

In situ formation of highly conducting covalent Au–C contacts for single-molecule junctions

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Charge transport across metal–molecule interfaces has an important role in organic electronics¹. Typically, chemical link groups such as thiols² or amines³ are used to bind organic molecules to metal electrodes in single-molecule circuits, with these groups controlling both the physical structure and the electronic coupling at the interface. Direct metal–carbon coupling has been shown through C₆₀, benzene and π -stacked benzene^{4–7}, but ideally the carbon backbone of the molecule should be covalently bonded to the electrode without intervening link groups. Here, we demonstrate a method to create junctions with such contacts. Trimethyl tin (SnMe₃)-terminated polymethylene chains are used to form single-molecule junctions with a break-junction technique^{2,3}. Gold atoms at the electrode displace the SnMe₃ linkers, leading to the formation of direct Au–C bonded single-molecule junctions with a conductance that is \sim 100 times larger than analogous alkanes with most other terminations. The conductance of these Au–C bonded alkanes decreases exponentially with molecular length, with a decay constant of 0.97 per methylene, consistent with a non-resonant transport mechanism. Control experiments and *ab initio* calculations show that high conductances are achieved because a covalent Au–C sigma (σ) bond is formed. This offers a new method for making reproducible and highly conducting metal–organic contacts.

In this work, we synthesize a series of SnMe₃-terminated polymethylene chains with 4–12 carbons in the backbone, and measure the conductance of single-molecule junctions formed from these molecules using a scanning tunnelling microscope (STM)-based break-junction method^{2,3}. We show that these junctions have a conductance that is significantly higher than those formed with conventional linkers such as thiols² and amines³. For example, with 1,4-bis-trimethylstannylbutane we form a single-molecule junction with a conductance that is about one-tenth of the quantum of conductance $G_0 = 2e^2/h$ (where e is the electron charge and h is Planck's constant). This conductance is \sim 100 times larger than that achieved with 1,4-diaminobutane³. The high conductance we observe suggests strongly that the SnMe₃ groups are cleaved *in situ*, leading to the formation of covalent Au–C bonds (Fig. 1a). Although other explanations (such as C–Sn–Au bonds; see below) are possible in principle, compelling evidence for direct Au–C sigma (σ) bond formation comes from the fact that the conductance of two control molecules that contain covalent Au–C bonds (1,6-bis-(triphenylphosphinyl)auryl)hexane (C6Au) and 1,8-bis-(triphenylphosphinyl)auryl)octane (C8Au) are the same as those of the respective SnMe₃-terminated alkanes⁸. Finally, calculations using density functional theory (DFT)

show that formation of a direct, covalent Au–C bond is energetically favourable and results in a high zero-bias conductance.

Single-molecule junctions were created by repeatedly forming and breaking Au point contacts² with a modified STM (Fig. 1a) in a 10 mM 1,2,4-trichlorobenzene solution of the target molecules. Conductance (current/voltage) was measured as a function of the relative tip/sample displacement to yield conductance traces, which were used to generate conductance histograms. The SnMe₃-terminated alkanes used in this study were prepared by coupling the corresponding di-Grignard reagents with SnMe₃Cl (see Supplementary Information) following known procedures taken from the literature⁹.

Figure 1b compares individual conductance traces from measurements of butane, hexane, octane and decane molecules terminated on both ends with SnMe₃ linkers (C4, C6, C8 and C10, respectively). We see clear conductance plateaux at molecule-dependent conductance values below G_0 that are due to conduction through a molecule bonded in the gap between the two Au point contacts. The position of the conductance plateaux is \sim 0.09 G_0 for C4, and decreases by about an order of magnitude for every two carbons added to the molecular backbone. Furthermore, sample traces show that the plateau length increases with molecule length, as has been observed for other linkers^{10,11}. For the longer molecules, we also see sharp dips within the conductance plateau, separated by about 2 Å. We will discuss these features later.

Repeated measurements give a statistical assessment of the junction properties. Figure 1c presents conductance histograms, generated without any data selection from over 10,000 measurements for each of the five alkanes studied (C4–C12). Each conductance histogram reveals a clear peak at a conductance value that decreases exponentially with molecule length. The positions of these peaks are shown in Fig. 1d, together with conductance measurements of the same linear alkanes terminated at both ends with amine linkers¹².

We find that conductance G decays as $G \approx e^{-\beta N}$ where $\beta = 0.97 \pm 0.02$ is the decay constant and N is the number of methylene groups on the backbone; this value of β is equivalently to a decay constant of 0.76 per Å using a C–C vertical separation of 1.27 Å. This β value is comparable to that of alkanedithiols (0.8 per Å in refs 2,13,14) or alkanediamines¹⁵ (0.79 per Å in Fig. 1d), indicating that the mechanism for electron transfer across these alkane junctions is by means of non-resonant tunnelling or super-exchange¹⁶. Thus, in these single-molecule junctions, we measure transport characteristics of the molecular backbone—tunnelling through the σ -system for alkanes—while achieving a very high coupling across the molecule–metal interface. Extending the fit in Fig. 1d towards the origin shows that we would achieve a G_0 conductance

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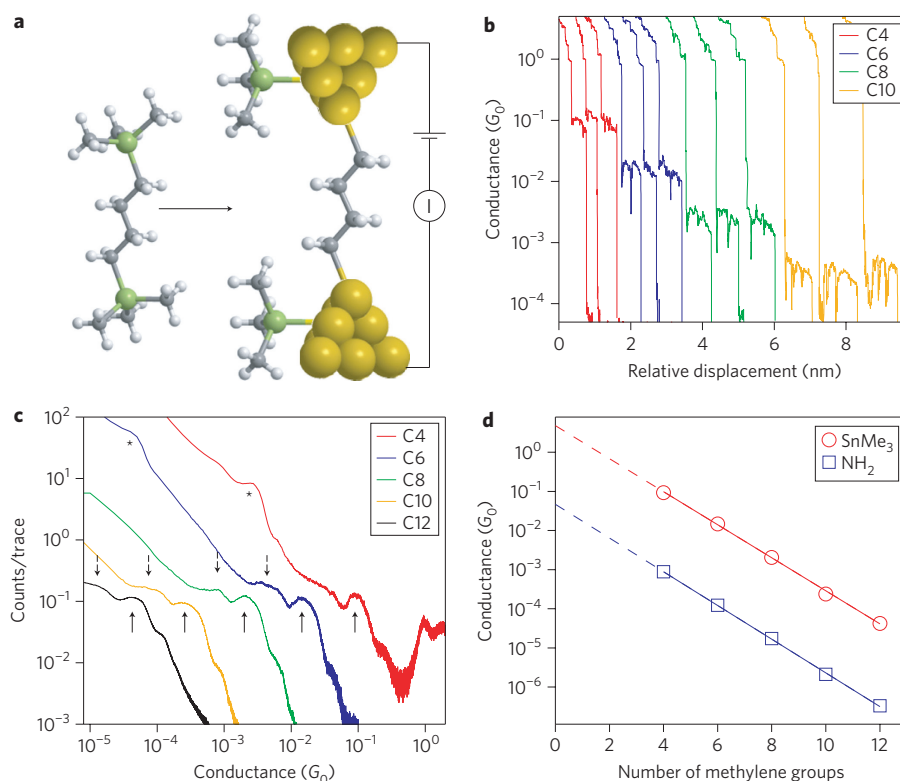


Figure 1 | Conductance data for SnMe₃-linked alkanes. **a**, Junction formation and conductance measurements with 1,4-bis(trimethylstannyl)butane molecules between gold electrodes. (H atoms, white; C atoms, grey; Sn, green). **b**, Sample traces showing conductance (on a logarithmic scale) versus relative displacement for SnMe₃-terminated alkanes with four (**C4**: red), six (**C6**: blue), eight (**C8**: green) and ten (**C10**: yellow) methylene groups in the backbone. **c**, Conductance histograms for **C4**, **C6**, **C8**, **C10** and **C12**. Each histogram is constructed from 10,000 traces, and is generated without any data selection. Bin size is $10^{-4}G_0$ for **C4**, $10^{-5}G_0$ for **C6** and **C8**, $10^{-6}G_0$ for **C10** and $10^{-7}G_0$ for **C12**. Upward arrows indicate primary conductance peaks; downward arrows indicate lower conducting shoulders; asterisks indicate conductance peaks due to the dimer molecule formed *in situ*. **d**, Conductance at the peak (as determined by fitting a Lorentzian to the histograms in Fig. 1c) on a logarithmic scale versus number of methylene groups in the backbone for SnMe₃-terminated alkanes (red) and diamine-terminated alkanes (blue; data from ref. 12).

with a backbone of 1–2 carbons, implying that the transport mechanism will change from non-resonant to resonant at this length. This view is supported by the calculations discussed in the following.

In addition to the main peaks discussed above, we see additional peaks for **C4** and **C6** at conductance values that correspond to the main peaks for **C8** and **C12**, respectively (indicated by asterisks in Fig. 1c). There are, therefore, a statistically significant number of junctions formed with conductance plateaux corresponding to the molecule that has twice the number of backbone carbons, which must be formed *in situ*. From analysing over 10,000 traces measured with a 10 mM solution of **C4**, we see that ~50% of traces show plateaux at the conductance value for **C8**. As a comparison, ~60% of the traces measured with a 10 mM solution of **C8** show plateaux at the conductance value corresponding to **C8**, but no conductance peak is seen if the **C8** solution is diluted to a concentration of 1 mM or lower. A similar analysis of the measurements carried out in a solution of **C6** shows that 85% of the traces have a step at the **C12** conductance value compared with measurements in a **C12** solution, where nearly 100% of the measured traces show a conductance plateau corresponding to **C12**.

Because we see a large number of traces with conductance plateaux of alkanes twice as long as those prepared synthetically, *in situ* dimerization of the carbon backbones must be occurring. This could only result if the C–SnMe₃ bond was cleaved during measurements. The Grignard reaction that we use for synthesis could also yield longer alkanes, but nuclear magnetic resonance (NMR) analysis of the synthesized compounds shows that we

could have only trace quantities (<1%). Such small quantities, corresponding to concentrations of 0.1 mM or less, do not yield a peak in the conductance histograms. These results confirm that we are measuring transport through a Au–(CH₂)_n–Au junction rather than through Au–SnMe₃–(CH₂)_n–SnMe₃–Au, because in the latter case, the ‘dimer’ molecular junction (Au–SnMe₃–(CH₂)_n–SnMe₃–SnMe₃–(CH₂)_n–SnMe₃–Au) would have a different conductance when compared with the molecular junction with twice the number of backbone carbon atoms (Au–SnMe₃–(CH₂)_{2n}–SnMe₃–Au). These results also support the idea that molecules could be bound on one side to the gold surface and can dimerize, making new C–C bonds before bridging the break-junction gap. Although the exact mechanism for dimerization cannot be determined from these measurements, dimerization could occur through a reductive elimination mechanism¹⁷.

Histograms in Fig. 1c also show a small shoulder at a conductance value below that of the main peak for all compounds other than **C4**, as indicated by the downward-pointing (dashed) arrows. The values of the conductance for these broad shoulders correspond to the values observed in the sharp dips seen, for example, in the individual conductance traces shown in Fig. 1b. This indicates that during junction formation and elongation, the conductance value can drop as a result of structural rearrangement within the junction. The fact that these dips occur with a separation of ~2–2.5 Å in traces with longer plateaux (see Supplementary Information for details) suggests that junction rearrangement involving gold periodicity is involved¹⁸. Finally, the lack of such dips for **C4** could indicate that for this molecule, where plateau lengths are

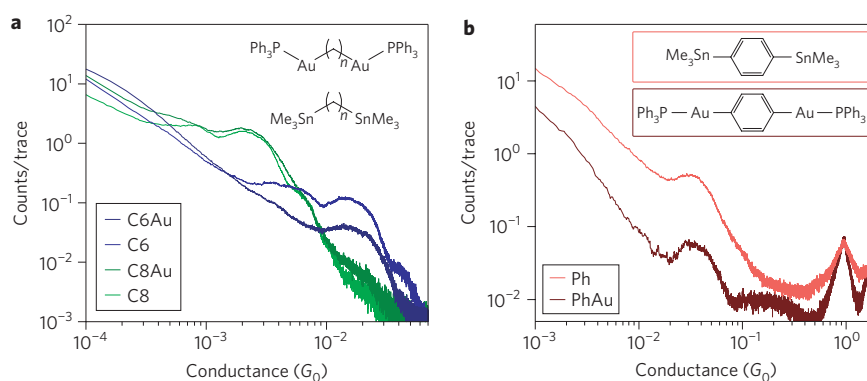


Figure 2 | Conductance histogram for SnMe₃- and Au-PPh₃-terminated compounds. **a**, Conductance histograms for two SnMe₃-terminated alkanes (**C6** and **C8**) and two Au-PPh₃-terminated alkanes (**C6Au** and **C8Au**). Bin size is 10⁻⁵G₀. Inset: structures for SnMe₃-terminated alkanes (bottom) and Au-PPh₃-terminated alkanes (top) with *n* = 6 or 8. **b**, Conductance histograms for SnMe₃-terminated benzene (**Ph**) and Au-PPh₃-terminated benzene (**PhAu**). Bin size is 10⁻⁴G₀. Inset: structures for **Ph** (top) and **PhAu** (bottom).

shortest, junction structures do not allow for reorganization of the molecular attachment point on the electrode¹⁰.

To provide conclusive experimental evidence that we do indeed measure the conductance of Au–C coupled single-molecule junctions, we measured transport through two molecules, **C6Au** and **C8Au**, which, by design, have a Au–C bond built into the structure (Fig. 2a, inset). These were made by reacting the corresponding di-Grignard reagents with triphenylphosphine gold bromide (see Supplementary Information) and were stored under argon until just before measurement because of their limited air stability¹⁹. Figure 2a shows conductance histograms for these and for **C6** and **C8**. We can see that the peaks are at precisely the same location, irrespective of the terminal group. Moreover, for these control molecules, we do not see a peak corresponding to the dimer molecule or the shoulder at lower conductance. As the **C6Au** and **C8Au** molecules have a direct Au–C link by design^{10,20}, these control measurements show that in the case of the SnMe₃-terminated alkanes, Au–C coupled single-molecule junctions are formed. However, these conductance measurements alone are not sufficient to determine whether the PPh₃ capping ligand remains bonded locally to the Au link atom or is removed when the junction forms.

To probe transport through a Au–C coupled conjugated molecule, we synthesized 1,4-bis(trimethylstannyl)benzene (**Ph**) and 1,4-bis-(triphenylphosphinyl)benzene (**PhAu**) (Fig. 2b, inset) as detailed in the Supplementary Information⁸. Conductance measurements of **Ph** and **PhAu** were carried out as described above for the alkanes. For **Ph**, we had to wait about 2.5 h after adding the ~10 mM solution of the compound in 1,2,4-trichlorobenzene before conductance traces demonstrated molecular plateaux, indicating that a chemical transformation was occurring before the conducting molecule was formed. We deduce that the Sn–C link is transformed to a Au–C link during this waiting period while the solution is in contact with the gold electrodes. This result also indicates that breaking the C–SnMe₃ bond is harder with the *sp*² benzene carbon than with the *sp*³ carbons of the alkanes. For measurements with **PhAu**, conductance plateaux were observed as soon as the measurement started (unlike with **Ph**), as we saw with the alkane–Sn compounds. In Fig. 2b, it can be seen that conductance histograms show a peak around 0.03G₀ for both **Ph** and **PhAu**. It is noteworthy that the conductance of these benzene derivatives is not very high; **C4** conducts better than a benzene connected directly to Au electrodes²¹, in contrast to what is observed with other linkers³. This is because the Au atoms are not well coupled to the benzene π system in these molecules, and mainly conduct through the *sp*² linked σ system.

To understand the energetics, physical structure and conductance for the junctions formed in these experiments, we carried out DFT-based first-principles calculations with a gradient-corrected exchange-correlation functional²², as detailed in the Supplementary Information. We first probed the initial C–SnMe₃ bond scission by calculating the energy required to break the C–Sn bond for an isolated molecule²³. We found the energy required to break the backbone C–SnMe₃ bond is ~0.3 eV lower than that required to break the Sn–CH₃ bond. This clearly favours direct binding of the C backbone to the gold tip over a scenario in which a single Me group is removed and a Sn–Au bond forms. We then analysed the binding of the resultant products to a model for the gold electrodes, which were represented by multilayer slabs and a small, localized structure of Au atoms to represent the tips of the electrodes²⁴. For this purpose, we used a shorter example, trimethylethyltin (C₂H₅SnMe₃) and considered several sites on an Au surface with a four- or six-atom model tip structure.

Two scenarios were compared, as shown in Fig. 3a,b. For cleavage at the C–SnMe₃ bond, the SnMe₃ group binds to different Au motifs, including an atop, hollow and bridge site on a flat Au surface, as well as to an apex atom on our tip structure. However, the C₂H₅ part binds only to an undercoordinated gold atom of our tip structure or to the atop site on the Au surface. The energy gained from breaking the C–SnMe₃ bond and forming a Au–C bond on the tip and a Au–SnMe₃ bond on the surface was found to be ~0.8 eV, and varied by ~0.05 eV depending on the location of the SnMe₃ group (see Supplementary Information). In contrast, for cleavage of the Sn–CH₃ bond, the resultant methyl bonds either to an apex atom on the tip structure (energy gain, 0.6 eV) or atop on the flat Au surface (energy gain, 0.3 eV; Fig. 3b). Although these energies do not provide details of the reaction path or transition barriers for rupturing the Sn–C bond and forming an Au–C and Au–Sn bond, they do show that the formation of an Au–C coupled single-molecule junction in the final state is favoured energetically and entropically. Finally, we find that the energy required to rupture the Au–C bond in a **C6** junction bonded to a single gold atom as a model of the electrode is 3.0 eV, which is substantially higher than the associative bond formed between gold and benzene^{6,7} or the links that form donor–acceptor bonds to gold^{10,12,15}.

We used a non-equilibrium Green function approach²⁵ to calculate electronic transmission through junctions formed between gold electrodes and alkane backbones, as illustrated in Fig. 3c. Transmission curves for three alkanes used in the experiments, **C4**, **C6** and **C8**, as well as for **C1**, are shown in Fig. 3d. Transmission at the Fermi level results primarily from the σ channel, as shown by

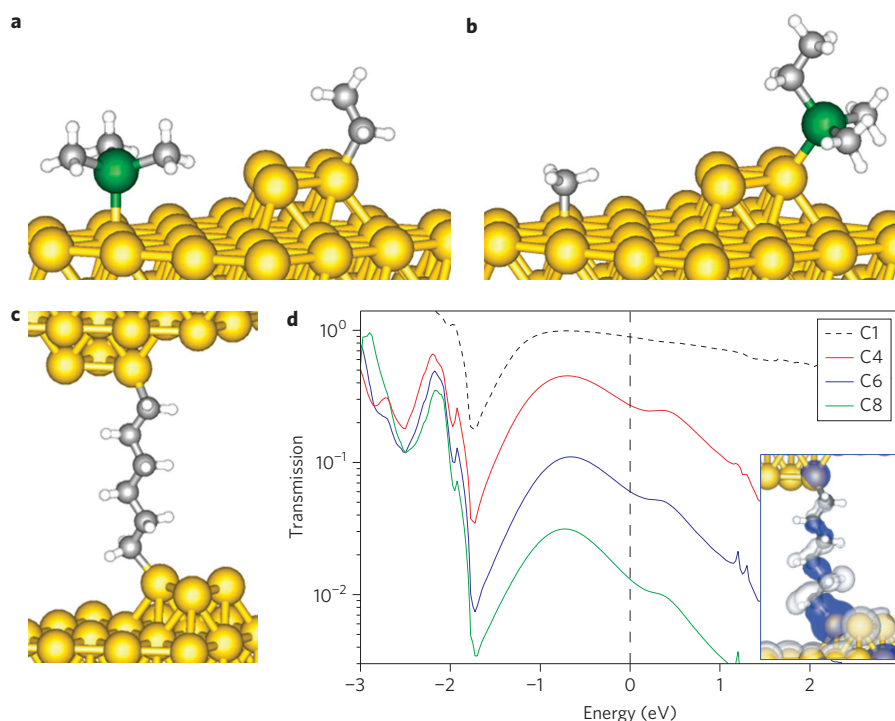


Figure 3 | Calculated geometry and transmission. **a**, Sample geometry used to determine the energy required to first cleave a C–SnMe₃ bond and then bond the SnMe₃ to the Au(111) surface and the C₂H₅ to a model electrode structure. **b**, Sample geometry used to determine the energy required to first cleave the Sn–CH₃ bond and then bond the CH₃ to the Au(111) surface and the SnMe₂C₂H₅ to a model electrode structure. **c**, Sample geometry used in transmission calculations for **C6**. **d**, Transmission (on a logarithmic scale) versus energy (relative to the Fermi energy) for **C1** (dashed back line), **C4** (red), **C6** (blue) and **C8** (green) junctions. Inset: molecular scattering state at the Fermi energy showing σ character.

the transmission channel for **C6** in the inset of Fig. 3d. The conductance is dominated by the occupied resonance that physically derives from the Au–C σ -bond orbitals. These transmission curves have not been corrected for the inherent errors of DFT, so calculated conductance values are larger than those in the experiment, as typically found for other junctions^{26–30}. For more quantitative comparison to experiment, the resonance positions are shifted to account for intramolecular self energy effects as well as the image potential in the junction with a simplified procedure that corrects the conductance³⁰ (see Supplementary Information). The corrected conductance at zero bias is $0.12G_0$, $0.02G_0$ and $0.004G_0$ for **C4**, **C6** and **C8**, respectively, falling within the conductance peak of the experiments. The computed decay constant β for **C4**, **C6** and **C8** is 0.86 per methylene group, somewhat smaller than that measured, but still indicative of non-resonant tunnelling. Calculations for **Ph** were also carried out (see Supplementary Information). We find that transmission near the Fermi energy is dominated by the σ channel, consistent with the low conductance measured and in agreement with recent calculations³¹.

Finally, we return to the trends in conductance seen for **C4–C12**. The exponential decay indicates that the conductance mechanism occurs by means of non-resonant tunnelling. Given the direct Au–C bond link to the electrode, the high conductance found here is due in part to the tunnelling path being shorter (no intervening link groups). Even taking this into account, and comparing, for example, **C6** with 1,4-diaminobutane, we find that the conductance for direct Au–C coupled junctions is a factor of 10 higher. The calculations show that electronic coupling is mediated by a broad resonance due to the Au–C σ -bond orbitals, which is relatively close to the Fermi energy, resulting in high electronic coupling at the interface. Extrapolating to the limit of a backbone with a single CH₂ group, the electronic coupling through that single unit is large enough that the calculated transmission for **C1** shows near unit

transmission over an extended energy range (Fig. 3d). A crossover from through bond tunnelling to single-channel resonant transmission should therefore occur at a backbone length between **C1** and **C4**. Unfortunately, attempts at synthesizing these shorter alkanes were not successful. Focusing on the contribution of the link groups, the high, measured conductance and the calculations suggest that the contact resistance has a value that is close to the minimum value ($1/G_0$) dictated by fundamental quantum mechanics for a single conducting channel.

In conclusion, we have created a class of single-molecule junctions that exhibit well-defined structure and high conductance. Starting with organo-tin compounds, *in situ* reactions result in junction formation where the Au electrodes are covalently bonded directly to the C backbone without an intervening link group. For these single-molecule junctions, the conductance depends on the molecular backbone, allowing molecule-dependent, selective highly conducting linkers for single-molecule junctions.

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Author contributions

Z.L.C., R.S., S.S. and W.C. synthesized the compounds. J.R.W. performed the experiments and data analysis. H.V. carried out all calculations. M.S.H., R.B. and L.V. conceived and designed the experiments and calculations, and co-wrote the paper.

Additional information

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