Quantum interference and heteroaromaticity of \textit{para} - and \textit{meta}-linked bridged biphenyl units in single molecular conductance measurements

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Is there a correlation between the (hetero)aromaticity of the core of a molecule and its conductance in a single molecular junction? To address this question, which is of fundamental interest in molecular electronics, oligo(arylene-ethynylene) (OAE) molecular wires have been synthesized with core units comprising dibenzothiophene, carbazole, dibenzofuran and fluorene. The biphenyl core has been studied for comparison. Two isomeric series have been obtained with 4-ethynlypyridine units linked to the core either at \textit{para}-\textit{para} positions (\textit{para} series 1–5) or \textit{meta}-\textit{meta} positions (\textit{meta} series 6–10).

A combined experimental and computational study, using mechanically controlled break junction measurements and density functional theory calculations, demonstrates consistently higher conductance in the \textit{para} series compared to the \textit{meta} series: this is in agreement with increased conjugation of the $\pi$–system in the \textit{para} series. Within the \textit{para} series conductance increases in the order of decreasing heteroaromaticity (dibenzothiophene $<$ carbazole $<$ dibenzofuran). However, the sequence is very different in the \textit{meta} series, where dibenzothiophene $\approx$ dibenzofuran $<$ carbazole.

Excellent agreement between theoretical and experimental conductance values is obtained. Our study establishes that both quantum interference and heteroaromaticity in the molecular core units play important and inter-related roles in determining the conductance of single molecular junctions.

The measurement and understanding of charge transport in single molecules is of fundamental interest and is relevant to the proposed future applications of molecules in electronic devices\textsuperscript{1–6}. Many studies have addressed correlations between molecular structure and transport properties of molecules wired into metal–molecule–metal nanoscale junctions\textsuperscript{7, 8}. Several experimental approaches are well established for measuring transport through single (or a few) molecules, notably the mechanically controlled break junction (MCBJ)\textsuperscript{9} and scanning tunnelling microscopy-break junction (STM-BJ) techniques\textsuperscript{10}. Combined experimental and theoretical studies\textsuperscript{11} have established that charge transport through molecular junctions is controlled by the intrinsic properties of the molecular backbone, the terminal anchoring group, and the metal leads. Key features are the molecular length, the molecular conformation, the gap between the highest occupied and the lowest unoccupied molecular orbitals (the HOMO-LUMO gap), the alignment of this gap to the Fermi level of the metal electrodes, and the...

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coordination geometry at the metal-molecule contacts. Oligo(arylene-ethynylene) (OAE)-type molecular wires have been widely explored in single molecular junctions12–16. They are π-conjugated, rod-like molecules and their functional properties can be systematically tuned over a wide range of parameters by chemical synthesis17.

In the present work we investigate a series of ten OAE molecules 1–10 whose structures are shown in Fig. 1. The molecular design combines three key structural features: (i) all of the molecules have terminal pyridyl anchoring units at both ends; (ii) each molecule has one of five different core units and (iii) there is either para-para or meta-meta conjugation through the core unit, providing two isomeric series. The dibenzothiophene (1, 6), N-ethylcabazole (2, 7), dibenzofuran (3, 8) and 9,9-dimethylfluorenes (4, 9) are rigid and planar. Heteroaromaticity, i.e., the resonance energy, will decrease in the sequence dibenzothiophene > carbazole > dibenzofuran, reflecting the extent of delocalization of a lone pair from the heteroatom into the π-system of the central ring (S > N > O)18. Fluorene, with no heteroatom and a bridging sp3 carbon atom instead, has a non-aromatic central ring. In contrast to the other molecules in Fig. 1, biphenyl derivatives 5 and 10 possess a flexible and twisted core. It is well known that increasing the torsion angle within a biphenyl unit leads to reduced single-molecule conductance24. This work did not consider the linkage of the anchor units to different positions on the core.

We are aware of only two related reports on the effect of heteroaromaticity on single-molecule conductance. Venkataraman, Breslow and co-workers studied three amine-terminated molecules comprising thiophene, furan and dimethycyclopentadiene cores (11–13, Fig. 2). Based on STM–BJ measurements the authors concluded that aromaticity in the core leads to a decrease in the single-molecule conductance, i.e. the non-aromatic cyclopentadiene derivative 13 has the highest conductance, while the most aromatic thiophene derivative 11 has the lowest conductance14. This work did not consider the linkage of the anchor units to different positions on the core.

A second study concerns multiple pathways through a molecular wire based on fluorene-like molecules25. Several studies have established that para (conjugated) connectivity through a core unit results in enhanced conductance compared to the isomeric meta (reduced conjugation) connectivity. This is ascribed to quantum interference and has been observed experimentally and theoretically in aromatic rings such as benzene26–29, naphthalene24, anthracene24, pyrene30 and anthanthrene31.

The motivation for the present work is to study for the first time the combined effects of two important molecular parameters on the single-molecule conductance of molecular wires: (i) heteroaromaticity in the core of the wire, and (ii) para versus meta conjugation through the core unit.

**Results**

**Synthesis.** For the synthesis of the para-linked 1–5 and meta-linked 6–10 molecules (Scheme 1) a tandem two-pot reaction sequence was followed. To enable the Sonogashira cross coupling of the corresponding aryl dibromide central units (structures 14–2332–39 in SI) at elevated temperatures, desilylation of 4-((trimethylsilyl) ethynyl)pyridine44 with TBAF (1 M in THF) was performed in 1,4-dioxane (room temperature for 30 min). Since the light-sensitive 4-ethynylpyridine is not stable in air, the mixture was directly subjected to the aryl dibromide in the presence of PdCl2(PhCN)2, Cul, t-BuP, and (i-Pr)2NH, to give the target structures 1–10 in very good yields (Supplementary Note 1). All the compounds were characterized by 1H and 13C NMR spectroscopy, mass spectrometry and elemental analysis. In addition, to assess the extent of conjugation within compounds 1–10 their UV–Vis absorption spectra were measured in a dilute and aerated dichloromethane solution at room temperature (Supplementary Figure 1). The optical HOMO–LUMO gaps ($E_g$) were calculated from the onset of the absorption spectra.

**Figure 1.** Structures of the molecules discussed in this work and their nomenclature. The structures represent the para-linked series 1–5 (top) and meta-linked series 6–10 (bottom).

**Figure 2.** Molecules studied in ref. 24. Amine-terminated molecules 11–13 measured by STM-BJ.
and are listed in Supplementary Table 1. Compounds 1–5, with the anchor groups attached in the para positions, show a smaller HOMO–LUMO gap compared to the meta isomers 6–10. This is consistent with reduced conjugation in the meta series.

**Single-molecule Conductance Measurements.** Single-molecule conductance measurements of 1–10 in molecular junctions were performed using a home-built mechanically controllable break junction (MCBJ) setup at a bias $V_{bias} = 0.1$ V. Figure 3a shows typical individual conductance $G$ (in units of quantum point conductance $G_0 = 2e^2/h$) versus distance ($\Delta z$) stretching traces in the measurement of $N_p$. The conductance in the molecule-free traces (black line) reveals exponential decrease characteristics upon the stretching process. When molecule $N_p$ is present a pronounced conductance plateau around $10^{-5}G_0$ could be detected (green line) after the Au–Au contact breaks, which is assigned to the gold–molecule–gold junction. Since the break junction method can create a large number of molecular junctions with different molecule–electrode contact geometries, more than 1,000 curves were recorded for statistical analysis to determine the most probable conductance of the molecular junctions. We further introduced a relative distance ($\Delta z$) and defined $\Delta z = 0.5 \pm 0.1$ nm corresponds to the “snap-back” nanogap which forms immediately upon breaking of the gold–gold atomic contact41. The all-data two-dimensional (2D) histogram (Fig. 3b) exhibits features of gold–gold contacts around $G \geq 1G_0$, followed by another well-defined conductance scatter group in the range of $10^{-1}G_0$ to $10^{-6}G_0$, which is attributed to the formation of single–molecule junctions. Figure 3c–d demonstrate the comparison between molecules with different bridging units and anchoring positions. For the compounds 1–3 with the para–para connectivity, the conductance clearly increases in the sequence $S_p < N_p < O_p$. However, for the isomers 6–8 where the anchoring groups are attached at meta–meta positions, the conductance reveals a different trend, $S_m \approx O_m < N_m$. Control experiments using analogues with a carbon bridge (4-Cp and 9-Cm) and without any bridging atom (5-2Hp and 10-2Hm) were also conducted. The conductance of 2Hm could not
in the experiments, including are presented in the Supporting Information (Supplementary Figures 24–33). No multiple features were observed higher conductance for the most probable conductance extracted from conductance histogram. O for the conductance of the fully-stretched configurations, while m shows a slightly m lower conductance than para junction obtained by linear fitting of the master curve. 

Table 1. Most Probable Conductance Values as Obtained from MCBJ Experiments and Computations.

| Compound | MCBJ (log(G/G0)) | DFT (log(G/G0)) | DFT vs. MCBJ (log(G/G0)) | JFP (%) | Electrode separation (nm) | Theoretical length (nm) |
|----------|------------------|-----------------|---------------------------|---------|--------------------------|------------------------|
| 1-Sp     | −5.79 ± 0.30     | −5.93 ± 0.16    | −5.50 − 5.74 0.72 0.66 69 | 2.04 ± 0.45 | 2.04                   |
| 3-Np     | −5.22 ± 0.40     | −5.74 ± 0.17    | −5.15 − 5.36 0.67 0.70 83 | 2.01 ± 0.23 | 2.02                  |
| 3-Op     | −5.04 ± 0.47     | −5.47 ± 0.22    | −5.10 − 5.33 1.37 1.19 99 | 1.92 ± 0.26 | 2.03                  |
| 4-Gp     | −5.55 ± 0.44     | −5.81 ± 0.12    | −5.44 − 5.66 0.09 0.68 70 | 1.84 ± 0.22 | 2.03                  |
| 5-2Hp    | −5.40 ± 0.36     | −5.68 ± 0.11    | −5.30 − 5.55 1.32 2.34 83 | 2.11 ± 0.23 | 2.08                  |
| 6-Sm     | −6.34 ± 0.47     | −6.65 ± 0.35    | −6.34 − 6.40                       | 1.64 ± 0.29 | 1.51                  |
| 7-Nm     | −5.76 ± 0.48     | −6.41 ± 0.25    | −6.06 − 6.06                       | 1.60 ± 0.14 | 1.56                  |
| 8-Om     | −6.32 ± 0.38     | −6.84 ± 0.24    | −6.40 − 6.52                       | 1.65 ± 0.19 | 1.55                  |
| 9-Cm     | −5.66 ± 0.82     | −5.90 ± 0.39    | −5.74 − 6.34                       | 1.46 ± 0.29 | 1.51                  |
| 10-2Hm   | <−7              | <−7            | −7.38 − 7.89                       | —        | 1.41                  |

be measured within the detection range of our setup. This can be explained by the meta coupling combined with a non-planar biphenyl core giving a conductance value below the direct tunneling conductance.

As the junction configuration is known to have a significant effect on the single–molecule conductance, we further explored the master curves composed of the fitted conductance with standard variation at each cross-sectional distance point. After a linear fitting, the Np junction conductance with a fully stretched molecular conformation before the junction rupture can be deduced as 10−5.74±0.17 G0, which should be closer to the theoretical predicted configurations.

It is found that there is some difference in the conductance comparison among different molecules: Om shows lower conductance than Sm for the conductance of the fully-stretched configurations, while Om shows a slightly higher conductance for the most probable conductance extracted from conductance histogram.

The key results of the MCBJ measurements are summarized in Table 1 and the corresponding original results are presented in the Supporting Information (Supplementary Figures 24–33). No multiple features were observed in the experiments, including 3-Op and 8-Om. The lower peaks covered by the grey area below 10−7 G0 is the noise level of the MCBJ experiments (Fig. 3(c,d)). All the curves were used for the statistical analysis without any data selection. Junction formation probability (JFP) is the proportion of molecular stretching traces with a pronounced plateau relative to the total number of traces (Table 1). It is judged by area ratio of the peak in the plateau length distribution. Direct tunneling traces have no plateau and decay faster to the noise level, corresponding to the smaller stretching peak alongside the molecular peak in the plateau length histogram. (Supplementary Figures 24–33).

Several interesting conclusions can be drawn from the comparative conductance values of these molecules. First, in all cases, molecules with para connectivity 1–5 present larger conductance values than their meta isomers, regardless of the bridging unit. This can be attributed to the partial de Broglie waves traversing in different paths through the core being in phase in the para isomers, giving rise to a constructive quantum interference (QI) effect. On the contrary, in the meta-anchored isomers the waves are out of phase leading to destructive quantum interference. The conductance relationship of the para and meta molecules is consistent with that of molecules with a central single benzene ring27–29, indicating the quantum interference effect can still operate in polycyclic compounds. Secondly, the structure of the central core plays an important role in the conductance of QI molecules. It is noted that the largest difference between the para– and meta–anchored molecules (ΔG) is for the dibenzofuran pair 3-Op and 8-Om, 1.37 log(G/G0). However, as we reported previously, the differences between para and meta linked molecules are nearly 1.50 log(G/G0) in benzene-cored analogs29. The lower experimental differences in the present study demonstrate that the quantum interference effect has not been amplified, and is even slightly reduced, by bridging the two benzene rings with a five-membered ring. Additionally, differences of the conductance in fully-stretched conformations between para– and meta–anchored molecules follow the increasing order of ΔGC < ΔGN < ΔGS < ΔGO, illustrating that the heteroatom can also contribute to the expression of the quantum interference. The electrode separations (zcorr in Table 1) are in good agreement with the theoretical molecular lengths. This indicates that in the fully stretched configuration, the molecular junctions are primarily linked by the gold–nitrogen bonds.

Moreover, there is no distinct correlation between the plateau length (or JFP) and the nature of the bridging atoms (S, N, O or C), demonstrating that these atoms have no significant influence on the conductance of the molecular junction. Furthermore, we did not observe any additional conductance group during the experiments for the ten molecules. We attributed this fact to three reasons. Firstly, pyridyl-terminated compounds have been reported to show well-defined peaks in the conductance histograms resulting from the high directionality of the donor-acceptor binding between N lone pair and Au15, 44, 45. Secondly, the alkyl groups connected to the bridged
atom (N and C) sterically hinder the interaction between the electrode and the core of the molecule as well as restricting any π-π interaction of two molecules. Thirdly, molecules with similar core structures have been reported19, 22, 23 to exhibit only one conductance statistical peak, suggesting that the junction formed by the core of the molecule is not robust enough during the elongation process. In the control experiments with 5-2Hp and 10-2Hm, however, we observed such an obvious difference that the conductance of 5-2Hp is higher than that of 10-2Hm by almost two orders of magnitude.

**Theory and Simulations.** To understand the effect of pendant groups on quantum interference in the molecules of Fig. 1, we first consider their two tight-binding representations shown in Fig. 4, connected to 1-dimensional external leads.

The tight binding model is introduced to illustrate the underlying trends in the transmission function and to allow us to obtain an analytic formula. Figure 5 shows results for various values of alpha, to reveal the evolution of the transmission curves with increasing coupling to the pendant groups. In Fig. 6a, to use the simplest possible description, the same value of alpha = 1 is used for all molecules (for more information see Supplementary Table 5). When α = 0, the pendant orbital is decoupled from the central core. Since the latter is a bipartite lattice, in the meta case, destructive interference should occur at the centre of the HOMO–LUMO gap (i.e. $E = 0$)11, 30, 31. The black curves in Fig. 5 show the resulting transmission coefficients $T(E)$, when $\varepsilon_b = 0$. The other curves in Fig. 5 show how the transmission coefficient evolves as the coupling $\alpha$ to the pendant orbital is increased from zero (black curves) to unity (red curves).

The above results show that in the absence of pendant groups (i.e. when $\alpha = 0$) the meta case shows a sharp transmission dip due to destructive interference at the gap centre, which is absent in the para case. In the presence of pendant groups (i.e. when $\alpha$ is non-zero) this destructive interference is alleviated in the meta case. In the para case, the non-zero coupling to the pendant group introduces a new conductance pathway, which can cause destructive interference within the gap, signaled by the Fano lineshape just below $E = 0$. Further examples of this evolution for different choices of $\varepsilon_b$ are presented in the SI. For the values of $\varepsilon_b$ shown in Supplementary Table 5, Fig. 6a shows the resulting transmission coefficients $T(E)$ at $\varepsilon_b = 0$. Other curves in Fig. 5 show how the transmission coefficient evolves as the coupling $\alpha$ to the pendant orbital is increased from zero (black curves) to unity (red curves).

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The electronic interference structure calculations leading to transmission curves (Fig. 6b) were performed using the DFT code SIESTA. The optimum geometry of the isolated molecules was obtained by relaxing the molecules until all forces on the atoms were < 0.05 V/Å. The SIESTA calculations employed a double-zeta plus polarization orbital basis set, norm-conserving pseudopotentials, an energy cutoff of 200 Rydbergs defined the real space grid and the exchange correlation functional was Local Density Approximation (LDA).

To calculate the conductance through these two groups of molecules, para and meta shown in Fig. 1, they were attached to gold leads via the pyridyl anchor groups. The leads were constructed of 6 layers of (111) gold each containing 30 gold atoms. Transport calculations were carried out both for flat electrodes and for electrodes containing adatoms, as shown in Fig. 7. According to DFT, the molecule binds most favourably to a top site, with a binding energy of about 0.8 eV at a distance of 2.3 Å (Fig. 7 and Supplementary Figure 34–35) between the terminal nitrogen atoms and a 'top' gold atom. This most-favourable binding geometry has been used in all simulations. A Hamiltonian describing this structure was produced using SIESTA and the zero-bias transmission coefficients \( T(E) \) were calculated using the Gollum code. An excellent agreement between theoretical and experimental conductance values has been obtained (Fig. 8), by choosing a Fermi energy of \( E_F = -0.8 \text{ eV} \) relative to the DFT-predicted value. Supplementary Figure 49 shows that the transmission coefficients of meta-connected molecules are all lower than those of para connected molecules over a wide energy range within their HOMO–LUMO gaps, in agreement with a tight-binding model of \( \pi \)-orbital transport (Supplementary Figures 44–48). In the latter case, in the absence of bridging atoms (5–2Hp and 10–2Hm) there appear sharp transmission dips due to destructive interference in the meta case, which are alleviated by the presence of pendant groups. In contrast, in the para case, constructive interference in the \( \pi \)-channel is preserved in the presence of bridging atoms. On the other hand, in the DFT-based transmission curves perfect destructive interference is masked by the presence of sigma orbitals, which provide a parallel path for conductance.

Discussion

We conclude, therefore, from our experimental and theoretical data for the para series 1–4 and the meta series 6–9, that there is a clear correlation between aromaticity of the central ring when heteroatoms are present and the single-molecule conductance value in the para series. Aromaticity follows the sequence: S > NEt > O > CMe₂. Our conductance trend for the heterocyclic para series, i.e. O > NEt > S is in agreement with a previous experimental study by Venkataraman, Breslow et al. on monocyclic core units (furan > thiophene) (Fig. 2). However, the fluorene derivative 4-Cp (which does not have a heteroatom in the core) shows a lower conductance than 2-Np and 3-Op although it exhibits a non-aromatic core. The reason for this exceptional behaviour of 4-Cp is not clear. However, we note that other workers have observed that the single-molecule conductance of fluorene-based cores do not follow expected trends.

These results demonstrates that a non-aromatic core unit does not necessarily lead to higher conductance since the polycyclic series 1–5 exhibits a clear difference in comparison to the monocyclic series shown in Scheme 2. However, our data show that the sequence is very different in the meta series where dibenzothiophene ≈ dibenzofuran < carbazole. Multiple factors (such as quantum interference, aromaticity and electronegativity) and their composite effects should be taken into consideration in explaining the trends in the conductance. Our results
show that bridging heteroatoms alleviate destructive quantum interference in the meta-connected molecules. The contribution of electronegativity of the bridging atoms should not be ignored. For the meta series dibenzothiophene 6-5m and dibenzofuran 8-0m represent both extremes. Dibenzothiophene 5m is the most aromatic and therefore it lowers the conductance. As was mentioned above, dibenzofuran 8-0m is the least aromatic core unit. Therefore, based on the conclusions of the series shown in Fig. 2, 8-0m should be the most conductive molecule. However, the lone pair of oxygen is tightly bonded due to oxygen’s high electronegativity, which hinders the delocalization of electrons and decreases the electron density of the conjugated π system in 8-0m. The carbazole derivative 7-Nm is the most conductive in this meta series because it is less aromatic than dibenzothiophene, but also bears a lone pair which allows transmission through the molecule. The conductance of model non-bridged compound 5-2Hp is reduced because of the dihedral angle between the two phenyl units. Model compound 10–2Hm shows no conductance within the detection limit of the MCBJ setup. This is consistent with the bridging atom of 6–9 planarizing the core, which is essential for raising the conductance in the meta-series.

We have studied the single-molecule conductance of ten oligo(arylene-ethynylene) derivatives with five different core units (dibenzotheniophene, carbazole, dibenzofuran, fluorene and biphenyl) attached to gold electrodes by pyrrolyl anchoring groups. Within the two series there is either para-para or meta-meta conjugation through the core unit. In all cases molecules with para connectivity present larger conductances than their meta isomers, regardless of the bridging unit. We have experimentally and theoretically observed clear and distinct trends in the para and meta series. In the para series there is a clear correlation between aromaticity of the central ring and the single-molecule conductance values in the sequence dibenzofuran > carbazole > dibenzothiophene, in agreement with a previous experimental study on monocyclic core units (furan > thiophene). However, in the meta series the carbazole derivative is the most conductive: the sequence dibenzothiophene ≈ dibenzofuran < carbazole. It is concluded that the nitrogen lone pair facilitates transmission through the molecule. Overall, we find that constructive quantum interference in the para-connected molecules persists in the presence of bridging atoms and is partly masked by the presence of sigma channels, whereas bridging atoms alleviate destructive quantum interference in the meta-connected molecules. Our comprehensive study establishes that both quantum interference and heteroaromaticity in the molecular core units play important and inter-related roles in determining the conductance of single molecular junctions. These results should assist in future research in the development of new molecules for incorporation into nanoscale molecular circuits.

Methods

Synthesis. Details of the synthesis and molecular characterization are in the Supplementary Notes 1–2. Synthetic procedures, characterization data; UV–Vis absorption; NMR spectra; and MCBJ conductance analysis of compounds 1–10; additional theoretical data.

MCBJ measurements. Electron transport characteristics in single-molecule junctions were studied by MCBJ measurements in solution at room temperature. The molecular solution contained typically 0.1 mM of the 1–10 molecules in a mixture of 1,3,5-trimethylbenzene (Aldrich, p.a.) and tetrahydrofuran (Aldrich, p.a.), 4:1 (v/v). Single-molecule conductance experiments were performed during the formation and breaking of a nanogap on a notched, freely suspended gold wire (0.1 mm diameter, 99.999%, Goodfellow) fixed on spring steel sheets (10 mm × 30 mm, 0.25 mm thick) with a two-component epoxy glue (Stycast 2850 FT with catalyst 9). A Kel-F liquid cell with a Kalrez O-ring was mounted onto the sample sheet fixed by two holders. During the
measurements, the steel sample could be bent with a pushing rod controlled by a stepper motor (or a piezo motor) and a piezo stack. The stepper motor initialized the bending process. Once the measured current reached a value corresponding to 15 $G_0$, the stepper motor paused and the piezo stack was activated. This strategy managed to decrease environmentally from the operation of the stepper motor. After the junction was completely opened, the piezo stack was reset and the stepper motor drove down the pushing rod. The movement of the piezo stack controlled the breaking and the reformation of nanoscale contacts and the stretching rate of the two gold leads controlled by the piezo stack is about 5–20 nm/s. Molecular junctions could form upon breaking the gold–gold nanotactests. More than 1000 conductance–distance curves were recorded for statistically relevant data analysis during the repeated cycles.

The MCBJ controller is based on a laboratory–built bipotentiostat. All current measurements were performed with two custom–designed bipolar and tunable logarithmic I–V converters operating in a wide dynamic range from 10 to below $10^{-3} G_0$. The tunneling current between the two ends of the ‘broken wire’ (taken as WE1 and WE2) could be recorded as a feedback signal at a given bias voltage 0.1 V. The distance between the two gold electrodes in the MCBJ setup is calibrated by the STM–BJ setup with the assumption that the tunneling decay is identical under the same experimental conditions. After breaking a gold–gold contact, the conductance of the junction drops to approximately $10^{-3} G_0$. Due to the so–called “snap–back” effect, the gap between the two gold electrodes increases instantaneously to a certain distance $\Delta z_{corr}$. A perfect linear atomic chain of gold has a conductance of $G_0$. Due to the tunneling theory, we assume that log ($G/G_0$) = $-\alpha \Delta z$ where $\Delta z = 0$ corresponds to the point where the distance between the terminating gold atoms is equal to the equilibrium gold–gold separation. Our measured separation is $\Delta z = \Delta z_{corr}$ where $\Delta z_{corr}$ is the snap–back distance. Then, the relationship between log ($G/G_0$) and $\Delta z$ is log ($G/G_0$) = $-\alpha \Delta z - \Delta z_{corr}$. The log($G/G_0$) plot has a slope of $-\alpha$ and an intercept of $-\alpha \Delta z_{corr}$. To calibrate the stretching distance in the absence of molecules, we measured the conductance $G$ versus $\Delta z$ for conductances ranging from $10^{-4}$ to $10^{-6} G_0$, and extracted the slope and intercept. From repeated measurements, we obtained a distribution of slopes and intercepts and from the most probable slopes and intercepts obtained the most probable values of $\alpha$ and $\Delta z_{corr}$. We concluded from individual experiments that in TMB: THF (v:v = 4:1), the $\Delta z_{corr}$ is determined as 0.5 nm and the addition of a low concentration of molecules in solution does not influence the snap–back distance. Further technical details and data evaluation methods have been described in our previous article by Hong et al.49.

**Theory and simulations.** Details of the theory and simulations are in Supplementary Notes 4–5.

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M.G., L.W. and A.A.A. contributed equally to the work in this manuscript. All authors have given approval to the final version of the manuscript. All authors provided essential contributions to interpreting the data reported in this manuscript. M.R.B., C.J.L. and W.H. originally conceived the concept and designed the experiments. Synthetic work was carried out in M.R.B’s laboratory by M.G.; break junction measurements were carried out in W.H.’s laboratory by L.W.; calculations were carried out in C.J.L’s laboratory by A.A.A., A.K.I. and M.G. coordinated the writing of the manuscript with input from all authors.

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