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Controlling single-molecule conductance through lateral coupling of π orbitals

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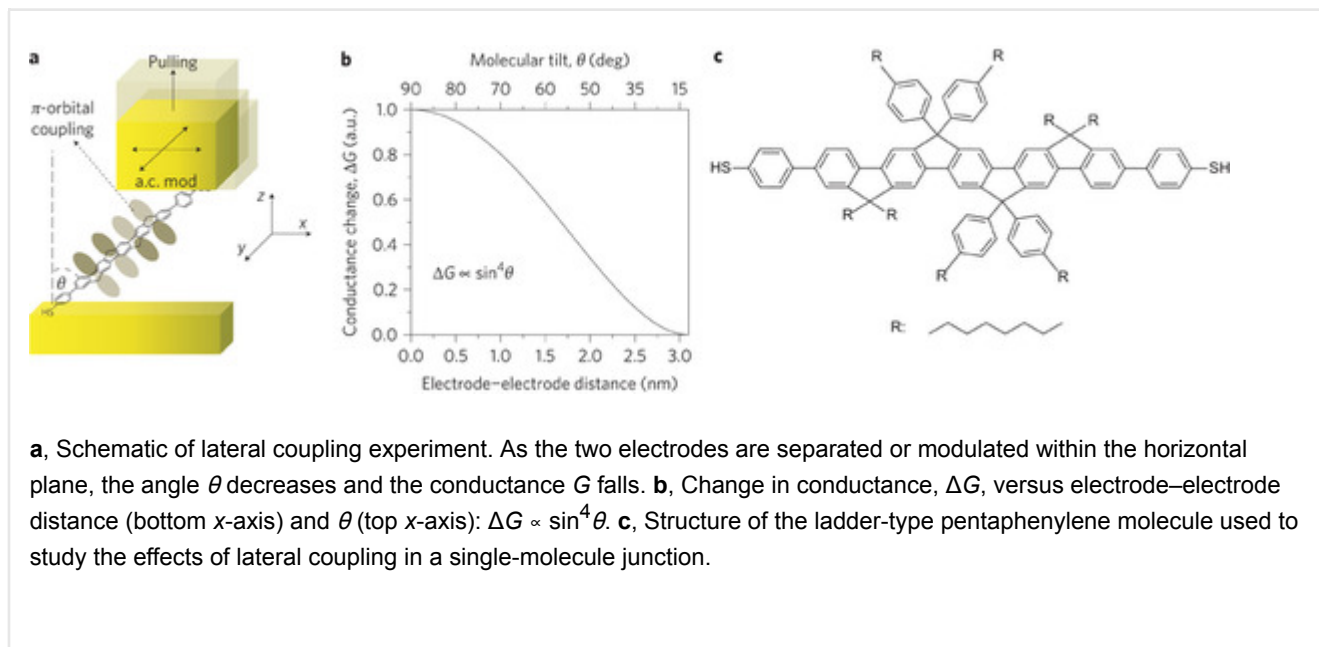
Abstract

In recent years, various single-molecule electronic components have been demonstrated[1]. However, it remains difficult to predict accurately the conductance of a single molecule and to control the lateral coupling between the π orbitals of the molecule and the orbitals of the electrodes attached to it. This lateral coupling is well known to cause broadening and shifting of the energy levels of the molecule; this, in turn, is expected to greatly modify the conductance of an electrode–molecule–electrode junction[2, 3, 4, 5, 6]. Here, we demonstrate a new method, based on lateral coupling, to mechanically and reversibly control the conductance of a single-molecule junction by mechanically modulating the angle between a single pentaphenylene molecule bridged between two metal electrodes. Changing the angle of the molecule from a highly tilted state to an orientation nearly perpendicular to the electrodes changes the conductance by an order of magnitude, which is in qualitative agreement with theoretical models of molecular π-orbital coupling to a metal electrode. The lateral coupling is also directly measured by applying a fast mechanical perturbation in the horizontal plane, thus ruling out changes in the contact geometry or molecular conformation as the source for the conductance change.

Subject terms: Electronic properties and devices
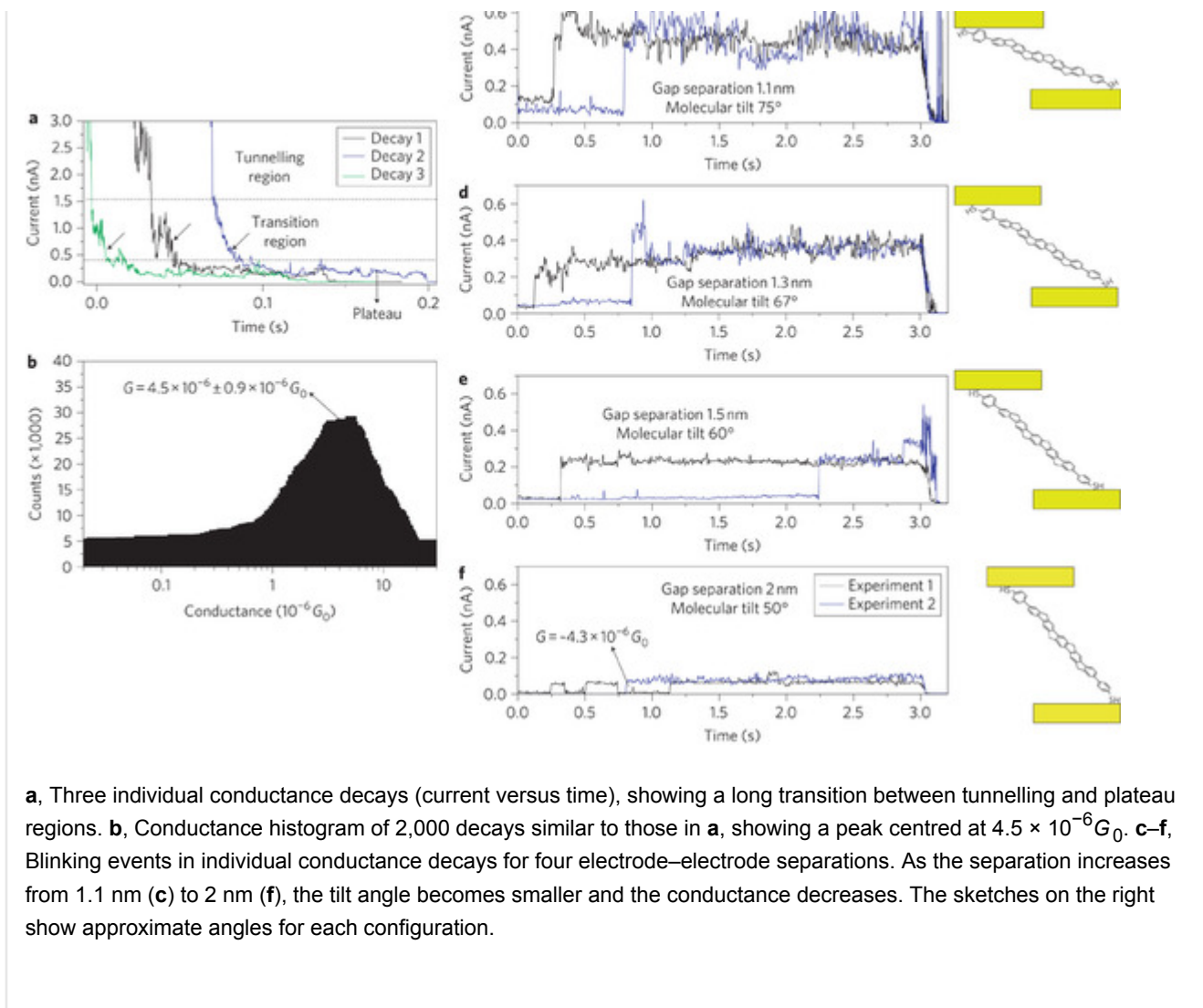
Main

Previous theoretical work has predicted that the conductance G of a molecular junction in the non-resonant tunnelling regime will change by up to one order of magnitude[2, 5, 6] as the angle θ between a π-conjugated molecular backbone and the vector normal to the surface of the electrode is varied (Fig. 1a). This lateral coupling was first discussed by Kornilovitch and Bratkovsky[2], who predicted that $G \propto \sin^4\theta$ (Fig. 1b). Further corroboration of this theoretical model has been provided by local density approximations[7]. These effects have been experimentally observed on self-assembled monolayers (SAMs) and explained by a localization–delocalization transition of the molecular orbitals as θ increases[8]. At the single-molecule level, a statistical method has been used to demonstrate that lateral coupling can play a significant role in molecular conductance[5], and several other studies have provided additional indirect evidence[9, 10, 11, 12, 13, 14]. However, it has not yet been shown that a continuous change in the angle of a single-molecule junction can provide a continuous change in the conductance. The ability to mechanically and reversibly control the conductance in this way could be exploited in future single-molecule electromechanical devices.

Figure 1: Lateral coupling.

a, Schematic of lateral coupling experiment. As the two electrodes are separated or modulated within the horizontal plane, the angle θ decreases and the conductance G falls. **b**, Change in conductance, ΔG, versus electrode–electrode distance (bottom x-axis) and θ (top x-axis): $\Delta G \propto \sin^4 \theta$. **c**, Structure of the ladder-type pentaphenylene molecule used to study the effects of lateral coupling in a single-molecule junction.

To study this lateral coupling effect, we chose the molecule shown in Fig. 1c. This molecule is ideal for several reasons. First, it has a highly conjugated, rigid and flat ladder-type pentaphenylene backbone that is 3.1 nm long and produces delocalized π-molecular orbitals along its main longitudinal axis. Second, even though the system is highly conjugated, there is still a large gap of ~3.0 eV between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (Supplementary Section 1), so the molecule conducts by means of non-resonant tunnelling[15]. Third, the presence of the long alkane side chains helps to avoid π–π stacking between neighbouring molecules, which would mask the single-molecule character of the measurement[16], and also ensures that the molecular π-orbital system is properly oriented towards the electrodes when the molecule is bound between the surfaces of the two electrodes. Finally, the long conjugated backbone provides a measurable current through the molecule with an almost negligible tunnelling current through space, even at high molecular tilt angles of $\theta > 70°$, so the change in conductance due to lateral coupling can be directly quantified without any further background subtraction.

Single-molecule conductance was first characterized using the scanning tunnelling microscope break junction (STM-BJ)[17] method (see Methods). For the molecule in Fig. 1c, the resulting conductance histogram (Fig. 2b) shows a single peak centred at $4.5 \times 10^{-6} G_0$, where $G_0 = 2e^2/h$. Moreover, if one looks at the individual traces (Fig. 2a), there are two important features that differ from previous junctions with shorter saturated alkane chains[18]. First, the conductance plateaux typically measure between 1 and 1.5 nm in length, which is significantly longer than the results for most molecules previously studied using this approach (typically ≤0.5 nm)[15, 19]. Second, there is a transition region in the decay curve before the plateau, as indicated in Fig. 2a. This behaviour is not observed for shorter saturated molecules displaying an exponential decay followed by a short plateau[19], and suggests the existence of molecule–electrode lateral coupling in the pentaphenylene case.

Figure 2: Break junction and blinking experiments on a pentaphenylene molecular junction.

a, Three individual conductance decays (current versus time), showing a long transition between tunnelling and plateau regions. **b**, Conductance histogram of 2,000 decays similar to those in **a**, showing a peak centred at $4.5 \times 10^{-6} G_0$. **c–f**, Blinking events in individual conductance decays for four electrode–electrode separations. As the separation increases from 1.1 nm (**c**) to 2 nm (**f**), the tilt angle becomes smaller and the conductance decreases. The sketches on the right show approximate angles for each configuration.

To test this hypothesis, we used the blinking technique, which has been described previously[5, 20, 21] (see Methods). Several example traces are shown in Fig. 2c–f. For each of these traces, a different initial current set point was used to change the electrode–electrode gap spacing so that the molecule would fit the gap with a different tilting angle. These results demonstrate that in the case of the pentaphenylene molecule the conductance increases as the electrode spacing decreases (or θ increases), which is not observed in other single-molecule junctions. For example, Fig. 3a,b shows similar blinking traces for a tetraphenyl single-molecule junction with different electrode–electrode distances. In this case, the blinking events have the same amplitude, regardless of electrode–electrode separation, indicating that there is poor or no coupling of the molecular π orbitals to the metal electrodes at different molecular tilt angles. Although one may think that the tetraphenyl molecule has a π-orbital system and should therefore also exhibit lateral coupling effects, the phenyl rings in this molecule have a dihedral angle of 34° at room temperature[14], which has two effects on junction conductance. First, the intramolecular coupling of the π orbitals at each phenyl ring is truncated, thus preventing an extended conjugation along the molecular backbone. Second, the localized π orbitals at each of the rings are not oriented relative to the metal electrodes in such a way as to observe lateral coupling. The tilt angle also has no effect on the conductance of linear non-conjugated single-molecule junctions such as those formed with decanedithiol, although in this case it is

not possible to probe as wide an angular range due to the short molecular length (Supplementary Section 3).

**Figure 3: Blink-and-pull experiments on a tetraphenyl junction.**
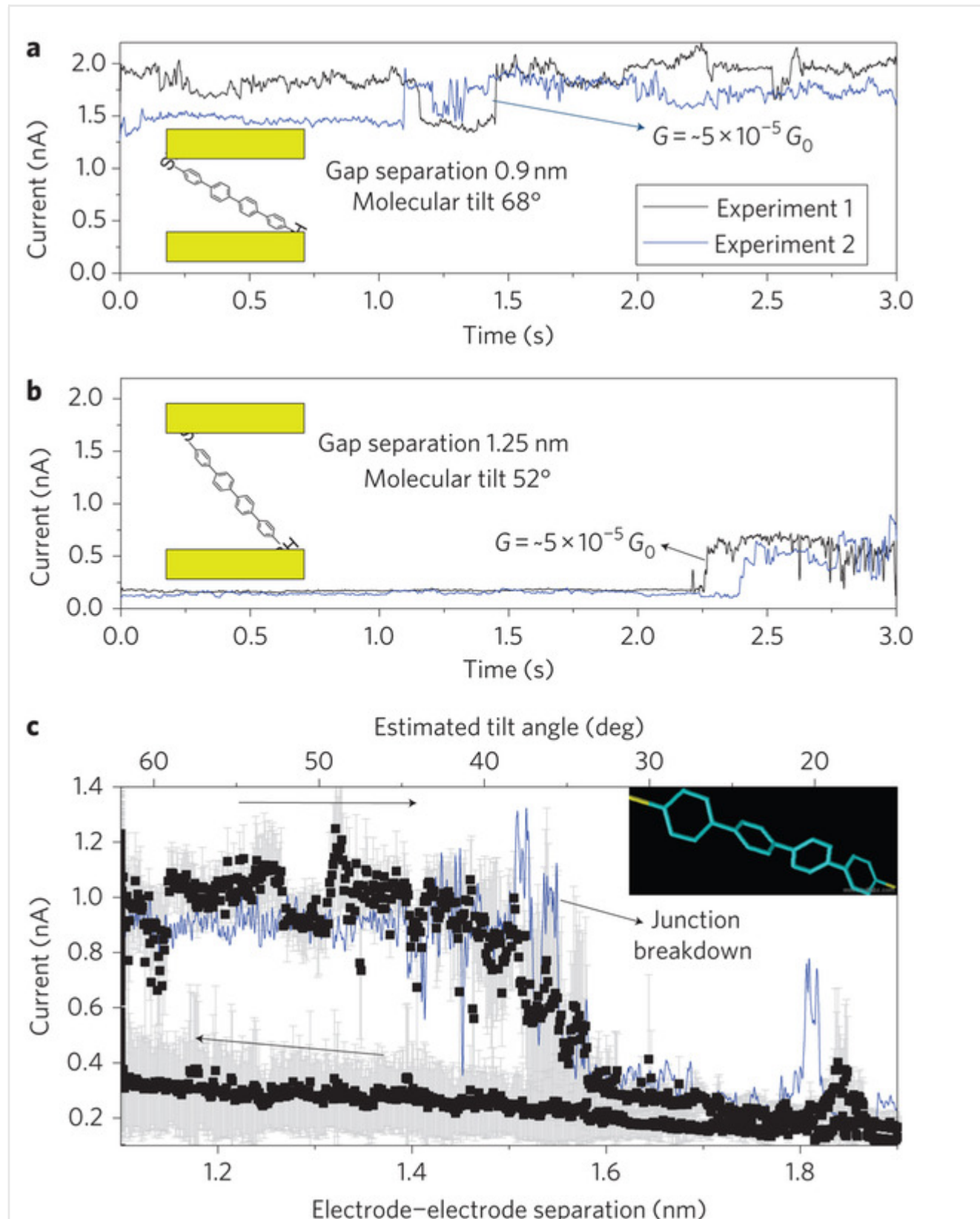
a,b, Current versus time traces for single tetraphenyl molecules at separations of 0.9 nm (**a**) and 1.25 nm (**b**). The amplitudes of the blinking events are the same for the two separations, indicating that there is only poor coupling to the electrodes or no coupling at all. **c,** Average of 15 blink-and-pull experiments (current versus electrode separation or tilt angle) on a tetraphenyl junction (solid squares) showing that the conductance does not change appreciably within the range of accessible angles. Grey background indicates standard deviation. The 'softening' effect in the breakdown region is due to the averaging process. The blue line is an individual pulling trace showing a sharp event during the junction breakdown. Inset: tetraphenyl molecule.

The blinking data suggest that the distance-dependent conductance changes are due to the lateral coupling of the molecular π orbitals to the electrodes. This implies that it should be possible to continuously change the conductance of the single-molecule junction by changing the electrode–electrode separation once a molecule is bound between the two electrodes. To further test this supposition, we performed a set of experiments we call 'blink-and-pull'. As the name suggests, blinking experiments were first performed as described for Fig. 2, but in this case, once the current jumped to the expected value, we cycled the distance between the electrodes to continuously modulate the tilt angle and therefore the lateral coupling of the molecule to the electrodes while simultaneously monitoring the current. The results of this experiment for pentaphenylene are summarized in Fig. 4. Figure 4a presents three individual blink-and-pull cycles, with the electrode–electrode distance initially held at 1.2 nm. Once a molecular bridge was formed, this distance was increased by 1 nm, then decreased back to the initial value (see scanned angles on the top x-axis). In these experiments, the junctions typically broke before the entire cycle was completed. This breakdown clearly demonstrates the presence of a single-molecule junction. It is also clear that there is a monotonic decrease in molecular conductance as the distance is increased (θ decreased). Similar experiments were performed with the initial electrode–electrode separation set to ~2 nm (Fig. 4b). However, in this case, because the angle was already small, there was very little change in the molecular conductance before the junction broke down, and only a short plateau was observed.

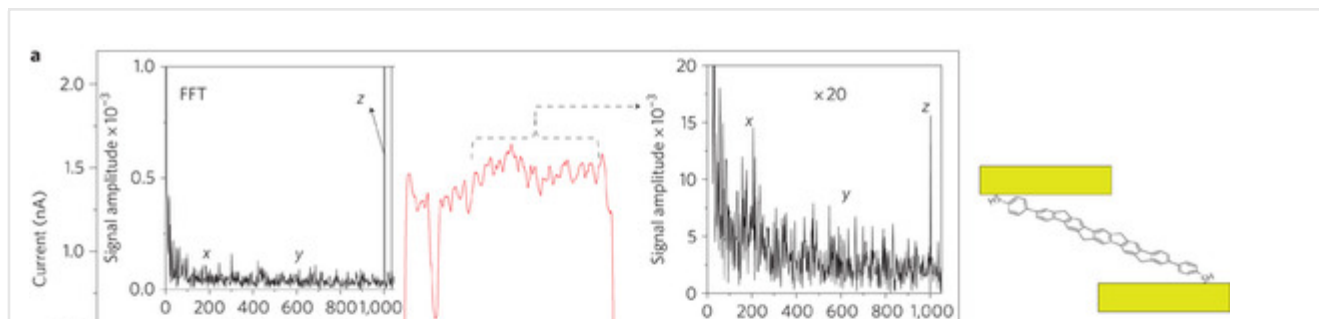**Figure 4: Blink-and-pull experiments on a pentaphenylene junction.**
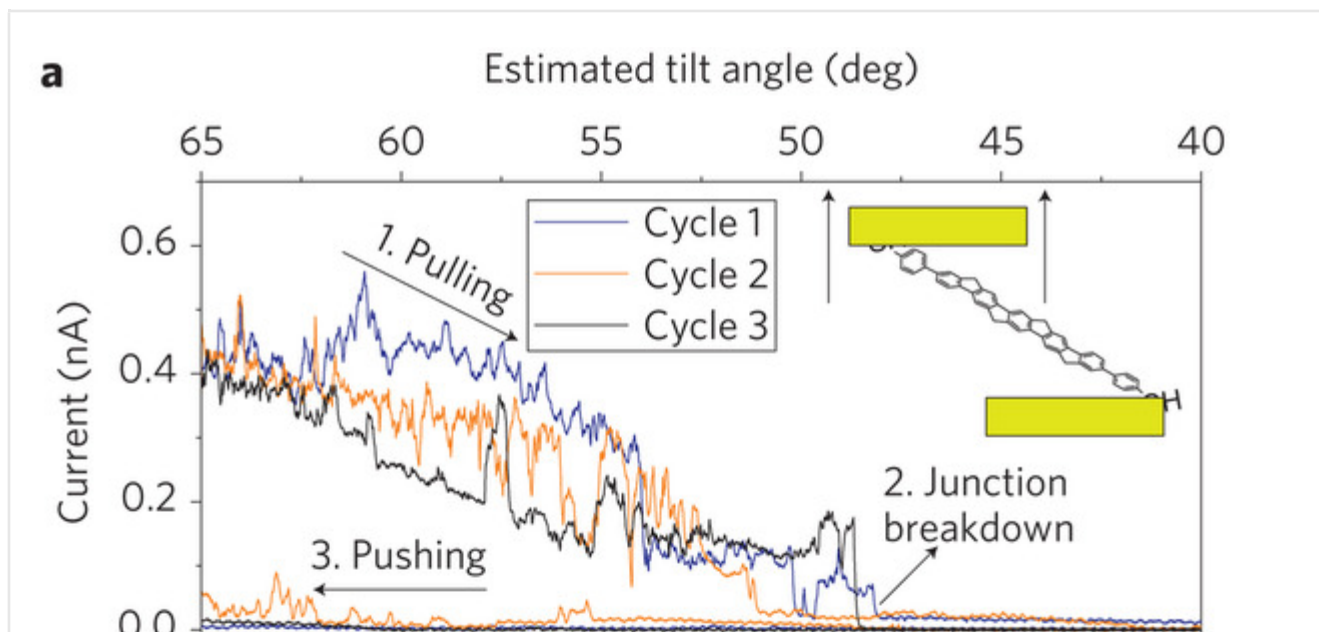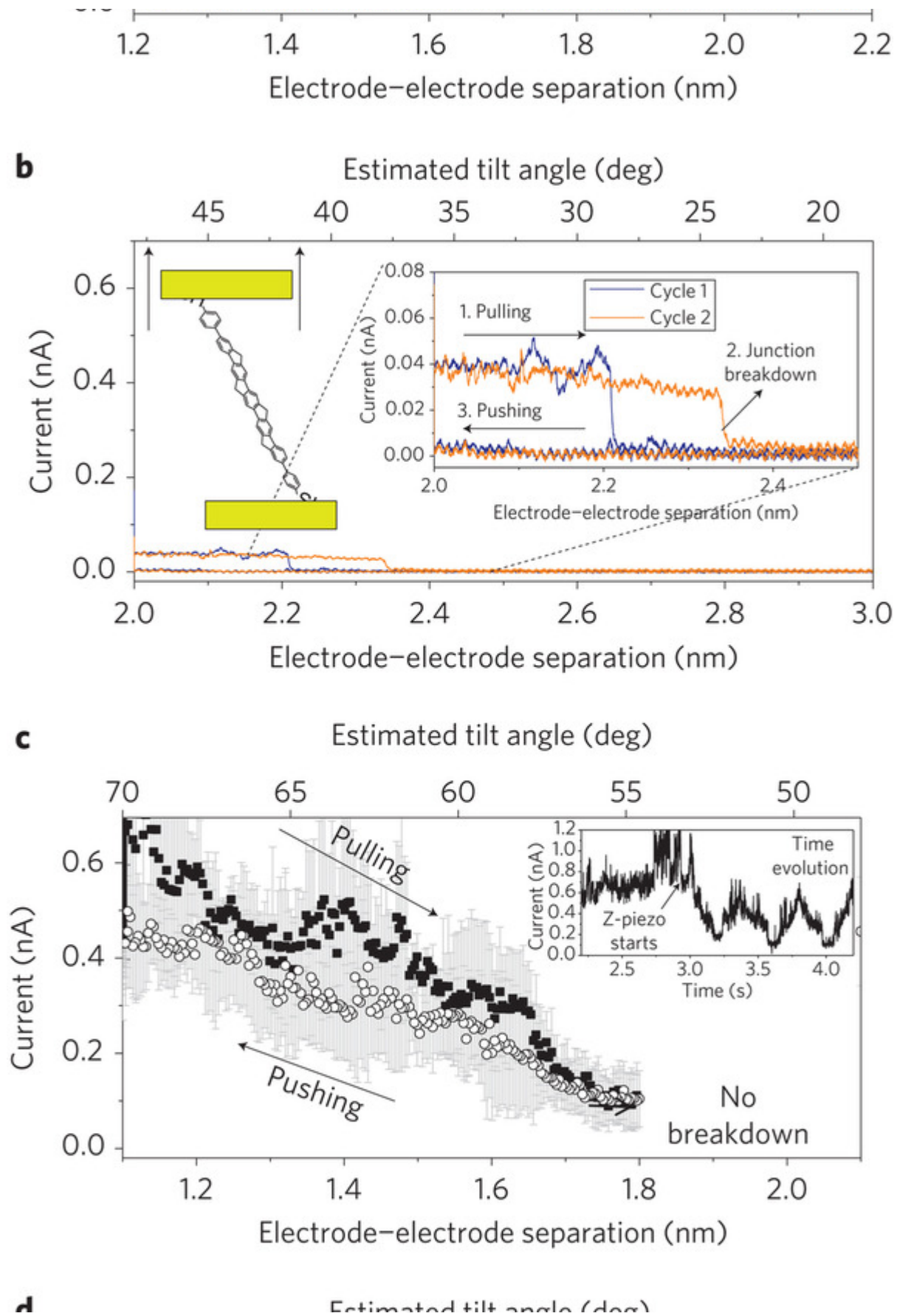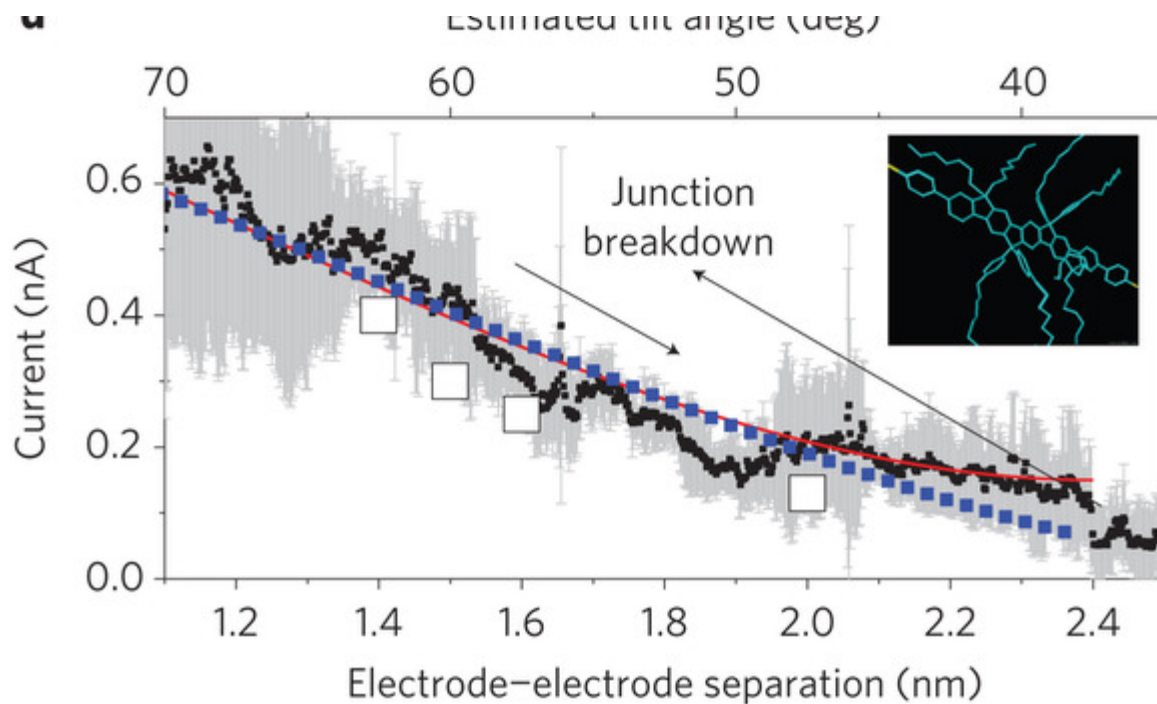
a, Three blink-and-pull traces (current versus electrode separation or tilt angle). The blinking events occur at an initial separation of 1.2 nm, and the conductance falls during the pulling process. The junctions typically break down at a separation of ~1.9 nm. **b**, Two blink-and-pull traces for experiments in which the initial separation is ~2 nm. Almost no change is seen in the conductance because the angle (and the lateral coupling) is already small. **c**, Average of ~40 pulling (filled squares)–pushing (open circles) cycles where the junction is not broken. There is an obvious change in conductance, and no hysteresis in the curves. Inset: time evolution of the experiments. **d**, Average of 10 long pulling curves where the junction breaks down at very low angles. The decrease follows the same trend as the theoretical model, $I \propto \sin^4\theta$ (red curve). Dashed blue line: best fit of the averaged curve to $y = I_0 \sin^n(\theta - \theta_0)$. Best fit occurs for $n = 4.4 \pm 0.01$. Open blocks are values from the blinking events in Fig. 2. Inset: pentaphenylene molecule. Grey shadow in **c** and **d** indicates standard deviation.
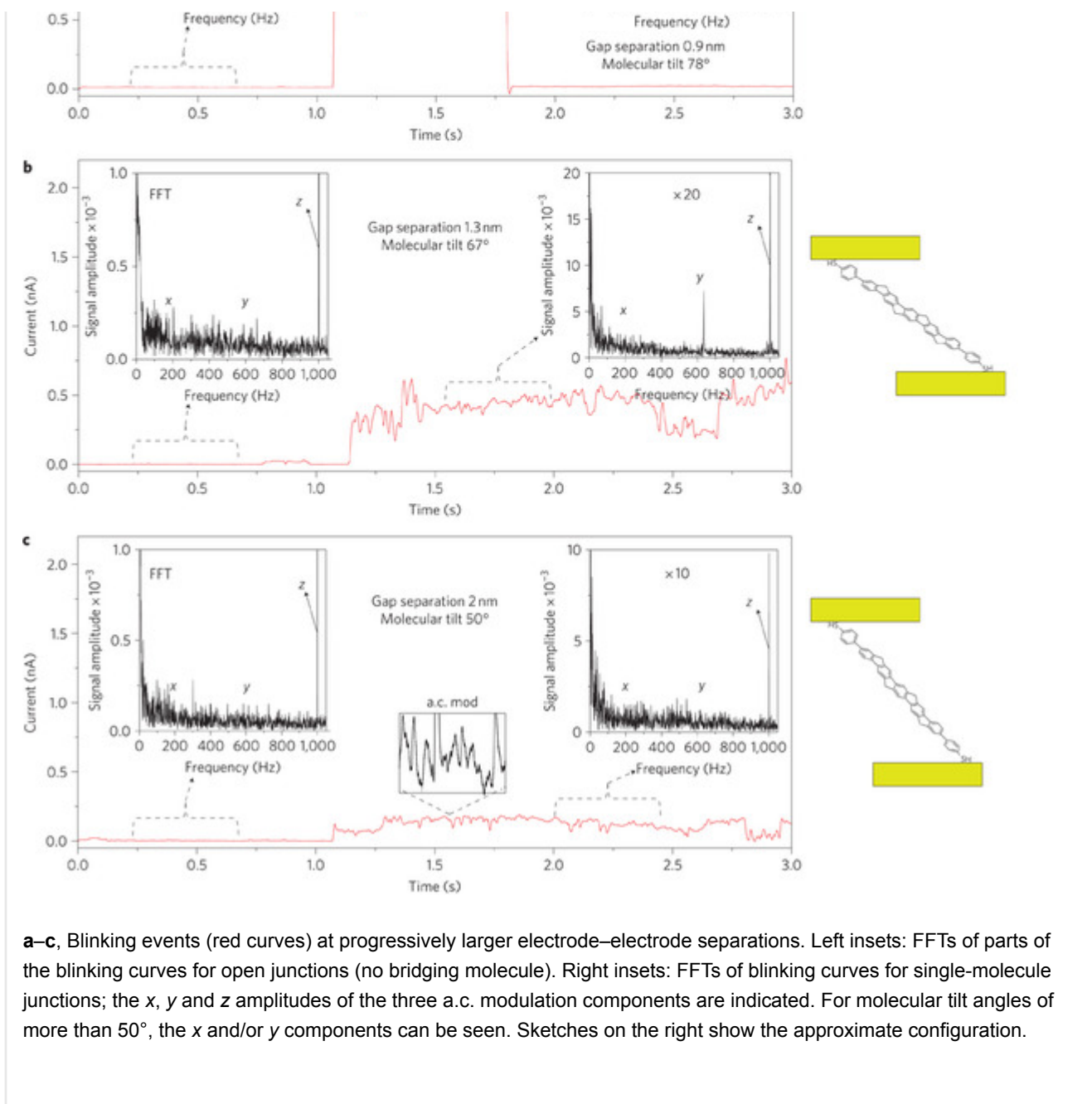
These experiments show that it is possible to separate the electrodes to a distance of 1.9 nm without causing the junction to break down. It should then be possible to move the tip back towards the surface to return to the original conductance value before the junction breaks down. Figure 4c shows an average of over 40 of these complete cycles on different molecular junctions, with the conductance of the single-molecule junction being modulated over time periods of several seconds. Changing the tilt angle of the molecular backbone from 70° to 45° resulted in an average change in conductance by a factor of ~6 to 7, and up to 10 in the best scenario. The inset of Fig. 4c shows the time evolution of this type of experiment. Typically, it was possible to complete several cycles (up to 10 in the best run) before the junction broke down. Figure 4d shows an average of 10 of the longest pulling curves stretched until breakdown of the junction. The average conductance change is in qualitative agreement with the theoretical $I = I_0 \sin^4\theta$ model[2] (red curve). Details on the fitting procedure are shown in Supplementary Section 2. The dependence of the tetraphenyl junction conductance on angle (control experiment) is significantly different from the behaviour of the pentaphenylene junction, as shown in Fig. 3c, where no clear dependence on tilt angle is observed.

Although the conductance changes are reproducible, stable, lack hysteresis effects, and match a qualitative fitting of the π-orbital lateral coupling model[2], it is still not possible to rule out conformational changes in the molecule, or to ignore the fact that because we are separating the electrodes by as much as 1 nm, electrode–molecule contact may change during the pulling–pushing cycles. To demonstrate that these effects are not dominating the observed conductance change, we developed a new method to probe the strength of the lateral coupling. This method works by applying a small periodic mechanical a.c. modulation to one of the electrodes in the x- and y-directions parallel to the substrate, at different frequencies (Fig. 1a), then monitoring the amplitude of the a.c. current response at each of the frequencies. If both electrodes are nearly perpendicular and no molecule is present between the electrodes, then these mechanical perturbations in the x–y plane would have no effect on the current, because the electrode–electrode separation is kept constant (see discussion of a.c. calibration in Supplementary Section 4). However, in the case of a bridging molecule that has some coupling with the electrodes at a certain angle θ, these perturbations will cause a small change in the angle, resulting in corresponding changes in the current due exclusively to lateral coupling. It is necessary to apply a modulation in both the x and y directions because it is impossible to know what the molecular orientation is in the x–y plane. There are cases where a molecule lies parallel to one axis and no modulation in the current is observed in the other, or for the molecule to be somewhere between the x- and y-axes, in which case some a.c. current response is measured at both frequencies. Therefore, the combination of the current amplitudes from the x and y components will directly demonstrate whether there is any lateral coupling in the molecular junction while discounting effects due to molecular conformational changes or changes in contact geometry.

We performed systematic blinking experiments and applied the previously described a.c. motion to one electrode in the x and y directions. The x and y modulation signals were typically 0.1 nm in amplitude and 203 Hz and 633 Hz in frequency, respectively. We also applied a small modulation to z (0.1 nm at 1 kHz) to identify the presence of a molecular junction (as previously described[21]), as well as to determine the electrode–electrode separation through the current decay relationship (Supplementary Section 2). Figure 5 summarizes the x–y modulation result, showing blinking events at three different electrode–electrode separations and FFTs of the current before and during the blinking event (insets). When the angle is small, at electrode–electrode separations greater than 2 nm, the x and y a.c. components of the FFT show almost no difference between the open (no molecule) and bridged junctions. However, as the tilt angle increases (electrode–electrode separation decreases), enhancement of the x–y a.c. components of the current is observed (Fig. 5a,b), suggesting lateral coupling between the molecular orbitals and the metal electrodes. Owing to the small distance modulation applied in the x and y directions, such changes in the current discount any effects due to conformational or contact changes as the electrodes are separated, providing direct proof that changes in the lateral coupling between the molecule and the metal electrodes can significantly alter the conductance of a single-molecule junction.

Figure 5: Blinking experiments coupled with a.c. horizontal and vertical distance modulation.

a–c, Blinking events (red curves) at progressively larger electrode–electrode separations. Left insets: FFTs of parts of the blinking curves for open junctions (no bridging molecule). Right insets: FFTs of blinking curves for single-molecule junctions; the *x*, *y* and *z* amplitudes of the three a.c. modulation components are indicated. For molecular tilt angles of more than 50°, the *x* and/or *y* components can be seen. Sketches on the right show the approximate configuration.
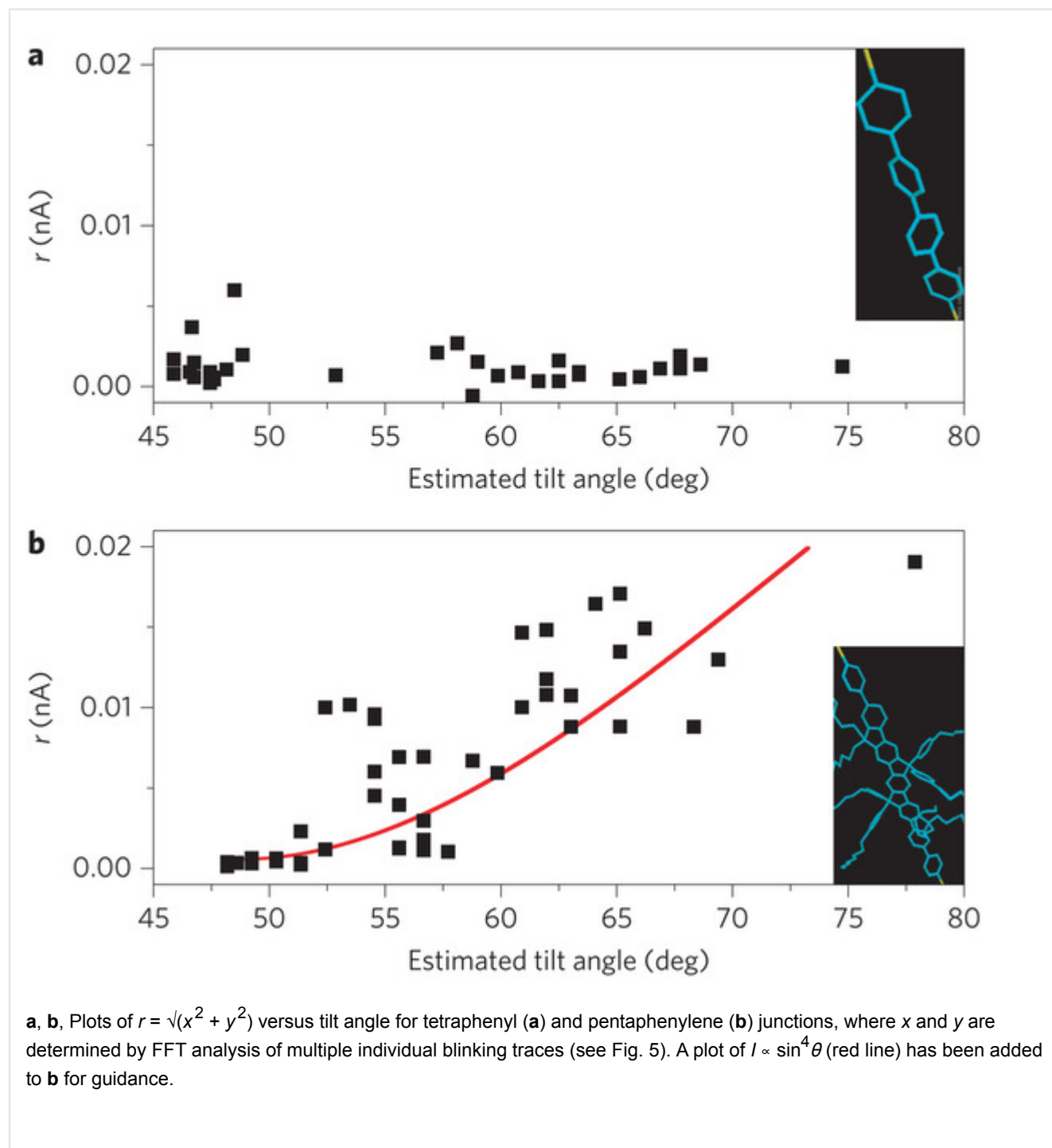
To obtain statistical information from the FFT data shown in Fig. 5, the total lateral coupling (*x* and *y* contributions) for a large number (*N* = 60) of single-pentaphenylene junctions is shown as a function of the molecular tilt angle in Fig. 6b. The orientation of the molecule in the *x*–*y* plane is unknown, so we plot the magnitude of the *x* and *y* components, $r = \sqrt{(x^2 + y^2)}$ versus angle to show the total current enhancement due to lateral coupling. Although a large dispersion is observed, most likely due to particular atomic configurations at the single-molecule junction, the trend observed in Fig. 4 is again observed here. Control experiments were performed using the tetraphenyl molecule, and the results, shown in Fig. 6a, show no apparent dependence of the *x* and *y* component amplitudes on molecular tilt angle. These results demonstrate that the lateral coupling is the main effect dominating charge transport during the molecular tilting process in this molecular system with extended conjugation. Other effects

such as the possible rotation of the phenyl rings at both ends can be ruled out by the use of the tetraphenyl block as a control experiment. However, the exact role of the metal–molecule contact detail[22, 23] in blink-and-pull experiments remains less thoroughly studied and needs to be explored in future experiments.

Figure 6: Total lateral coupling magnitude.

a, **b**, Plots of $r = \sqrt{(x^2 + y^2)}$ versus tilt angle for tetraphenyl (**a**) and pentaphenylene (**b**) junctions, where x and y are determined by FFT analysis of multiple individual blinking traces (see Fig. 5). A plot of $I \propto \sin^4 \theta$ (red line) has been added to **b** for guidance.

This work clearly demonstrates that it is possible to mechanically control the conductance of a single-molecule device under appropriate conditions. Furthermore, introduction of the horizontal mechanical perturbation technique

provides a new method for understanding conductance changes in molecular-scale systems.

Methods

In the STM-BJ method, a gold STM tip (electrode 1) was repeatedly brought into contact with a gold substrate (electrode 2) in the presence of molecules with anchor groups capable of binding to both electrodes. As the tip is withdrawn, there is some probability that a molecule will bridge both electrodes, and when this occurs, a plateau appears in the current versus distance trace (otherwise, an exponential decay is observed). By performing a statistical analysis of thousands of these curves it is possible to determine the most likely conductance of a single-molecule junction[12, 17, 24].

In the blinking method, the STM tip was placed at a certain distance from the surface in the presence of a dilute coverage of molecules. To determine the distance, a low set-point tunnelling current was set through the STM feedback loop, and the tunnelling current decay β was evaluated by applying a small mechanical a.c. perturbation along the vertical direction[21]. When the electrode–electrode gap was open (no molecules bridging), the current decay values obtained from the vertical a.c. modulation were ~10 nm^{-1}, and the electrode–electrode gap distance could be evaluated. The final electrode–electrode separation could be set by applying an additional vertical translation to the STM tip through the piezoactuator.

Errors in the determination of electrode–electrode distance could arise if too high a concentration of target molecule was used, because the values of decay (β) over a self-assembled monolayer can be much lower and may not be constant along the entire electrode–electrode gap. For this reason, very low molecular concentrations were used in the blinking experiments. This method also implies no physical contact between the STM tip and the Au(111) surface, a fact that minimizes possible tip-induced roughness effects (Supplementary Section 2). Once the distance was set, the feedback system was disabled. Occasionally, a molecule would bridge between the tip and the surface, and this occurrence was accompanied by a sudden jump in current, because the molecule was much more conductive than the tunnelling gap through the solvent (no molecule bridging) before junction formation. These blinks typically lasted several seconds and could be used to extract the conductance of a single-molecule junction[20]. Furthermore, because this molecule was so long and the conductance was relatively high compared to its length, the initial tunnelling currents could be set to very low values (large electrode–electrode distances) and still result in pronounced blinking events.

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Acknowledgements

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Contributions

N.J.T. conceived the transport experiment. I.D.-P., J.H. and T.H. conducted the experiments and analysed the data. K.M. supervised the design and synthesis of the molecule. Z.-S.W. and G.Z. synthesized the molecule.

Competing financial interests

The authors declare no competing financial interests.

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Supplementary information

PDF files

1. Supplementary information (1,323 KB)
   Supplementary information