Nearfield trapping increases lifetime of single-molecule junction by one order of magnitude.

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ABSTRACT

Progress in molecular electronics (ME) is largely based on improved understanding of the properties of single molecules (SM) trapped for seconds or longer to enable their detailed characterization. We present a plasmon-supported break-junction (PBJ) platform to significantly increase the lifetime of SM junctions of 1,4-benzendithiol (BDT) without the need for chemical modification of molecule or electrode. Moderate far-field power densities of ca. 11 mW/µm² lead to a >10-fold increase in minimum lifetime compared to laser-OFF conditions. The nearfield trapping efficiency is twice as large for bridge-site contact compared to hollow-site geometry, which can be attributed to the difference in polarizability. Current measurements and tip-enhanced Raman spectra confirm that native structure and contact geometry of BDT are preserved during the PBJ experiment. By providing a non-invasive pathway to increase short lifetimes of SM junctions, PBJ is a valuable approach for ME, paving the way for improved SM sensing and recognition platforms.

Keywords: Molecular electronics; PBJ; STM-BJ; single-molecule junction; nearfield optical trapping, junction lifetime, tip-enhanced Raman spectroscopy.

INTRODUCTION

The field of molecular electronics (ME) aims at miniaturising electronic devices and surpassing the space limitation of conventional silicon circuit integration.1 In ME, the functionality of the electric circuitry relies on the electronic properties of individual molecules or small molecular ensembles. To improve our understanding of single-molecule electronic properties, ME research fundamentally relies upon the development of novel techniques to reliably and reproducibly study the diverse properties of individual molecules that are inaccessible in conventional ensemble experiments.2 Robust tools have been developed for high-precision single-molecule trapping and detection to characterize individual molecules, enabling, for example, molecular sensing,3 recognition,4 Raman characterisation5,6 or single-molecule reactors.7 Most of these approaches rely on the detection of individual molecular binding events in an electrode-electrode gap of a fixed size as a function of time.6–10 One of the most promising approaches to trap and study single molecules bridged in precisely sized, motionless nanogaps is the blinking approach,11 a scanning tunnelling microscope (STM)-based break-junction technique (STM-BJ).12 In the blinking approach, a sub-nm precise inter-electrode distance is kept between the STM-tip and substrate electrodes to create a molecular-scale metal-metal gap in which an individual target species can be trapped to form a single-molecule electronic junction. When the tunnelling-current (I_t) feedback control is disabled, molecular junctions form (and break)10 stochastically (Figure 1a) in the electrode gap.13 The formation of a single-molecule junction can be monitored in situ by a sudden increase of the measured current signal to the molecular junction current, I_m, whose amplitude equals the conductance of the single-molecule junction (Figure 1b).10 A molecular junction lasts for a finite period of time, i.e. the junction lifetime τ, after which the current suddenly drops again to I_t due to the spontaneous disconnection of the molecule from one of the two electrodes.11 Typical τ are rather short in the order of tens to hundreds of ms, thus hindering elaborate junction characterization over longer time periods.6,7,10,11 Immobilising target molecules for longer timescales, i.e. increasing τ, has remained one of ME’s central challenges. Strategies to obtain enduring and mechanically robust molecular junctions include the usage of various electrode materials3,15,16 and anchoring groups.17–19 While these strategies have resulted in improved τ of up to a factor 2 compared to routinely employed Au-SH or Au-NH₂ electrode-anchoring systems,16,18 they are typically rather system specific, which hinders a wide applicability to diverse sets of target molecules and electrode materials.

Preprints are preliminary reports that have not undergone peer review. They should not be considered conclusive, used to inform clinical practice, or referenced by the media as validated information.
One versatile way to secure particles in a specific location is optical (far-field) trapping. An optical trap is created by tight focusing of a laser beam to generate a strong field gradient in the focal region. This field gradient attracts dielectric particles and directs them to the centre of the focus where the field is strongest, reaching typical trapping forces in the order of a few (tens of) pN. Downscaling far-field optical trapping to the single-molecule scale is not straightforward because of the Abbe diffraction limit of approx. $\lambda/2$ ($\lambda$ is the trapping laser wavelength, which for typical applications lies in the visible regime between 500 and 750 nm) of the far-field focus size. Furthermore, the gradient of the optical force becomes weaker with decreasing object size (scaling with the third power of the object size) and results in significantly smaller capturing efficiency and thus a simpler escape from the trap of small objects compared to larger ones. Nanophotonics offer a useful nanoscale alternative to conventional optical traps: plasmonic traps. Plasmonic traps are based on nanostructures that confine and enhance an electromagnetic field well beyond the diffraction limit due to (surface) plasmon excitation by (far-field) light. The resulting near-field induces strong gradient forces capable of increasing the efficiency and the precision of optical trapping. The intensity of the near-field can be up to three orders of magnitude stronger than the far-field intensity, in this way rendering feasible even the capturing of nanoparticles and molecules, to date down to the 100 to 10 nm range.

In recent works, plasmonic trapping was employed to lock bio-molecules into position at Ag nanoaggregates or Au surfaces for surface enhanced Raman spectroscopic measurements. Here, we combine nearfield trapping with the blinking STM-BJ approach to enable plasmon-supported break-junction (PBJ) experiments. For the PBJ approach, we integrate an STM-BJ platform into an STM-based solid/liquid tip-enhanced Raman spectrometer (EC-TERS) that allows us to build, stabilize and characterize well-defined single-molecule junctions in situ in terms of $\tau$ and other common junction characteristics such as molecular conductance, junction yield and adsorption geometry. We form single-molecule junctions of showcase 1,4-benzenedithiol (BDT), a prototypical single-molecule component in ME research, that has been shown to interact through one of the terminal $\text{S(H)}$ groups with the Au(111) surface as thiolate while the second thiol group is accessible by the tip to form stable molecular junctions. We analyse $\tau$ in the presence or absence of a nearfield to assess the stability of the Au-BDT-Au junctions. From the PBJ results in correlation with solid/liquid TER spectra, we find that the presence of a nearfield gradient in the order of $6.3 \times 10^7$ V/m leads to a significant increase of $\tau$ of the single-molecule junction by up to one order of magnitude. As such, we demonstrate that nearfield trapping provides a straightforward way to increase molecular junction robustness without the need for chemical modification of target molecule and/or electrode and in this way opens up new possibilities for single-molecule characterization during prolonged time scales of >1 s without compromising the chemical integrity of the junction.

RESULTS AND DISCUSSION

Assessing the nearfield effects over single-molecule junction characteristics

Figure 2 a and b shows example telegraphic current traces recorded from Au-BDT-Au junctions of constant size of 10 Å in water with or without 632.8 nm laser illumination of the junction, i.e. with or without nearfield (technical details in the Supplemental Experimental Procedures; additional current traces in Figure S1). The telegraphic noise pattern in blinking experiments is associated with thermally activated stochastic junction formation and breaking. According to thermodynamic theory, the molecule-tip bond is considered as a dynamic state and the probability to spontaneously break down the bond due to thermal fluctuations increases with time (see detailed information including the S-Au junction specific case in Note S1). Independent of the illumination setting, the single-molecule junction can be found in either one of two discrete conduction states of ca. $2.66 \pm 0.21 \times 10^{-3}$ G$_0$ and $1.10 \pm 0.06 \times 10^{-2}$ G$_0$, where G$_0$ is the conductance quantum unit of 77.4 µS (respective conductance 1D histogram and 2D maps in Figures S2 and S3). The low conductance (LC) and high conductance (HC) states have been previously assigned to hollow and bridge BDT-Au adsorption configurations, respectively. The corresponding current/voltage (I(V)) characteristics (see Note S2 and Figure S4) indicate symmetric hollow or bridge molecule/electrode contact geometries at both electrodes. Complementary TER spectra (see analysis in Note S3, Figures S5-7 and Table S1) recorded prior to and after the PBJ experiments corroborate the presence of intact BDT molecules in the gap through the detection of their characteristic vibrational fingerprint. Furthermore, the stable spectral background provides an independent proof of the gap (plasmonic) stability over the course of a few-hour long PBJ experiment.
In the absence of the nearfield, the recorded junction mean lifetimes are \( \tau_{\text{OFF-LC}} = 0.14 \pm 0.07 \text{ s} \) and \( \tau_{\text{OFF-HC}} = 0.08 \pm 0.03 \text{ s} \) for the LC and HC junctions, respectively. LC junctions possess an inherently lower resistance than LC junctions because of the stronger bridge-contact geometry compared to the hollow Au site geometry of LC junctions. The lower resistance negatively affects the HC-junction \( \tau \) because the inherent local heating due to stronger electron-phonon interactions lowers the junction stability compared to LC junctions.\(^{34} \) Interestingly, we observe a drastic increase in mean lifetimes for both LC and HC type junctions to \( \tau_{\text{ON-LC}} = 0.80 \pm 0.22 \text{ s} \) and \( \tau_{\text{ON-HC}} = 0.58 \pm 0.15 \text{ s} \) when the tip-sample gap is illuminated and a nearfield is created. For the highest employed far-field power density of 11 mW/\( \mu \text{m}^2 \) (3.3 mW far-field laser power at the diffraction-limited focus spot measured in air; the one in water cannot be measured but is likely to be a factor 3 to 5 smaller,\(^{35} \) (details in Note S4 and values in Tables S2 and S3), the mean \( \tau \) increase thus amounts to a factor 6 and 7 for LC and HC junctions, respectively. 1 \% of the runs show an unprecedented increase in BDT junction lifetime of more than one order of magnitude, \( i.e. \) detected HC and LC lifetimes of 1.1 s and 1.8 s, respectively. These results demonstrate that creating a nearfield in the tip-sample gap constitutes a highly effective means to stabilize single-molecule junctions already at moderate far-field laser power densities of ca. 11 mW/\( \mu \text{m}^2 \). In addition to the increase in \( \tau \), we observe an increase in the detected junction yield of up to factor 8 between laser OFF and ON conditions, which indicates that the presence of the nearfield also facilitates the formation of single-molecule junctions (see Figure S8 and Table S4; detailed analysis in Note S5). A similar plasmon-supported increase in single-molecule junction probability has been recently reported by Zhan et al. who were able to tune the capturing and releasing of molecules in a nearfield-gap in solution during pulling captures between two electrodes.\(^{36} \) The single-molecule conductance, on the other hand, is independent of the absence or presence of the nearfield at the investigated laser powers (see Figure S9 and Table S5; detailed analysis in Note S6). The electron transmission eigenchannel of BDT is dominated by the highest occupied molecular orbital (HOMO) level that is located about 2 eV below the Fermi level of Au.\(^{32} \) At 3 mV bias applied here, the overlap of the Au hot-hole energy distribution with the BDT HOMO level is apparently insufficient to create a detectable hot-carrier induced current.\(^{37} \)

Figure 2c displays how \( \tau \) depends on the employed laser power. The data have been extracted from 1D lifetime histograms obtained from hundreds of accumulated PBJ current captures (histograms in Figure S10 and extracted lifetimes in Tables S6-9) for far-field laser power densities ranging from ca. 1.2 mW/\( \mu \text{m}^2 \) to 11 mW/\( \mu \text{m}^2 \) (0.38 to 3.3 mW far-field laser power). For each set of experiments at a specific laser power density, complementary 0 mW/\( \mu \text{m}^2 \) \textit{in situ} control experiments were performed by completely blocking the laser beam (see Note S7 and Figure S11). The 0 mW/\( \mu \text{m}^2 \) data depicted in Figure 2c is the mean value of all control experiments. We can fit the laser power dependence of \( \tau \) to an Arrhenius-like exponential function with degrees of confidence, \( r^2 \), of 0.997 and 0.987 for the LC and HC traces, respectively:

\[
\tau = A \cdot \exp \left( \frac{P}{k_B T} \right), \quad (\text{Equation 1})
\]

with \( A \) as a constant, \( P \) incident laser power density, \( k_B \) Boltzmann constant and \( T \) temperature. As such, our single-molecule nearfield trap exhibits a logarithmic increase in \( \tau \) with employed laser power (density), comparable to the one that has previously been observed for the trapping of large 100 nm-sized particles in liquid medium in a nanoaperture-based optical trap.\(^{38} \) The slight difference in the slopes of the HC (0.49) and LC (0.61) traces attests to different susceptibilities of the two types of BDT-Au bonding motifs to the nearfield optical trap. Even though \( \tau_{\text{HC}} < \tau_{\text{LC}} \), apparently the HC state is more strongly stabilised by the presence of the nearfield than the HC state.

To understand the different magnitude of the nearfield effect on LC and HC junctions, let us consider the physical origin of the lifetime increase. In a plasmonic trap, the emerging gradient force of the nearfield (at a given laser power) acting on the (trapped) species is proportional to the polarizability of the particle or molecule.\(^{39} \) Observing differences in nearfield trapping efficiencies for LC and HC states therefore points to the fact that the two Au-BDT-Au related adsorption configurations exhibit different polarizabilities. In fact, it has been demonstrated that the conductance of molecules scales with their polarizability.\(^{40} \) Even more importantly, also small differences in molecule-metal contact geometry result in significant changes in polarizability and correlated conductance.\(^{41} \) In general, the junction polarizability is described by the induced electronic dipolar transition between the frontier orbitals.\(^{42} \) For Au-BDT, this transition is largely dominated by the HOMO-LUMO gap that, in turn, depends on the contact geometry.\(^{43} \)
Accordingly, the fact that we find the HC Au-BDT-Au state to exhibit a larger susceptibility to the nearfield than the LC state can be associated with the higher polarizability of the HC state compared to the LC state.

To exclude additional parameters inherent to the system that potentially affect \( \tau \), such as intrinsic lifetime differences between LC and HC junctions due to current-induced local heating, or the lifetime variance between sets of experiments under equivalent conditions, and thus to isolate and more precisely quantify the effect of the plasmonic nearfield on \( \tau \), we calculate a normalised nearfield trapping efficiency (\( \eta \)) for each junction. Here, \( \eta = \frac{\tau_P - \tau_{OFF}}{\tau_{OFF}} \), with \( \tau_P \) the lifetime under laser illumination at a specific incident laser power density and \( \tau_{OFF} \) the lifetime measured under identical conditions with the laser beam blocked. Furthermore, we convert the employed power density (\( P \)) to an approximate far-field strength (\( E \)) following a \( P = \frac{E^2}{Z_0} \) conversion where \( Z_0 \) is the characteristic impedance of free space and then calculate an approximate nearfield gradient by assuming an enhancement of a factor 30, typical for the given TERS Au-Au gap (see Table S1).35

Figure 2d shows how \( \eta \) increases exponentially with increasing nearfield gradient for LC (HC) junctions from ca. 0.47 (0.44) to 6.3 (4.2) with a slope of 2.9 \( \times \) 10\(^{-8} \) (3.4 \( \times \) 10\(^{-8} \)) at a degree of confidence of 0.972 (0.984). Except for the lowest laser power conditions employed here, HC junctions display higher nearfield trapping efficiency values than LC junctions, reaching twice as high a nearfield susceptibility at 6.3 \( \times \) 10\(^7 \) V/m. The differences in slope and \( \eta \) values again indicate a correlation between the nearfield trapping efficiency and the contact geometry, i.e. the distinctive feature between LC and HC junctions.

Note that when the laser is OFF (no nearfield), there is still a small electric field of ca. 3.0 \( \times \) 10\(^6 \) V/m present in the gap that is associated with the applied bias voltage of 3 mV (cross marker data in Figure 2d).7 This bias-related field is present during all experiments and can thus be viewed as an offset to the applied nearfield. Fitting the OFF data points together with the ON data points, we obtain an estimation for the bias-induced contribution to \( \eta \) of 0.13 and 0.16 for LC and HC junctions, respectively. In our experiments, the bias contribution to the stabilization of the junction is thus at least one order of magnitude smaller than the nearfield contribution. In principle, one could increase the bias voltage to create stronger field gradients and thus more stable junctions. However, large biases always imply higher currents and thus greater instabilities of the junctions because of increased electron-phonon interactions.34 These instabilities then could lead to a net decrease of \( \tau \), as has been recently reported for single-protein trapping in plasmonic nanopores.45

Nearfield trapping and junction breakdown behaviour

How can we understand the blinking lifetime increase of the Au-BDT-Au junction in the presence of a nearfield? First, we need to assess the capability of the employed incident power densities (1.2 to 11 mW/\( \mu \)m\(^2\)) to trap individual BDT molecules. Already early works by Novotny39 and Käll42 describe the theoretical possibility to trap individual molecules in nearfield traps with power densities as small as 1.0 mW/\( \mu \)m\(^2\) and three orders of magnitude field enhancement, i.e. conditions similar to the ones we employ here.35 In a recent publication, Long et al. theoretically predict the plasmon-based trapping effects of individual molecules in an illuminated STM (TERS) nanogap.46 According to their results, the highly localised electric nearfield creates a radial (restoring) force in the order of 10\(^{-4} \) pN/[mW/\( \mu \)m\(^2\)] in the nanosized region in the tip-sample gap that is sufficiently strong to orient and stabilize a molecule in the junction. Long et al. use a PBJ tip-sample nanogap geometry of 2 nm size, a 60˚ excitation geometry, a factor 500 of field intensity enhancement and a molecule polarizability, \( \alpha \), of 4.5 Cm\(^2\)/V. These conditions are comparable to our system with 1 nm gap size, side-illumination geometry, a field intensity enhancement of 2 to 3 orders of magnitude35 and \( \alpha_{BDT} = 4.1 \times 10^{-39} \) Cm\(^2\)/V (as obtained from the Clausius-Mossotti equation, see Supplemental Experimental Procedures). As such, we conclude that, under the given experimental conditions, the generated nearfield optical trapping force in our PBJ experiments is sufficient to direct the BDT molecule toward the centre of the illuminated nanogap and trap it there, in this way increasing the junction lifetime.

In the absence of external forces or fields and at low bias voltage regimes <100 mV,31 \( \tau \) exhibits spontaneous junction breakdown behaviour following the thermodynamic theory,30

\[
\tau = t_d \cdot \exp \left( \frac{E_b}{k_B T} \right), \quad \text{(Equation 2)}
\]
with \( t_d \) the diffusion time inherent to the system and \( E_b \) the Au-BDT dissociation energy barrier (details in Note S1). When \( E_b \) is modified by an external parameter, such as a mechanical force, \( \tau \) will be affected accordingly.\(^{30} \) For example, a pulling force from electrode retraction has previously been shown to decrease \( E_b \) and thus \( \tau. \)\(^{31} \) As evident from comparing Equations 1 and 2, \( E_b \) can be understood to be a function of \( P. \) We can then separate \( E_b \) into field-independent (\( E_{\text{ind}} \)) and field-dependent (\( E_{\text{field}} \)) terms, as the field contribution that modifies \( \tau, \) accordingly to the field gradient:

\[
\tau = t_d \cdot \exp \left( \frac{E_{\text{ind}} + E_{\text{field}}}{k_B T} \right), \quad \text{(Equation 3)}
\]

\[
\tau = t_d \cdot \exp \left( \frac{E_{\text{ind}}}{k_B T} + \frac{E_{\text{field}}}{k_B T} \right),
\]

\[
\tau = t_d \cdot \exp \left( \frac{E_{\text{ind}}}{k_B T} \right) \cdot \exp \left( \frac{E_{\text{field}}}{k_B T} \right)
\]

With Eq. 3, the increase in \( \tau \) can be estimated from the field gradient values for a given power density \( P. \) For the maximum \( P \) of 11 mW/\( \mu \)m\(^2\), the calculated nearfield gradient equals ca. 6.3 \( \times 10^7 \) V/m (or 2.2 \( k_B \)T/\( \mu \)m), a value comparable to a previously estimated one of ca. 6 \( k_B \)T optical potential well resulting from 10s of mW/\( \mu \)m\(^2\) excitation power.\(^{42} \) In other words, the nearfield associated with the maximum \( P \) employed here leads to an increase in the Au-BDT dissociation barrier by 2.2 \( k_B \)T. For the lowest power density, Eq. 3 yields ca. 2.1 \( \times 10^7 \) V/m (or 0.7 \( k_B \)T/\( \mu \)m) and for the 0 mW/\( \mu \)m\(^2\) control, the small electric field of 3 \( \times 10^5 \) V/m corresponds to 0.12 \( k_B \)T/\( \mu \)m. According to Eq. 3, we should thus expect an increase in \( \tau \) by factors 2 and 8 for the minimum and maximum power laser densities employed here, respectively, compared to the 0 mW/\( \mu \)m\(^2\) case. Despite the given approximation in field enhancement, the calculated values agree quantitatively very well with the experimentally observed ones for HC (LC) junctions of 2 (\(<2\)) and 7 (5). The stabilizing effect of the nearfield can be expected to break down at some point when heating effects – contributing to the destabilization of the junction – in the gap become non-negligible. For TERS configurations with field enhancements in the order of 20 to 30 comparable to ours, the local temperature rise has been estimated to lie below 10°C.\(^{47} \) This temperature increase is likely insufficient to promote Au-S desorption\(^{48} \) or Au-Au fracture.\(^{49} \) It has been estimated that instabilities of thiol-Au junctions may be relevant above a \( T \) increase of 30 K.\(^{50} \) However, even at these elevated temperatures, blinking experiments did not show signs of lifetime decrease for Au-S based molecular junctions.\(^{51} \)

To corroborate that the nearfield is the driving force for the increased lifetime of single-molecule junctions, two additional types of experiments were performed besides the 0 mW/\( \mu \)m\(^2\) controls. To deliberately suppress or switch off the nearfield trapping in the hotspot region (experimental details in Note S8), we defocus the laser in a controlled way or block the laser immediately after a set of experiments (see Figures S12 and 13). The first additional control allows us to exclude far-field effects related to laser illumination, like photocurrent\(^{34} \) or photo-thermal effects,\(^{52} \) that could influence the conductance and the stability of the single-molecule junction. Turning off the laser immediately after a power-dependent experiment, on the other hand, allows us to confirm the reversibility of the plasmon-supported enhancement of \( \tau. \) Both controls give the same result, namely, that \( \tau \) is reduced to the original (0 mW/\( \mu \)m\(^2\)) value in the absence of a nearfield, in this way confirming that the nearfield is responsible for the observed lifetime increase under focused illumination.

**Insights into lifetime’s dependence on the nearfield gradient**

To provide a more in-depth lifetime characterization in the presence of the nearfield, we plot 2D \( \tau \) vs. conductance distribution maps for the PBJ current captures as a function of applied laser power density (Figure 3). The 2D maps allow us to visualize the \( \tau \)-distribution envelope and extract the mean lifetimes, and to directly correlate them to the conductance-distribution envelope for each power density (detailed description in Note S7). Figure 3 neatly visualizes the transition from \( \tau_{\text{LC}} = 0.20 \pm 0.06 \) s and \( \tau_{\text{HC}} = 0.11 \pm 0.03 \) s at 1.2 mW/\( \mu \)m\(^2\) power density to \( \tau_{\text{LC}} = 0.80 \pm 0.22 \) s and \( \tau_{\text{LC}} = 0.58 \pm 0.15 \) s at 11 mW/\( \mu \)m\(^2\) power density (horizontal lines). From the 2D maps, it is evident that the
conductance values (envelopes) are independent of the $\tau$ distributions at any given power density, with the mean $\tau$ regions corresponding to the mean conductance values (cf. 1D histograms in Figure S2 a-e). This observation proves that the $\tau$ increase is not related to any structural modification of the molecule or to a contact alteration, since such geometric changes would lead to changes in conductance. As we only observe conductance values assigned to single-molecule junctions (and not integer multiples of these values), multi-molecule contacts can also be ruled out. Such an assessment of individual molecular contacts is relevant for a $\tau$ analysis in plasmonic traps, since multi-molecule cooperative effects have been reported to affect the trapping time.

The spatial distribution of the 2D envelopes around the mean $\tau$ values contains information about how $\tau$ evolves with the laser power density. Interestingly, both minimum and maximum envelope $\tau$ values are displaced to higher values with increasing nearfield strength (overview in Table S8). For LC (HC) junctions, we observe an increase of the largest 1% $\tau$ values (< 10 junctions) by a factor of ca. 7 (5) and of the shortest 1% $\tau$ values by a factor of 11 (5) compared to the 0 mW/µm² values. As such, the presence of the nearfield tunes both lower and higher $\tau$ thresholds, but in a non-uniform way. The asymmetric $\tau$ increase is further corroborated by the broadening of the full-width-at-half-maximum (FWHM) of the Gaussian fit of the 1D lifetime histograms (Table S9). With increasing power density, the FWHM increases by up to a factor 5 for both LC and HC junctions with respect the 0 mW/µm² laser power. We can potentially attribute the broadening of the $\tau$ distributions to two effects, namely to the increase in experimental error with increase of detected events and/or to an increase of heating effects causing small structural variations in the junction. As stated above, heating effects should be negligible under the given conditions. As such we speculate that the major contribution to the observed increase in the FWHM is the increase in the experimental error associated with the larger number of events. In any case, we wish to stress that, despite the broadening, the entire $\tau$ distribution is displaced to larger values in the presence of the nearfield. The result that less stable junctions are stabilized to a larger extent than more stable junctions may be of relevance for ME applications where the minimum junction lifetime is a limiting factor for junction screening or device applications for sensing and recognition.

**OUTLOOK**

In summary, with PBJ, we present a combined STM-BJ and EC-TERS platform to investigate how a gap nearfield can be exploited to strengthen spontaneously formed single-molecule junctions. PBJ experiments on Au-BDT-Au junctions are shown to efficiently increase the junction lifetime without the need for chemical modification of molecule and/or electrode. The nearfield is employed to overcome the native stochastic disconnection of the junction, in this way imposing a deterministic lifetime. We quantify experimentally and theoretically how the presence of a nearfield increases the junction lifetime exponentially due to the mechanical stabilization of BDT in the Au-Au gap with help of an optical gradient force. A moderate far-field power density of ca 11 mW/µm² is found to lead to an effective increase in the junction dissociation barrier by about 2.2 k_BT. For the given experimental parameters, we achieve an average increase in lifetime by a factor 7, increasing the lifetimes of hundreds of junctions from hundreds of milliseconds to the order of seconds, reaching values up to 1.8 s. The detected minimum lifetimes increase by more than one order of magnitude. Interestingly, the nearfield trap affects differently the two observed contact geometries, i.e. LC hollow and HC bridge geometry, respectively. HC junctions are up to twice as susceptible to the nearfield trapping as LC junctions. This difference can be attributed to the larger polarizability of HC junctions compared to LC ones. The development of PBJ represents a significant contribution to the ME field by implementing plasmonic trapping to increase the lifetime of a single-molecule junction while preserving the target molecule’s native structure and contact geometry. Our findings can benefit the broad range of existing fixed-gap molecular platforms where short lifetimes are often the main bottleneck limiting practical applicability such as sensing and recognition.
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SUPPLEMENTAL INFORMATION
Supplementary Experimental Procedures and Supplementary References accompanies this paper at https://doi.org/xxxxxx

ACKNOWLEDGMENTS
A.C.A thanks European Union for a H2020-MSCA-IF-2018 Fellowship (TECh-MoDE, #844668). K.F.D. is grateful for generous funding through the “Plus 3” program of the Boehringer Ingelheim Foundation.

DECLARATION OF INTERESTS
The authors declare no competing interests.
Figure 1. Schematic of the blinking approach for single-molecule junction formation.
(a) Left: Fixed tip-sample gap distance, no molecular conductive junction, tunnelling current $I_t$. Centre: Spontaneous formation of Au-BDT-Au junction with characteristic molecular current $I_m$. Right: Disconnection of the molecule from one electrode and current drop to $I_t$. (b) Corresponding detected current response to the sequence depicted in (a). The duration of $I_m$ is the junction lifetime $\tau$. 

Tip electrode

Junction formation

Junction breakdown

Surface electrode

Detected current

Capturing time

$I_m$

$I_t$
Figure 2. Example of PBJ captures and mean junction lifetime with the nearfield trapping powers under the employed power laser densities.

Example of PBJ captures of (a) low conductance (LC, orange) and of (b) high conductance (HC, blue) junctions with laser (i.e. nearfield) ON or OFF. (c) Mean junction lifetime $\tau$ as a function of laser power density for LC (orange) and HC (blue) junctions. Shaded areas mark the minimum to maximum 1% distributions (average values marked with bright orange triangles and blue squares, respectively) of all runs. Error bars indicate the dataset standard deviation for each laser power density condition. (d) Calculated nearfield trapping efficiency $\eta$ as a function of the estimated nearfield gradient for LC (orange) and HC (blue) junctions. Asterisk field gradient corresponds to bias-induced field. 0 mW control values are an average from all experiments with the laser beam fully blocked.
Figure 3. Junction lifetime 2D distribution maps for the employed power laser densities. HC (blue) and LC (orange) 2D distribution maps of junction lifetime $\tau$ as a function of junction conductance for indicated power laser densities. Counts (number of datapoints with a given lifetime-conductance relation) are normalised to the total number of processed captures to have equivalent ranges of counts (and colour scales) between sets of experiments.
References


