

Detection of Single-Molecule Reaction Using STM Approach

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Method Article

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Abstract

Scanning tunneling microscopy (STM) was first designed to image conductive surfaces at the atomic scale resolution and can be used to perform electrical measurements at the single-molecule level [1–5]. Herein, we present a protocol based on single-molecule STM electrical measurements that enables monitoring a chemical reaction at the single molecule level. This was made possible by combining a surface chemistry that enables attaching molecules via self-assembled monolayers on the electrodes with the STM capability to control the distance between electrodes, hence to control the distance and trajectory between the approaching reactants. The reaction studied here is a Diels-Alder reaction between a furan derivative representing the diene (2-methyl-3-furanthiol) which is attached to the tip electrode and a norbornylogous bridge with a terminal double bond as the dienophile attached to the substrate electrode [6,7]. The product molecules are detected by specific current signatures as a consequence of a single product molecule bridging the two STM electrodes. This protocol allows to impose an oriented electrical field of specific magnitude along the approaching reactants at the single-molecule level.

Introduction

The reaction studied is a Diels-Alder (DA) coupling reaction between a diene and a dienophile, which is monitored via single-molecule conductance measurements. The Norbornylogous bridge NB (dienophile) and 2-methyl-3-furanthiol (diene) molecules are attached to the gold substrate and tip electrodes, respectively. The synthesis of these and related molecules can be found in the Supporting Information (SI) of the Nature article DOI 10.1038/nature16989. Details about the single-molecule junction technique can be found in several articles and reviews [1–5]. The procedure described herein is an adapted version of the spontaneous formation of single-molecule junctions approach by Richard Nichols and co-workers [2,3]. Functionalized tip and substrate electrodes are fixed at a distance of ca. 1 nm by imposing an initial set point tunneling current. After reaching the set point current, the feedback loop is turned off and the current is continuously monitored. Current jumps referred to as “blinks” appear when a molecular bridge spans the gap between the electrodes. The formation of these junctions is only seen when both reactants are present. When either reactant is removed from its respective electrode, or when their saturated analogues are used instead (i.e., 2-methyl-3-tetrahydrofuranthiol, DA unreactive) on the tip electrode or an hydrogenated version of NB (DA unreactive) on the substrate electrode, the molecular bridge does not form.

Reagents

Au substrate (Matech-Germany) Mesitylene (Acros Organics) 2-methyl-3-furanthiol (Sigma Aldrich) NB, tricyclo[4.2.1.0^{2,5}]non-7-ene-3,4-dimethanethiol (Custom synthesized) Absolute ethanol (Panreac) CH₂Cl₂ (Sigma-Aldrich) Piranha [3:1 H₂SO₄ (Sigma-Aldrich)/H₂O₂ by volume] H₂ flame (Carbueros Metálicos) Ar (Carbueros Metálicos) Milli-Q water (Millipore)

Equipment

Homemade PTFE Cell PicoSPM-I microscope head controlled using a Picoscan-2500 electronics (both from Agilent-USA) NI-DAQmx (National Instruments-USA) BNC-2110 (National Instruments-USA) LabVIEW software package (National Instruments-USA) Au wire, 0.25 mm diameter (99.99%) (Goodfellow-UK) Au (111) single crystal substrate (10 mm x 1 mm) of 99.9999% purity and orientation accuracy < 0.1 degrees from (MaTeck-Germany)

Procedure

A. Preparation: 1. All glassware and PTFE parts of the STM cell are cleaned with piranha solution (3:1 H₂SO₄/H₂O₂ by volume) before usage followed by rinsing with 18.2 MΩ cm⁻¹ Milli-Q water (Millipore) and finally dried with a stream of N₂. ▲ TROUBLESHOOTING 2. The Au wire is mechanically cut to produce sharpened apex at its distal end (confirmed via optical microscope) and used as the STM tip electrode. The formed tip is briefly H₂ flame-annealed to remove impurities and immediately immersed for 12 h in 0.05 mM 2-methyl-3-furanthiol (Sigma-Aldrich) in CH₂Cl₂ solution previously purged with Ar gas for 20 min. Each tip is then thoroughly rinsed with CH₂Cl₂ and then dried under a stream of Ar before being used in the STM experiment. 3. Before modification of the Au substrate, the single crystal Au (111) surface is electro-polished for a 1 min period to eliminate possible residual contaminations and then annealed for a 10 min in a H₂ flame to improve surface orientation. The clean substrates are then immediately immersed for a 12 h period in an ethanol solution containing 0.1 mM of the dienophile (NB), previously purged by means of Ar gas bubbling. The substrates are then washed thoroughly with absolute ethanol, dried under a stream of Ar and placed in the homemade STM PTFE cell. A volume of 80 μL of mesitylene is then added to protect the substrate surface against external contamination and to keep the electrodes in an electrically isolated medium. B. Measurement: 1. A variable direction and magnitude working bias is imposed between tip and substrate electrodes. 2. The electrodes are fixed at a specific distance by imposing an initial set-point current. ▲ TROUBLESHOOTING 3. After 1 h of equilibration time to reach an appropriate mechanical stability, the feedback loop is turned off and the current is externally monitored and recorded through a LabVIEW acquisition system. When both reactants are joined, the product molecule spans the gap between the electrodes and closes the electrical circuit. As a consequence, the current flowing between both electrodes increases above the background tunneling current (tunneling through the gap). This is reflected in the monitored current as a sudden jump in the form of telegraphic signatures or “blinks” (Figure 1) [3,8–10]. The net current crossing the molecule is then obtained by subtracting the tunneling current background from the blink. 4. Measuring the effect of the electrical field over the Diels-Alder reaction: Under the employed working bias between tip and substrate electrodes all the blinking events are recorded during 1 h periods. At the end of each 1 h period, we changed the furan-modified STM tip and its lateral position with respect to the surface to compensate for the loss of reactants. This procedure is repeated 8 times giving each bias point (magnitude and direction) a total experimental time of 8 h. The chronology of the selected biases for each repeat is randomly selected to minimize the experimental error. ▲ TROUBLESHOOTING 5. Testing the junction mechanical stability: the appearance of a blink when a product molecule closes the circuit between the tip and substrate electrodes is an indication of a mechanically stable junction. The molecular signature

of this junction can be confirmed by collecting pulling curves during the “blinks”. Pulling curves collected over the “blinks” show a plateau corresponding to the stretching of the single-molecule bridge. When a pulling force is exerted over the tunneling background, a clean exponential decay is observed (Figure 2 and 3). Pulling decay captures are applied via a code written in LabVIEW which applies a voltage ramp to the piezo to force a defined tip electrode retraction distance during a selected time. C. Data treatment - All the collected data from the blinking experiments are plotted as 2D conductance maps (Figure 4) by the accumulation of hundreds of individual “blinks”. No selection procedures were applied to the data i.e. all blinking traces were accumulated to build the 2D maps. - To build 2D maps all the blinks are accumulated and set into a common time origin and baseline, in order to compare the lifetimes of the blinks in the 2D maps and subtract the background tunneling current, respectively. 2D maps were built by a code written in LabVIEW.

Timing

- STM gold tips were immersed in 2-methyl-3-furanthiol solutions (Preparation stage): 12h. - Au 111 substrates are immersed in NB solution (Preparation stage): 12h. - “Blinking” (Current measurement stage): 8h for each applied bias after 1h of stabilization time.

Troubleshooting

- Preparation stage (step 1): Caution, Piranha solution should be handled with extreme caution, it is corrosive and achieves high temperatures quickly. - Current measurement stage (step 2): the tip and substrate electrodes were set to a distance comparable to the molecular length of the product molecule (1 nm). A drift of 2-fold away from the setpoint current was corrected by turning on the current feedback. This was applied to ensure that the variation in tip-surface distance is kept to minimum. - Current measurement stage (step 4): To keep all the experiments at the same initial conditions and to keep the same distance between electrodes across the bias range, the same initial set point current and bias are used. The working bias is then changed while the current feedback is turned off.

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Figures

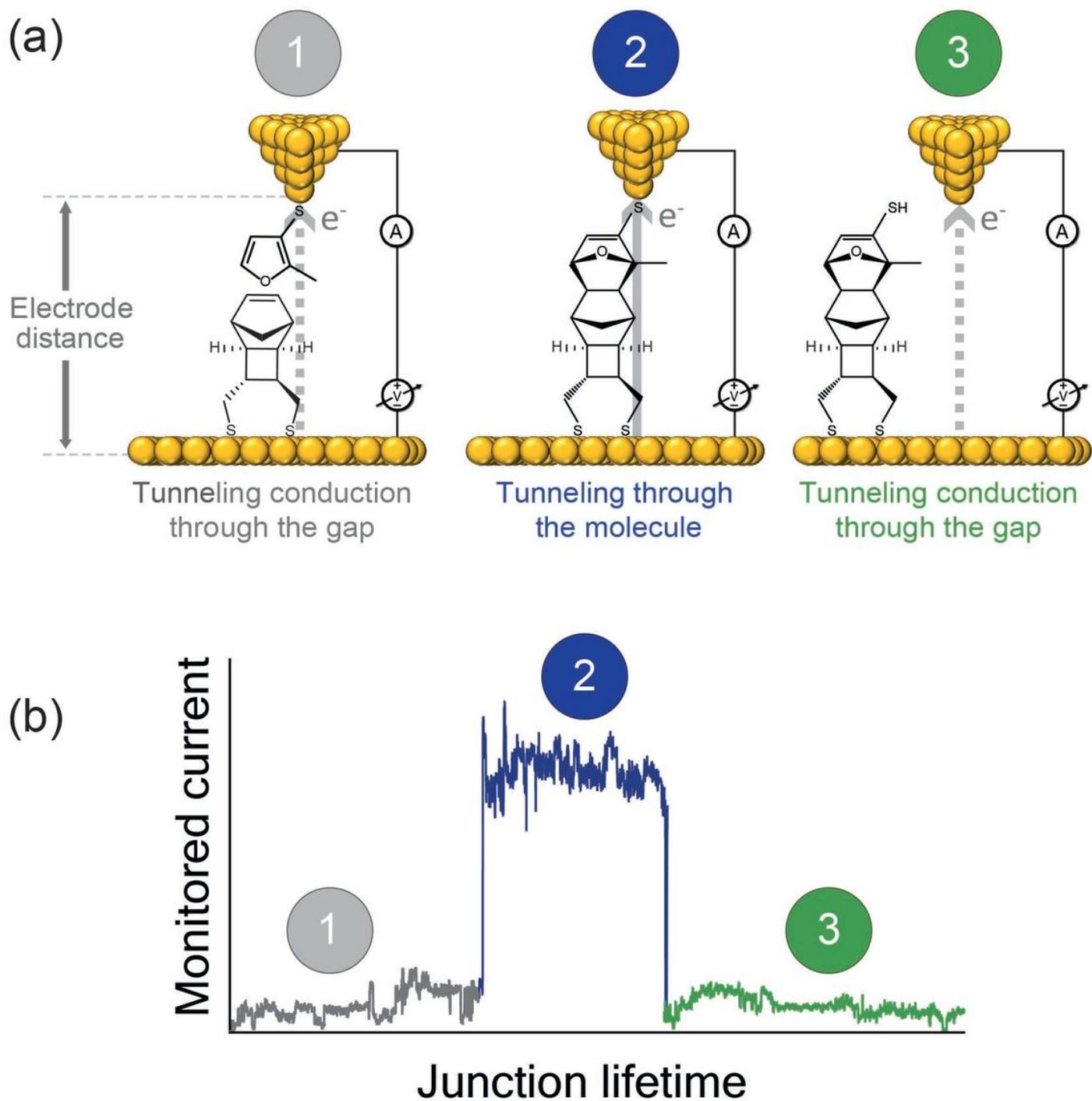


Figure 1

Graphical scheme of blinking Fig. 1 (a) Graphical scheme detailing the stages of a blink and (b) the typical current response during a blinking event. Stages marked as “1”, “2” and “3” represent the response before, during and after the formation of a representative blink, respectively.

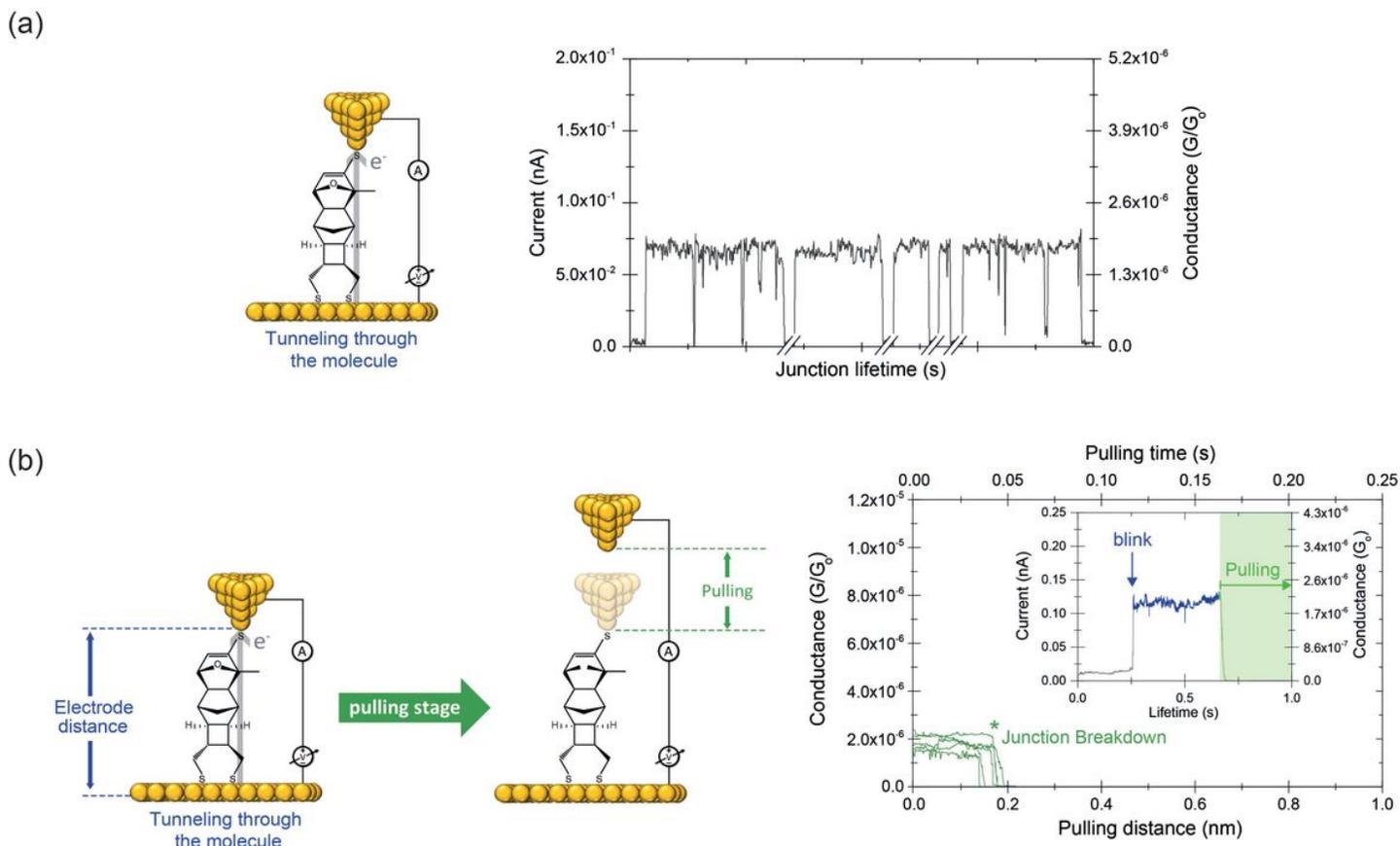


Figure 2

Mechanical pulling of blinking events Fig. 2 (a) A real-time data capture of blinking events at surface bias of -0.5 V as a consequence of the formation of molecular junctions between the product molecule and the electrodes. The time breaks in the x-axis are about 2 minutes. The sudden current jumps are due the tunneling current flowing through the molecule between the tip and substrate electrodes. The tunneling current abruptly decays to the background current value due the spontaneous breakdown of the junction. (b, left panel) Mechanical pulling exerted during the blinking events. The pulling is exerted while a product molecule is forming a junction between the electrodes. (b, right) Representative pulling curves during the blinking events at $1.5 \times 10^{-6}\text{ G} \sim 0 \sim$. The inset shows the blink before and after the pulling stage. The blink can be stretched by ca. 0.2 nm , which demonstrates that the junction possesses significant mechanical resistance to the pulling attempt and testify for the formation of robust molecular junction between the 2 electrodes.

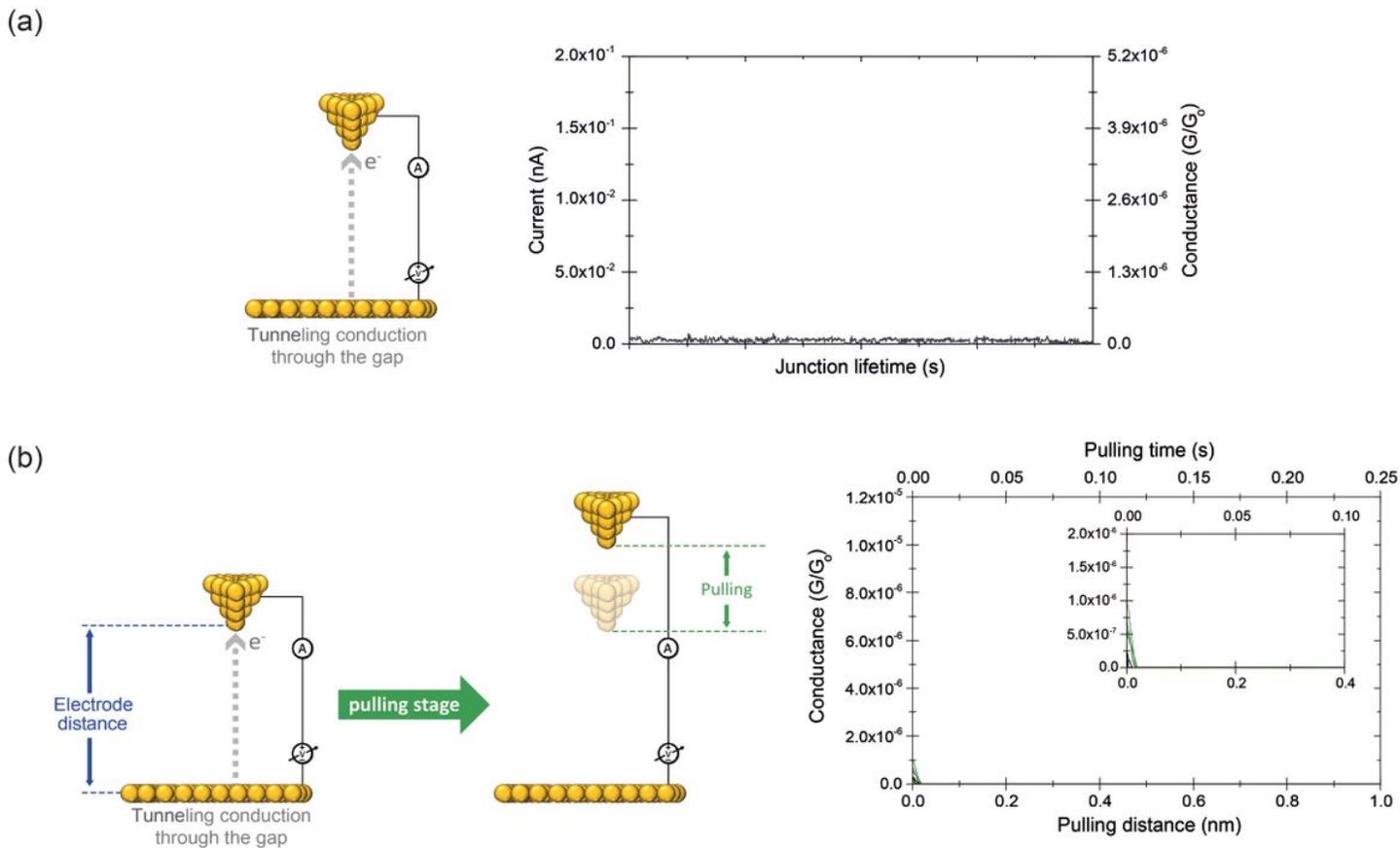


Figure 3

Mechanical pulling in the absence of a molecular junction Fig. 3 (a) The STM current response in the absence of a molecular junction; only the tunneling current-background flowing between the tip and substrate electrodes is observed. (b, left panel) Schematic of the pulling procedure exerted during the time when the current is showing only the tunneling current-background (b, right panel) the pulling results immediately in an exponential decay in the monitored current without any mechanical resistance.

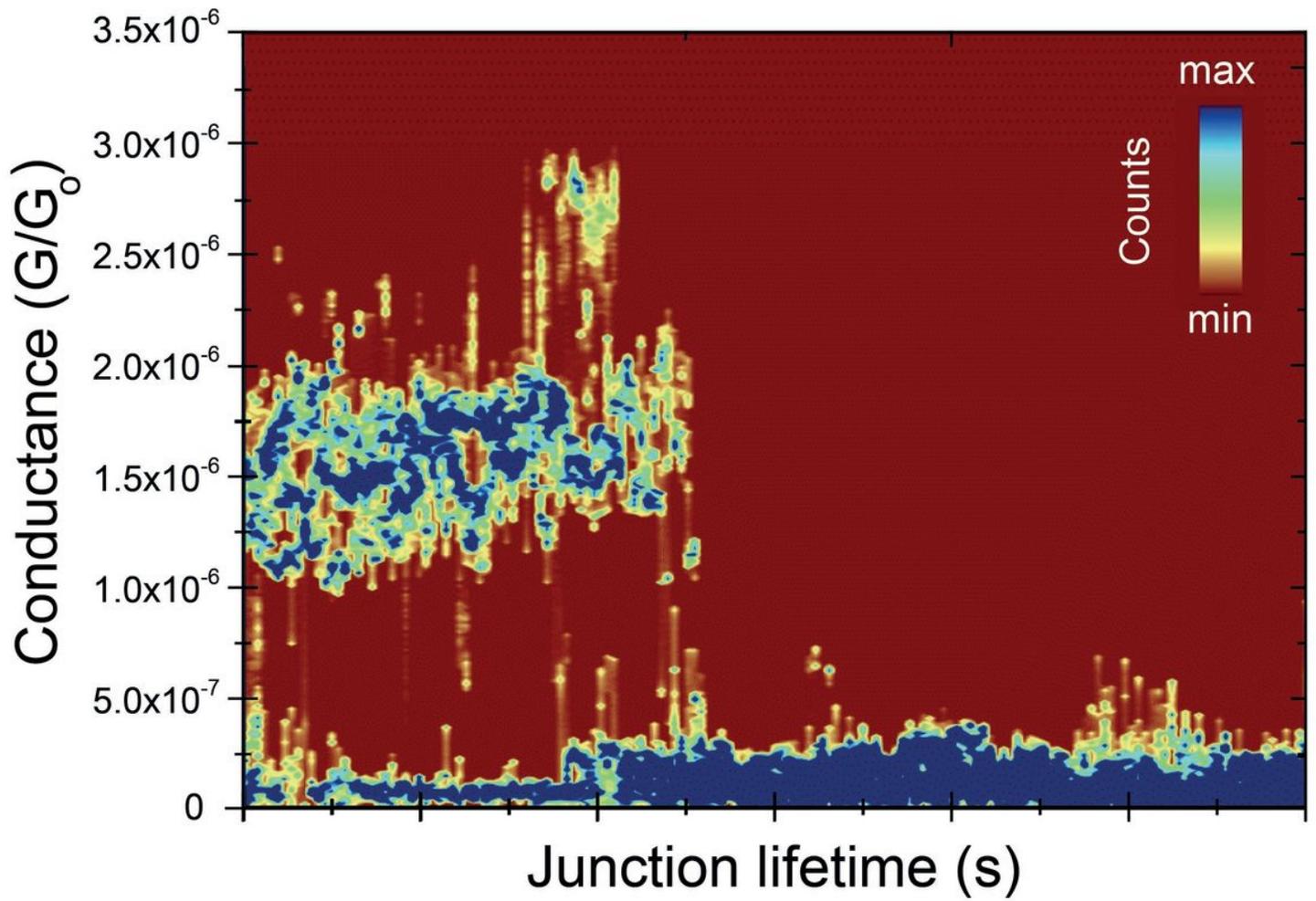


Figure 4

2D maps of blinking events Fig. 4 2D maps overlaying hundreds of blinks. Counts have been normalized to a color scale with 100 representing the maximum and 0 representing the minimum.