

# Observation of molecular orbital gating

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**The control of charge transport in an active electronic device depends intimately on the modulation of the internal charge density by an external node<sup>1</sup>. For example, a field-effect transistor relies on the gated electrostatic modulation of the channel charge produced by changing the relative position of the conduction and valence bands with respect to the electrodes. In molecular-scale devices<sup>2–10</sup>, a long-standing challenge has been to create a true three-terminal device that operates in this manner (that is, by modifying orbital energy). Here we report the observation of such a solid-state molecular device, in which transport current is directly modulated by an external gate voltage. Resonance-enhanced coupling to the nearest molecular orbital is revealed by electron tunnelling spectroscopy, demonstrating direct molecular orbital gating in an electronic device. Our findings demonstrate that true molecular transistors can be created, and so enhance the prospects for molecularly engineered electronic devices.**

The demonstration of a true three-terminal molecular device, one that depends on external modulation of molecular orbitals, has been the outstanding challenge of the field of molecular electronics since soon after its inception<sup>5</sup>, but until now it has defied experimental efforts. Theoretical proposals indicate that field-effect gating of a molecular junction is possible<sup>6,7</sup>. Carrier modulation in molecular junctions can be achieved by alternative non-molecular mesoscopic mechanisms such as Coulomb blockade and Kondo effects<sup>8–10</sup>, and has been claimed to be observed in an electrochemical break junction<sup>11</sup>, but until now proof of direct orbital gate control of a solid-state device has been elusive. Single-molecule orbital modulation has been demonstrated in two-terminal, non-device scanning tunnelling microscopy experiments<sup>12</sup>, lending encouragement to the development of three-terminal device implementations, notwithstanding concerns of the degree of gate control that can be achieved in a field-effect transistor (FET) configuration<sup>6,13</sup>. Here we demonstrate direct electrostatic modulation of orbitals in a solid-state molecular FET configuration, with both effective gate control and enhanced resonant coupling of the molecular orbitals to the source and drain electrodes. We show this using a multiprobe approach combining a variety of transport techniques that give a self-consistent characterization of the molecular junction.

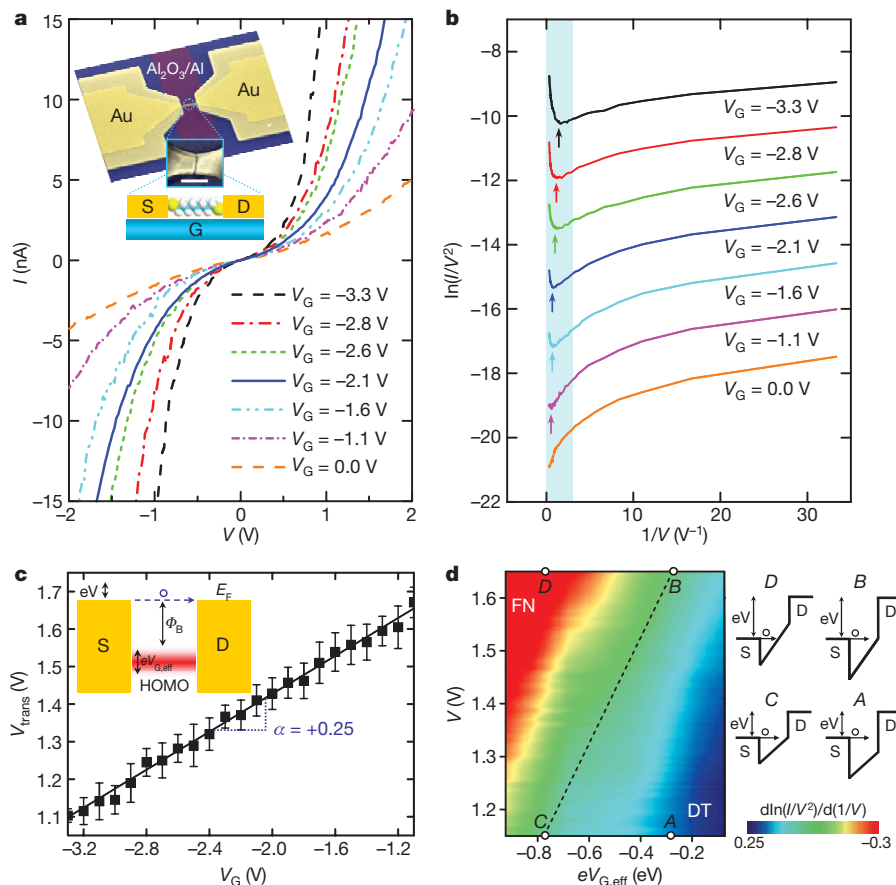
As illustrated in the inset of Fig. 1a, individual molecules are connected to source and drain electrodes with a bottom-gate control electrode in a FET configuration. In such devices, the energies of the molecular orbitals with respect to the Fermi level of the electrodes can be directly tuned by adjusting a gate voltage,  $V_G$ . We make such devices using the well-known electromigration technique of fracturing a continuous gold wire (coated with the desired molecules, in vacuum, at 4.2 K) that is placed over an oxidized aluminium gate electrode<sup>8,9</sup> (Methods Summary). This produces source and drain electrodes with a nanometre-scale gap, which are often bridged by single or very few molecules, creating molecular junctions. We have examined a sample size of 418 devices containing two prototype molecules: the control, a 1,8-octanedithiol (ODT) with an alkyl

backbone as a  $\sigma$ -saturated aliphatic molecule; and the active device, a 1,4-benzenedithiol (BDT) with a delocalized aromatic ring as a  $\pi$ -conjugated molecule. We found 35 devices with sigmoidal and significantly gate-dependent source–drain current ( $I$ )–voltage ( $V$ ) characteristics. The measured low-bias conductance is in good agreement with single-molecule conductance values of the molecules of interest (Supplementary Fig. 4). Coherent, off-resonance tunnelling with a strong molecule–metal contact coupling (for example, the thiol–gold bond) can be reasonably expected as a conduction mechanism for these junctions, in accordance with the form of the symmetric  $I(V)$  curves<sup>14,15</sup>, the lack of a significant conductance gap<sup>14,15</sup>, the exponential dependence of conductance on molecular length<sup>15–17</sup> (Supplementary Fig. 6) and the temperature-independent  $I(V)$  behaviour<sup>17</sup> (Supplementary Fig. 5).

Figure 1a shows representative  $I(V)$  curves for a Au–ODT–Au ( $\sigma$ -saturated aliphatic) junction measured at different  $V_G$  values. The tunnelling current passing through the ODT junction increases as  $V_G$  becomes increasingly negative. The corresponding analysis of  $\ln(I/V^2)$  versus  $1/V$ , the graph of which is known as a Fowler–Nordheim plot, is shown in Fig. 1b. Here two distinct transport regimes are evident; the boundary between them, which occurs at the transition voltage,  $V_{\text{trans}}$ , is indicated with an arrow and exhibits a clear gate dependence. In the low-bias region, the logarithmic dependence is characteristic of direct tunnelling ( $V < \Phi_B/e$ , where  $\Phi_B$  is the barrier height and  $e$  is the elementary charge), whereas in the high-bias region above  $V_{\text{trans}}$ , the curves yield a linear relation with a negative slope, indicative of Fowler–Nordheim tunnelling or field emission ( $V > \Phi_B/e$ ). The measurement of  $V_{\text{trans}}$  allows an experimental determination of the height of the energy barrier associated with the tunnelling transport in molecular junctions, given by the difference between the electrode Fermi energy,  $E_F$ , and the energy of the nearest molecular orbital (the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO)<sup>18</sup>; see Supplementary Information for details).

We observe a controllable gate-voltage dependence of  $V_{\text{trans}}$  in the molecular junction. For Au–ODT–Au junctions,  $V_{\text{trans}}$  shifts to a lower bias as a more negative  $V_G$  is applied (Fig. 1b). To explore this further, we plot the measured  $V_{\text{trans}}$  values against  $V_G$  in Fig. 1c. We find that  $V_{\text{trans}}$  scales linearly and reversibly as a function of  $V_G$ . The slope,  $\alpha = \Delta V_{\text{trans}}/\Delta V_G$ , is the gate efficiency factor, which describes the effectiveness of molecular orbital gating; for example, if  $e|\alpha| = 0.25 \text{ eV V}^{-1}$  (from the linear fit in Fig. 1c) then the molecular orbital energy changes by 0.25 eV when 1 V is applied to the gate electrode. This large gate coupling probably indicates that the molecule resides close to the gate metal–dielectric interface to reduce screening by the electrodes; future improvements to the device performance may be made by using a tapered-electrode approach<sup>13</sup>. We can also determine the actual amount of molecular orbital shift produced by the applied gate voltage in terms of an effective molecular orbital gating energy,  $eV_{G,\text{eff}} = e|\alpha|V_G$ .

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**Figure 1 | Gate-controlled charge transport characteristics of a Au-ODT-Au junction.** **a**, Representative  $I(V)$  curves measured at 4.2 K for different values of  $V_G$ . Inset, the device structure and schematic. S, source; D, drain; G, gate. Scale bar, 100 nm. **b**, Fowler–Nordheim plots corresponding to the  $I(V)$  curves in **a**, exhibiting the transition from direct to Fowler–Nordheim tunnelling with a clear gate dependence. The plots are offset vertically for clarity. The arrows indicate the boundaries between transport regimes (corresponding to  $V_{\text{trans}}$ ). **c**, Linear scaling of  $V_{\text{trans}}$  in terms of  $V_G$ . The error

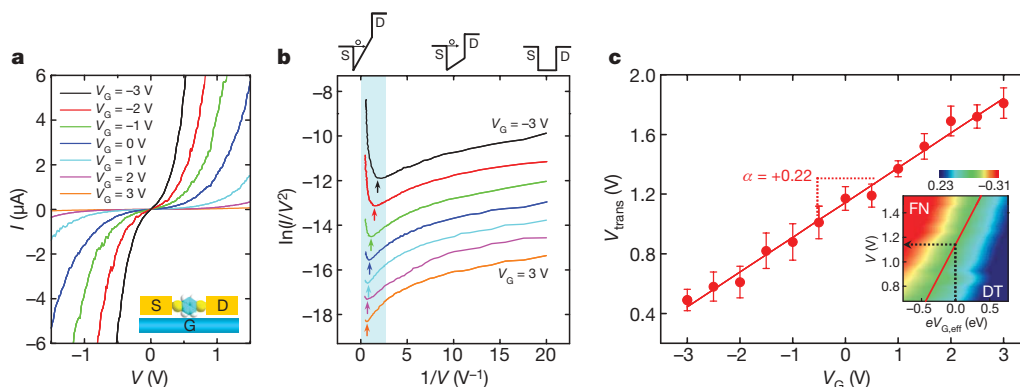
bars denote the s.d. of individual measurements for several devices and the solid line represents a linear fit. Inset, the schematic of the energy band for HOMO-mediated hole tunnelling, where  $eV_{G,\text{eff}}$  describes the actual amount of molecular orbital shift produced by gating. **d**, Two-dimensional colour map of  $d\ln(I/V^2)/d(1/V)$  (from Fowler–Nordheim plots). Energy-band diagrams corresponding to four different regions (points A–D) are also shown. FN, Fowler–Nordheim tunnelling; DT, direct tunnelling.

The gate-controlled tunnelling transport is fully illustrated in Fig. 1d, where we show a two-dimensional colour map of  $d\ln(I/V^2)/d(1/V)$  (from Fowler–Nordheim plots) in the transition region, as a function of  $V$  and  $eV_{G,\text{eff}}$ . The dashed line indicating the linear fit of  $V_{\text{trans}}$  versus  $V_G$  defines the boundary between two distinct transport regimes (direct and Fowler–Nordheim tunnelling). In Fig. 1d, the transport at point A shows typical direct tunnelling across the trapezoidal barrier at given values of  $V$  and  $eV_{G,\text{eff}}$ . If the applied bias increases further, to reach  $V_{\text{trans}}$  (point B), a transition from a trapezoidal to a triangular barrier shape occurs. This indicates the onset of Fowler–Nordheim tunnelling, corresponding to an inflection point in the plot of  $\ln(I/V^2)$  against  $1/V$ . Point C shows  $V_{\text{trans}}$  to be at a lower bias than at point B, which is attributed to a decrease in the  $|E_F - E_{\text{HOMO}}|$  offset (where  $E_{\text{HOMO}}$  is the energy of the HOMO level), arising from a more negative  $V_G$  value. Finally, at point D, the barrier is a completely triangular shape and the charge transport is dominated by Fowler–Nordheim tunnelling.

In a three-terminal device, a negative or positive gate voltage would respectively raise or lower the orbital energies in the molecules relative to  $E_F$  (refs 1, 6). Hence, a positive value of  $\alpha$  indicates HOMO-mediated hole tunnelling (p-type-like; Fig. 1c, inset). Conversely,  $\alpha$  would be negative for LUMO-mediated electron tunnelling (n-type-like); for example, a Au–1,4-benzenedicyanide–Au junction (Supplementary Fig. 8). By extrapolating the  $y$ -intercept from the linear fit in Fig. 1c, we obtain the zero-gate transition voltage,  $V_{\text{trans},0} = 1.93 \pm 0.06$  V, which provides an estimate of the original position (at  $V_G = 0$  V) of the HOMO level relative to  $E_F$  in Au–ODT–Au junctions.

Now let us examine a  $\pi$ -conjugated BDT molecule, the prototypical molecular transport junction<sup>4,6,14</sup>. Figure 2a shows the gate-modulated transport of a Au–BDT–Au junction. The tunnelling current flowing through the BDT junction is enhanced when a negative  $V_G$  is applied, whereas a positive  $V_G$  suppresses the current level (p-type-like; see also Supplementary Fig. 7). Figure 2b and Fig. 2c respectively display plots of  $\ln(I/V^2)$  versus  $1/V$  and  $V_{\text{trans}}$  versus  $V_G$  for this molecular system. The positive sign of  $\alpha = +0.22$  in the BDT junction explicitly indicates that HOMO-mediated tunnelling is the dominant transport channel. The colour map of  $d\ln(I/V^2)/d(1/V)$  (from Fowler–Nordheim plots) is shown as a function of  $V$  and  $eV_{G,\text{eff}}$  (Fig. 2c, inset); the solid line and the dotted arrow indicate the linear fit and the  $y$ -intercept obtained from the plot of  $V_{\text{trans}}$  versus  $V_G$ , respectively. We find that  $V_{\text{trans},0} = 1.14 \pm 0.04$  V for the BDT junction, which is much less than the value for the ODT junction owing to the  $\pi$ -conjugated BDT molecule having a smaller HOMO–LUMO gap.

These results demonstrate relative movement of the molecular orbitals with respect to  $E_F$ , accomplished by gating. This should give rise to a modified coupling of the molecular orbitals to the electrodes, depending both on the orbital Fermi level spacing and on the character of the molecular orbital (that is,  $\sigma$ -saturated or  $\pi$ -conjugated). An unambiguous method of investigating this in current-carrying molecular junctions is inelastic electron tunnelling (IET) spectroscopy, which is a powerful tool for investigating the molecular role in charge transport, specifically the coupling between charge carriers and molecular vibrations<sup>3,19–22</sup>. We performed IET spectroscopy



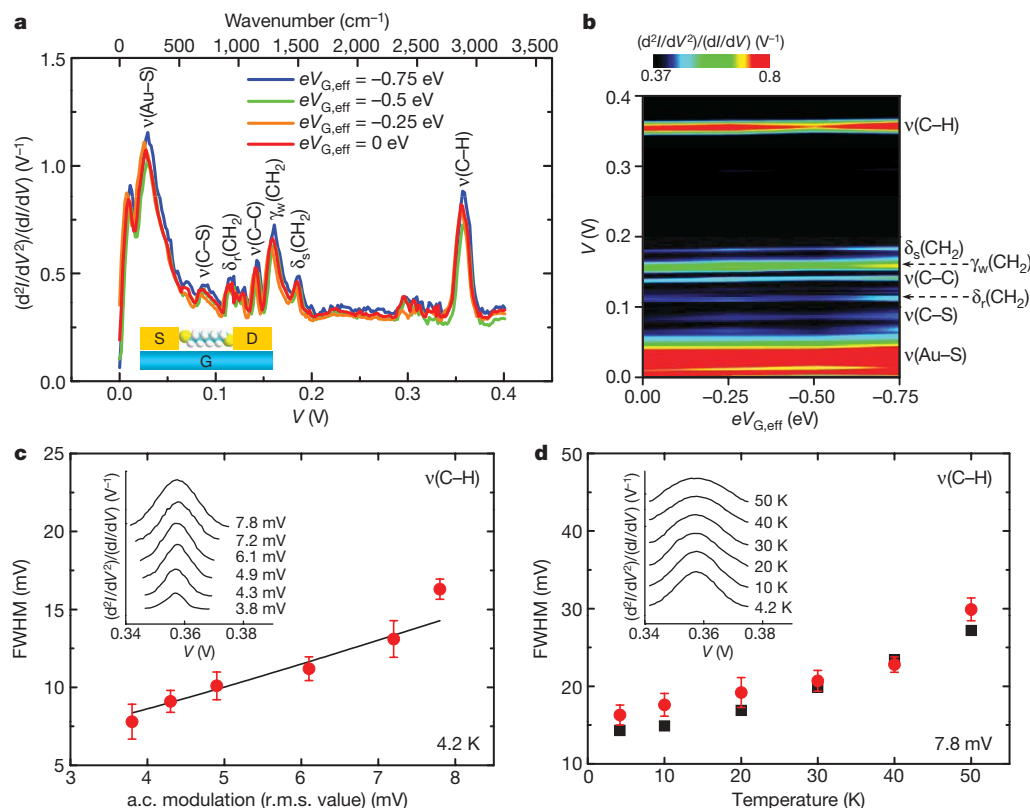
**Figure 2 | Gate-controlled charge transport characteristics of a Au-BDT-Au junction.** **a**, Representative  $I(V)$  curves measured at 4.2 K for different values of  $V_G$ . **b**, Fowler–Nordheim plots demonstrating the gate-variable transition from direct to Fowler–Nordheim tunnelling (colour-coded as in **a**). The plots are offset vertically for clarity. Also shown are drawings of the

barrier shape with increasing bias. **c**, Plot of  $V_{\text{trans}}$  versus  $V_G$ . The solid line is a linear fit and the error bars denote the s.d. of the individual measurements. Inset, the colour map of  $d\ln(I/V^2)/d(1/V)$  (from Fowler–Nordheim plots) with linear fit (solid line) obtained from the plot of  $V_{\text{trans}}$  versus  $V_G$ . The zero-gate transition voltage is indicated by the dashed arrow.

measurements on the two types of molecules (ODT and BDT). Figures 3a and 4a show the IET spectra of ODT and BDT junctions measured at various values of  $eV_{G,\text{eff}}$  respectively. A standard a.c. modulation technique with a lock-in amplifier is carried out at 4.2 K to directly acquire the first ( $dI/dV$ ) and second ( $d^2I/dV^2$ ) harmonic signals (see Supplementary Information for details). We assign the observed spectral features to specific molecular vibrations by comparison with previously reported infrared, Raman and IET spectroscopy measurements, and also by density functional theory (DFT) calculations (Supplementary Table 1). All of the spectral features are

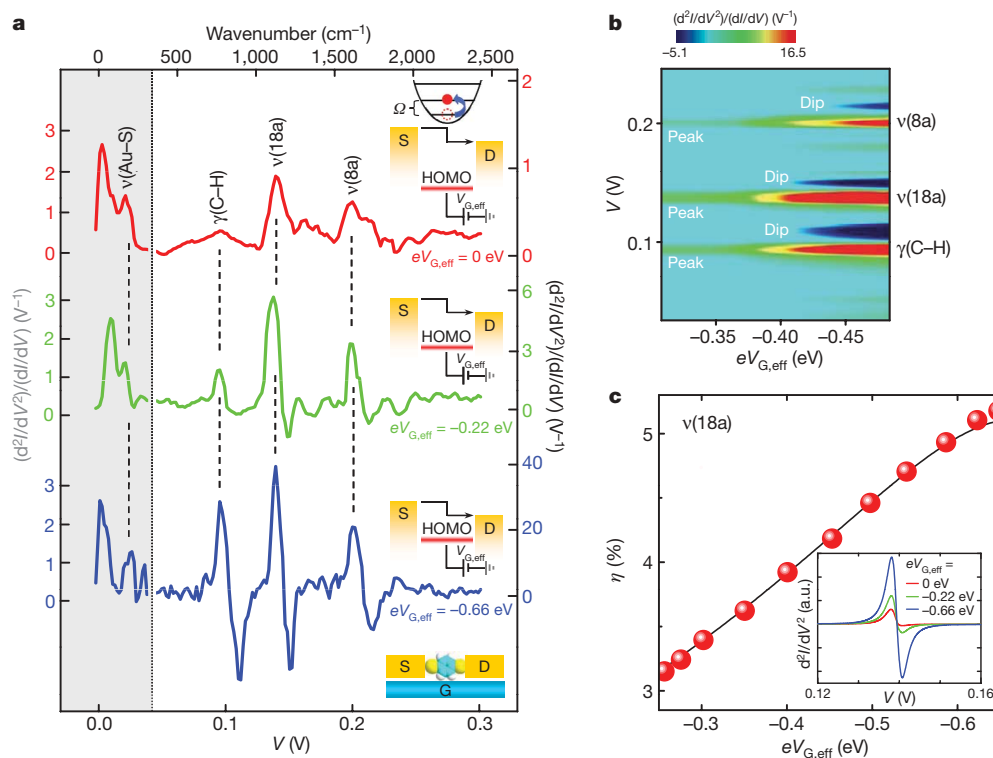
attributable to vibrational modes associated with the molecular species, which provides additional verification of the constituent molecules.

A well-established validation method for IET spectroscopy is to examine the linewidth broadening as a function of modulation voltage and temperature<sup>20,21</sup>. Figure 3c shows the modulation broadening of a representative IET spectroscopy feature (the 357-mV  $\nu(\text{C-H})$  stretching mode in the ODT junction) at a constant temperature of 4.2 K. The data points show the FWHM of the experimental peak. Taking into account the known thermal broadening ( $5.4k_B T$ ,



**Figure 3 | Gated IET spectra and linewidth broadening of a Au-ODT-Au junction.** **a**, IET spectra measured at 4.2 K for different values of  $eV_{G,\text{eff}}$  with vibration modes assigned. **b**, Two-dimensional colour map of the gated IET spectra, indicating near independence with respect to  $eV_{G,\text{eff}}$ . **c**, **d**, Full-width at half-maximum (FWHM) of the peak corresponding to the  $\nu(\text{C-H})$  stretching mode ( $\sim 357$  mV) as a function of a.c. modulation voltage (**c**) and

temperature (**d**). The circles indicate experimental data, and the solid line (**c**) and squares (**d**) show theoretical values. The error bars are determined by the Gaussian fitting. Insets, successive IET spectroscopy scans for the  $\nu(\text{C-H})$  mode under increasing a.c. modulation voltage (**c**) and increasing temperature (**d**), as indicated. r.m.s., root mean squared.



**Figure 4 | Resonantly enhanced IET spectra of a Au-BDT-Au junction.** **a**, IET spectra measured at 4.2 K for different values of  $eV_{G,\text{eff}}$  with vibration modes assigned. The left-hand  $y$  axis corresponds to the grey shaded region of the spectra, and the various right-hand  $y$  axes (with different scales) correspond to the related (colour-coded) spectra in the non-shaded region. The vertical dotted line corresponds to  $V = 45$  mV ( $363\text{ cm}^{-1}$ ). Significant modification in the spectral intensity and line shape for the benzene ring modes,  $\gamma(\text{C-H})$ ,  $v(18a)$  and  $v(8a)$ , was observed for different values of  $eV_{G,\text{eff}}$  as indicated. Insets, energy diagrams illustrating inelastic tunnelling

where  $k_B$  is Boltzmann's constant and  $T$  denotes temperature) and modulation broadening ( $1.7V_{\text{ac}}$ , where  $V_{\text{ac}}$  is the a.c. modulation voltage), the intrinsic linewidth,  $W_I$ , can be determined from a fit to the modulation broadening data (Fig. 3c, solid line), giving  $W_I = 4.94 \pm 0.89$  meV. Figure 3d shows the thermal broadening of the same  $v(\text{C-H})$  peak at a fixed modulation, demonstrating excellent agreement between experimental FWHM values (circles) and theoretical values (squares) (see Supplementary Fig. 9 for the BDT junction).

We now focus on the gate-voltage dependence of the IET spectra measured in the two types of molecular junction. The spectra of the ODT junction remain essentially unchanged at different values of  $eV_{G,\text{eff}}$  as shown in Fig. 3a. This constancy with respect to  $eV_{G,\text{eff}}$  can be also identified in Fig. 3b, which shows a colour map of the gated IET spectra. This result implies that, although the total current is sensitively dependent on the  $|E_{\text{F}} - E_{\text{HOMO}}|$  barrier height (because it is tunnelling), the inelastic tunnelling features that correspond to vibrational excitations of the molecule are nearly independent of the energetic parameters in the  $\sigma$ -saturated ODT junction, indicating little orbital coupling. However, the IET spectra of the  $\pi$ -conjugated BDT junction are drastically modified by gating (Fig. 4a, b), exhibiting an enhanced spectral intensity and a change in line shape for specific vibrational modes. As  $eV_{G,\text{eff}}$  becomes more negative in Fig. 4a (that is, as  $E_{\text{HOMO}}$  is brought closer to  $E_{\text{F}}$ ), the normalized amplitude  $(d^2I/dV^2)/(dI/dV)$  of some IET spectroscopy features in the BDT junction increase in magnitude by a factor of more than 30 and peak shapes of the zero-gate spectrum change to distinct peak-derivative-like (or Fano-shaped) features.

The difference between the Fermi energy and the energy of the molecular orbital has been shown to be an important factor in

as the position of the HOMO resonance shifts as a result of gating. **b**, Two-dimensional colour map of the gated IET spectra, showing that IET spectroscopy intensity and line shape vary significantly as functions of  $eV_{G,\text{eff}}$ . **c**, The relative change,  $\eta$ , in the normalized conductance for the  $v(18a)$  mode as a function of  $eV_{G,\text{eff}}$ . The circles show the experimental data and the solid curve represents the theoretical fit calculated from equation (1). Inset, the gate-variable IET spectra for the  $v(18a)$  mode, simulated using equation (1). a.u., arbitrary units.

determining the IET spectroscopy intensity and line shape<sup>23,24</sup>. As illustrated in Figs 1 and 2, the HOMO level for ODT is energetically much farther away from  $E_{\text{F}}$  than it is for BDT. Owing to the far-off-resonant nature of the ODT junction, the  $eV_{G,\text{eff}}$  values observed in the device (Fig. 3a) are predicted not to produce any significant changes in the IET spectra<sup>25</sup>. However, in the opposite limit of near resonance as in the BDT case, the dominant transport orbital (that is, the HOMO) will be strongly coupled to the internal vibrational modes (Fig. 4a, insets), resulting in resonantly enhanced IET spectra<sup>26–28</sup>. In addition, strong coupling between the molecular resonance and the vibrational modes is expected only when the energy states of the molecular orbitals are distributed around the bond directly related to the vibrational modes<sup>28,29</sup>, which has been shown to be prominent for  $\pi$ - $\pi$  orbitals (for example for BDT) and minimal for  $\sigma$ - $\sigma$  orbitals (for example for ODT)<sup>30</sup>. This is corroborated by DFT calculations showing that the HOMO of BDT has a significant contribution from the benzene ring, whereas there is essentially no contribution from the alkyl chain in the HOMO of ODT (Supplementary Fig. 10). We note that the vibrational modes associated with the benzene ring are the only modes enhanced by molecular orbital gating. The zero-bias features within  $\sim 40$  mV, including the shoulder features assigned as  $v(\text{Au-S})$  modes, are commonly attributed to phonon interactions in the metal leads<sup>21,22,29</sup>, and we observe that this metallic phonon regime is not affected by gating, as shown in Fig. 4a (grey shaded region).

For the enhanced resonant coupling in near-resonance IET, it has been shown that near the excitation threshold,  $|eV| = \Omega$ , for a molecular vibration, the corresponding change in the total tunnelling conductance (normalized to its elastic background) is<sup>27</sup>

$$\eta = \frac{\delta E^2}{(E_M - \bar{E}_F)^2 + \Gamma/2} \left[ \frac{(E_M - \bar{E}_F - \Omega)^2 - (\Gamma/2)^2}{(E_M - \bar{E}_F - \Omega)^2 + (\Gamma/2)^2} \theta(eV - \Omega) - \frac{1}{\pi} \frac{(E_M - \bar{E}_F - \Omega)\Gamma}{(E_M - \bar{E}_F - \Omega)^2 + (\Gamma/2)^2} \ln \left| \frac{eV - \Omega}{\Delta} \right| \right] \quad (1)$$

Equation (1) implies that the IET spectroscopy intensity and line shape can be varied, depending on the orbital energy,  $E_M$ , and the width,  $\Gamma$ , of the molecular resonance and its coupling,  $\delta E$ , to a particular molecular vibration (where  $\Delta$  is the cut-off energy, which is much smaller than  $\Gamma$ , and  $\bar{E}_F = E_F - eV$ ). Recently, theoretical models based on the non-equilibrium Green's function formalism have also described such variations in the IET spectroscopy features as the energy of the resonant level shifts<sup>23,24,26</sup>. Using equation (1), we can reproduce the experimental results for the gate-variable IET spectra (see Supplementary Information for details). In Fig. 4c, we show the agreement between the experimental values (data points) and calculated values (solid curve) of  $\eta$  for the  $\sim 138$ -mV  $v(18a)$  stretch mode of the BDT junction as a function of  $eV_{G,\text{eff}}$  which suggests that equation (1) can provide useful estimates of the contribution from the resonant coupling to the gate-variable IET spectra. We also quantitatively fit the observed IET spectroscopy line shapes for the  $eV_{G,\text{eff}}$  values shown in Fig. 4a. The agreement between theory and experiment is good for both the spectral line shape and the relative magnitude (Fig. 4c, inset). The same analysis for other vibration modes in the spectra generates essentially similar results to that for the  $v(18a)$  mode.

Our results demonstrate direct gate modulation of molecular orbitals. The IET spectra reveal which orbitals are resonantly enhanced, and dramatic differences are seen in the comparison between near-resonant and far-from-resonant systems. This demonstration validates the concept of molecular-orbital-modulated carrier transport, allowing new designs of molecular-based devices and elucidating both carrier transport mechanisms and the electronic structure of molecular junctions.

## METHODS SUMMARY

We used electron-beam lithography to pattern continuous thin gold wires with minimum widths of approximately 100 nm on top of an aluminium gate electrode, previously oxidized in a fresh oxygen atmosphere to form an  $\text{Al}_2\text{O}_3$  layer typically  $\sim 3$  nm thick that acts as a gate dielectric. Molecular deposition on the gold surface was performed in a dilute ethanol solution (1 mM) of each molecule inside a nitrogen-filled glove box. Before use, each sample was rinsed in ethanol and gently blown dry in a nitrogen stream. Then we immediately cooled the samples coated with the molecules to 4.2 K (in a vacuum cryostat), and used electromigration to form electrode pairs with a nanometre-scale separation by ramping up a d.c. voltage across the wire while monitoring the resistance. Full details on methods are presented in the Supplementary Information.

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