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A MULTIVARIATE APPROACH TO SINGLE-MOLECULE THERMOPOWER AND ELECTRIC CONDUCTANCE MEASUREMENTS

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ABSTRACT: We report a method using scanning tunnelling microscope single molecular break junction to simultaneously measure and correlate the single-molecule thermopower and electrical conductance. In contrast to previously reported approaches, it does not require custom-built electronics and takes advantage of a trace-by-trace calibration of the thermal offset at the Au/Au contact, thus greatly facilitating thermoelectric measurements at the single-molecule level. We report measurements of three molecules: 1,4-di(4-(ethynyl(phenylthioacetate)) benzene, 1,8-octanedithiol, and 4,4'-bipyridine, and determine single-molecule Seebeck coefficients of 12(3), 5(2), and -5(2) $\mu\text{V K}^{-1}$, respectively. Furthermore, the method statistically correlates the Seebeck voltage offset, electrical conductance, and stretching displacement of the single-molecule junction, and allows for direct comparison with current-distance spectroscopy results obtained at constant bias.

Keywords: charge transport; thermoelectrics; quantum interference; polycyclic aromatics; energy conversion; sustainability

Introduction

Thermoelectric energy generation is an environmentally friendly approach to improving the energy efficiency by converting waste heat into electricity. It has previously been estimated that approximately 63% of the global primary energy consumption is lost during combustion and heat transfer processes, with waste heat being a major contributor.^{1,2} Efficient conversion of at least part of this loss into a usable form of energy would thus be an exciting prospect. While the theoretical efficiency of thermoelectric processes is not high and is bound by the Carnot limit (as well as other factors), they do have advantages, compared to other energy generation technologies, such as heat engines. For example, they are typically all-solid-state devices, which do not require cooling liquids or have any moving parts, and they are usually less bulky. This means they find application in areas, where maintenance is difficult or costly, such as in space travel or deep-sea exploration, or where power demands are low, for example in some sensing applications in remote environments.

Thermoelectric energy generation is rooted in the Seebeck effect,³ where a temperature difference ΔT across a material induces a potential difference, the thermal voltage ΔV . This is a consequence of the temperature dependence of the Fermi distribution, thus resulting in the redistribution of charge carriers in the material and in charge separation along the temperature gradient.⁴ To generate a high ΔV for a given ΔT materials for thermoelectric applications must have a high Seebeck coefficient, defined by

$$S = -\frac{\Delta V}{\Delta T} .^5 \quad (1)$$

The efficiency of a thermoelectric material is related to its electric and thermal conductances, G and K , via the figure of merit ZT (assuming that the geometric factors for electric and thermal transport are the same):

$$ZT = \frac{GS^2T}{K} . \quad (2)$$

Hence, it is clear from Eq. 2 that, to maximise ZT , G and S need to be as large as possible (thus maximising the power factor, $f = GS^2$), while K must be minimized, for example by minimising phonon transport.⁶

Molecular materials equally lend themselves to such optimisation, due to their compositional and structural variety and synthetic flexibility. This is illustrated by eq. 3, which relates the thermopower to the transmission function $T(E)$ of a molecular junction⁷.

$$S = - \frac{\pi^2 k_B^2 T}{3e} \left. \frac{\partial \ln(T(E))}{\partial E} \right|_{E=E_F} , \quad (3)$$

where E is the energy, E_F the Fermi energy, k_B Boltzmann's constant, T the temperature and e the elemental charge.

Specifically, S is determined by the gradient of the (logarithmic) transmission function $T(E)$, which can be altered by an appropriate choice of substrate material and anchor group, thus controlling the Fermi level alignment. In addition, it has also been shown that molecular design can affect the thermal conductance, for example via phonon interference, the introduction of heavy-atom side chains or the choice of anchor groups minimising phonon coupling to the substrates.⁸ In combination, these features may offer the prospect of decoupling electric and thermal conductance in the spirit of the Wiedemann-Frantz law and potentially lead to further increases in ZT .

Experimental testing of theoretical predictions for molecular conductance and thermopower generally rely on two conceptual approaches, namely measurements at the single-molecule level, and in thin films, and one would expect these to be largely complementary. To this end, single-molecule measurements allow for more direct insight into structure-property relationships, and are unaffected by uncertainties around molecular surface coverage or structure, for example. On the other hand, they may also reveal a variance in the measured properties, which is not representative of thin-film devices, where high coverage and close packing in the molecular adlayer may reduce the structural

variability. Thin-film measurements are more likely to represent structurally averaged characteristics as large number of molecules are sampled simultaneously.

However, measuring the thermoelectric properties of single molecules reliably is not trivial. Apart from challenges around addressing individual molecules immobilised on a surface, the thermal voltages induced by practical temperature gradients in molecular systems (perhaps 20-100 K) are small, e.g., in the region of 1-5 mV for $S = 50 \mu\text{V K}^{-1}$. Scanning probe techniques, and in particular STM break junction (STM BJ) configurations, have been adapted to perform such measurements,^{9,10,11,12,13} but this has typically involved customised hardware, purpose-built electronics, and sophisticated data acquisition schemes. For example, the pioneering work by Reddy et al. involved approaching a room temperature (RT) STM tip towards a heated substrate until a certain conductance value ($0.1 G_0$) was reached (G_0 , the conductance quantum, is theoretically defined as $G_0 = 2e^2/h$, where e is the elemental charge and h is Planck's constant). The applied tip/substrate bias voltage and the current amplifier was then switched off, the tip retracted, and a voltage amplifier switched on to measure the thermal voltage directly during tip withdrawal.¹⁴ A similar approach has been used by Malen and Segalman et al.¹⁵ Widawsky et al. also used an STM BJ, first approaching the tip to a conductance value of $5 G_0$, followed by tip retraction by a certain distance, holding the tip in position for 50 ms and another retraction. The first and last quartile of the 50 ms window were used to measure the molecular electric conductance at finite applied bias, while the bias was switched off during the middle 25 ms to record the thermal current. Finally, the measured thermal current and the electrical conductance were used to determine the thermal voltage.¹⁶ Tao et al. performed thermoelectric measurements on DNA by soft-contact current/distance spectroscopy (the substrate was cooled), where molecular bridge formation during tip withdrawal was detected as a plateau in the tunnelling current (even though in their paper the authors do not seem to state how a plateau was identified during this process).¹⁷ The withdrawal process was then stopped, a current/voltage (I/V) ramp performed between ± 10 mV and tip withdrawal continued until the molecular junction broke. This measurement simultaneously provided the molecular conductance from the slope of the I/V trace as well as the thermal voltage as

the offset of the I/V trace at zero (applied) bias. A conceptually simpler approach based on distance-dependent I/V spectroscopy in a customised setup was employed by Yzambart, Agraït et al.¹⁸ In their experiment, the (heated) tip was brought into contact with the substrate surface, then withdrawn in a stepwise manner (40-60 pm/step) and at each step an I/V trace recorded (± 10 mV, relative to a tip/substrate bias of 0.2 V). Again, both the conductance and the thermal voltage were extracted from the slope and the offset at zero bias, respectively.

In the present work, we employed a similar method, except that in our case the substrate was heated while the tip remained at RT, and we used the 'as supplied' logarithmic current pre-amplifier in the commercial STM setup, rather than custom-built electronics. Employing distance-dependent I/V spectroscopy (STM BJ IV), we recorded multiple sets of I/V traces to determine the voltage offset for $I = 0$ nA, corresponding to either direct tip/substrate contact (close contact), a tip/molecule/substrate bridge, or direct tunnelling through a tip/substrate gap. The voltage offset at the Au/Au contact ($\sim 1 G_0$) was then subtracted from all other voltage offsets in a given set, thereby reducing instrumental fluctuations and drift on a trace-by-trace basis. In combination with multivariate data analysis, this yielded an accurate measurement of the molecular thermal voltage and largely eliminated instabilities in the voltage offset that sporadically occurred over the duration of an experiment. This approach thus greatly facilitated the determination of single-molecule thermopower. It also provided distance-dependent data for the thermopower and electric conductance, as well as the break-off distance, and thereby enabled direct comparison with results from complementary constant-bias STM break-junction experiments, STM BJ.

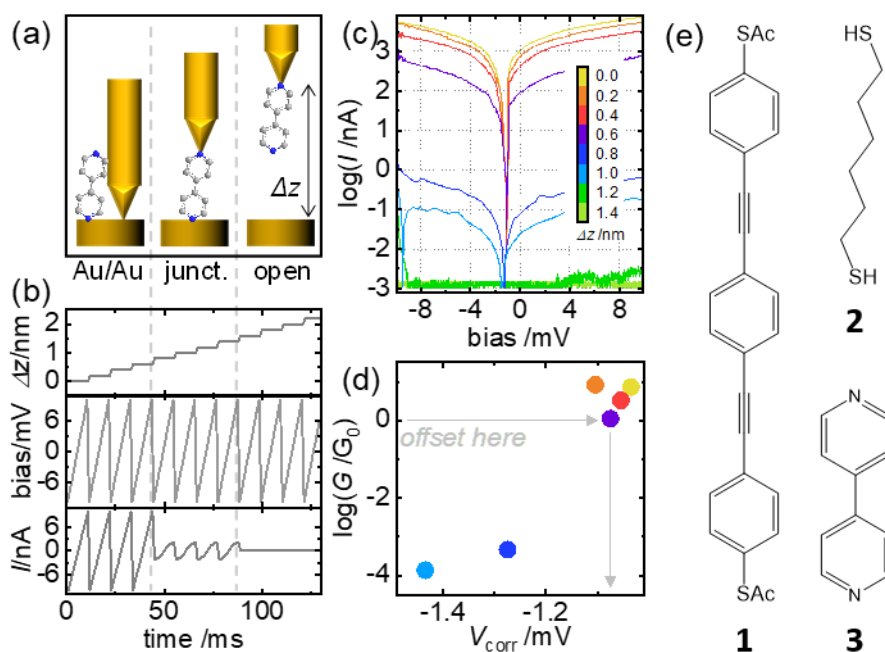


FIG. 1: Depiction of an STM BJ IV experiment and example data. (a) Au STM tip is retracted from the substrate while a bias is applied, and the current is measured. (b) In STM BJ IV mode the tip is retracted in steps, and at each step the bias is swept, yielding a series of I/V traces across the junction. (c) Example series of I/V traces from a single tip withdrawal at $\Delta T = 27$ K, with four high-current traces across the Au/Au junction (yellow, orange, red, purple), two medium-current traces across molecule **3** (blue), and two traces at the noise level (greens). Note, asymmetry in these I/V traces was a result of drift in the electronics and corrected in subsequent procedures. (d) Each trace in (c) can be parameterized by determining the displacement, Δz , within the series (colour scale), the differential conductance, G , and the voltage offset, V_{corr} . The trace closest to $1 G_0$ (purple trace) defines the voltage and displacement offset corrections for that series (here $V_{\text{corr}} = -1.074$ mV). (e) Chemical structures of molecules **1**, **2** and **3**.

Materials and Methods

The three molecules used in this study were 1,4-di(4-(ethynyl(phenylthioacetate)) benzene (molecule **1**), 1,8-octanedithiol (molecule **2**), and 4,4'-bipyridine, (molecule **3**), and chosen to reflect different structure and anchor group chemistry. The samples were purchased from Sigma-Aldrich with purity grades of 97% (molecules **1** and **2**) and 98% (molecule **3**), respectively, and were used without further purification, cf. section S1.1 in the Supporting Information (SI) for further details.

Constant-bias STM BJ and distance-dependent I/V spectroscopy measurements were conducted on an Agilent 5100 (Keysight) Scanning Tunnelling Microscope fitted with a logarithmic pre-amplifier and sample heating plate (Lake Shore Cryotronics Model 331, USA, controlling an Agilent Model N9647A, USA, sample plate). Substrate and STM tip were of Au; the tip was left at room temperature during all measurements. The main purpose of the constant-bias STM BJ experiments as a well-established technique was to determine G_{mol} and Δz_{mol} for each molecule, as described in section S1.2,^{19, 20, 21,22} and to validate results obtained from STM BJ IV spectroscopy.

In STM BJ IV mode, I/V sweeps were measured as a function of tip/substrate distance, as depicted in figure 1(a) and (b), in discrete steps of 0.2 or 0.3 nm (larger for molecule **1**, to ensure breaking of the junctions), from direct Au/Au contact ($\Delta z \leq 0$ nm) to large tip/substrate distances ($\Delta z \gg \Delta z_{\text{mol}}$). At intermediate distances, when $\Delta z \approx \Delta z_{\text{mol}}$ or smaller, a molecule may be caught between the tip and the substrate until the distance becomes too large the junction eventually ruptures. In a typical experiment, ≈ 1000 withdrawals were performed in 25 steps at each ΔT , yielding ≈ 25000 I/V curves total.

At each step, an I/V trace was recorded, typically between ± 10 mV at a sweep rate of 2.0 V/s (see section S1.4 in the SI for detailed discussion on the effect of sweep rate, direction and voltage range as well as linearity), providing information on the thermal voltage (from the offset of I at $V = 0$ mV, *vide infra*), the electric conductance G (from the slope of the I/V trace, calculated from 41 data points centred around $V = -5$ mV, cf. S1.4.4 in the SI for further details), and the displacement of the tip

relative to the substrate, Δz . Hence, for the three cases described above, one would expect $G \geq 1 G_0$ for sweeps across the Au/Au junction (yellow to purple traces in fig. 1(c)); $G \approx G_{\text{mol}}$ for sweeps across the Au/molecule/Au junction (blue traces); and $G \approx 0$ once the molecular bridge has been broken at sufficiently large Δz . By convention, G was scaled by G_0 and plotted on a logarithmic scale.

The determination of the molecular thermopower, ΔV_{mol} , required a more detailed analysis. For $\Delta T = 0$ and in the absence of random noise and drift in the electronics, ϵ_{STM} , one would expect each I/V trace to pass through $I = 0$ nA at $V = 0$ mV. For $\Delta T > 0$, the thermal voltage from the junction is superimposed on V , but in practice, ϵ_{STM} also contributes to ΔV , cf. eq. (4). Detailed analysis has shown, however, that these interferences may be removed and the thermopower of the molecular junction, ΔV_{mol} , be extracted, see section S1.3.2 for details. Briefly, the approach takes advantage of characteristic properties of the data, namely that a) random fluctuations may be averaged out using sufficiently large datasets, and b) electronic drift occurs on a different (slower) timescale than recording a set of I/V traces, allowing for a voltage calibration on a trace-by-trace basis. Indeed, we found that the Au/Au contact with $G \approx G_0$ and $\Delta z = 0$ also serves as a suitable internal reference for the voltage offset of the I/V traces and thus subtracted its value V_{corr} from all ΔV values measured in I/V traces in a given set of distances Δz , cf. fig. 1(d).

$$\Delta V = \epsilon_{\text{STM}} + \Delta V_{\text{Au}}(+\Delta V_{\text{mol}}) = \Delta V_{\text{corr}}(+\Delta V_{\text{mol}}) \quad (4)$$

However, a number of points are worth noting. Firstly, the thermopower of the Au/Au contact itself has been found to be small, albeit somewhat dependent on the contact geometry.^{23,24} To this end, Ludoph and van Ruitenbeek have reported a negative value of $-0.5 \mu\text{V/K}$ for Au/Au contacts at G_0 and positive values up to $+1 \mu\text{V/K}$ for G up to $10 G_0$. The former compares well with a value of approximately $-1 \mu\text{V/K}$ reported by Agrait et al.²⁵, but is significantly smaller than the molecular thermopower values found for molecules **1** to **3** (see below). Secondly, while ΔV_{Au} determined at $G \approx G_0$ serves as an internal calibration here, it does not directly correspond to the thermal voltage of the contacts - namely the immediate atomic environment around the anchor groups - in the presence of

a molecular bridge. Accordingly, we found that in the absence of a molecular bridge, after correcting V_{corr} , the average voltage offset was close to, but not exactly zero. We also explored whether differences in the load resistance would cause a systematic voltage offset, given that the load resistance during a STM BJ IV experiments changes by several orders of magnitude. To emulate this effect, we performed control experiments by bridging the tip and substrate electrodes with well-defined resistors in the range of $R_0 = 1/G_0$ and $R_{\text{mol}} = 1/G_{\text{mol}}$, and measured the voltage offset in a way similar to the experiments with molecular systems, cf. section S1.3.1. In the results, we did not observe a simple correlation between voltage offset and load resistance for the chosen range of values, fig. S5. However, there appeared to be small positive voltage offsets when comparing R_{mol} against R_0 . Crucially, while those factors may contribute to the observed absolute voltage offset, they seemed to be independent of ΔT within experimental error and are therefore unlikely to affect the determination of S , *vide infra*.

To proceed with the analysis, a three-dimensional ($\Delta z, G, \Delta V_{\text{mol}} = -\Delta V_{\text{therm}}$) scatter plot was produced and clustered using a Gaussian Mixture Model (GMM) with three clusters, cf. fig. 2(d) and section S1.3 in the SI.^{13,20,26,27,28,29,30,31,32} This value was chosen because in most cases, the measurements were expected to include a cluster containing Au/Au junctions ($G > G_0$, yellow cluster in fig. 2 (c)), one cluster with molecular events (blue) as well as a separate cluster capturing noisy or poorly defined traces (red). Histograms of all ΔV values in the molecular, Au/Au, and noise clusters at given ΔT were then plotted, as shown in fig. 2 (d) for molecule **3** at $\Delta T = 27$ K. In accordance with eq. (1), S was then determined from a linear fit of all ΔV values plotted against ΔT , as shown in fig. 3 (a) for molecule **3**, and figs. S7 (a) and (d) in the SI for molecules **1** and **2**. Replicates were performed on independent samples for each molecule and on separate days.

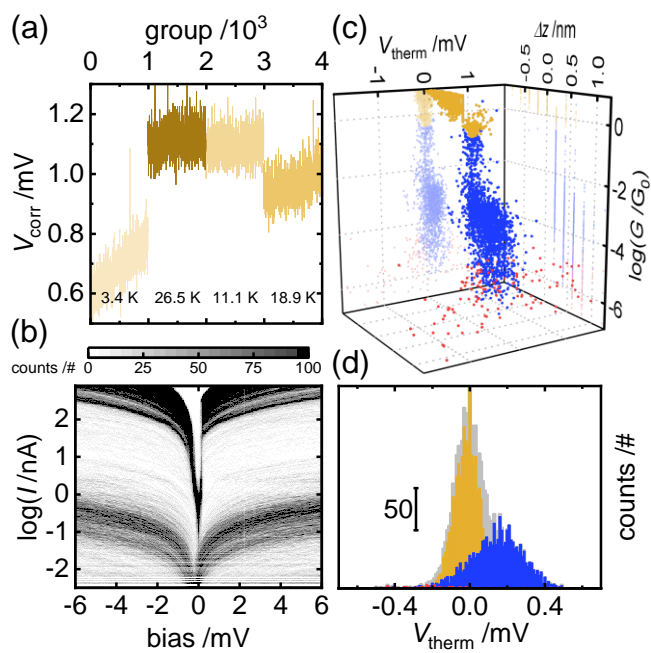


FIG. 2: Example STM BJ IV experiment performed on an adlayer of molecule **3**. (a) V_{corr} for each withdraw group over the time of the experiment. (b) 2D current vs bias intensity plot after V_{corr} is removed from each group. (c) 3D scatter plot of displacement, Δz , conductance, G , and voltage offset, V_{therm} , from each trace clustered using Gaussian mixture model into a Au/Au cluster (yellow), a molecular cluster (blue), and a noise cluster (red) (sweeps across open junctions had been removed). (d) 1D histograms of V_{therm} for the three clusters above, and for the entire data set (grey) at $\Delta T = 27$ K.

Results and Discussion

We now turn to the results obtained for molecules **1-3**, as well as "empty" Au/Au tunnelling junctions, following the above methodology. Fig. 3 (a-c) show results for **3**, similar data for **1** and **2** can be found in the SI, fig. S7. Panels (d) and (e) show the ΔV vs. ΔT plots, including the 95% confidence intervals, for all four configurations as well as the results obtained for *S*, including the individual replicates for each. The numerical results can be found in Table 1 (bottom rows), along with the power factor $f = G \cdot S^2$. The combined result for molecule **1** lies slightly below each of the individual replicates due to a constant offset between replicates 1 and 2, as seen in Fig. S7(a). Individually, both replicates have

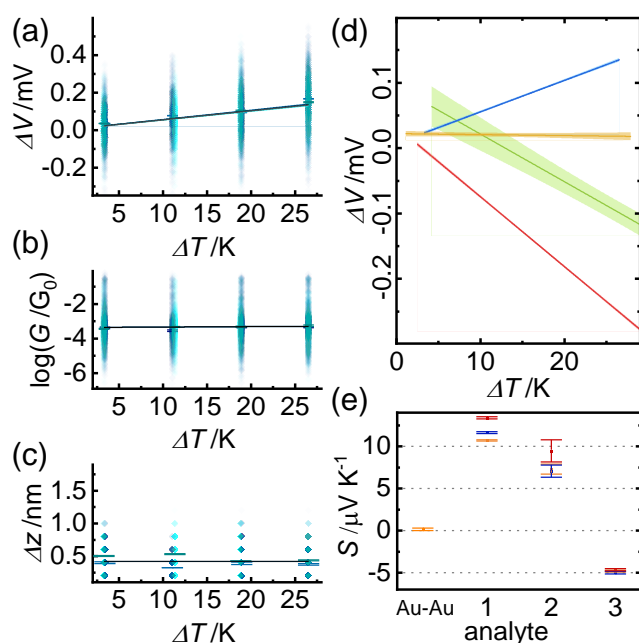


FIG. 3. (a) Scatter plots of ΔV vs ΔT measurements of **3** with separate trend lines, and combined trend line with 95% confidence interval. (b) Scatter plots of G vs ΔT , and (c) Δz vs ΔT for the same measurements, with G_{mol} and Δz_{mol} from each separate measurement calculated as the mean of a Gaussian fit of the distribution, and standard deviation as error bars. Black trend line is guide for the eye. (d) ΔV vs ΔT trend lines with 95% confidence intervals for **1** (red), **2** (green), **3** (blue), and clean Au/Au (yellow). (e) Summary of S_{mol} for all molecules in this study, and clean Au/Au junctions. Blue/red represent trial 1/2, and orange is the combined result. Error bars are standard error on the fit of the slope.

nearly identical results, except for a small constant offset. When the two results are combined, this offset reduces the magnitude of the slope overall.

Focusing initially on panel (a), the ΔV vs. ΔT plot shows a positive correlation, in accordance with eq. (1). A linear fit yields a value $S = -4.82 \pm 0.09 \mu\text{V/K}$ (in short 4.82(9) $\mu\text{V/K}$). $\log(G_{\text{mol}}/G_0)$ and Δz_{mol} were determined to be -3.3(9) and 0.4(2) nm, as discussed in more detail below. Finally, there does not appear to be a strong or consistent correlation between $\log(G/G_0)$ and ΔT for the three molecules, as expected for tunnelling-based transport, and a weak negative one for Δz_{mol} vs. ΔT with a slope of 1 pm/K or less for molecules **1** and **2**, but not for molecule **3** within experimental error, see Table S3 in the SI. A negative correlation could indicate that the stability of the junctions is reduced at larger ΔT , perhaps because molecular bonds rupture more easily when the substrate is hotter or because of increased thermal drift. However, the observed effect is rather weak and a fuller explanation would clearly require further study.

Fig. 3 (d) also includes the ΔV vs. ΔT data for molecules **1** (red) and **2** (green) as well as data for the Au/Au tunnelling junction (yellow), namely in the absence of a molecular bridge ("empty" junction). ΔG_{mol} and Δz_{mol} for the latter formally arise because the analysis method is agnostic as to whether a molecule is present in the junction or not. As a result, in an "empty" Au/Au junction, a small number of I/V sweeps are still recorded in sub- G_0 conductance region, before the conductance drops below the cut-off defining value for Δz_{mol} ($10^{-4.5} G_0$, *vide supra*). Numerically, those feature a mean conductance of $\log(G_{\text{mol}}/G_0) = -3(1)$ and a (short) mean displacement of 0.4 nm, consistent with pure tunnelling with a decay constant of ca. 10 nm^{-1} . After correcting for V_{corr} the remaining voltage offset - effectively the offset shift between a single-point contact and a tunnelling junction at distance Δz - is very small and remains unchanged as ΔT increases, with a slope of 0.2(2) $\mu\text{V K}^{-1}$.

For molecules **1** and **2**, the correlation between ΔV and ΔT is opposite in sign, compared to molecule **3**. The thermopower values have been determined as +10.69(8) $\mu\text{V/K}$ and +7.3(6) $\mu\text{V/K}$, and

$\log(G/G_{\text{mol}})$ and Δz_{mol} as -3(1) and 1.1(8) nm for molecule **1**, and -4(1) and 0.6(3) nm for molecule **2**, respectively.

Table 1: Results from current/distance spectroscopy at constant bias (top) and distance dependent I/V spectroscopy (bottom). Values for Δz_{mol} and G_{mol} are sample mean and standard deviation for all ΔT and all replicates; S values are slope and standard error of the slope for the trend line through all ΔT and all replicates. Note that the values for Au/Au have a different meaning, as discussed in the main text.

<i>Molecule</i>	Δz_{mol} nm	G_{mol} $\log(G G_0^{-1})$	S_{mol} $\mu\text{V K}^{-1}$	f aW K^{-2}
1	2.02(3)	-3.49(1)		
	1.1(8)	-3(1)	10.69(8)	6.7
2	1.0(5)	-4.3(5)		
	0.6(3)	-4(1)	7.3(6)	0.33
3	0.8(3)	-3.2(8)		
	0.4(2)	-3.3(9)	-4.82(9)	0.86
Au/Au	0.4(2)	-3(1)	(-0.2(2))	

Before we return to the discussion of the (thermo)electric properties of the junctions, for validation we have also compared the STM BJ IV results with data obtained using the more widely established constant-bias STM BJ method. While the latter does not provide information on ΔV , it does yield G_{mol} and molecular break-off distances, in the present case with higher spatial resolution in our implementation of the STM BJ IV approach. The results are shown in fig. 4 (for molecule **3**) and figs. S2 and S3 (for molecules **1** and **2**) and summarised in Table 1 (top rows). In each case, the

conductance/distance traces show the well-known feature around G_0 , corresponding to direct contact between the tip and the substrate. As the distance is increased, the conductance either drops exponentially (for "empty" junctions) or enters a plateau-like feature (for molecular junctions). In the case of molecule **1** and molecule **3**, molecular junctions seem to dominate, suggesting that the hit rate is close to 100%; for **1**, the plateau feature is noticeably slanted. For molecule **2**, both exponential decays and plateau features are observed, and the hit rate is 40%, based on the area-type Gaussian fit of the break-off distance histogram. STM BJ data for molecule **3** appear to show two sub-populations with plateaus at higher and lower conductance, with $\log(G_{\text{mol}}/G_0) = -3.2(8)$ and approximately -4. The high-conductance population appears to be the dominant population. This is in-line with findings by Venkataraman et al., who rationalise the presence of two sub-populations based on different binding geometries and Fermi alignment in the junction.³⁵ Notably, we did not observe two clear sub-populations in the STM BJ IV data, see blue cluster in fig. 2 (c), but at present it is unclear whether this is due to a lack of resolution or differences in the pulling process.

For comparison, we have included mean G_{mol} and Δz_{mol} values and standard deviations from the STM BJ IV measurements in the 2D conductance-distance histogram in Fig. 4(a) (dark/light blue cross hairs: independent datasets 1 and 2; orange: combined values). They clearly match the conductance plateau of the high-conductance population, while the displacement appears to be somewhat shorter. Qualitatively similar behaviour is observed for molecules **1** and **2**, namely that the conductance values match within experimental error, while the mean displacements obtained from STM BJ IV are systematically shorter than those measured in STM BJ, Table 1 and section S1.2 in the SI for further details. The differences are approximately twice or thrice the size the piezo step between consecutive I/V sweeps (either 0.2 nm or 0.3 nm, *vide supra*).

Hence, this observation can be rationalised, considering how the mean junction displacements are defined in the two cases: in STM BJ IV mode, the displacements are determined while the molecular junctions is still intact (before break-off, judged by the measured G value). In STM BJ mode, on the

other hand, the displacement histogram was calculated when the trace had reached the lower conductance cut-off, for example $10^{-4.5} G_0$ (i.e., after the junction had ruptured). Thus, the observed systematic difference in Δz_{mol} is unsurprising and the otherwise close correspondence between the two methods supports the assignment of the molecular cluster in the STM BJ IV data that was ultimately used to derive S_{mol} .

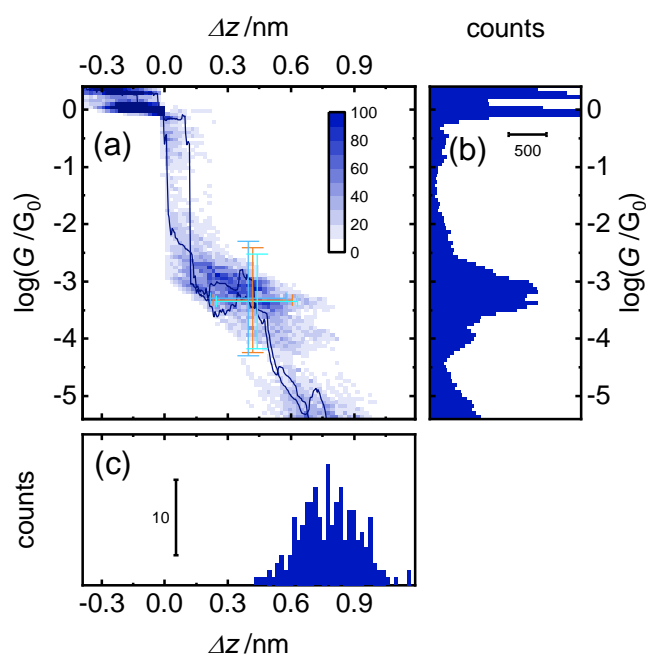


FIG. 4: Constant-bias STM BJ experiment performed on adlayer of molecule **3**. (a) 200 traces combined in a 2D conductance vs displacement intensity plot with two example traces (navy). Crosshairs are (z_{mol}, G_{mol}) from the STM BJ IV measurements with standard deviation (blues are trial 1 and 2, orange is combined). (b) 1D conductance histogram of all traces obtained in the constant-bias measurement. (c) 1D displacement histogram, determined at a conductance of $10^{-4.5} G_0$.

Having consolidated the methodology, we will now briefly discuss our single-molecule conductance and thermopower results in a wider context. Generally, our conductance data are in good agreement with previous literature. For example, for molecule **1**, we previously measured $\log(G_{mol}/G_0) = -3.74$ using soft-contact current distance spectroscopy,¹³ while Linke et al. found a conductance of $\log(G_{mol}/G_0) = -4.22 \leq -3.92 \leq -3.74$ and a thermopower value $10.8 \pm 9.5 \mu\text{V/K}$,³³ which compares

favourably to $-3.49(1)$ and $-3(1)$ and $10.69(8)$ $\mu\text{V}/\text{K}$, Table 1. In the case of molecule **2**, we found $-4.3(5)$ and $-4(1)$ for $\log(G_{\text{mol}}/G_0)$ and $S = 7.3(6)$ $\mu\text{V}/\text{K}$, in agreement with $\log(G_{\text{mol}}/G_0) = -4.3$ in our previous work, again employing soft-contact current-distance spectroscopy (see reference 34 for a more detailed comparison). Moreover, Majumdar et al. determined the thermopower as 2.4 ± 0.4 $\mu\text{V}/\text{K}$,¹⁵ which is somewhat smaller than the value of $7.3(6)$ we obtained in our experiments. Interestingly, for **3**, we observed two conductance groups in STM BJ experiments, a more abundant one at $\log(G_{\text{mol,H}}/G_0) = -3.2(8)$ and a less abundant one at ~ -4 , in line with previous work by Venkataraman et al.^{16,35} They observed the high-conductance group at $\log(G_{\text{mol,H}}/G_0) = -3.40$ and the low-conductance group at $\log(G_{\text{mol,L}}/G_0) = -4$, with thermopower values of -8.4 $\mu\text{V}/\text{K}$ and -7.5 $\mu\text{V}/\text{K}$, respectively. In our STM BJ IV measurements, we only observed one molecular cluster, for reasons discussed above, with a mean conductance of $-3.3(9)$ and a thermopower of $-4.82(9)$. This conductance value is in agreement with the high-conductance values above, even though our thermopower is formally lower than both values reported by Venkataraman et al.

The observed sign of the thermopower reflects the electronic structure of the junction around the Fermi level.^{10,36} In particular, pyridine anchors typically bring the Fermi level towards alignment with the lowest unoccupied molecular orbital (LUMO), resulting in positive slope in $T(E)$, a negative Seebeck, and electron-dominated charge transport. Conversely, thiol anchors typically bring the Fermi level towards alignment with the highest occupied molecular orbital (HOMO), resulting in a negative slope in $T(E)$, a positive Seebeck, and hole-dominated charge transport. The results presented in this paper confirm these results, where the thiol anchors in molecules **1** and **2** yield positive Seebeck coefficients and the pyridine anchors in molecule **3** yield a negative Seebeck.

Conclusions

Taken together, we find that the conductance, the sign and magnitude of the thermopower values for molecules **1-3** agree well with literature values, thereby validating previous results obtained on

different measurement platforms. In comparison with the best performing molecular and solid-state materials, the thermopower values for those molecules are small,³⁷ likely due to the Fermi level being close to the middle of the HOMO/LUMO gap in these molecules. We note that in the case of molecular materials, however, the magnitude of S can be significantly increased, for example by chemical design and quantum interference (QI),^{38,39} which has been demonstrated experimentally and theoretically at the single-molecule and thin-film levels.³³ In the present work, we have mainly focused on the development and validation of STM BJ IV spectroscopy, as a new and comparatively facile way to measure single-molecule thermopower. We have also characterised the molecular conductance and break-off distances systematically in a range of temperature gradients, which we found to be negligible, and cross-validated STM BJ IV results with the more established constant-bias STM BJ method, finding close agreement in all three cases. On this basis, we are confident that our methodology can readily be applied to new molecular systems and facilitate the discovery of high-performing thermoelectric materials based on new paradigms in chemical design.

Supporting Information

Details on sample preparation and tunneling spectroscopy measurements; assessment of experimental parameters, instrumental effect, sensitivity and noise on measurement performance; constant-bias tunneling spectroscopy data for molecules **1** and **2**.

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