), electroreduction peak features remain the same after the whole process (i. e. current peak is located at −1.07 ± 0.06 V and its charge density is 67 ± 2 μC cm-2). Furthermore, the CVs in the double layer region (the window potential where the SAM is stable and non-faradaic reaction takes place) are also similar in intensity (inset in Figure S4 (b)), indicating that the chemical structure of the monolayer remains intact.



*Figure S4. (a) Current density vs E profiles for (full black line) the reductive desorption of BPDT SAMs from Au (111) and (dotted grey line) Au (111) substrate. Shadowed areas correspond to the integration area employed for charge peak calculation. (b) Electrodesorption curves of BPDT SAMs on Au (111) before and after the removal of photoresist layer. Inset shows the double layer region for both samples.*

## Fabrication Procedures of Vertical Transport Devices

**Figure S5** presents the detailed fabrication procedures of graphene/BPDT/Au device. The Cr (2 nm)/Au (60 nm) was chosen as the electronic contacts and thermally evaporated onto SiO2 substrate via photoresist mask, as shown in Figure S5 (1). After the lift-off process, the substrate with patterned electrodes was immersed into 1 mM BPDT ethanol solution to immobilize the BPDT molecules onto gold surface, as shown in Figure S5 (2). The BPDT molecules at the junction area were protected by a layer of photoresist 1813 through another lithograph step (Figure S5 (3)) and the rest BPDT molecules at the contacting area were etched away by oxygen plasma (Figure S5 (4)). The protective photoresist on BPDT was removed by immersing the substrate into photoresist remover 1165 for 30 mins. The residue of photoresist remover was washed away by 5 mins DI water rinsing. CVD graphene was transferred following the wet transfer procedures [4], as shown in Figure S5 (6). The top layer of CVD graphene on Cu foil was spin-coated by a 200 nm PMMA layer and the bottom graphene layer was removed using oxygen plasma treatment at 100 W for 2 mins. The supporting Cu foil is etched away by immersing the sample in 15g/L ammonium persulfate solution, followed by a thorough rinse in DI water. The floating graphene/PMMA was carefully picked up by a SiO2 substrate with patterned gold electrodes on top and post-baked at 60°C to promote a stronger graphene/substrate interaction. The post-baking temperature here differs from standard one (180 - 220 °C) to protect SAM layer from oxidation. PMMA layer was then removed by immersing the sample into warm acetone at 60°C for 30 min.

The fabrication yields of devices with different channel sizes are summarised in Figure S5 (b). Originally, the device numbers of each channel size are 32 (red histograms). After the fabrication of graphene top electrodes, the device numbers decrease (blue histograms) due to the fragile nature of graphene and the surface complexity of BPDT modified electrodes. Among them, a number of devices are short-circuited, as the graphene forms contact with Au via the pin holes of SAM layer, leading to a further reduced number of working devices (yellow histograms). The smaller devices are more likely to fail during the fabrication. The corresponding current density of working devices at 0.05 V are summarised in Figure S5 (c).

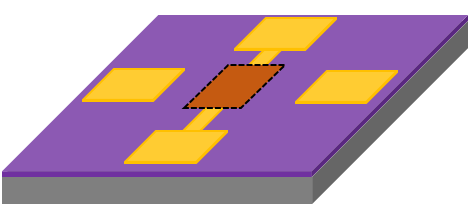
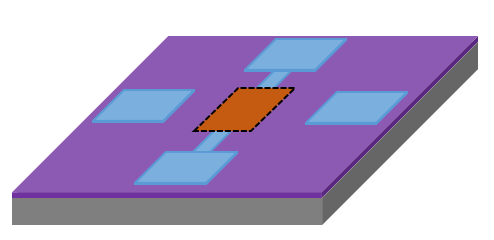
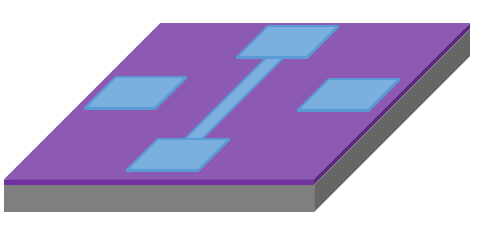
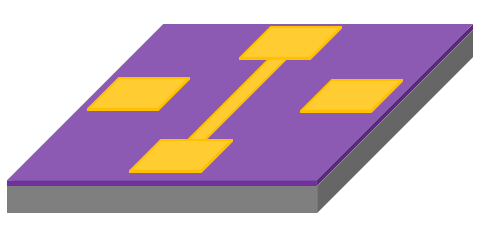
(1) Au layer deposition.

(2) SAM immobilization.

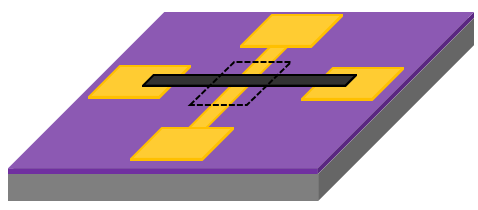
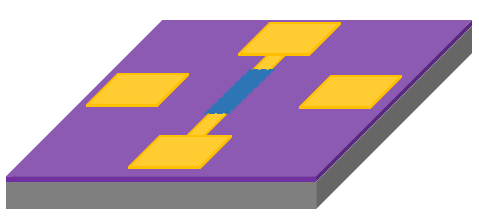
The Au layer will be fully covered by SAM.

(4) Use oxygen plasma etch away the SAM on “contacting area”.

(6) Wet transfer graphene onto this sub, one more lithograph to pattern the channel.



(5) Removal of photoresist.



(3) Protect SAM at “cross area” using photoresist.

a

b

c



*Figure S5. Detailed schematic illustration of device fabrication procedures and the statistical analysis of graphene/SAM/Au junctions. (a) Device fabrication procedures. (b) Histogram of fabrication yields for different junctions. (c) Statistics of current density measured from final working devices.*

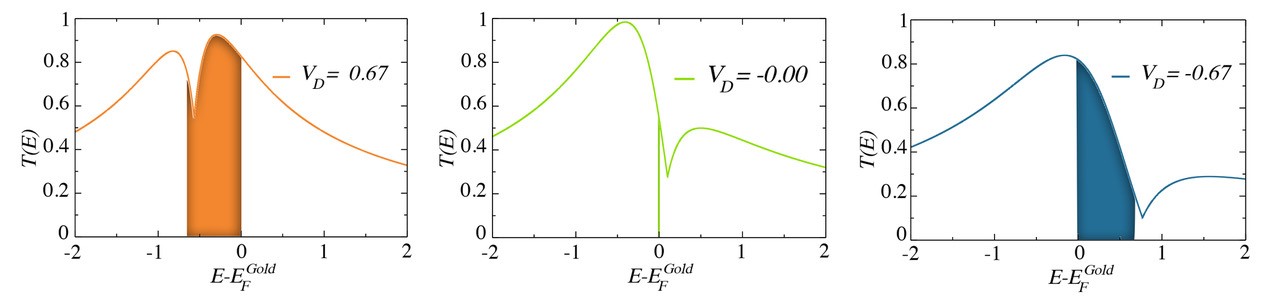
# **Theoretical Supplementary Information**

## Theoretical Calculations

### 3.1 The asymmetry and dip in curve

In the curve and the position of the Lorentzian relative to the Dirac point would create the A-symmetry in the , Figure S6 shows examples of transmission functions at three different drain voltages.

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| --- | --- |
|  | (S1) |



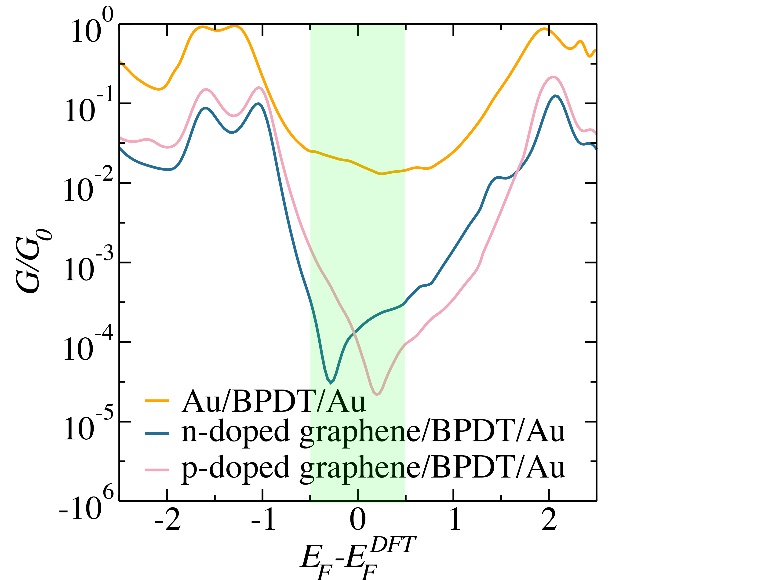
*Figure S6: The current at a given source and gate voltage is obtained by integrating the transmission curve over energies between to .*

### 3.2 DFT Method

To gain insight into the transport properties of graphene/molecule/Au junctions, the geometry of the isolated molecule was optimised using the SIESTA implementation of density functional theory (DFT) [5]. Then the geometry of each contact (BPDT with gold and BPDT with graphene) was optimised in the vicinity of a 111 gold surface and a graphene sheet separately. Thiol anchor groups bind to gold by losing the hydrogen and forming a covalent bond. The gold-thiol distance was found to be about 2.6 nm in our calculations. In contrast, thiol does not form a covalent bond with graphene contact and consequently the hydrogen remains bound to the thiol. In this case we find that thiol-graphene binding distance is 2.9-3 nm. In both systems, the molecule forms an angle with graphene and gold surface due to the nature of thiol anchor group [6]. Finally, a system with Au/BPDT/Au contact and graphene/BPDT/Au contact was constructed and the geometry of the system was optimised using the same method. The mean field Hamiltonian obtained from DFT, was combined with our quantum transport calculation code, GOLLUM to calculate the Green’s function in the presence of the electrodes [7]. The transmission coefficient of electrons of energy E passing from the graphene to gold electrodes is calculated using where is the self-energy due to the contact between the molecule and the electrodes. All calculations were performed using the local-density approximation (LDA) functional of the exchange and correlation functional is used with the CA parameterization along with a double-ζ polarized (DZP) basis set, a real-space grid defined with an equivalent energy cut-off of 185 Ry.

The structure in Figure 1 (c) is periodic in the transverse direction and the molecule is allowed to interact with neighbouring images. Summation over transverse k points therefore describes a periodic array of parallel molecules. In contrast the junction of **Figure S7** is not periodic and contains only a single molecule.

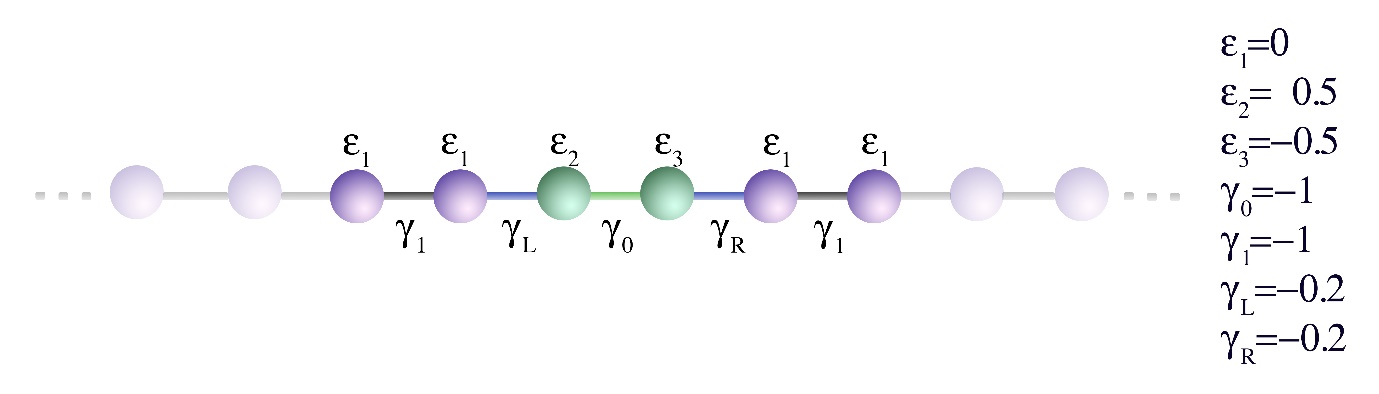
The following figure shows the transmission curves used to obtain Figure 2 (a) of the main text.



*Figure S7. The predicted room-temperature electrical conductance of a n-doped graphene/BPDT/Au junction (blue) and a p-doped graphene/BPDT/Au (pink), and Au/BPDT/Au (yellow) in units of G0. The predicted ratio of conductance per molecule for graphene/BPDT/Au to Au/BPDT/Au depends on the doping of the graphene and on precise location of the Fermi energy EF relative to the frontier orbitals of the molecule. However, over a range of such values in the vicinity of the DFT-predicted Fermi energy the ratio varies from 10-2 to 10-3.*

### 3.3 Applying Source Drain Voltage to Hamiltonian

Tight binding model demonstration of differential conductance (shown in **Figure S8**):



*Figure S8. Tight binding model where the onsite energies are and the hopping elements are .*

In order to introduce a voltage in to the system which shifts the energy levels consider the Bloch Hamiltonian

|  |  |
| --- | --- |
|  | (S2) |

Assuming to be a plane wave:

|  |  |
| --- | --- |
|  | (S3) |

We have

|  |  |
| --- | --- |
|  | (S4) |

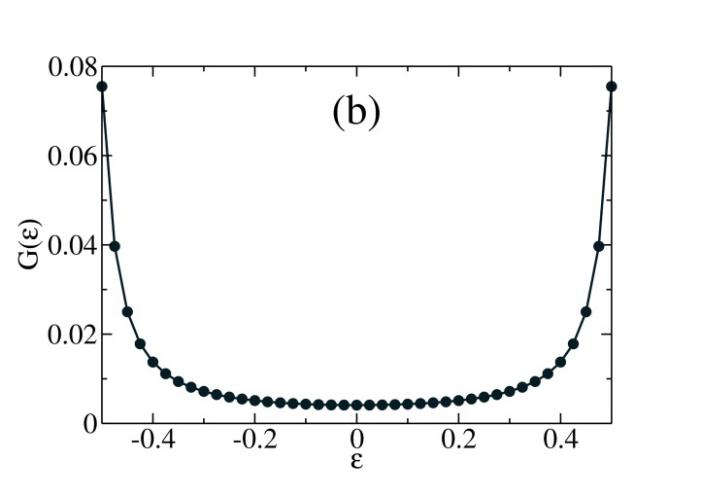
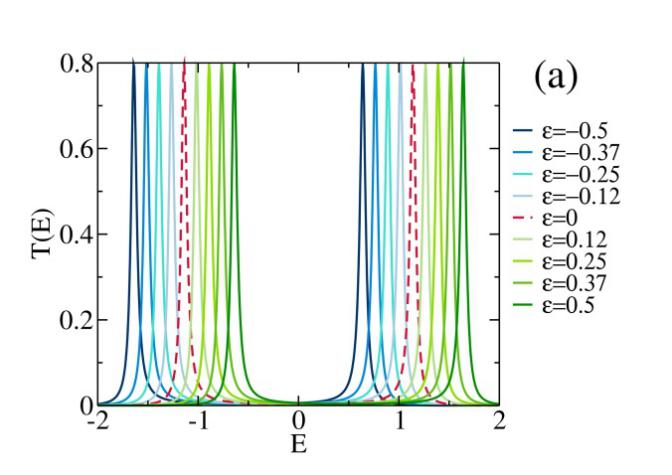
In order to shift the energy spectrum, we make the following changes to the Hamiltonian:

|  |  |
| --- | --- |
|  | (S5) |

To obtain conductance vs voltage, we evaluate the value of conductance at each voltage were the new Fermi energy is

|  |  |
| --- | --- |
|  | (S6) |

To test this approach, the shift in the voltage has been applied to all sites in the chain, shown in **Figure S9**.

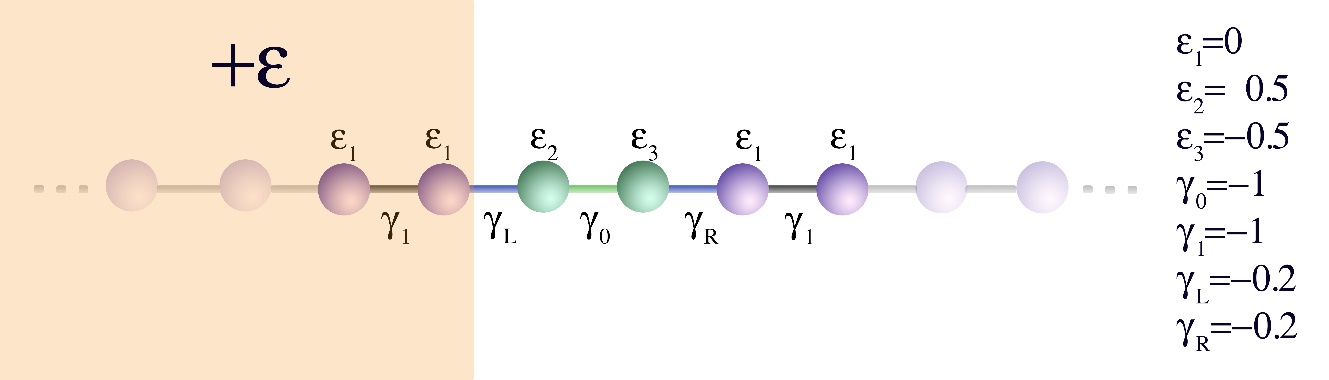


*Figure S9: (a) The transmission coefficient T(E) vs energy (E) for various bias voltages() introduced in equation S5 (b) conductance vs evaluated using equation S6.*

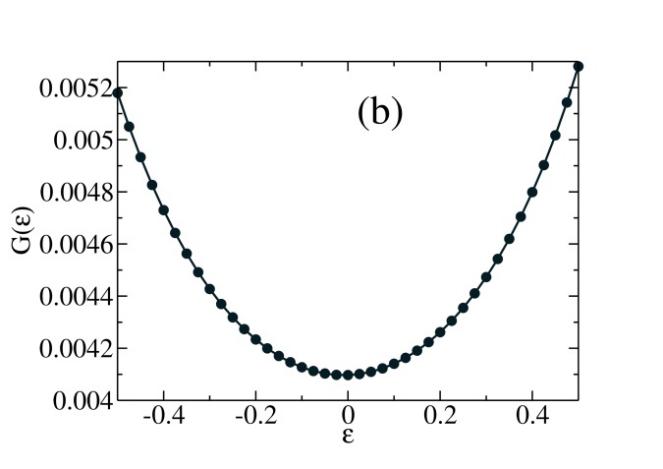
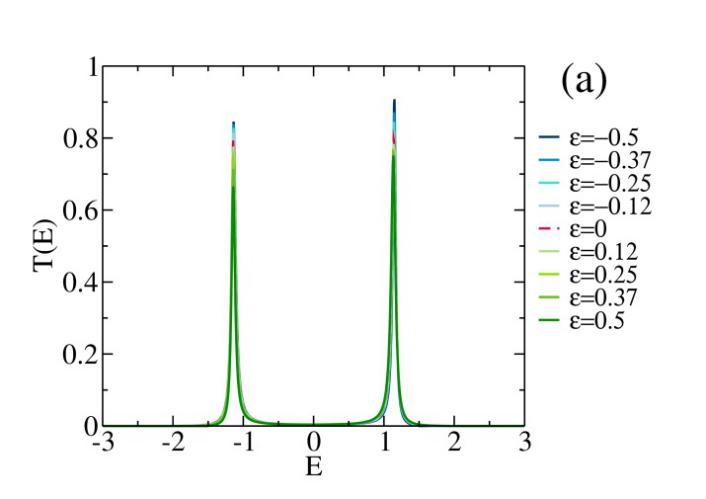
As expected the whole transmission curve and band structure of both leads shifts.

### 3.4 Modelling the Experiment Using Tight Binding Model

For modelling the experiment with a tight binding model, we apply voltage to the left lead as shown in **Figure S10** and **S11**.

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*Figure S10: In a tight binding chain, varying the voltage in one lead. This figure is illustrating method adopted in equation S5.*

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*Figure S11: (a) Transmission coefficient vs Energy for different values of (b) vs . Since the energies of molecular levels remain the same all transmission curves remain the same.*

**Toy Model for z = 2** is shown in **Figure S12.**

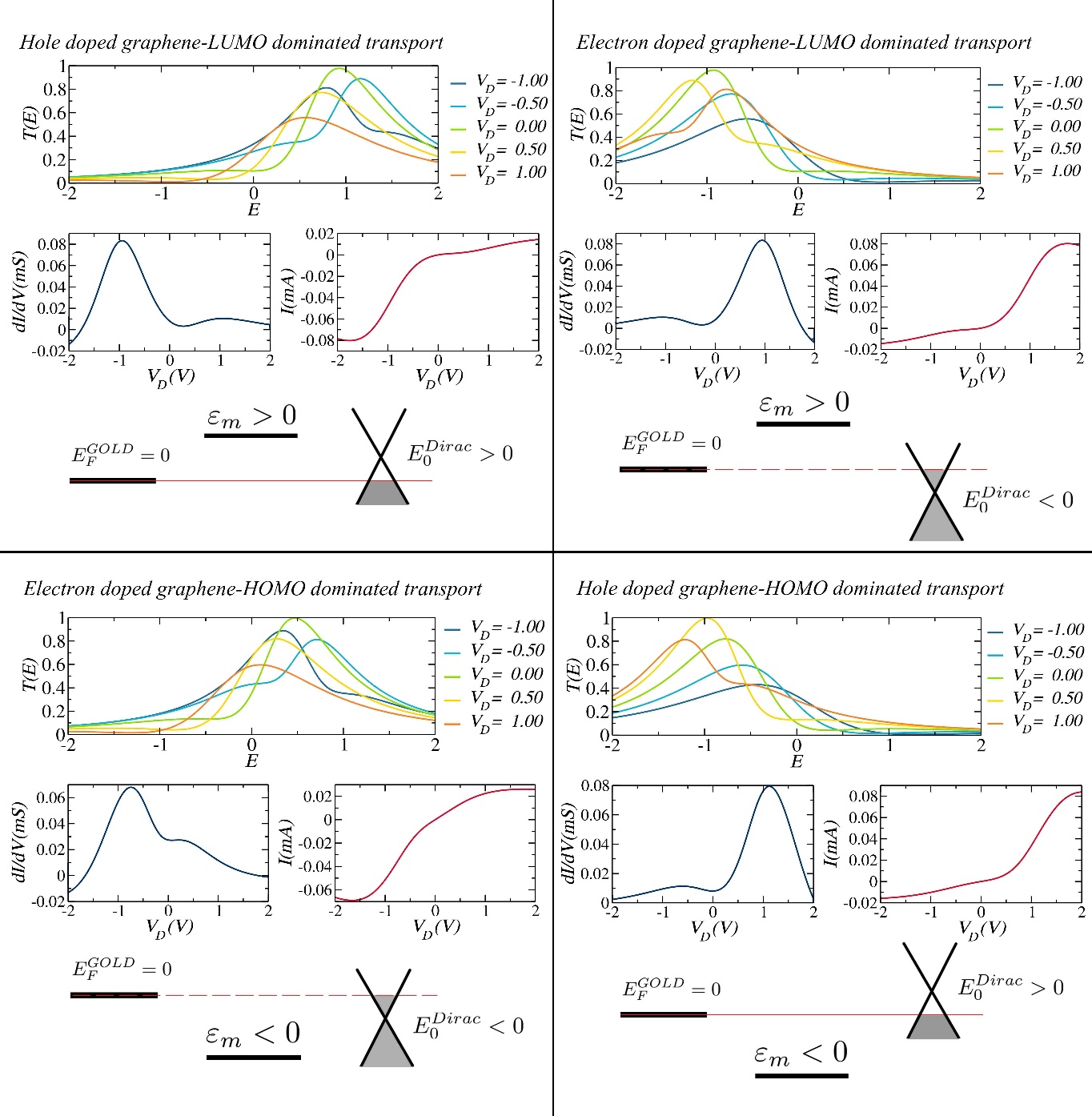
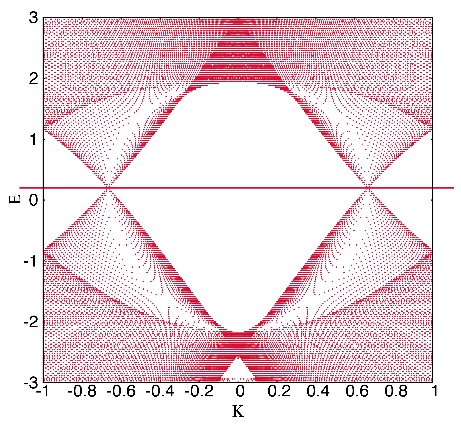
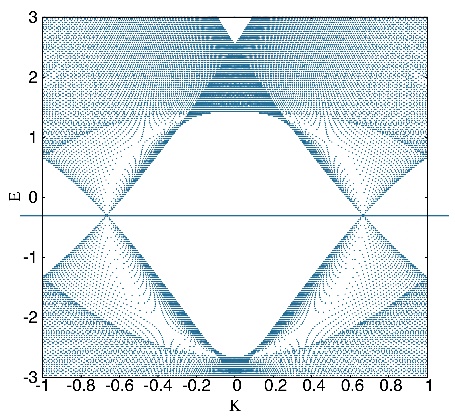
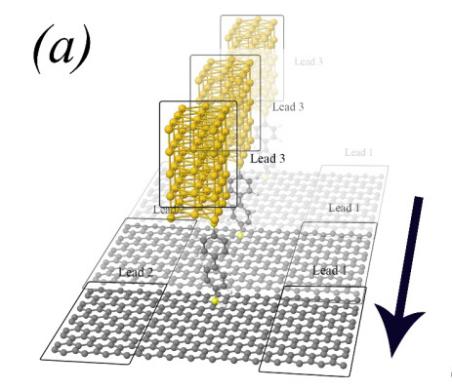


Figure S12. *Four different possibilities for the asymmetry and the dip in the curve, when .*

Graphene base SAMs could be made with various molecules, which have a variety of anchor groups. The electron affinity of these anchor groups would affect the doping of the graphene electrode and determine whether or not transport is LUMO or HOMO dominated. Doping the graphene with boron or nitrogen would also increase of decrease the Dirac point respectively.

### 3.5 Doped and undoped graphene band structures in this work is shown in Figure S13.



c 

b

Figure S13. (a) An illustration of the system under study. (b) Pristine graphene band structure from DFT where , (c) artificially doped band structure.

The monolayer graphene can be doped by the physisorbed molecules on top graphene surface. The calculation in the figure below shows that when decreasing the distance between one unit of BPDT from 6Å to its optimum distance from the graphene (2.9Å), the charge on the molecule becomes more negative. This means that the electrons are transferred from graphene to the molecule resulting in a hole doped graphene.

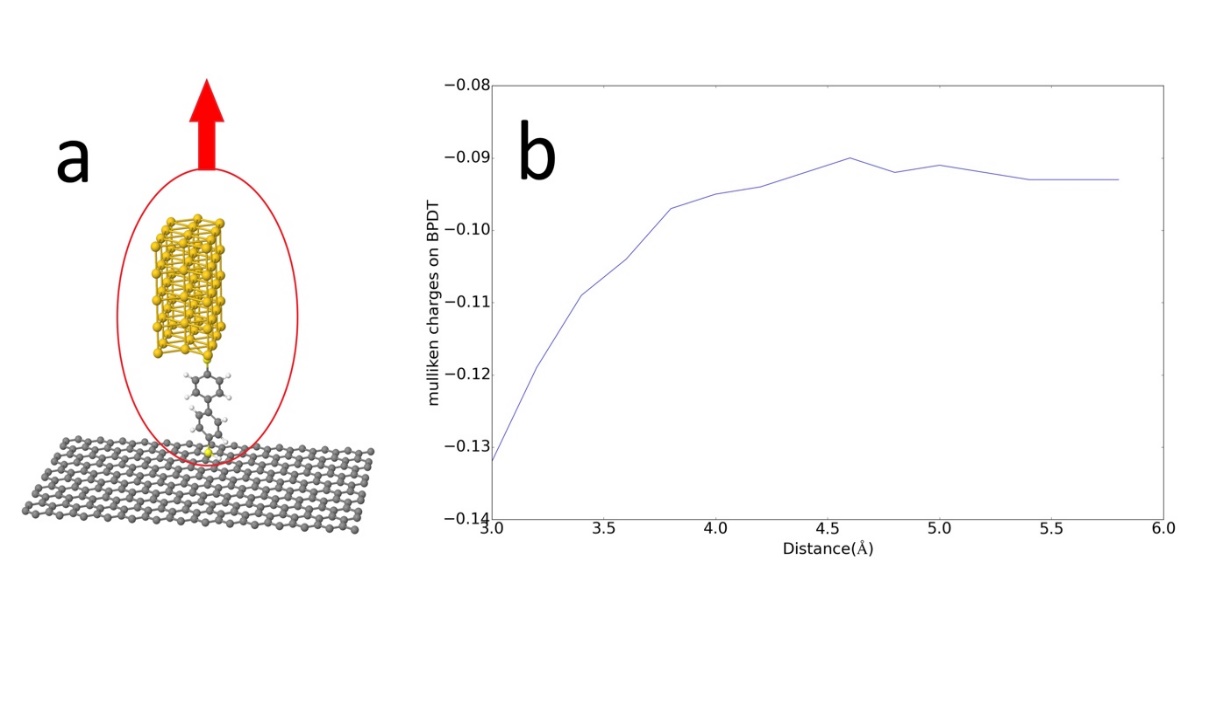


Figure S14: (a) Demonstration of molecule being pulled away from the graphene. (b) The total Mulliken charges on the molecule as it is moved from a distance of 6Å from graphene to its optimum distance from the graphene (2.9Å).

The graphene doped by physisorbed molecules has been reported before in the literature [8-10].

### 3.6 Conductance Ratios

The ratio of theoretical current to experimental current for a molecule in Au/Au junction:

The ratio of experimental current for Au/SAM/graphene and Au/SAM/Au:

The ratio of theoretical current for a single molecule in Au/Au junction to Au/graphene junction:

The ratio of theory to the experiment for a single molecule in Au/graphene junction:

[1] M. S. Inkpen, M. Lemmer, N. Fitzpartrick, D. C. Milan, R. J. Nichols, N. J. Long, et al. New Insights into Single-Molecule Junctions Using a Robust, Unsupervised Approach to Data Collection and Analysis. J Ame Chem Soc 2015, 137, 9971-9981.

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