Voltage-Controlled Binary Conductance Switching in Gold–4,4′-Bipyridine–Gold Single-Molecule Nanowires

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ABSTRACT: We investigate gold–4,4′-bipyridine–gold single-molecule junctions with the mechanically controllable break junction technique at cryogenic temperature (T = 4.2 K). We observe bistable probabilistic conductance switching between the two molecular binding configurations, influenced both by the mechanical actuation and by the applied voltage. We demonstrate that the relative dominance of the two conductance states is tunable by the electrode displacement, whereas the voltage manipulation induces an exponential speedup of both switching times. The detailed investigation of the voltage-tunable switching rates provides an insight into the possible switching mechanisms.

The field of single-molecule electronics envisions the exploitation of single molecule interconnects between conducting electrodes as functional devices. A key component toward this goal is the well-controlled manipulation of the conductance states by external parameters. Single-molecule conductance switching was already induced by mechanical actuation, by light irradiation, or by the voltage applied on the junction. In the latter case, usually complex molecules are applied, where either a charged or polarizable segment of the molecule is actuated by the electric field or the charge state of the molecule is manipulated. Here, we demonstrate voltage-tunable probabilistic conductance switching with a simple benchmark molecule, 4,4′-bipyridine (BP).

Previous measurements on Au–BP–Au single-molecule structures have shown, that the BP molecule can attach to gold electrodes in two different binding geometries resulting in double-step molecular plateaus on the conductance versus electrode separation traces after the rupture of a single-molecule gold junction with . In the following, we refer to these two binding geometries as HighG and LowG configurations, which are also reflected by two clear peaks on the conductance histograms. A mechanically controlled binary conductance switching between these two configurations was also reported, however, the voltage-controlled manipulation of the conductance states was hindered by the limited junction stability in the room temperature break junction environment.

Here we utilize a cryogenic temperature (T = 4.2 K) mechanically controllable break junction (MCBJ) setup to investigate the voltage-controlled binary conductance switching in Au–BP–Au single-molecule junctions. The superior low-temperature stability enables us to map the response of the junction to the manipulation of the external parameters in detail. We observe bistable switching between the two molecular configurations, influenced both by the mechanical actuation and by the applied voltage. We find that, at low bias voltage, the electrode separation determines the preferred junction configuration, similarly to prior room temperature measurements. However, as the voltage is increased, a probabilistic switching is induced. We demonstrate that the relative dominance of the two configurations can be tuned through adjusting the electrode separation, while the switching rates are controlled by the applied voltage. This behavior resembles the characteristics of probabilistic bit devices. Finally, we confront the measured switching phenomena with possible switching models, like (i) simple two-level system models, (ii) temperature activated switching models, (iii) a vibrational pumping model, (iv) a double-well potential...
inversion model, and (v) a heuristic model relying on the molecule’s energy dependent transition probability.

We performed measurements using a cryogenic MCBJ setup with high purity gold wires. After cooling the setup, a histogram is recorded to ascertain the cleanliness of the junction; then molecules are dosed using an in situ evaporation technique.\(^{23,25}\) We show an example pair of conductance traces in Figure 1a, black corresponds to the opening while gray to the closing trace, both exhibiting molecular plateaus. While the room temperature conductance histograms acquired by the same setup\(^{6,20,22}\) reproduce the common double-peak structure,\(^{6,20,22}\) the histogram for our low-temperature measurement shows a significant difference (black curve on Figure 1b), exhibiting an enhanced peak at the LowG interval and only a slight shoulder in the HighG region. In our previous work,\(^{25}\) we have shown that this phenomenon is related to the low-temperature single-atomic-chain-pulling mechanism typical for gold.\(^{28}\) The probable atomic chain formation process in the stable low-temperature environment yields such wide gaps after the chain rupture that are unable to accommodate the HighG molecular configuration.

Compared to the low-temperature opening histogram, the peaks in the closing histogram (gray curve in Figure 1b) are shifted toward higher values. Furthermore, the HighG peak becomes more pronounced, although the LowG peak remains dominant. We explain this by the adhesive instability of the junction.\(^{25}\) In the opening process a stretched molecular junction is formed inside a wider gap between the gold electrodes, whereas in the closing process, the electrodes and the molecule are relaxed, which leads to a somewhat higher conductance.

Next, we investigate how changing the electrode separation affects the molecular binding configuration. In their prior study Quek et al. reported mechanically controlled binary conductance switching between the two binding configurations.\(^{6}\) This was realized by stopping the opening process and applying a short (~60 ms) periodic signal to the piezo actuator to mechanically perturb the junction by repeatedly compressing and stretching it with 2 Ångstroms amplitude. When a molecule was caught in the junction during the period of the mechanical perturbation, the conductance indicated periodic switching between the two binding configurations. In Figure 1c,d,e, we reproduce this mechanical switching at 2 orders of magnitude longer time scales, utilizing the enhanced mechanical stability of the junction in the low-temperature environment. Thanks to the superior stability, we can also resolve the sub-Ångstrom displacement interval, where a conductance hysteresis is observed along the displacement cycles (Figure 1c).

We continue by investigating the current—voltage characteristics of BP single-molecule junctions. Typical \(I(V)\) curves (Figure 2a,b) show that at low bias voltage, the present state of the junction is stable. However, when the applied voltage is increased, the junction exhibits binary probabilistic switching between two distinct conductance states. Upon further increasing the voltage, the switching rates also increase. Figure 2c shows the distribution of the high and low conductance states (i.e., the on and off conductances) deduced from a statistical amount of switching \(I(V)\) curves. As a reference, the closing conductance histogram is reproduced from Figure 1b as a gray area graph. The similar positions of the peaks in the closing histogram and the distributions of the on and off

\[\text{Figure 1. (a) Sample opening (black) and closing (gray) trace pairs at } T = 4.2 \text{ K temperature. (b) Opening (black) and closing (gray) conductance histograms at } T = 4.2 \text{ K. (c) Hysteretic conductance switching is observed during repeated displacement cycles. (d, e) Time dependence of the measurement in panel c. The periodical displacement modulation (d) yields a repeated conductance switching between the HighG (red) and LowG (blue) configurations (e). Utilizing the atomic chain pulling mechanism of gold,}\]

\[\text{the probable atomic chain formation process in the stable low-temperature environment yields such wide gaps after the chain rupture that are unable to accommodate the HighG molecular configuration.}\]

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conductance states suggest that the molecular junction is switching between the HighG and LowG binding configurations, as observed during the closing of the junction. This result is consistent with our previous argument that the difference between the opening and closing histograms is caused by the strain acting on the junction in the opening process. During these I(V) measurements, the junction has time to relax, so that the strain acting on the molecule is reduced, leading to similar HighG and LowG conductance values as seen in the closing conductance histogram. These findings demonstrate that besides mechanical, we can also achieve electric switching between the two configurations of the BP molecule.

Next, we correlate the bistable electric switching with the displacement of the electrodes. During this measurement, we identify the displacement interval of the hysteretic conductance switching at low bias (V = 30 mV; see black line in Figure 3a), and afterward we stop at distinct displacement values (green signs in Figure 3a) to record the temporal evolution of the junction conductance under an elevated bias voltage (V = 150 mV). The gray hysteresis was recorded with \( \approx 400 \) s time delay after the black hysteresis. Between these two measurements the time dependence of the conductance was recorded at the signed displacement values (green dots) at \( V = 150 \) mV bias voltage, as demonstrated in panels b–d. Outside of the hysteresis at large displacement the LowG configuration is stable and no switching was observed. (c) At somewhat smaller displacement a bistable switching occurs and the LowG configuration is preferred. (d) At even smaller displacement the switching is reversed and most of the time is spent in the HighG configuration. (e) The distribution of the times spent in the on (red) and off (blue) states between subsequent switching events at the displacement position c. The histogram bins are equally spaced on the logarithmic scale. The dashed lines demonstrate the average \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \) times, whereas the solid lines represent the best fitting exponential probability density functions (see the Supporting Information for more details). (f) Similar distributions at the displacement position d.

![Figure 3](image-url)

**Figure 3.** (a) Hysteretic conductance jumps between the HighG and LowG states along piezo ramp cycles recorded at low bias (V = 30 mV). The gray hysteresis was recorded with \( \approx 400 \) s time delay after the black hysteresis. Between these two measurements the time dependence of the conductance was recorded at the signed displacement values (green dots) at \( V = 150 \) mV bias voltage, as demonstrated in panels b–d. (b) Outside of the hysteresis at large displacement the LowG configuration is stable and no switching was observed. (c) At somewhat smaller displacement a bistable switching occurs and the LowG configuration is preferred. (d) At even smaller displacement the switching is reversed and most of the time is spent in the HighG configuration. (e) The distribution of the times spent in the on (red) and off (blue) states between subsequent switching events at the displacement position c. The histogram bins are equally spaced on the logarithmic scale. The dashed lines demonstrate the average \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \) times, whereas the solid lines represent the best fitting exponential probability density functions (see the Supporting Information for more details). (f) Similar distributions at the displacement position d.

and afterward we stop at distinct displacement values (green signs in Figure 3a) to record the temporal evolution of the junction conductance under an elevated bias voltage (V = 150 mV). The corresponding representative segments of these time traces are shown in Figure 3b–d. Panels e and f of Figure 3 demonstrate the distribution of the times spent in the HighG (\( \tau_{\text{on}} \), red) and LowG (\( \tau_{\text{off}} \), blue) conductance states between two subsequent switching events for the entire length of the time traces (22 s) at the displacement points c and d, where a telegraph-like conductance fluctuation was observed. By recording the low bias conductance hysteresis at the end of the measurement again (gray line in Figure 3a), we estimate the stability of the junction to be on the scale of \( \approx 40 \) pm on the time scale of the entire measurement (\( \approx 400 \) s). This displacement inaccuracy is \( \approx 15\% \) of the Au–Au interatomic distance in a gold chain. On the basis of these measurements and further similar measurements, we find the following clear tendencies: (i) The bistable electrical switching is focused around the displacement range of the low-bias conductance hysteresis (see Figures 3c,d). (ii) Within this range the average times spent in the two states cross, i.e., at a smaller displacement the HighG state, whereas at larger displacement the LowG state is dominant (Figures 3e,f). (iii) Further away from the hysteresis, the electrical switching vanishes (Figure 3b), and the corresponding state is stable even under an elevated voltage. Note that the sub-Ångstrom displacement interval of the conductance hysteresis is almost an order of magnitude narrower than the \( \approx 2\) Å average displacement between the centers of the HighG and LowG conductance plateaus on the two-dimensional conductance–displacement histograms.\(^{5,25}\)

To resolve the temporal dynamics of the switching, we have performed a statistical amount of time-resolved measurements at various driving voltages. This was achieved by an automated measurement setup, where a real-time FPGA controller monitored the conductance and stopped the junction elongation once the predefined trigger conductance of \( G = 0.005 \) \( G_0 \) was reached. At this point, the displacement (i.e., the voltage on the piezo actuator) was fixed, and a voltage staircase was applied on the junction (see the scheme of the measurement in Figure 4a). Around 8% of the 8000 automated measurements yielded molecular contacts that were stable throughout the voltage sweep. Note that this number is partly related to the low molecular pick-up rate in the low-temperature measurements.\(^{25}\) Out of these stable molecular contacts \( \approx 5\% \) matched the displacement range, where the voltage dependent bistable switching was observable. These 35 independent traces are used to investigate the voltage dependence of the bistable switching in Figures 4b–j. One of these measurements is exemplified in Figure 4c–f showing the distribution of the times spent in the HighG and LowG conductance states at 50, 100, 125, and 150 mV driving voltages, respectively. We find that the distributions of the \( \tau_{\text{on}} \) and \( \tau_{\text{off}} \) times are all well fitted by exponential probability density functions (see the solid lines in Figure 4c–f and in Figure 3e–f as well). The exponential distribution implies stochastic switching events, independent of the elapsed time since the last switching event. The voltage dependence of the average times \( \langle \tau_{\text{on}} \rangle \) and \( \langle \tau_{\text{off}} \rangle \) are plotted in Figure 4b by red and blue dots, respectively. The solid lines show that both voltage dependencies are well fitted with a linear function once a logarithmic time scale is applied, i.e.,

\[
\log(\tau_{\text{on/ff}}) = a_{\text{on/ff}} + b_{\text{on/ff}} \cdot V,
\]

where we use the reference time \( \tau_0 = 1 \) s to make the argument of the logarithm dimensionless. This means that the switching exponentially speeds up upon linearly increasing the voltage. Furthermore, the red and blue lines demonstrate that the switching simultaneously speeds up in the two states. To confirm these tendencies for a statistical amount of data, we investigate the correlations between the \( a_{\text{on/ff}} \) intercept and \( b_{\text{on/ff}} \) slope values for all measurements (Figure 4g–j). Despite
Figure 4. Statistical investigation of the voltage dependent switching times using an automated measurement setup. (a) Scheme of the measurements (see text). (b)–(f) Voltage dependence of the switching times in one of the measured single-molecule junctions. (c)–(f) Distribution of the times spent in the on/off states between subsequent switching events at various bias values together with the best fitting exponential probability density functions (see the Supporting Information). The histogram bins are equally spaced on the logarithmic scale. (b) Voltage dependence of the average switching times deduced from the distributions in panels c–f. The solid lines represent the fitting curves considering an exponential speedup of the switching time upon linearly increasing voltage (see text). The black horizontal dashed lines illustrate the limiting time scales, i.e., the length of the measurement, and the bandwidth limit of the measurement. The red and blue dashed lines represent the best fitting curves considering a simple two-level system model with a well-defined excitation energy and a voltage independent coupling strength, i.e., \( \tau = \frac{A}{e(V - \epsilon)} \). The shaded areas illustrate the statistical scattering of the slope values at the fixed intercept values (see text). (g)–(j) the dependence of the \( b_{\text{on}}/b_{\text{off}} \) intercept and \( b_{\text{on}}/b_{\text{off}} \) slope values on each other for all the measured data together with the best fitting linear functions (dashed lines): (g) \( a_{\text{on}} = -2.135 - 0.151b_{\text{off}} \); (h) \( a_{\text{off}} = -2.006 - 0.134b_{\text{on}} \); (i) \( b_{\text{on}} = -9.588 + 0.487b_{\text{off}} \); (j) \( a_{\text{off}} = 0.23 + 0.400a_{\text{on}} \). The bright dots represent the example data in panel b.

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Figure 4 demonstrates the following major conclusions: (i) the switching times are well-fitted with an exponential probability density function (Figure 4c–f); (ii) for both states the switching speeds up exponentially along the linear increase of the applied voltage (Figure 4b); (iii) the on and off switching times speed up simultaneously, and the dominance of a certain state is usually preserved in the investigated voltage range (Figure 4b). Note that the latter is in sharp contrast to the mechanical manipulation, which clearly reverses the dominance of the states, as demonstrated in Figure 3e,f. The clear difference between the response to the mechanical actuation and the voltage manipulation also implies that the applied voltage does not influence the junction displacement.

Finally, we discuss our results on the bistable resistance switching in terms of simple model considerations. According to the model fitting of force measurements in ref 32, the binding energies of the HighG and LowG molecular configurations are respectively 1.6 and 0.9 eV with a large, 700 meV energy difference. A hypothetical switching between states with such energy offset would rely on an even higher barrier value in the lower energy configuration. These values, however, correspond to relaxed configurations. In our case the switching happens in the sub-Ångstrom hysteretic conductance region, where both states are stable. In this region, we anticipate a stretched HighG and a compressed LowG configuration with significantly smaller energy difference and energy barrier between the two states. This is consistent with the observation, that a voltage range of \( \approx 100 \text{ mV} \) can induce the switching.

We model the bistable molecular states as a double-well potential in the molecule’s configuration space considering an \( E \) energy release by the electrons to the molecule during a single switching event (see Figure 5). From the electrons’ point of view a Fermi-function integral describes this process giving the probability of scattering from an occupied state in the higher chemical potential electrode to a lower energy unoccupied state in the lower chemical potential electrode (see the Supporting Information). Once the molecule receives this energy, it switches to its other metastable state with \( \Gamma(E) \) probability (see the illustration in Figure 5). In the following, we consider different switching models as various limiting cases of this model.

(i) Simple two-level system models. We can consider either a coherent two-level system model with a finite tunneling probability between the two states and a fixed \( E \) excitation energy \( E_{\text{exc}} \), or an incoherent two-level system model where the tunneling transition is not possible, and the switching requires an excitation above the \( E_{\text{on}} \) barrier height in the actual state. In
both cases, we consider a constant $\Gamma = \Gamma_0$ transition probability at $eV < E$ or $eV > E_0$, respectively. These models respectively yield a $\tau \sim (eV - E)^{-1}$ or $\tau \sim (eV - E_0)^{-2}$ voltage scaling of the switching times (see Supporting Information). The red and blue dashed lines in Figure 4b illustrate the best fits with the former voltage scaling, which is clearly inconsistent with the measured data. Even if the divergence at $eV = E$ is blurred due to a broader energy distribution, the high bias $1/V$ scaling of this simple model is much shallower than the measured voltage dependence of the data, which also holds for the $1/V^2$ scaling in the incoherent model. Note that a $1/V$ and $1/V^2$ dependencies would yield a factor of 3 or 9 speedup between 50 and 150 mV driving in contrast to the observed $2$ orders of magnitude speedup (see Figure 4b). In Figure 4g,h this 3-fold and 9-fold speedup would relate to slope values of $b \approx -5 V^{-1}$ and $b \approx -10 V^{-1}$, which are also much shallower slopes than the typically observed $b \approx -30$ to $-20 V^{-1}$ values. Accordingly, these models are excluded.

(ii) Temperature activated switching model. In the former two-level system models the direct voltage excitation is not possible at $eV < E$ or $eV < E_0$ voltage. In this limit the temperature activation can still induce a transition with $\tau \sim \exp((E - eV)/kT)$ or $\tau \sim \exp(E_0 - eV)/kT$ switching times (see Supporting Information). Such a temperature-activated process is unrealistic at $T = 4.2$ K temperature, as the energy scale in the numerator of the exponent is almost $3$ orders of magnitude larger than the thermal energy in the denominator. Furthermore, this scaling would provide a slope of $b = -e\log(e)/kT \approx -10^3 V^{-1}$, whereas the largest measured slopes are restricted to $b \approx -30 V^{-1}$ (see Figure 4g,h).

(iii) Vibrational pumping model. So far we have considered models where the energy release from the electrons kicks the molecule to its other state within a single event. Alternatively, the electrons may release smaller $E = \hbar \omega$ vibrational quanta to the molecule, and the transition happens once this vibrational degree of freedom is pumped to an energy exceeding the barrier height. According to the consideration in the Supporting Information, the average occupation number of a vibrational mode can be estimated as $\bar{n} = (\hbar/2)(eV/\hbar \omega - 1)$. Considering the $T \approx 10^{-3}$ transmission probability of the molecule, the $eV < 150$ mV voltage range and $\approx 100$ mV typical vibrational energies $\omega \approx 1$ follows, i.e., the vibrational pumping, and related local overheating of the junction is unrealistic. As a simple explanation this result is related to the fact that the vibrational mode is much more efficiently cooled than excited in the $T \ll 1$ limit.

(iv) Double-well potential inversion model. Recent studies reported single-molecule switching, where the voltage excitation reversed the dominance of the two molecular states; i.e., it induced an inversion of the minima in the double-well potential (see the illustration in the Supporting Information). This was reflected by the clear crossing in the voltage dependence of the switching times. In our system the dominance of the states is manipulated by the displacement, but at a fixed electrode separation the switching of the two configurations speeds up simultaneously, and the initially dominant state remains dominant throughout the studied voltage train; i.e., the double-well potential inversion model is also excluded.

(v) Heuristic model relying on the molecule’s energy dependent transition probability. To be able to describe the simultaneous exponential decay of the switching times with linearly increasing voltage, we consider a strong (exponential) energy dependence of the molecule’s transition probability $\Gamma(E)$ (see left illustration in Figure 5). This may relate to an energy dependent tunneling probability between two conformational states, as implied on the figure, but several other processes, like the reduction of the barrier with the applied voltage, or the influence of electron-phonon forces may play a role. A more detailed understanding of the precise microscopic processes would require first principle model calculations.

In conclusion, we have demonstrated well-controlled voltage-induced probabilistic conductance switching in cryogenic temperature Au–BP–Au single-molecule junctions. This behavior resembles probabilistic bit devices with two tunable parameters: the relative dominance of the two conduction states is manipulated by the electrode displacement, whereas the voltage manipulation induces an exponential speedup of both switching times.

We have compared our experimental results with possible model considerations and argued against simple two-level system models, temperature activated switching models, a vibrational pumping model, and a double-well potential inversion model. Finally, we proposed a heuristic model relying on the exponential energy dependence of the molecule’s transition probability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c02185.

Discussion of the model considerations and details on the fitting of the switching time distributions (PDF)
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