Mechanical stretching-induced electron transfer reactions and conductance switching in single molecules

Yueqi Li^{1,2}, Naomi L. Haworth³, Limin Xiang^{1,2}, Simone Ciampi^{4*}, Michelle L. Coote^{3*} and
Nongjian Tao^{1,5*}

Affiliations: ¹Center for Bioelectronics and Biosensors, Biodesign Institute, Arizona State University, Tempe, Arizona 85287-5801, USA

²School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287-5801, USA

³ARC Centre of Excellence for Electromaterials Science, Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory 2601, Australia

⁴Department of Chemistry, Curtin University, Bentley, Western Australia 6102, Australia

⁵School of Electrical, Energy and Computer Engineering, Arizona State University, Tempe, Arizona 85287-5801, USA

njtao@asu.edu, +1 480 965 4456,

michelle.coote@anu.edu.au, +61 2 61253771,

simone.ciampi@curtin.edu.au, +61 8 9266 9009.

Abstract: A central idea in electron transfer theories is the coupling of the electronic state of a molecule to its structure. Here we show experimentally that fine changes to molecular structures by mechanically stretching a single metal complex molecule via changing the metal-ligand bond length can shift its electronic energy levels and predictably guide electron transfer reactions, leading to the changes in redox state. We monitor the redox state of the molecule by tracking its characteristic conductance, determine the shift in the redox potential due to mechanical stretching of the metal-ligand bond, and perform model calculations to provide insights into the observations. The work reveals that a mechanical force can shift the redox potential of a molecule, change its redox state, and thus allow the manipulation of single molecule conductance.

Main text:

Introduction

Electron transfer reactions are responsible for many chemical and biological processes, including photovoltaic energy conversion, photosynthesis, and metabolic activities in living systems.¹ Central to electron transfer reaction theories² is that the electronic state of a molecule is coupled to the nuclear degrees of freedom of the molecule and its surrounding solvent, and thermal fluctuations create a favorable nuclear geometry that allows electron transfer to take place³. Here we show via single molecule conductance measurements that mechanically stretching a redox molecule can help create the favorable geometry, shift the redox potential and induce electron transfer reactions. We measure electron transfer in a single metal complex molecule that is covalently connected to two electrodes⁴ while stretching the metal-ligand bond length. This allows us to detect mechanical stretching-induced switching of the metal ion between reduced and oxidized states, and to establish experimentally a link between changes in nuclear geometry and

redox potential. Our theoretical modeling of the system confirms that the mechanical distortion in the metal-ligand bond is responsible for the observed shift in the redox potential. The work points to a way to examine the interplay between electronic and structural properties of molecules in electron transfer reactions, and to switch the conductance of a single molecule via mechanically changing its redox state without bond rupture.⁵

Results and discussions

We study the electron transfer reactions of a ferrocene compound by monitoring its conductance while mechanically stretching the molecule under electrochemical control. Ferrocene can reversibly donate an electron to an electrode (become oxidized), and accept an electron from the electrode (become re-reduced) without bond rupture⁶. The ferrocene compound studied here is 1,1'-Ferrocenyl diester (Fc-Lip, see Fig. 1a for structure and Supporting Methods for synthesis protocols), which consists of a ferrocene redox center connected to two linker groups that can bind to the gold electrodes (Fig. 1a and Supporting Figs. 1-2). As a control experiment, we also study 1,4-Phenylene bis(5-(1,2-dithiolan-3-yl) pentanoate) (Lip-ctr, see Supporting Methods for synthesis protocols) which is similar to Fc-Lip but lacks the ferrocene redox center (Fig. 1a and Supporting Figs.3-4). We measure the redox states of Fc-Lip from its characteristic conductance with the scanning tunneling microscope (STM) break junction technique^{7,8} (details in Methods section), where the gold tip and gold substrate serve as the two electrodes to change the geometry of the molecule via mechanical stretching, and also to determine its conductance. During the measurement, we control the potential of the molecules with respect to a reference electrode (Fig. 1b). The redox reaction of Fc-Lip immobilized on the electrodes (See Supporting Methods for

immobilization procedures) is reversible with a redox potential at ~ 405 mV vs. Ag/AgCl (Fig. 1c), which agrees with the previous report⁹.

Figure 1. (a) Structures of 1,1'-Ferrocenyl diester (Fc-Lip) and 1,4-Phenylene bis(5-(1,2-dithiolan-3-yl)pentanoate)(Lip-ctr). (b) Experimental setup showing a redox molecule bridged between a gold STM tip and gold substrate for interrogating the redox state of the molecule via conductance measurement, and for stretching the molecule. The tip and substrate potentials are controlled with respect to a reference electrode (silver wire as quasi-reference, potential calibrated in Supporting Fig. 11) in 0.1 M NaClO₄ solution. A small bias (30 mV) is maintained between the tip and substrate electrodes for conductance measurement. A platinum wire (not shown) is used as a counter electrode for stable potential control. (c) Cyclic voltammogram of Fc-Lip on a gold surface showing well-defined oxidation and reduction peaks at ~ 0.4 V vs. Ag/AgCl, characteristic

of fully reversible redox reaction (potential sweeping rate: 100 mV/s). **(d)** Conductance of Fc-Lip vs. overpotential ($E - E_{\text{ox/red}}$, where E is potential and $E_{\text{ox/red}}$ is the redox potential), revealing low conductance reduced state, high conductance oxidized states, and switching between the two states (potential sweeping rate: 1 V/s).

To study the electron transfer reaction of single Fc-Lip molecules, we bridge a Fc-Lip molecule between the STM tip and substrate electrodes, and then sweep the potential while recording the conductance of the molecule (Fig. 1d). At low potentials, the redox molecule is in the reduced state, and its conductance is $0.011 \pm 0.002 G_0$, where $G_0 (=7.748 \times 10^{-5} \text{ S})$ is the conductance quantum. However, at high potentials, Fc-Lip becomes oxidized, which is observed as a sudden conductance increase by 5x to $0.053 \pm 0.007 G_0$. This finding is consistent with literature ⁶, and further validated by performing a large number of measurements and statistical analysis discussed below. The measured discrete low and high conductance levels of a single Fc-Lip molecule provide “fingerprinting” for us to determine if the molecule is in the reduced (low conductance) or oxidized (high-conductance) states, and switching between the two levels measures the individual electron transfer reaction events in single molecules.

Electron transfer theories assume a coupling between the electronic states and the structure of a molecule and surrounding solvent. Mechanically stretching the molecule is expected to distort the molecular structure, and thus the energy levels of the molecule, which could affect electron transfer reactions. To verify or falsify this idea, i.e., a link between stretching and changes to redox states, we stretch the molecule by progressively separating the tip and substrate electrodes, and monitor the redox state of Fc-Lip from the discrete conductance switching (See Methods section for details). We perform the measurements by holding the potential at different values: below, at, or above the redox potential of unstretched Fc-Lip (marked on Fig. 2a). At potentials well below the redox potential (e.g., -88 mV), Fc-Lip is in its reduced state with a probability of 97% according

to the Nernst equation. The individual conductance vs. distance traces reveal plateaus corresponding to the formation of single Fc-Lip molecules bridged between the two electrodes, followed by abrupt conductance drops as the bonds at the molecule-electrode contact break (Fig. 2b)¹⁰. The conductance plateaus are located near $0.01 G_0$, which correspond to the low conductance level of the reduced Fc-Lip state. The lack of conductance switching to the high conductance level indicates that the molecule remains in the reduced state during stretching. The corresponding conductance histogram displays a single pronounced peak near $0.01 G_0$ (Fig. 2c), further confirming that mechanical stretching at low potentials does not induce the electron transfer reaction (Fig. 2d).

Figure 2. Mechanical stretching and conductance measurement of Fc-Lip at different potentials. **(a)** Cyclic voltammogram of Fc-Lip, where the colored dots mark the potentials at which the mechanical stretching and conductance measurements in (b-i) are carried out. Note that the potential is referred to overpotential, $E-E_{\text{ox/red}}$. **(b-d)** $E-E_{\text{ox/red}}=-88$ mV. The individual conductance traces (b) show plateaus and the conductance histogram (c) shows a single peak at the low conductance level, indicating that the molecule remains in the reduced state under stretching (d). **(e-g)** $E-E_{\text{ox/red}}=+78$ mV. The individual conductance traces (e) show plateaus and the conductance histogram (f) shows a single peak at the high conductance level, indicating that the molecule remains in the oxidized state under stretching (g). **(h-j)** $E-E_{\text{ox/red}}=-7$ mV, close to the redox

potential. The individual conductance traces (h) show plateaus at **both** the low and high conductance levels, and switching from the low to high conductance levels, and the conductance histogram (i) shows two peaks, indicating coexistence of reduced and oxidized species (j).

At potentials well above the redox potential, Fc-Lip is expected to be in the oxidized state. For example, at +78 mV, the molecule has a probability of 95% in the oxidized state. The individual conductance traces at +78 mV display plateaus around $0.05 G_0$ (Fig. 2e), and the conductance histogram also reveals a single well-defined peak near $0.05 G_0$ (Fig. 2f), showing that the molecule is in the oxidized state during stretching. Like the case where the potential is held well below the redox potential, mechanical stretching at high potentials does not induce electron transfer reaction either (Fig. 2g).

When the potential is held close to the redox potential, e.g. -7 mV, both reduced and oxidized states coexist; this is shown by the presence of plateaus at both the low and high conductance levels in the conductance traces (Fig. 2h). At this potential, the conductance often switches abruptly from low to high conductance levels during the stretching of the molecule (curves 2 and 3), suggesting that the molecule switches from the reduced to the oxidized state under stretching. The conductance histogram reveals two peaks, at $0.013 \pm 0.001 G_0$ and $0.050 \pm 0.0011 G_0$, respectively, corresponding to the reduced and oxidized states, respectively (Fig. 2i). We note that previous studies have also observed changes in the conductivity of a molecular linker in response to stretching.[Beratan, Ratner] In these investigations, pulling in an STM experiment caused unfolding of a compacted linker, resulting in a decrease in the observed conductance. The change in conductivity was ascribed to an increase in the transport distance,[Beratan] and also to changes in the transport mechanism (the loss of a π transport pathway due to stretching)[Ratner]. While these mechanisms appropriately describe the reduction in charge transport with stretching

observed in these earlier studies, they cannot explain the stretching induced **increase** in conductance observed in Fig 5h. The fact that experiments performed at potentials significantly above and below the redox potential of Fc-Lip (Fig. 5b and 5e) do not show this conductance increase, confirms that it does not result from a change the electron transport mechanism in the same way as seen in the investigation of Franco, et al.[Ratner] A small drop in conductance is observed in some of our pulling curves (eg Fig. 2h, curve 4), consistent with an increase in the transport distance hindering electron movement. However, the large conductance increase in Fig. 2h, curves 2 and 3, and the small decrease in Fig. 2h, curve 4, are clearly different effects. Indeed, the fact that these conductance changes are only observed when the potential of the system is close to but slightly below the redox potential of the linker (-7 mV) and the strong correlation between conductance in the initial and final states in the pulling curves and those of the reduced and oxidized linkers, respectively, provides strong evidence that mechanical stretching is inducing switching of Fc-Lip from the reduced to the oxidized state (Fig. 2j).

To further examine the roles of electrode-molecule contact in Fc-Lip, we perform the same measurement on Lip-ctr (control molecule), where the phenyl ring replaces the ferrocene redox center in Fc-Lip (Fig. 1a and Supporting Fig. 5a). Unlike Fc-Lip, we do not observe stretching-induced conductance switching at various potentials (Supporting Figs. 5b and c), and the conductance histograms display only a single peak (Supplementary Figs. 5d and e). This control experiment shows that the conductance change in Fc-Lip originates from the ferrocene redox center.

We obtain quantitative relationship between mechanical stretching and redox states by constructing a 2D histogram of conductance vs. stretching distance by counting all the traces that show conductance switching at $E - E_{\text{ox/red}} = +30 \text{ mV}$ (Fig. 3a). The 2D histogram reveals two

conductance regions, corresponding to the low conductance reduced state (“R”) at short stretching distances, and high conductance oxidized state (“O”) at long stretching distances, respectively. 1D conductance histograms for at different stretching distances reveal the ratio of the two states and the progressive increase of the oxidized population with stretching (Figs. 3b-e). The peak areas are proportional to the numbers (thus probabilities) of Fc-Lip in the reduced and oxidized states^{11,12,13} (further evidence in Supporting Discussion 1 and Supporting Fig. 6). The ratio of the high to low conductance peak areas (including conductance traces with and without switching events (Supporting Fig. 7)) is plotted vs. stretching distance in Fig. 3f, showing that the probability of the molecule in the oxidized state increases with stretching distance. Data measured at +30 mV are shown in Fig. 3 as the example to clearly illustrate the stretching effect on the the redox reaction.

Figure 3. Mechanical stretching-induced oxidation of single Fc-Lip ($E-E_{\text{ox/red}} = +30$ mV). **(a)** 2D histogram of conductance plateaus vs. stretching distance (counts are normalized for each distance bin), where “R” and “O” mark the reduced and oxidized states. **(b-e)** 1D conductance histograms for stretching distances between 0-0.1 nm (b), 0.1-0.2 nm. (c), 0.2-0.3 nm (d), and 0.3-0.4 nm (e), where the red and blue curves are Gaussian fits of the oxidized and reduced conductance peaks,

respectively. **(f)** Logarithmic ratio of the conductance histogram peak area for the oxidized state to that for the reduced state, showing increasing probability of oxidation with stretching distance.

By studying the probabilities of the molecule in the reduced and oxidized states at different potentials and stretching distances, we determine the relationship between mechanical stretching and redox potential (Supplementary Fig. 8). Fig. 4 plots the logarithmic ratios of the probability of the molecule in the oxidized state to that in the reduced state at unstretched (black) and stretched (red) stages. The former refers to data collected during the initial stage of the stretching process with a stretching distance between 0 and 0.1 nm, and the latter corresponds to a fully stretched molecule (0.3-0.4 nm), beyond which the junction breaks down. The breakdown takes place due to the cleavage of an Au-Au bond, which is the weakest bond in the molecular junction with an average breakdown force of ~ 1.5 nN^{10,14,15}. For unstretched redox molecules, the relative probabilities of the molecule in the oxidized and reduced states are expected to follow the Nernst equation (Supporting Discussion 1). Indeed, the data for the unstretched molecule can be fitted by the Nernst equation with a slope of $2.3nF/RT$ (where n , the number of electron transfer per molecule, is 1, F is the Faraday constant, and R is the gas constant). The data for the stretched molecule is also consistent with the Nernst equation (red line, Fig. 4), but the redox potential is shifted negatively by 34 ± 6 mV. The negative shift in the redox potential indicates that the molecule favors the oxidized state under mechanical stretching, which is consistent with the observations in Figs. 2 and 3. The data of the stretched state show some deviation from the Nernst equation. Whether this was due to experimental errors or real effect requires further study.

Figure 4. Shift of redox potential with mechanical stretching. Logarithmic ratio of the conductance histogram peak area for the oxidized state to that for the reduced state of unstretched (black dots) and stretched (red dots) Fc-Lip vs. potential, where the dashed black line is the Nernst equation prediction (with $n=1$) for unstretched Fc-Lip. The solid black line is a linear fit to the data for the unstretched molecule, and the solid red line is a linear fit to that for the stretched molecule. In both fits, the slope is $2.303nF/RT$ with $n=1$. The blue arrow marks the shift in the redox potential caused by stretching the molecule over ~ 0.3 nm.

It has been found that the coordination bond strengths and lengths for many metal complex are different for the reduced and oxidized states.¹⁶ Related to the present work, X-ray crystallography^{17,18} has shown that the cyclopentadienyl(Cp)-Fe-Cp distance in ferrocene increases by 0.006 nm upon oxidation. This is because the electron that is lost upon oxidation is removed from an Fe-Cp bonding orbital, thus weakening the Fe-Cp interaction. We thus expect that mechanically stretching of Fc-Lip drives the electron transfer reaction towards oxidation, and shifts the redox potential negatively. The redox potential shift can be calculated with a single reaction coordinate model (Cp-Fe-Cp bond) in the spirit of the Marcus theory², which assumes

parabolic energy profiles for the reduced and oxidized states (Fig. 5a). In the absence of mechanical stretching, electron transfer occurs when thermal fluctuations bring the molecule to the favorable geometry, corresponding to the interception of the energy profiles of the reduced and oxidized states. Mechanical stretching^{19,20} shifts the redox potential, given by (Supporting Discussion 2)

$$\Delta G_0 = \frac{F^2}{2} \left(\frac{1}{k_{red}} - \frac{1}{k_{ox}} \right) - Fq_0, \quad (1)$$

where F is the force, k_{red} and k_{ox} are the effective spring constants of Cp-Fe-Cp bond in the reduced and oxidized states, respectively, and q_0 is the Cp-Fe-Cp bond length increase associated with the oxidation of Fc-Lip. Using $F=1.5$ nN for the breakdown force of the molecular junction^{10,14,15}, $q_0=0.006$ nm^{17,18}, and spring constants determined from the vibrational frequencies by IR spectroscopy²¹ ($\nu_{red} = 402$ cm⁻¹ and $\nu_{ox} = 406$ cm⁻¹ for the tilting modes) and density functional theory (DFT) calculations (Supporting Table 1 and Supporting Discussion 2), Eq. 1 predicts -51 mV shift in the redox potential, which is in reasonable agreement with the observation.

The simple model that leads to Eq. 1 does not consider stretching-induced changes in the electronic coupling along the charge transport pathway in the molecular junction and solvent reorganization, which could also affect the conductance^{22,23}. The STM break junction method measures the very last stage of a molecular stretching process. In the present system, from the beginning of stretching to the breakdown of the molecule, the total measured increase in distance is as small as 0.3 nm, which includes ~0.25 nm at the Au-Au bond near the molecule-electrode contacts. In other words, the conformational change in the molecule during stretching measured in the experiment is small. As such, we expect that the associated stretching-induced changes in the electronic coupling strengths and solvent effect are small. The good agreements between the

simple model and the DFT calculations that include the solvent effect, and also between the calculations and the experimental data further indicate that the simple model captures most of the effect.

Figure 5. Theoretical model and computational results. **(a)** Free energy surfaces of the reduced (blue) and oxidised (red) species vs. bond length (reaction coordinate) with (dashed curve on the right) and without (solid curve on the left) mechanical stretching. **(b)** Molecular structure of Fc-Lip. **(c)** DFT calculation of the structural distortion of reduced and oxidized molecule during mechanical stretching. For clarify only the central portion of the molecule is shown. **(d)** DFT calculation of the potential energy surfaces of the reduced (blue) and oxidised (red) Fc-Lip vs.

stretching distance (between atoms S1 and S2), which are parabolic (solid lines), supporting the simple model in (a). Energies are given relative to the global minimum (ring substituents at $\sim 72^\circ$) for each redox state. **(e)** Changes in the adiabatic ionization potential (aIP) of Fc-Lip vs. stretching distance. The aIP is relative to that of unstretched molecule. In (d) and (e), a stretching distance of 0.2793 nm corresponds to an applied force (1.5 nN), breakdown of Au-Au bond (thick dashed line).

The model above includes only one coordinate. To consider all possible degrees of freedom, we perform DFT calculations (Fig. 5b) using the B97-D3 functional²⁴ (See Methods section for calculation details, and see Supporting Methods and Supporting Table 2 for benchmarking study). Under stretching, the molecule undergoes various conformational changes (Fig. 5c, and Supporting Table 3). Initially, the added strain is accommodated by a slight curvature in the linker side chains. As the stretching increases, the Cp rings begin to twist with respect to each other until the dihedral angle reaches 180° ; beyond this point the strain can only be accommodated by stretching bond lengths and angles. The energies of the reduced and oxidized states in the twisting and stretching regimes are parabolic functions of the stretching distance (Fig. 5d, cf. Supporting Fig. 9 and Supporting Table 4). The calculation reveals that stretching takes place at multiple bonds, but predominantly at Fe-C1 (C9), which is stretched by 0.01 nm at 1.5 nN (Supporting Fig. 10). The corresponding adiabatic ionization potential shifts negatively by ~ 65 mV (Fig. 5e and Supporting Discussion 3). Assuming the thermal and entropic contributions are not affected by stretching, this corresponds to a decrease in the redox potential of 65 mV. The value predicted by the analytical model calculation is in good agreement with this more accurate result. It is important to note that neither of our modelling approaches consider any potential differences in the outer sphere reorganization energies (solvent reorganization) associated with the oxidation of the stretched and unstretched species. Although these effects are expected to be small, this approximation is a potential explanation for the slightly larger redox potential changes

predicted by the DFT and modelling studies. Nevertheless, the results of both modelling approaches are in good agreement with the experimental data within error margins.

Conclusions

Mechanical forces can be an effector of chemical changes^{20,25} as demonstrated by ball milling/grinding^{26,27}, and ultrasound bath^{28,29} and atomic force microscopy³⁰⁻³³, but measuring a relationship between forces and redistribution of redox equilibria within intact single molecules has been an elusive task. Our study demonstrates that mechanical stretching induces redox reactions in single metal complex molecules as the stretching changes the bond length and drives the reaction towards the final state that favors the bond length change. This observation supports the thesis that electronic-nuclear coupling is responsible for redox reactions in electron transfer theories. The observation that a mechanical stretching can control redox states of a single molecule also provides a way to mechanically switch the electronic properties of a single molecule, which supports the vision of molecular machines with electromechanical functions³⁴.

Materials and Methods:

Measurement of stretching-induced shift in redox potential of single Fc-Lip molecules

A scanning-tunneling microscope (STM), consisting of a controller (Nanoscope IIIA, Digital Instruments Inc.) and a STM scanner (Molecular Imaging), was used for the break junction measurements. The STM tip was freshly prepared by cutting a gold wire (0.25 mm diameter, 99.95%, Alfa Aesar) and coated with Apiezon wax to reduce the leakage current. The gate voltage was controlled by the bipotentiostat (Agilent). A silver wire and a platinum coil were used as quasi-

reference electrode and counter electrode, respectively. To determine errors in the potential associated with the quasi-reference electrodes, cyclic voltammetry was performed before and after each experiment (Supporting Fig. 11), and the measured variation in the redox peak potential of Fc-Lip was taken as errors in the gate voltages.

STM break junction experiments were performed with the following two approaches. In the first approach, a small voltage bias (10 mV) was applied between the STM tip and substrate electrode, and the potential was held initially at -0.1 V. The STM tip was brought into contact with the Fc-Lip molecules on the gold substrate, allowing binding of the gold tip to the linker group, and then retracted from the substrate, during which a conductance was monitored. Once a plateau in the conductance was detected, signaling the formation of a single molecule bridged between the tip and substrate, the STM tip was held in position and the potential was swept at 1 V/s to record the conductance of the molecule vs. potential (Fig. 1d). In the second approach, both the tip-substrate bias and potential were fixed (see Supporting Table 5 for the applied bias and gate voltages). The STM tip was repeatedly brought into contact and retracted from the substrate repeatedly, during which the individual conductance traces (conductance vs. the STM tip-substrate distance) were collected (Figs. 2b, 2e, and 2h) and a conductance histogram (Figs. 2c, 2f, and 2i) was constructed from the individual conductance traces. The measurement was repeated at differential potentials. Conductance vs. distance histograms (2D) were also obtained from the conductance vs. distance traces (Supporting Fig. 7a), from which 1D conductance histograms at different stretching distances were obtained (Supporting Figs. 7c-f).

Computational methods:

The changes in adiabatic ionization potential (aIP) of the Fc-Lip with stretching and the associated geometric distortions were explored using DFT using Gaussian 09³⁵. After an extensive benchmarking study (see Supporting Methods and Supporting Table 2 for benchmarking study), the B97-D3²⁴ functional was chosen to describe the system, along with the def2-svp³⁶ basis sets for C, H, O and S atoms and the more extensive def2-tzvp³⁶ basis set for Fe. Solvent effects (water) were included using the SMD³⁷ implicit solvation model. Relaxed potential energy surface (PES) scans were performed for both the reduced and oxidized species, with the distance between atoms S1 and S2 being scanned (Supporting Fig. 9), and all other geometric coordinates being allowed to fully relax. Only conformations where the side chains were fully extended were considered, as the redox potential changes are expected to be primarily associated with strain on the ferrocene moiety and comparatively insensitive to the conformations of the alkyl chains. This was confirmed for a smaller model compound. To ensure the lowest energy electronic configuration was obtained for the oxidized species, the optimized orbitals from the minimum energy structure were used as an initial guess for each new geometry when scanning the PES. Scans were performed iteratively for both stretching and relaxation of strain until a smooth curve was obtained. A harmonic curve was fitted to the PES data to obtain the force constant (second derivatives of the curves). These could be used to determine the degree of stretching the system could undergo before sufficient force had been applied to cleave an Au-Au bond (1.5 nN)^{10,14,15}.

Due to mechanical stretching the molecule, the data points do not correspond to stationary points on the PES. Additionally, due to the fixed ends of the linker, the system cannot undergo free rotation and translation. As a result, standard statistical mechanics formulae (which are derived for an ideal gas) cannot be applied to calculate the thermal and entropic effects on this system, and hence the free energy and redox potential changes as the molecule is stretched cannot be

determined. Instead, only the response of the aIP (in the presence of a solvent field) to stretching is reported. We note that this would be equivalent to the change in redox potential if the thermal and entropic effects are unaffected by increasing strain.

Supporting information:

Supporting experimental methods and DFT calculation methods.

Supporting discussions on 1 Relationship between conductance peak area and surface coverage of redox species; 2 Derivation of Eq.1, spring constant calculation and further estimation; 3 Theoretical description of the stretching process.

Supporting figures of NMR spectra, control experiment, plateau length statistics, analysis of both switched and unswitched curves at +30 mV, peak ratio vs. stretching distance at all potentials, calculated potential energy surface vs. distance, calculated significant structural parameters vs. stretching distance, and calibration of quasi-reference electrode.

Supporting tables of spring constants and shifts in Gibbs free energy, benchmark study of theoretical calculation, calculated molecular geometries, calculated potential energy surface, applied overpotential in each experiments.

Acknowledgements:

The authors would like to thank Drs. Wolfgang Schmickler and Andrew Gilbert for stimulating discussions. Financial support from the Office of Naval Research (N00014-11-1-0729) and from the Australian Research Council (CE140100012 and DE160100732), and generous allocations of supercomputing time on the National Facility of the Australian National Computational Infrastructure are gratefully acknowledged.

References

- (1) Kuznetsov, A. M.; Ulstrup, J. *Electron transfer in chemistry and biology. An introduction to the theory*; Wiley: Chichester, 1999.
- (2) Marcus, R. A. *Annual Review of Physical Chemistry* **1964**, *15*, 155.
- (3) Spiros S. Skourtis, D. H. W., David N. Beratan *Annual Review of Physical Chemistry* **2010**, *61*, 461.
- (4) Schmickler, W.; Rampi, M. A.; Tran, E.; Whitesides, G. M. *Faraday Discussions* **2004**, *125*, 171.
- (5) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384.
- (6) Xiao, X.; Brune, D.; He, J.; Lindsay, S.; Gorman, C. B.; Tao, N. *Chemical Physics* **2006**, *326*, 138.
- (7) Xu, B.; Tao, N. J. *Science* **2003**, *301*, 1221.
- (8) Li, Y.; Xiang, L.; Palma, J. L.; Asai, Y.; Tao, N. *Nature Communications* **2016**, *7*, 11294.
- (9) Zanello, P. *Inorganic Electrochemistry, Theory, Practice and Application*; The Royal Society of Chemistry: UK, 2003.
- (10) Huang; Chen, F.; Bennett, P. A.; Tao *Journal of the American Chemical Society* **2007**, *129*, 13225.
- (11) Artés, J. M.; López-Martínez, M.; Díez-Pérez, I.; Sanz, F.; Gorostiza, P. *Small* **2014**, *10*, 2537.
- (12) Arielly, R.; Vadai, M.; Kardash, D.; Noy, G.; Selzer, Y. *Journal of the American Chemical Society* **2014**, *136*, 2674.
- (13) Xiang, L.; Palma, J. L.; Li, Y.; Mujica, V.; Ratner, M. A.; Tao, N. *Nature Communications* **2017**, *8*, 14471.
- (14) Rubio, G.; Agraït, N.; Vieira, S. *Physical Review Letters* **1996**, *76*, 2302.
- (15) Xu, B.; Xiao, X.; Tao, N. J. *Journal of the American Chemical Society* **2003**, *125*, 16164.
- (16) Hao, X.; Zhu, N.; Gschneidner, T.; Jonsson, E. Ö.; Zhang, J.; Moth-Poulsen, K.; Wang, H.; Thygesen, K. S.; Jacobsen, K. W.; Ulstrup, J.; Chi, Q. **2013**, *4*, 2121.
- (17) Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Crystallographica* **1956**, *9*, 373.
- (18) Martinez, R.; Tiripicchio, A. *Acta Crystallographica Section C* **1990**, *46*, 202.
- (19) Bell, G. I. *Science* **1978**, *200*, 618.
- (20) Stauch, T.; Dreuw, A. *Chemical Reviews* **2016**, *116*, 14137.
- (21) Duggan, D. M.; Hendrickson, D. N. *Inorganic Chemistry* **1975**, *14*, 955.
- (22) Lin, J.; Beratan, D. N. *The Journal of Physical Chemistry A* **2004**, *108*, 5655.
- (23) Franco, I.; George, C. B.; Solomon, G. C.; Schatz, G. C.; Ratner, M. A. *Journal of the American Chemical Society* **2011**, *133*, 2242.
- (24) Grimme, S.; Ehrlich, S.; Goerigk, L. *Journal of Computational Chemistry* **2011**, *32*, 1456.
- (25) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friscic, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. *Chemical Society Reviews* **2012**, *41*, 413.
- (26) Boldyrev, V. In *Treatise on Materials Science & Technology*; Herbert, H., Ed.; Elsevier: 1983; Vol. Volume 19, Part B, p 185.
- (27) Balaz, P.; Achimovicova, M.; Balaz, M.; Billik, P.; Cherkezova-Zheleva, Z.; Criado, J. M.; Delogu, F.; Dutkova, E.; Gaffet, E.; Gotor, F. J.; Kumar, R.; Mitov, I.; Rojac, T.; Senna, M.; Streletskii, A.; Wiczorek-Ciurowa, K. *Chemical Society Reviews* **2013**, *42*, 7571.
- (28) Basedow, A. M.; Ebert, K. H. In *Physical Chemistry*; Springer Berlin Heidelberg: Berlin, Heidelberg, 1977, p 83.

- (29) Hickenboth, C. R.; Moore, J. S.; White, S. R.; Sottos, N. R.; Baudry, J.; Wilson, S. R. *Nature* **2007**, *446*, 423.
- (30) Rief, M.; Gautel, M.; Oesterhelt, F.; Fernandez, J. M.; Gaub, H. E. *Science* **1997**, *276*, 1109.
- (31) Wiita, A. P.; Perez-Jimenez, R.; Walther, K. A.; Gräter, F.; Berne, B. J.; Holmgren, A.; Sanchez-Ruiz, J. M.; Fernandez, J. M. *Nature* **2007**, *450*, 124.
- (32) Baldus, Ilona B.; Gräter, F. *Biophysical Journal* **2012**, *102*, 622.
- (33) Dopieralski, P.; Ribas-Arino, J.; Anjukandi, P.; Krupicka, M.; Kiss, J.; Marx, D. *Nat Chem* **2013**, *5*, 685.
- (34) Browne, W. R.; Feringa, B. L. *Nat Nano* **2006**, *1*, 25.
- (35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc.: Wallingford CT, 2009, p Gaussian 09.
- (36) Weigend, F.; Ahlrichs, R. *Physical Chemistry Chemical Physics* **2005**, *7*, 3297.
- (37) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *The Journal of Physical Chemistry B* **2009**, *113*, 6378.