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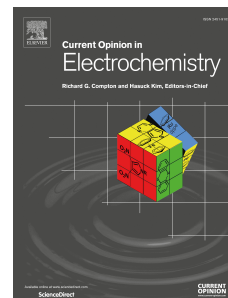
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Electric fields as actuators in unimolecular contacts

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Abstract

Single-molecule detection is essential for investigating individual molecules and (electro)chemical processes at the molecular level. Often, interrogation of individual molecules is achieved by fixating them in nanogaps to minimise the masking effect of surrounding molecular ensembles common to bulk analysis. Electrical detection methods are reliable options for single-molecule studies as they are label-free and provide a robust real-time readout easy to monitor. Here we review how the electric field generated in the nanogap between two electrodes can be employed to achieve active control over the target molecule beyond simple molecular sensing. First, we describe the use of electric fields to build the inter-electrode nanogap, to orient the molecular contact, to steer molecule-electrode interaction, and to promote reactivity of the trapped molecule. Second, we focus on the use of the electric field as a contact stabilising agent, to address the main drawbacks of single-molecule sensing, such as detection rate and timescales.

Keywords: Single-molecule detection, Single-molecule conductance, Unimolecular contact, Molecular contact geometry, PBJ, STM-BJ, MCBJ, CEM-SMJ, (Di)electrophoresis, Electromigration, Optical nearfield trapping, Bioelectrochemistry, Electrocatalysis.

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Single-molecule detection

Single-molecule (SM) detection is critical for investigating individual molecules and physico-chemical processes at the molecular level[1, 2, 3, 4, 5] and is one of the most heavily pursued research goals in (bio-electrochemical) molecular analysis.[6] SM sensing is extraordinarily beneficial when attempting to better comprehend the behaviour of analyte or reactant species at extremely low concentrations and/or in small sample volumes.[7] Therefore, this research area is gaining increasing attention also in electrochemical research.[8, 9, 10, 11, 12]

SM detection relies on the confinement of individual analyte molecules in space and time during the analytical measurement. Ideally, the analytical geometric space or sensing volume should be equivalent to the size of the analyte molecule to allow SM occupancy, *i.e.*, SM sensing sensitivity.[7, 13] Nanogaps have perfect analytical dimensions for SM detection because they possess a volume in the molecular-size regime. Thus, SM detection in nanogaps provides a twofold benefit: a readout with SM selectivity that at the same time minimises the masking ensemble effect[7, 14] common in micro and macroscopic measurements.

Among the extensive variety of SM detection approaches,[15] electrically based detection methods are most attractive because, in contrast to common photon-based approaches, they work without the need for tethers or labelling, are less expensive and complex, and avoid photon-related issues such as photobleaching.[6] The fixation of a molecule, electrically contacted, between two electrodes placed close to each other in a nanometric interelectrode gap to form a quantum tunnelling junction (Fig. 1) is one of the most often employed approaches for electrically based SM detection methods in gas-phase or liquid (electrochemical) environments (Fig. 1).[16] In such an SM detection set-up, the electrons that tunnel across a molecular contact, driven by the electric field (EF) related to the bias voltage between the electrodes, provide a simple, yet robust, real-time readout in form of a traceable current. While the SM electrical contact is formed in the nanogap, the detected current is altered from the

contact-free (vacuum) tunnelling current, I_t , (Fig. 1 a,c), giving rise to a characteristic molecular contact current signal, I_m , whose amplitude can characterise the analyte and reveal its nature and properties.

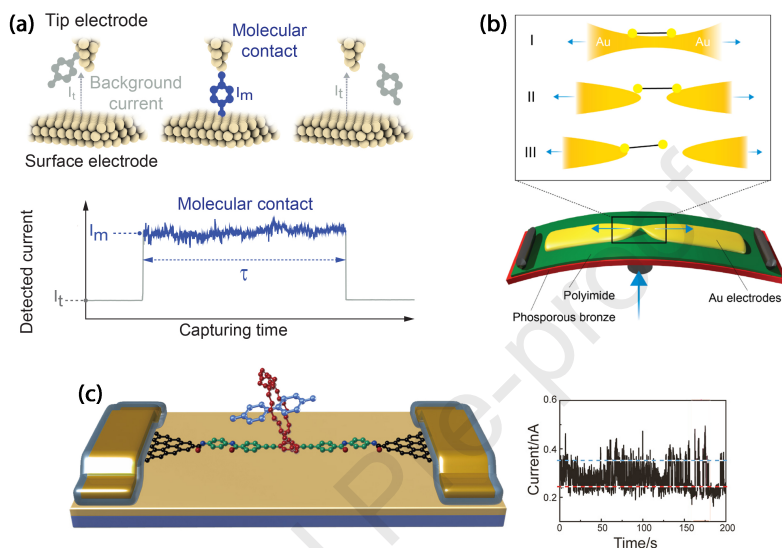


Figure 1: Panel (a), SM electrical detection in a nanogap. I_t is the tunnelling current through the nanogap (grey) and I_m through the molecule (blue). Top: Representation of the molecular contact (blue, center) and the other scenarios in which I_m is the only detected signal given that the molecule either contacts only one electrode (grey, left) or none (grey, right). Bottom: Current response during a molecular-contact event with I_t and I_m . τ is the lifetime of the molecular contact. Panel (b), schematics of the mechanically controlled break-junction (MCBJ) SM detection setup and graphical description of the formation process of the molecular contact. Reprinted with permission from Frisenda et al.[2] Panel (c), schematics of the carbon electrode-molecule (CEM) SM detection setup (left) and of the I_m readout (right) oscillating between high and low conductance values due to the trapping and release (blue and red traces, respectively) of an individual viologen molecule. Reprinted with permission from Wen et al.[4]

Building a nanogap with an electric field

35 In electromigration (EM), nanogaps are built at current densities high enough to promote the travelling electrons' momentum (partial) transfer to the atoms of the electrode.[17] As a result, the nanogap between two electrodes narrows to a range of a few Å where the target molecule can be allocated (Fig. 2 a). Unlike in other break-junction techniques, molecular contacts built by EM can only be
40 broken once and cannot be re-formed.[1, 18] Analyte molecules can be attached to the electrode surface before the EM process and then may diffuse together with the electrode atoms during the EM process.[19, 20] Alternatively, they can be added after the EM process, spontaneously attach to the nanogap and be electrically detected.[21, 22] The high stability of EM nanogaps has led to the
45 development of different SM detection approaches such as the ones coupled with gate electrodes[23, 24] or with enhanced Raman spectroscopy.[25]

Very recently, Naitoh et al. have developed an EM-based methodology dedicated to SM trapping by tuning the size of the nanogap via the applied voltage between both electrodes, continuously elongating and contracting it
50 (Fig. 2 b).[26]* This size tunability of the nanogap renders feasible the future integration of this approach into detection systems based on static structures.

Electrically tuning the contact: molecular orientation and reactivity

Both strength and orientation of the EF in the nanogap have been demonstrated to affect the molecular contact. The dipole-dipole interaction between
55 the trapped molecule and the EF induces the alignment of the molecule with the EF direction. Xiang et al., for example, have shown how an individual water molecule in an SM contact changes its orientation from a planar configuration (parallel to the electrode surface) to a less planar one with the two hydrogen atoms pointing away from the surface as a function of the EF strength.[27]

60 It is also possible to take advantage of the dipole-dipole interaction to promote the contact of a specific type of molecule. Contreras et al. have selectively

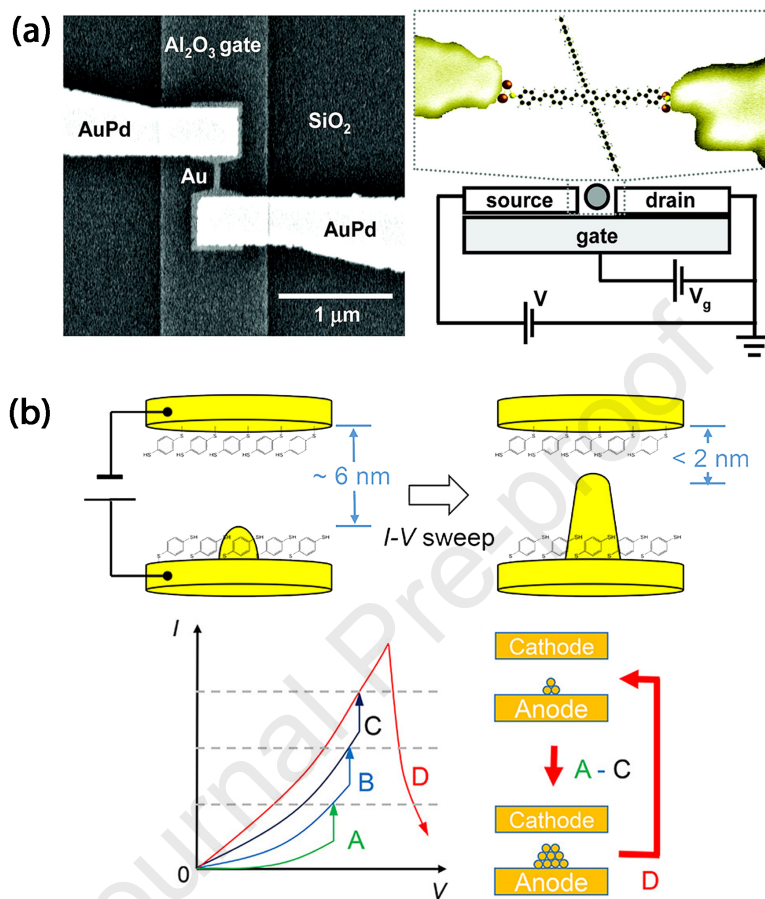


Figure 2: Examples of Au interelectrode nanogaps fabricated via EM processes. Panel (a), SEM image of a static Au interelectrode gap with a three-electrode configuration (left) and its schematic representation with the SM contact (right). Reprinted with permission from Osorio et al.[22] Panel (b), schematics of a tunable Au interelectrode nanogap by current–voltage sweeps. Top: representation of the EM stretching process to allow SM detection. Bottom: I vs. V profiles (left) with the corresponding electrode formation sequences (right). Reprinted with permission from Naitoh et al.[26]

captured flat conformers from a mixture with non-flat conformers.[28] Magnitude and orientation of the dipole moment of the flat conformers are notably

different from the ones of the non-flat conformers due to the orientation of the
65 terminal methylthiolated (anchoring) groups, in this way promoting a selective
contact via the molecular (dipole) alignment with the EF. More recently, Zeng
et al. have extended the use of dipole-dipole interactions to orient molecules
in the nanogap with help of the applied EF (Fig. 3 a).[29]* They have proven
that the EF can facilitate molecular contact formation with specific anchoring
70 groups, such as methylthiols, and in this way increase the SM detection rate.
The authors suggest that the EF induces a directional change of the molecular
dipole moment that, in turn, enhances the molecule–electrode coupling strength.
Since the contact-formation probability is correlated to the coupling strength,
the molecular contact formation frequency is proportional to the magnitude of
75 the EF-induced molecular dipole moment.

In addition, works by Tang[30] and by Gao[31] have shown that the EF can
strategically and reversibly tune the molecular contact geometry. More specifi-
cally, they attested that the connectivity of the analyte molecule at the contact
can be modified by adjusting the EF strength to promote specific interactions
80 between the electrodes and the anchoring points of the trapped molecule’s back-
bone. On the one hand, Tang et al. have modulated a molecular contact con-
nectivity via the EF. Contacts with a para-connectivity showed a significantly
stronger interaction with the EF than the ones with a meta-connectivity due to
the larger dipole moment of the former (Fig. 3 b).[30] On the other hand, Gao
85 et al. have studied how the EF induces a molecule–electrode contact through
the middle N atoms at the in-backbone anchoring point rather than through
the available terminal N atoms in aniline units.[31]

Lately, the SM detection field has turned its attention to monitoring chem-
90 ical conversion processes of individual molecules that occur during detection.
Here, the EF plays a crucial role because of its capability to affect, for exam-
ple, intermediate transition states by stabilising or destabilising their charge-
separated resonance contributors.[32, 33, 34, 35] We have demonstrated how the
EF stabilises and catalyses the transition state in an intermolecular liquid-phase

95 *Diels-Alder* reaction between two reactant molecules (*diene* and *dienophile*) at-
tached to distinct electrodes (Fig. 3 c).[3] When an EF is present, specific minor
resonant contributors may be stabilised when the EF is aligned in a specific
way with respect to the reaction centre, namely, pointing from the *diene* with
the associated negative charge to the *dienophile* with the associated positive
100 charge. In addition, apart from affecting the orientation of the reactants, the EF
strength also regulates the catalytic conversion, as evidenced by the observed in-
terrelation between EF strength and detection rate of the product molecules.[3]
Yang et al. have extended this *Diels-Alder* research, focusing mainly on the
reaction kinetics by monitoring the increase in SM product detection rate.[36]
105 The authors have revealed the reaction mechanism by unveiling the presence of
zwitterionic contributors during the reaction and deciphered the role of charge
transfer complexes with *endo* or *exo* configurations for the reaction pathway.

The stabilisation effects of the EF can be exerted over intramolecular pro-
cesses, such as the isomerisation process of a trapped molecule during its de-
110 tection, similarly to the well-known isomerisation in SM contacts driven by the
irradiation of UV or visible-light photons.[37] Recently, we have achieved to
promote and monitor, in real-time, a *trans-to-cis* isomerisation of a carotenoid
molecule trapped between two electrodes (Fig. 3 d).[38]* According to our cal-
culations, the EF polarises the molecule in a way that results in a mixing of
115 its excited states with allowed electronic transitions, in this way enhancing the
trans-to-cis switching probability. Zang et al. employing a dynamic approach of
the STM junction-breaking technique based on electrode displacement[39] pro-
moted, under strong EFs, the detection of SM contacts of cumulene *trans-* over
cis- conformers.[5] The former possess a more efficient charge delocalisation that
120 facilitates their formation under the EF. Despite the electrode motion and the
associated variable EF in the nanogap, a clear correlation between the increase
of the reaction rate and the net field strength of up to 2 orders of magnitude was
established. Tang et al. have combined sequentially intra- and intermolecular
processes (Fig. 3 E) to form single-stacked SM contacts *in situ* with terphenyl
125 molecules.[40]* The EF strength decreases the dihedral angles between adjacent

phenyl rings, which, in turn, promotes the formation of the dimer bond. The process is helped by the increase of the terphenyl dimer stacking energy in the EF.

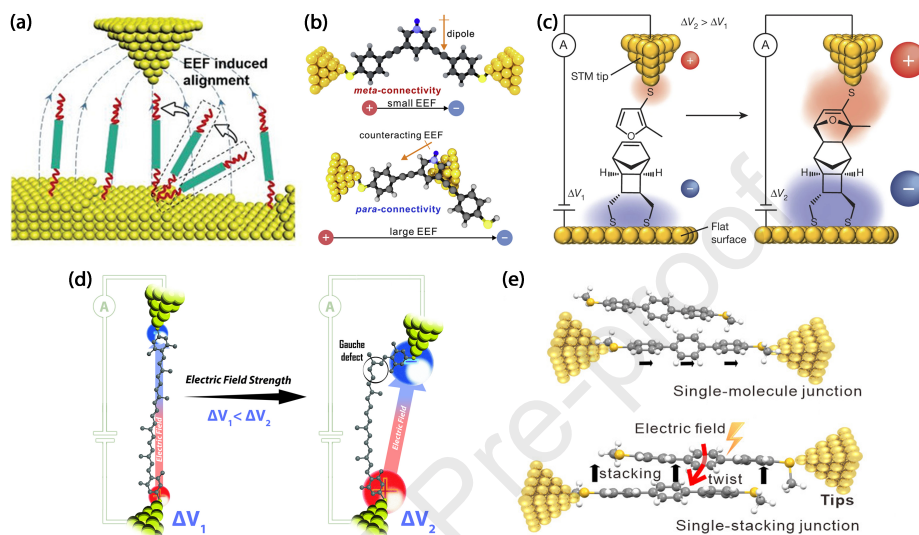


Figure 3: Panel (a), SM conductance detection facilitated by the EF-induced dipole alignment of the molecule in the nanogap. Reprinted with permission from Zeng et al.[29] Panel (b), schematics of connectivity switching between *meta*- and *para*-connectivity in a SM contact tuned by the EF. *Para*-connectivity is favoured when a large EF is applied. Reprinted with permission from Tang et al.[30] Panel (c), representation of a SM intermolecular reaction in the nanogap promoted by the EF. Reprinted with permission from Aragonès et al.[3] Panel (d), sketch of a SM intramolecular isomerisation process promoted by the EF in an SM contact. Reprinted with permission from Quintans et al.[38] Panel (e), depiction of an EF-promoted single-stacking contact of two terphenyl molecules in a nanogap during the SM detection process. Reprinted with permission from Tang et al.[40]

Overcoming stochastic drawbacks associated with SM detection

130 SM detection in confined nanospaces involves the localisation of the target molecule in the analytical geometric space, which is an entropically unfavourable process mainly ruled by stochastic events.[41] On the one hand, Brownian motion, *i.e.*, the random motion of particles in a liquid or in gas-phase, is of great relevance for platforms using electrodes immersed in a solution that contains
135 the analyte molecules. The diffusion pathways of the analyte molecules are governed by Brownian motion, eventually leading them to the sensing region to be detected when they come into contact with both electrodes. Therefore, the Brownian motion affects the detection rate.[42, 43, 38, 44] Explained below are some strategies that have focused on overcoming the Brownian motion with help
140 of the EF by providing a potential energy that is larger than the thermal energy inherent to Brownian motion and thus restricting the translational freedom of the analyte molecule in the nanogap. On the other hand, molecular contact formation and breaking are thermally activated stochastic processes that define the formation frequency and lifetimes (*i.e.*, detection rate and timescale) of the
145 molecular contact.[45, 46] These processes are underlying any kind of molecular contact, including scenarios where the analyte molecule is firmly attached to the electrodes and Brownian motion therefore is suppressed.[47]

Electrokinetic trapping forces

SM confinement in the nanogap of an electrically based detection platform
150 can exploit electrokinetic phenomena that result from the applied voltage between the two electrodes. In this way, Brownian motion can be overcome and molecules can be trapped for prolonged electrical detection and characterisation timescales.[48] Electrophoresis (EP) has proven to be effective for SM trapping of dissolved nucleotides in the nanogap formed between two electrodes, increasing the trapping yield by one order of magnitude compared to that without
155 EP.[49] Similarly to EP, also dielectrophoresis (DEP) is suitable for SM trapping purposes[48] and can be coupled to SM electrically based trapping platforms.[50]

Here, applying an AC voltage to exert a non-uniform EF promotes SM trapping. In this way, *e.g.*, DNA origami structures in solution have been guided and retained individually in nanogaps (Fig. 4 a) by controlled DEP forces.[51]

160 In a complementary study, Ghomian et al. have improved the electrically based monitoring of the trapping process by employing a novel and reliable methodology that overcomes a relevant drawback for the DEP trapping, namely the lack of uniformity in the electrode fabrication.[52]

165 Tang et al. very recently have achieved SM detection of individual DNA (mononucleotides and oligonucleotides) and proteins molecules by DEP-enhanced trapping (Fig. 4 b).[53]**

They have reported an increase of five orders of magnitude in detection rate due to DEP trapping, even at low voltages.

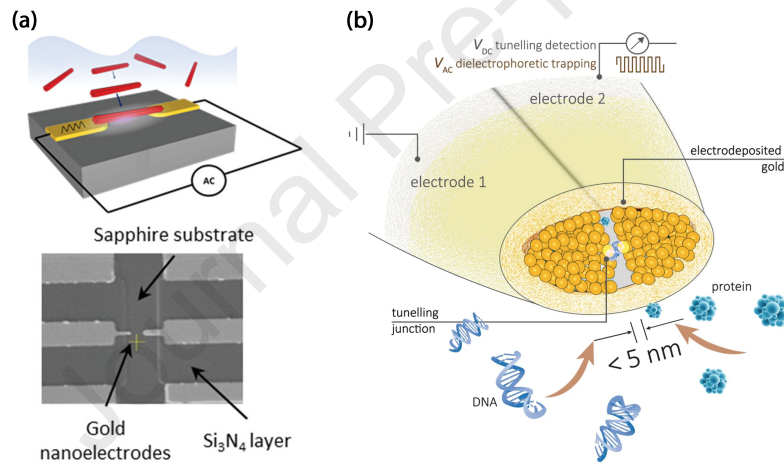


Figure 4: DEP-based SM detection platforms. Panel (a), top: Device schematic showing the DNA-based contact. Bottom: SEM image of the device showing the Au nanoelectrodes. Reprinted with permission from Ghomian et al.[52]

Panel (b), detailed sketch of an enhanced SM trapping DEP platform based on a quantum tunnelling junction. Reprinted with permission from Tang et al.[53]

Optical nearfield trapping approaches

170 One viable way to fixate individual molecules of a size much smaller than the
interacting wavelength (Rayleigh regime[54]) inside a nanogap is plasmonic, or
nearfield, trapping.[55] In metallic nanogaps, localised surface plasmon (LSP)
resonances can be excited when irradiated with laser photons of a suitable
energy.[56] In this way, a strong electromagnetic field, *i.e.*, a nearfield, can
175 be generated in the center of the nanogap.[57] This nearfield is confined to a
nm-sized region and typically shows an increase of two to three orders of mag-
nitude in intensity compared to the laser excitation farfield.[58] As a result of
the extreme electric field strength increase, its electric field gradient generates
strong attractive forces inside the nanogap[59, 58] that can promote and sta-
180 bilise molecule trapping.[60, 55] Since electrically based SM detection platforms
are based on a molecular contact in an interelectrode nanogap, they are perfect
candidates to implement nearfield-enhanced trapping. Nearfield trapping allows
to exploit strong electrical fields without the need of high applied voltages, thus
avoiding the associated instabilities.[61, 62]

185

The pioneering work of Ikeda et al. has proven that the nearfield exerts a
torque effect on the molecule trapped in a nanogap that causes the alignment
of the molecular dipole with the nearfield vector parallel to the long axis of
the junction.[63, 60] The authors have observed that the molecule alignment
190 is proportional to the optical excitation power (nearfield intensity) with help
of surface-enhanced Raman spectroscopy. In our recent work, we have made
use of this increased stability of the SM contact in the nearfield to improve the
SM electrical detection timescales:[64]** the plasmon-supported break-junction
technique (PBJ) is based on a motionless STM break-junction approach called
195 blinking,[65] wherein the electrodes that form the nanogap keep an interelec-
trode distance that is adjusted to the size of the target molecule. Considering
the relevant dependence between nanogap size and nearfield enhancement,[66]
one of the strengths of our approach is the strict control over and stability of

the sub-nanometer precise interelectrode nanogap. The PBJ approach improves
200 the (classic) SM blinking detection in different ways. Owing to the presence of
the nearfield, we overcome the native stochastic disconnection of the molecular
contact and achieve longer contact lifetimes, enabling longer SM interrogation
times.[46] Under nearfield conditions, we have achieved an increase in SM de-
205 tection timescale (Fig. 5 a) of up to one order of magnitude compared to the
laser OFF conditions, proportional to the employed optical power that ranged
from ca. 1 to 10 mW/ μm^2 . [64] Furthermore, the presence of the nearfield also
improves the detection rate. The experiments have shown up to eight times
more detected SM contacts under laser ON conditions than OFF conditions,
depending on the applied laser power density, even when using submonolayer
210 amounts of analyte.[64] The enhancing effects of the presence of a nearfield on
the detection rate were also reported by Zhan et al.[67]** in a mechanically
controlled break-junction (MCBJ) setup.[18] The authors have investigated the
suppression of Brownian motion in the presence of a plasmonic field. They
were able to modulate the ratio between the capture and release of individual
215 molecules from a solution between the two moving trapping electrodes through
the employed optical power (Fig. 5 b).

Combined electrochemical and nearfield trapping

Electrochemical control has not been commonly coupled to conventional or
220 nearfield optical trapping,[68, 69, 70, 71] but constitutes a versatile way to fur-
ther tune and improve the nearfield trapping, as we have demonstrated in our
recent work (Fig. 5 c).[70]** Electrochemical (potential) control brings a twofold
capability to nearfield-enhanced SM detection in nanogaps: (i) The tuning of
the Fermi level energy of the electrodes that form the nanogap affects the LSP
225 resonance energy of the nanogap. The LSP profile, in turn, is correlated with
magnitude of the (near)field enhancement through the laser resonance and thus
with the efficiency of the nearfield trapping. (ii) The promotion of certain redox

states of the trapped molecule and of the optical properties associated with the redox state through electrochemical control. In our work, we use the target
230 cuproprotein Azurin, which, when oxidised, possesses a ligand-to-metal charge transfer energy in resonance with the excitation laser line. Under such resonant optical excitation, the SM nearfield trapping efficiency increases, as theoretical works predict[72, 73] and other experimental works have shown.[74] We have demonstrated that, in combination, the two electrochemical effects result in an
235 increase in capture efficiency by three orders of magnitude (Fig. 5 d), even when working with moderate optical powers in the range of $10 \text{ mW}/\mu\text{m}^2$. [70] Similarly, Oyamada et al. have observed an abrupt increase in the SERS signal in the vicinity of the nearfield hotspot under the conditions of resonant electronic excitation when working under electrochemical control at an electrified interface.[75]
240 The authors have attributed the effect to an accumulation of molecules due to the attractive force of the nearfield gradient in the nearfield.

Summary

In this review, we have summarised the advances made to date in the field of SM detection, mainly based on molecular contacts, focusing on the potential
245 of the electrical approaches. We have revised their use for both nanogap formation and molecular contact modification, including molecule-nanogap structural and interaction alterations. Finally, we have gathered the most innovative approaches to guide, trap and immobilise individual molecules in the sensing region to improve the SM detection. From all the presented trapping approaches,
250 we want to highlight that nearfield-based ones where the electric field gradient forces are sufficiently strong to overcome the major drawback related to SM electrically detection without the need to apply high voltages: Namely, thermal fluctuations driven by the Brownian motion can in this way be suppressed and thermal stochastic contact disconnection counterbalanced. The net effect is remarkable in that the molecular contact formation process and its stability are
255 strongly promoted, thereby increasing the SM contact formation rates and pro-

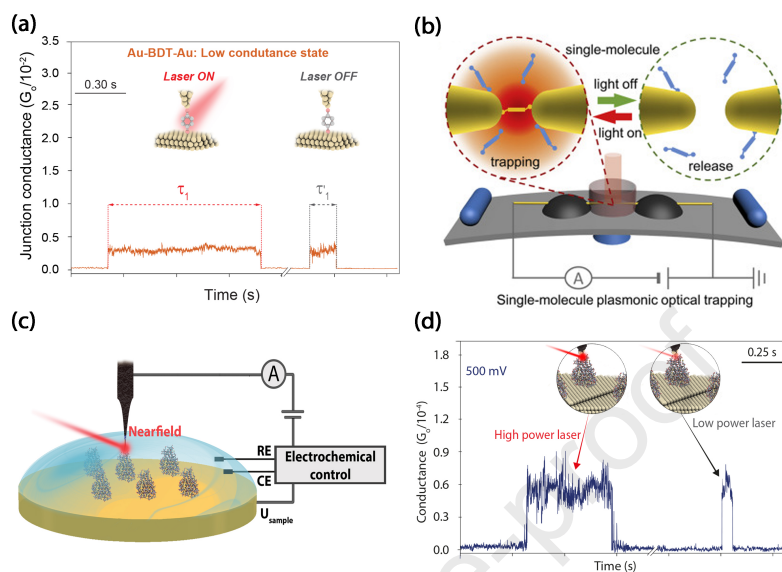


Figure 5: Optical nearfield-enhanced SM trapping. Panel (a), I_m lifetime (τ) in the presence (red) or absence (grey) of the nearfield. Reprinted with permission from Aragonès et al.[64] Panel (b), schematic depicting how SM capture (release) is favoured in the presence (absence) of the nearfield. Reprinted with permission from Zhan et al.[67] Panel (c), schematic representation of the electrochemically gated plasmon-supported break-junction technique. Reprinted with permission from Aragonès et al.[70] Panel (d), SM Azurin protein detection shows a clear correlation between lifetime and nearfield intensity as tuned by the laser power. Reprinted with permission from Aragonès et al.[70]

longing detection and interrogation timescale. Nearfield-enhanced SM trapping is still in its infancy, but already represents one of the most effective candidates for next-generation SM detection schemes, particularly also for electrochemical
 260 single-entity research, given the recently proven compatibility and synergy of electrochemical and nearfield SM trapping.

Credit author statement

K. F. D. acquired funding, contributed to conceptualisation, and performed writing, reviewing and editing. A. C. A. acquired funding, performed writing
265 of the original draft, contributed to conceptualisation and performed reviewing and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported
270 in this paper.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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