Molecular electronics at electrode-electrolyte interfaces.

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Electron transfer at interfaces lies at the heart of electrochemistry and methods with increasing sensitively have been evolved in waves over the last 100 years. Mercury electrodes and polarography were hugely important in providing well defined platforms for studying electron transfer and in the development of many areas of electrochemistry, including its hugely important role as an analytical technique. For example, mercury electrodes enabled well defined studies of inner and outer sphere electron transfer processes and helped relationships between molecular structure and rates of heterogeneous electron transfer to be established. Advances in modern interfacial electrochemistry have been defined by developments in electrodes. For example, microelectrodes have been so important in the evolution of modern electrochemistry,[1-2] including fundamental studies of interfacial electron transfer. Well defined single crystal surfaces emerged in the 1970s and 1980s as a new cornerstone for physical electrochemistry.[3] As well as providing highly defined electrodes for electron transfer studies they enabled the study of structure and dynamics of the electrode-electrolyte interface with unprecedented detail. Important here was the combination with spectroscopic and modern imaging techniques such as STM. A more recent innovation has been the growing interest and development of "single entity electrochemistry".[4-5] Single entities have now been studied in many diverse ways and there have even been conferences devoted to such. [4-6] Such studies have been very diverse, ranging from the electrochemistry of cells to small molecules,[4] and from microelectrodes used in scanning electrochemical microscopy (SECM) to STM tips contacting just a single molecule. Key methods for achieving such feats have relied on ultra-sensitive ways of measuring current and controlling electrode positioning. An example here is scanning ultramicroelectrodes of an scanning electrochemical microscope (SECM) being used to repeatedly oxidise and reduce single molecules shuttling between the SECM ultra-micro tip and a very close adjacent surface.[7] A quite different example is the use of STM to form single molecular bridges between two electrodes and to study the resulting current flow across this junction in electrolyte solution.[8-19] This latter example of is the topic of this opinion piece.

Molecular electronics is concerned with the study and application of electrical properties of molecules. At its limit molecular electronics can probe the electrical properties of single molecules

wired between two contacts or in some cases in 3-terminal (gated) configurations. Since many interesting properties arise from the redox and electrochemical properties of the target molecules there is a strong affiliation with electrochemistry. This connection has been strengthened by the capabilities to make defined electrical measurements on redox active single molecules within an electrochemical environment.[8, 20-21] This can be achieved by use of an STM [8-9] or a mechanically controlled break junction[22-23] within electrochemical environments, although the electrochemical STM (EC-STM) has been much more commonly deployed. The EC-STM has a bipotentiostat, so the electrode potential of both contacts is controlled. In brief, the STM is used as the tool to form single molecule junctions with molecules chemically bound at one of their ends to the surface and the other end of the tip. So, in effect single molecules are wired between two contacts and the minute current flow across this junction is measured. This is different to electrochemical scanning tunnelling spectroscopy (EC-STS) in which the molecular target is adsorbed on the electrode surface but not attached to the STM tip to form a "wired junction". [24-29] This is a very brief synopsis of the method and further details such as variations in the mode of junction formation and data analysis are given elsewhere.[30] Importantly, these techniques share the commonality of having to repeatedly make and break the single molecule junctions many times. The resulting data is then viewed in 1-D conductance histograms and/or 2-D conductance- junction elongation histograms to enable reliable statistical determination of junction electrical properties.

Four contemporary examples, all published in recent years, of studies of molecular electronics at electrode-electrolyte interfaces are described in this opinion article. The *first illustrative example* involves the switching of the redox active molecular wire between redox states, with concomitant changes in molecular conductance. This example illustrates how molecular electronics at electrode-electrolyte interfaces can be used to analyse mechanisms of electron transfer, to distinguish electrolyte effects and to provide details not readily available from large ensemble measurements. The *second example* shows that the fluctuations of molecular conductance of a redox active molecular wire can be followed as a function of electrode potential. This shows how the stochastic kinetics of individual reaction events at an electrode-electrolyte interface can be followed. The *third example* demonstrate how electrochemistry can be used to control quantum interference in single molecular wires. The *fourth example* shows a single molecule electrochemical transistor concept for well-defined metal cluster containing molecular wires.

The *first example* involves viologen molecular bridges spanning between gold electrode contacts.[8, 31-37] Figure 1A shows a "wired" viologen molecular junction in an EC-STM setup, with Figure 1B showing the viologen moiety surrounded by electrolyte ions. The viologen molecular bridge is connected to the gold electrodes by gold-thiol bonds, which provide the molecular crocodile clips for

wiring the single molecule junction. The 4-electrode setup of the EC-STM can be seen, enabling the electrode potentials of both gold contacts to be individually controlled and the viologen to be electrochemically switched (gated) between different redox states. Surrounding the redox group by the controllable electrolyte medium has been referred to as "electrolyte gating" in a single molecule electrochemical transistor configuration. Note that the central viologen (bipyridinium) is electronically decoupled from the metal electrodes by the $(CH_2)_6$ chains. This decoupling encourages electron transfer to be by a two-step type mechanism through the central redox moiety. This is the so called Kuznetsov-Ulstrup (KU) 2-step mechanism (see [25] and references therein). Charge flow across the molecular bridge is achieved by the central viologen group first reorganising through environmental and internal fluctuations. As molecular orbitals approach the Fermi level of one of the metal contacts charge transfers onto one of the redox centres thereby reducing it. Following partial (adiabatic limit) or full (diabatic limit) relaxation the electron then transfer across to the other contact, in a sequential process.[25] In the adiabatic limit the second electron transfer occurs when only partial relaxation of the molecule and its environment has occurred; this is much more efficient than the non-adiabatic (or diabatic) limit. This conclusion about the electron transfer mechanism is reached from the single molecule data described in the next paragraph.

Single molecule conductance versus electrode potential data for a viologen molecular bridge with $(CH_2)_6$ linking chains and thiol contacting groups is shown in Figure 1C for ionic liquid electrolytes.[32] A central part of this study was to analyse how different electrolytes influence the charge transfer, with a comparison between water electrolytes and ionic liquids.[32] Ionic liquids had been previously demonstrated as effective media for EC-STM and electrochemical tunnelling spectroscopy[26] and have also been shown as effective media for molecular electronics studies.[38] The influence of the electrolyte medium can be clearly seen in conductance versus overvoltage plots for this viologen system in Figure 1C (ionic liquid electrolytes) and Figure 1D (water electrolytes). Zero overvoltage on these plots refers to the reversible potential for the reduction of viologen dication (V^{2+}) to its corresponding radical cation ($V^{+\cdot}$). Note that when moving from positive overpotentials in the negative direction the conductance increases towards the reversible potential and then falls. This is a consequence of the KU mechanism with maximum current flow through the molecule close to the equilibrium potential where both the oxidized and reduced forms contribute comparably to the current flow across the junction. The solid curves in these plots are fitting to the KU model.[32] One parameter obtained here is the proportion of the applied potential felt by the redox centre in the double layer, which can be termed the "electrolyte gate coupling". The ionic liquid shows strong electrolyte gate coupling (~1) compared with the aqueous electrolytes (~0.2).[32] These data show

how molecular electronics can give insights into the potential dropped across double layers and electrostatic interactions between the double layer and surface attached redox moieties.[32]
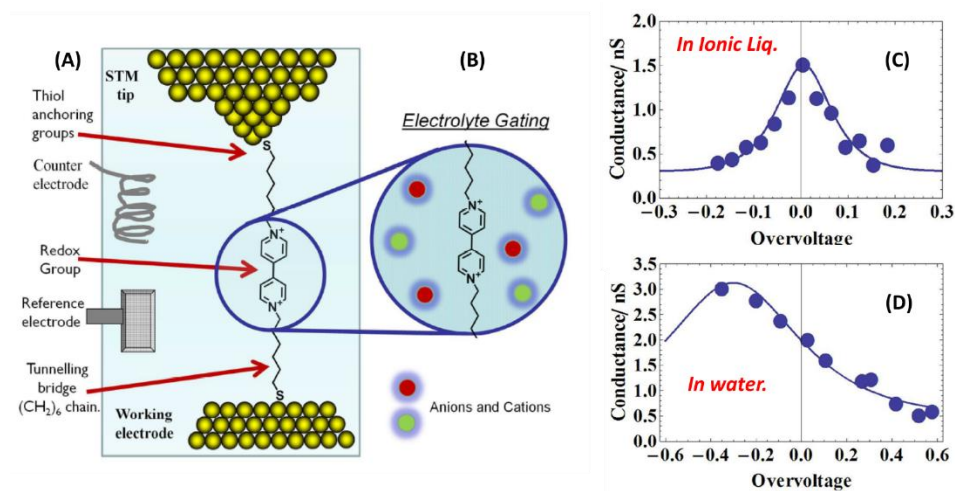

Figure 1 (A) Illustrates single molecule gating using an electrochemical STM. The electrode potential of the substrate and STM tip are controlled with a bipotentiostat control. The single molecule bridge contains a central redox active viologen moiety. (B) Illustrates the electrolyte gating concept with the electrolyte ions surrounding the viologen group. (C) & (D) Single molecule conductance data (blue circles) and fitting with the KU model (solid blue lines) for the viologen junction in ionic liquid (C) and for comparison in aqueous electrolyte (D). Adapted from ref. [32]. Copyright 2015 American Chemical Society.

The *second example* shows how fluctuations in the conductance of single redox molecules can be followed and how this can be used to track the stochastic kinetics of individual redox events as a function of electrode potential.[39] This example employs ferrocene molecular bridges with different lengths of linking chains, with the 3C-Fc and 5C-Fc exemplars shown in Figure 2.[39] The EC-STM is used to form molecular junctions and conductance is studied as a function of electrode potential (E). Many individual conductance- potential sweeps are plotted into heat maps, shown for 3C-Fc and 5C-Fc in Figure 2A. As the electrode potential is swept from negative to positive overpotentials the conductance increases in a sigmoidal fashion with no peak as in the previous example. By contrast in this case rather than a 2-step mechanism electron transport is by superexchange tunnelling mediated by a low-lying intermediate state at the redox centre.[39] Here tunnelling is through either the reduced or oxidised state of the molecules which have different conductance values and an average conductance can be simply seen as related to the probability of whether the molecule is in the reduced or oxidised state. This balance between reduced and oxidised states is clearly shifted by changing the electrode potential and in figure 2A the ferrocene molecule is nearly fully in it reduced

(neutral) form at the negative overpotential side of the scale and fully oxidised at the most positive overpotentials. The sigmoidal rise of the conductance traced by the dashed black average conductance curve then simply follows the Nernstian distribution between the reduced and oxidised states, with the latter state having the higher tunnelling conductance.[39]
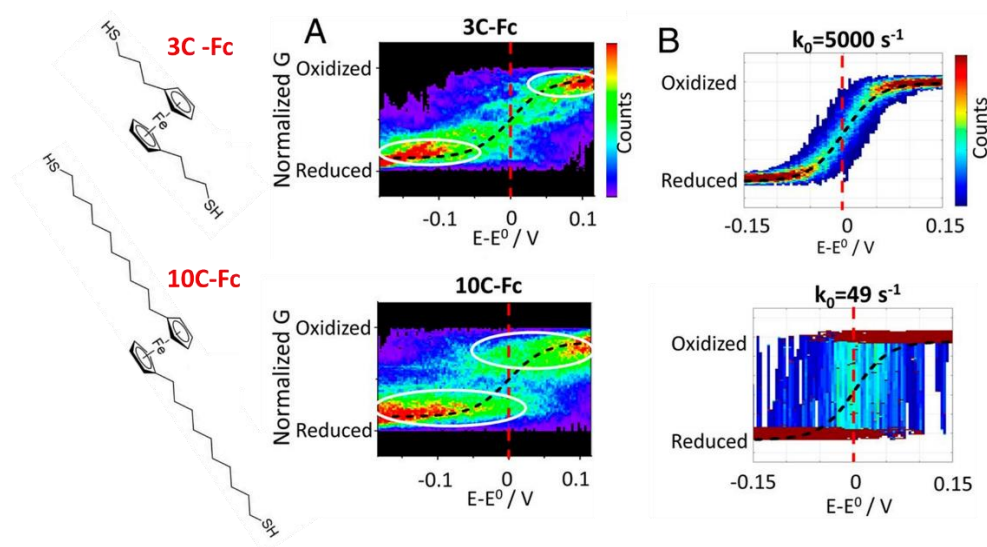

Figure 2 (A) Single molecule conductance versus electrode potential for the molecular bridges 3C-Fc and 10C-Fc (Structures shown on the left). Data statistically represented in 2D heat-maps by overlaying 150 individually measured conductance–potential curves. The vertical dashed red lines mark the equilibrium potentials of the ferrocene groups. The white ovals mark the conductance bands of the reduced (Fc) and oxidized (Fc$^+$) ferrocene states. (B) 50 theoretically simulated conductance–potential curves overlaid in 2D conductance–potential histograms for two standard rate constants (5000 versus 49 s^{-1}). The 5000 s^{-1} simulation best matches the 3C-Fc data, while the 49 s^{-1} simulation is matched with the 10C-Fc system. Adapted from reference [39].

The previous paragraph highlights the behaviour averaged from the many conductance-potential sweeps collected together on these heatmaps in Figure 2A. However, the wide distribution of colours in the heatmap and "spikiness" of the traces, which is best seen in individual scans, is related to large conductance fluctuations in the single molecule data. [39] At the sufficiently negative overpotentials the conductance is that of the reduced state giving a band highlighted into Figure 2A by one of the white line ovals. A band is also highlighted at positive overpotential and attributed to the oxidised state. The conductance stochastically fluctuates between these states and this is most apparent for the longer analogue (10C-Fc) where these high and low conductance bands overlap around zero overpotential, giving the appearance of two-state switching. The dynamics of this

switching is modelled in the framework of first-order kinetics with the interfacial electrochemical rate constant described by the Butler–Volmer relation with a standard rate constant of k_0. Simulated conductance-potential histograms are then produced with different values of k_0, two of which are shown in Figure 2B. [39] It is apparent that the high k_0 (k_0 = 5000 s^{-1}) simulation most resembles the experimental data for 3C-Fc, with the sigmoidal conductance increase and superimposed larger stochastic conductance fluctuations around the equilibrium potential. The low k_0 (k_0 = 49 s^{-1}) simulation on the other hand resembles the 10C-Fc data with the long low and high conductance bands and clearly apparent two-state switching. The overall importance of this work is to show that the stochastic kinetics of single molecule electron transfer reactions can be followed and the transition of this single molecule behaviour can be mapped to ensemble average behaviour as manifested by the Nernstian behaviour of the aggregated traces. [39]

Example three concerns the phenomenon of quantum interference (QI). QI has been an actively pursued contemporary topic in molecular electronics since molecular devices offer new opportunities arising from their quantum mechanical properties. Molecules cannot be viewed as molecular conductors following classical behaviour, for example Kirchoff's circuit rules. On the contrary, charge flow through molecules and "molecular circuits" will be governed by quantum mechanical phenomena, with the wave-like interference of electrons playing centre stage. QI arises from destructive or constructive interferences of the transmission of electron waves through molecules. This is probably most straightfordwardly explained with the conceptual example of a benzene ring which is hypothetically electrically wired through either para connectivity (X-Y in figure 3A) or meta connectivity (X-Z in figure 3A). Although X-Y involves a longer through-bond pathway, higher current can flow through this route compared to the shorter X-Z connectivity. This is because the X-Z (meta) displays QI. This is a rather simple example and "quantum circuits" rules have been devised to rationalise interference effects in single-molecule electrical junctions,[40] and determination of local currents[41] has given clear insight into interference effects and current flow in molecular junctions.

There are now several examples of QI being tuned using electrochemistry. [13, 42-47] A recent illustration is from Bai et al. who used an electrochemistry to tune the electronic behaviour of thiophene based molecular junctions, for structures see Figure 3B.[42] The electrode potential is used here to tune the relative position of the metal Fermi energies and molecular orbitals (or transmission resonance). Figure 3C shows a gradual shift of the conductance histogram peak to lower values as the electrode potential is stepped negative. Figure 3D shows a comparison of conductance versus electrode potential for 2,5-TP-Ac (top curve, purple) versus 2,4-TP-SAc (lower curve, orange-red); the latter shows a pronounced decrease of conductance as the electrode potential is taken negative and the

system is shifted to an anti-resonance arising from destructive QI. The relatively small differences in structure between the two compounds in Figure 3B leads to rather pronounced differences in the QI tuning of their conductance. Furthermore, a sharp anti-resonance feature is shown in the computed transmission coefficients of 2,4-TP-SAc (see ref. [42]), which can be tuned with the charge added to the molecule, underpinning that QI is being tuned by the electrochemistry. This study thereby demonstrates novel ways in which electrochemistry can be used to control and understand charge flow through molecules.
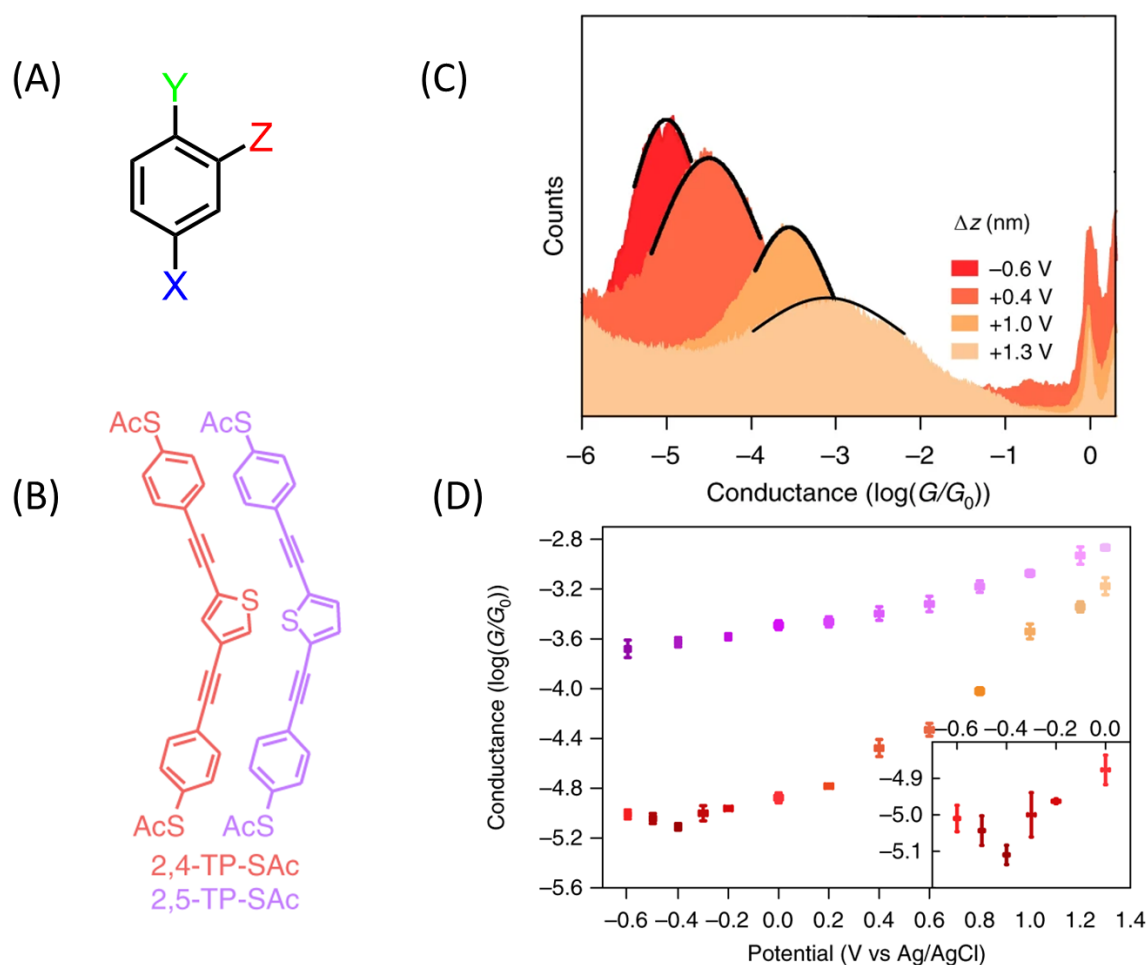

Figure 3 (A) A benzene ring with para (X-Y) or meta (X-Z) electrical connectivity. Even though the through bond distance is less for the meta connectivity, quantum interference ensures that this is less conductive. (B) 2,4-TP-SAc and 2,5-TP-SAc used by Bai et al. in a study of electrochemically controlled destructive quantum interference. (C) 1D conductance histograms of single molecule thiophene junctions (2,4-TP-SAc) at four different applied electrode potentials as marked (of the coated Au STM tip relative to Ag/AgCl). (D) Comparison of conductance versus electrode potential for 2,5-TP-Ac (top curve, purple) and 2,4-TP-SAc (lower curve, orange-red); the latter shows a

pronounced decrease of conductance as the electrode potential is taken negative and the system is shifted to an anti-resonance arising from destructive QI. The inset shows a zoom-in around the curve minimum. Adapted from reference [42] copyright 2019, Springer Nature.

The final example shows how electrochemical single molecule gating ("electrochemical transistor") studies have been recently extended to cluster-containing molecular wires.[48] Although metal nanoparticles featured in much earlier molecular electronics studies, which exploited Coulomb blockading of current flow through a metal nanoparticle,[49] this new example featured well defined metal cluster containing molecular wires which showed pronounced multiple electrochemical switching features. Figure 4 shows a single polyoxometalate (POM) molecular wire with 4-pyridyl termini caught between gold electrode contacts in an ionic liquid electrolyte. This metal cluster molecular wire contained 1 Mn atom and six Mo atoms. As shown in Figure 4 the charge of the polyoxomolybdate is electrochemically switched between the 2- , 3- and 4- states. This 3-state conductance switching gates current flow across the junction by over one order of magnitude.[48] This offers new perspectives for coupling electrochemistry and molecular device function, which could also deploy electrochemistry to control the tuneable optical and electrical properties of the clusters within the molecular wires.
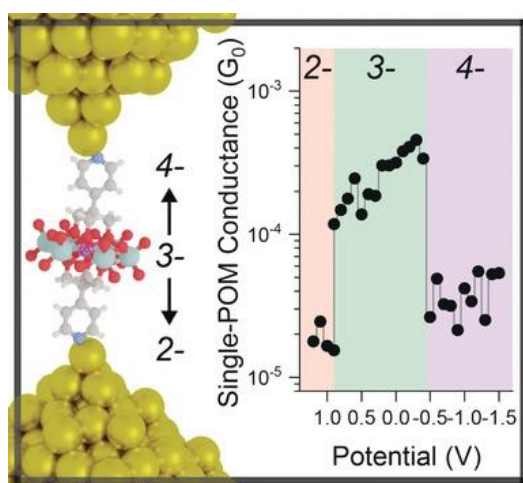

Figure 4 This shows how a polyoxometalate (POM) molecular wire with 4-pyridyl termini has been used to fabricate single molecule junctions in an electrochemical environment. The fabricated device shows a single molecule electrochemical transistor behaviour with conductance being electrolyte gated by more than one order of magnitude. Reprinted from reference [48].

In summary, techniques such as the electrochemical STM can be used to "wire" and study current flow through single molecules in an electrochemical environment with electrode potential control. This has enabled detailed studies of mechanisms of charge transport through molecules in electrolyte environments ranging from aqueous to ionic liquids. Mechanisms have been seen to vary

from 2-step ones to superexchange tunnelling. Quantitative properties such as reorganisation energies or double layer potential drops at the redox centre have been obtained from the single molecule data by applying theoretical models. Although not covered here, electrochemistry has also promoted the use of other less inert metal contacts, including Cu, Fe, Pd[50] and Ni and Co [17, 51-52]. Recently the methodology has moved into the time domain with fluctuations of molecular conductance of a redox active molecular being followed as a function of electrode potential. Single molecule methodology has also been used to study and control phenomena such as quantum interference and electrochemically gated single molecule transistor behaviour.

Declaration of interest: none.

REFERENCES

1.   Bond, A. M.; Fleischmann, M.; Robinson, J., ELECTROCHEMISTRY IN ORGANIC-SOLVENTS WITHOUT SUPPORTING ELECTROLYTE USING PLATINUM MICROELECTRODES. *Journal of Electroanalytical Chemistry* **1984,** *168* (1-2), 299-312.
2.   Clavilier, J.; Faure, R.; Guinet, G.; Durand, R., PREPARATION OF MONO-CRYSTALLINE PT MICROELECTRODES AND ELECTROCHEMICAL STUDY OF THE PLANE SURFACES CUT IN THE DIRECTION OF THE (111) AND (110) PLANES. *Journal of Electroanalytical Chemistry* **1980,** *107* (1), 205-209.
3.   Kolb, D. M., Electrochemical surface science. *Angewandte Chemie-International Edition* **2001,** *40* (7), 1162-1181.
4.   Long, Y. T.; Unwin, P. R.; Baker, L. A., Single-Entity Electrochemistry: Fundamentals and Applications. *Chemelectrochem* **2018,** *5* (20), 2918-2919.
5.   Baker, L. A., Perspective and Prospectus on Single-Entity Electrochemistry. *Journal of the American Chemical Society* **2018,** *140* (46), 15549-15559.
6.   Crooks, R. M., Concluding remarks: single entity electrochemistry one step at a time. *Faraday Discussions* **2016,** *193*, 533-547.
7.   Fan, F. R. F.; Bard, A. J., Electrochemical Detection of Single Molecules. *Science* **1995,** *267* (5199), 871-874.
8.   Haiss, W.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Hobenreich, H.; Schiffrin, D. J.; Nichols, R. J., Redox state dependence of single molecule conductivity. *Journal of the American Chemical Society* **2003,** *125* (50), 15294-15295.
9.   Xu, B. Q.; Tao, N. J. J., Measurement of single-molecule resistance by repeated formation of molecular junctions. *Science* **2003,** *301*, 1221-1223.
10.   Guo, S.; Manuel Artes, J.; Diez-Perez, I., Electrochemically-gated single-molecule electrical devices. *Electrochimica Acta* **2013,** *110*, 741-753.
11.   Diez-Perez, I.; Li, Z.; Guo, S.; Madden, C.; Huang, H.; Che, Y.; Yang, X.; Zang, L.; Tao, N., Ambipolar Transport in an Electrochemically Gated Single-Molecule Field-Effect Transistor. *ACS Nano* **2012,** *6* (8), 7044-7052.
12.   Darwish, N.; Diez-Perez, I.; Guo, S. Y.; Tao, N. J.; Gooding, J. J.; Paddon-Row, M. N., Single Molecular Switches: Electrochemical Gating of a Single Anthraquinone-Based Norbornylogous Bridge Molecule. *Journal of Physical Chemistry C* **2012,** *116* (39), 21093-21097.
13.   Darwish, N.; Diez-Perez, I.; Da Silva, P.; Tao, N. J.; Gooding, J. J.; Paddon-Row, M. N., Observation of Electrochemically Controlled Quantum Interference in a Single Anthraquinone-Based Norbornylogous Bridge Molecule. *Angewandte Chemie-International Edition* **2012,** *51* (13), 3203-3206.

14.   Li, Z.; Li, H.; Chen, S.; Froehlich, T.; Yi, C.; Schoenenberger, C.; Calame, M.; Decurtins, S.; Liu, S.-X.; Borguet, E., Regulating a Benzodifuran Single Molecule Redox Switch via Electrochemical Gating and Optimization of Molecule/Electrode Coupling. *Journal of the American Chemical Society* **2014,** *136* (25), 8867-8870.

15.   Li, C.; Stepanenko, V.; Lin, M.-J.; Hong, W.; Wuerthner, F.; Wandlowski, T., Charge transport through perylene bisimide molecular junctions: An electrochemical approach. *Physica Status Solidi B-Basic Solid State Physics* **2013,** *250* (11), 2458-2467.

16.   Diez-Perez, I.; Li, Z.; Hihath, J.; Li, J.; Zhang, C.; Yang, X.; Zang, L.; Dai, Y.; Feng, X.; Muellen, K.; Tao, N., Gate-controlled electron transport in coronenes as a bottom-up approach towards graphene transistors. *Nature Communications* **2010,** *1*.

17.   Brooke, R. J.; Jin, C.; Szumski, D. S.; Nichols, R. J.; Mao, B.-W.; Thygesen, K. S.; Schwarzacher, W., Single-Molecule Electrochemical Transistor Utilizing a Nickel-Pyridyl Spinterface. *Nano Letters* **2015,** *15* (1), 275-280.

18.   Zhou, X.-S.; Liu, L.; Fortgang, P.; Lefevre, A.-S.; Serra-Muns, A.; Raouafi, N.; Amatore, C.; Mao, B.-W.; Maisonhaute, E.; Schoellhorn, B., Do Molecular Conductances Correlate with Electrochemical Rate Constants? Experimental Insights. *Journal of the American Chemical Society* **2011,** *133* (19), 7509-7516.

19.   Chen, F.; He, J.; Nuckolls, C.; Roberts, T.; Klare, J. E.; Lindsay, S., A molecular switch based on potential-induced changes of oxidation state. *Nano Letters* **2005,** *5* (3), 503-506.

20.   Nichols, R. J.; Higgins, S. J., Single molecule electrochemistry in nanoscale junctions. *Current Opinion in Electrochemistry* **2017,** *4* (1), 98-104.

21.   Nichols, R. J.; Higgins, S. J., Single Molecule Nanoelectrochemistry in Electrical Junctions. *Accounts of Chemical Research* **2016,** *49* (11), 2640-2648.

22.   Shu, C.; Li, C. Z.; He, H. X.; Bogozi, A.; Bunch, J. S.; Tao, N. J., Fractional conductance quantization in metallic nanoconstrictions under electrochemical potential control. *Physical Review Letters* **2000,** *84* (22), 5196-5199.

23.   Tian, J.-H.; Yang, Y.; Zhou, X.-S.; Schoellhorn, B.; Maisonhaute, E.; Chen, Z.-B.; Yang, F.-Z.; Chen, Y.; Amatore, C.; Mao, B.-W.; Tian, Z.-Q., Electrochemically Assisted Fabrication of Metal Atomic Wires and Molecular Junctions by MCBJ and STM-BJ Methods. *Chemphyschem* **2010,** *11* (13), 2745-2755.

24.   Tao, N. J., Probing potential-tuned resonant tunneling through redox molecules with scanning tunneling microscopy. *Physical Review Letters* **1996,** *76* (21), 4066-4069.

25.   Zhang, J.; Kuznetsov, A. M.; Medvedev, I. G.; Chi, Q.; Albrecht, T.; Jensen, P. S.; Ulstrup, J., Single-molecule electron transfer in electrochemical environments. *Chemical Reviews* **2008,** *108* (7), 2737-2791.

26.   Albrecht, T.; Moth-Poulsen, K.; Christensen, J. B.; Hjelm, J.; Bjornholm, T.; Ulstrup, J., Scanning tunneling spectroscopy in an ionic liquid. *Journal of the American Chemical Society* **2006,** *128* (20), 6574-6575.

27.   Albrecht, T.; Moth-Poulsen, K.; Christensen, J. B.; Guckian, A.; Bjornholm, T.; Vos, J. G.; Ulstrup, J., In situ scanning tunnelling spectroscopy of inorganic transition metal complexes. *Faraday Discussions* **2006,** *131*, 265-279.

28.   Albrecht, T.; Guckian, A.; Kuznetsov, A. M.; Vos, J. G.; Ulstrup, J., Mechanism of electrochemical charge transport in individual transition metal complexes. *Journal of the American Chemical Society* **2006,** *128* (51), 17132-17138.

29.   Albrecht, T.; Guckian, A.; Ulstrup, J.; Vos, J. G., Transistor-like behavior of transition metal complexes. *Nano Letters* **2005,** *5* (7), 1451-1455.

30.   Nichols, R. J.; Higgins, S. J., Single-Molecule Electronics: Chemical and Analytical Perspectives. In *Annual Review of Analytical Chemistry, Vol 8*, Cooks, R. G.; Pemberton, J. E., Eds. 2015; Vol. 8, pp 389-417.

31.   Zhang, W.; Gan, S.; Vezzoli, A.; Davidson, R. J.; Milan, D. C.; Luzyanin, K. V.; Higgins, S. J.; Nichols, R. J.; Beeby, A.; Low, P. J.; Li, B.; Niu, L., Single-Molecule Conductance of Viologen–Cucurbit[8]uril Host–Guest Complexes. *ACS Nano* **2016,** *10* (5), 5212-5220.

32.   Osorio, H. M.; Catarelli, S.; Cea, P.; Gluyas, J. B. G.; Hartl, F.; Higgins, S. J.; Leary, E.; Low, P. J.; Martin, S.; Nichols, R. J.; Tory, J.; Ulstrup, J.; Vezzoli, A.; Milan, D. C.; Zeng, Q., Electrochemical Single-Molecule Transistors with Optimized Gate Coupling. *Journal of the American Chemical Society* **2015,** *137* (45), 14319-14328.

33.   Kolivoska, V.; Valasek, M.; Gal, M.; Sokolova, R.; Bulickova, J.; Pospisil, L.; Meszaros, G.; Hromadova, M., Single-Molecule Conductance in a Series of Extended Viologen Molecules. *Journal of Physical Chemistry Letters* **2013,** *4* (4), 589-595.

34.   Pobelovt, I. V.; Li, Z. H.; Wandlowski, T., Electrolyte Gating in Redox-Active Tunneling Junctions-An Electrochemical STM Approach. *Journal of the American Chemical Society* **2008,** *130* (47), 16045-16054.

35.   Leary, E.; Higgins, S. J.; van Zalinge, H.; Haiss, W.; Nichols, R. J.; Nygaard, S.; Jeppesen, J. O.; Ulstrup, J., Structure-property relationships in redox-gated single molecule junctions - A comparison of pyrrolo-tetrathiafulvalene and viologen redox groups. *Journal of the American Chemical Society* **2008,** *130* (37), 12204-12205.

36.   Li, Z. H.; Pobelov, I.; Han, B.; Wandlowski, T.; Blaszczyk, A.; Mayor, M., Conductance of redox-active single molecular junctions: an electrochemical approach. *Nanotechnology* **2007,** *18* (4).

37.   Haiss, W.; Albrecht, T.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Hoebenreich, H.; Schiffrin, D. J.; Nichols, R. J.; Kuznetsov, A. M.; Zhang, J.; Chi, Q.; Ulstrup, J., Single-molecule conductance of redox molecules in electrochemical scanning tunneling microscopy. *Journal of Physical Chemistry B* **2007,** *111* (24), 6703-6712.

38.   Kay, N. J.; Higgins, S. J.; Jeppesen, J. O.; Leary, E.; Lycoops, J.; Ulstrup, J.; Nichols, R. J., Single-Molecule Electrochemical Gating in Ionic Liquids. *Journal of the American Chemical Society* **2012,** *134* (40), 16817-16826.

39.   Li, Y. Q.; Wang, H.; Wang, Z. X.; Qiao, Y. J.; Ulstrup, J.; Chen, H. Y.; Zhou, G.; Tao, N. J., Transition from stochastic events to deterministic ensemble average in electron transfer reactions revealed by single-molecule conductance measurement. *Proceedings of the National Academy of Sciences of the United States of America* **2019,** *116* (9), 3407-3412.

40.   Manrique, D. Z.; Huang, C.; Baghernejad, M.; Zhao, X. T.; Al-Owaedi, O. A.; Sadeghi, H.; Kaliginedi, V.; Hong, W. J.; Gulcur, M.; Wandlowski, T.; Bryce, M. R.; Lambert, C. J., A quantum circuit rule for interference effects in single-molecule electrical junctions. *Nature Communications* **2015,** *6*.

41.   Solomon, G. C.; Herrmann, C.; Hansen, T.; Mujica, V.; Ratner, M. A., Exploring local currents in molecular junctions. *Nature Chemistry* **2010,** *2* (3), 223-228.

42.   Bai, J.; Daaoub, A.; Sangtarash, S.; Li, X.; Tang, Y.; Zou, Q.; Sadeghi, H.; Liu, S.; Huang, X.; Tan, Z.; Liu, J.; Yang, Y.; Shi, J.; Mészáros, G.; Chen, W.; Lambert, C.; Hong, W., Anti-resonance features of destructive quantum interference in single-molecule thiophene junctions achieved by electrochemical gating. *Nature Materials* **2019,** *18* (4), 364-369.

43.   Baghernejad, M.; Zhao, X. T.; Ornso, K. B.; Fueg, M.; Moreno-Garcia, P.; Rudnev, A. V.; Kaliginedi, V.; Vesztergom, S.; Huang, C. C.; Hong, W. J.; Broekmann, P.; Wandlowski, T.; Thygesen, K. S.; Bryce, M. R., Electrochemical Control of Single-Molecule Conductance by Fermi Level Tuning and Conjugation Switching. *Journal of the American Chemical Society* **2014,** *136* (52), 17922-17925.

44.   Li, X.; Tan, Z.; Huang, X.; Bai, J.; Liu, J.; Hong, W., Experimental investigation of quantum interference in charge transport through molecular architectures. *Journal of Materials Chemistry C* **2019,** *7* (41), 12790-12808.

45.   Li, Y.; Buerkle, M.; Li, G.; Rostamian, A.; Wang, H.; Wang, Z.; Bowler, D. R.; Miyazaki, T.; Xiang, L.; Asai, Y.; Zhou, G.; Tao, N., Gate controlling of quantum interference and direct observation of anti-resonances in single molecule charge transport. *Nature Materials* **2019,** *18* (4), 357-363.

46.   Huang, B.; Liu, X.; Yuan, Y.; Hong, Z.-W.; Zheng, J.-F.; Pei, L.-Q.; Shao, Y.; Li, J.-F.; Zhou, X.-S.; Chen, J.-Z.; Jin, S.; Mao, B.-W., Controlling and Observing Sharp-Valleyed Quantum Interference

Effect in Single Molecular Junctions. *Journal of the American Chemical Society* **2018,** *140* (50), 17685-17690.

47.   Liu, J.; Huang, X.; Wang, F.; Hong, W., Quantum Interference Effects in Charge Transport through Single-Molecule Junctions: Detection, Manipulation, and Application. *Accounts of Chemical Research* **2019,** *52* (1), 151-160.

48.   Wu, C. L.; Qiao, X. H.; Robertson, C. M.; Higgins, S. J.; Cai, C. X.; Nichols, R. J.; Vezzoli, A., A Chemically Soldered Polyoxometalate Single-Molecule Transistor. *Angewandte Chemie-International Edition* **2020,** *59*, 2.

49.   Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger, R., ''Coulomb staircase'' at room temperature in a self-assembled molecular nanostructure. *Science* **1996,** *272* (5266), 1323-1325.

50.   Zhou, X. S.; Wei, Y. M.; Liu, L.; Chen, Z. B.; Tang, J.; Mao, B. W., Extending the capability of STM break junction for conductance measurement of atomic-size nanowires: An electrochemical strategy. *Journal of the American Chemical Society* **2008,** *130* (40), 13228-13230.

51.   Brooke, R. J.; Szumski, D. S.; Vezzoli, A.; Higgins, S. J.; Nichols, R. J.; Schwarzacher, W., Dual Control of Molecular Conductance through pH and Potential in Single-Molecule Devices. *Nano Letters* **2018,** *18* (2), 1317-1322.

52.   Catarelli, S. R.; Higgins, S. J.; Schwarzacher, W.; Mao, B.-W.; Yan, J.-W.; Nichols, R. J., Ionic Liquid Based Approach for Single-Molecule Electronics with Cobalt Contacts. *Langmuir* **2014,** *30* (47), 14329-14336.

REFERENCES with ANNOTATIONS

1.   Bond, A. M.; Fleischmann, M.; Robinson, J., ELECTROCHEMISTRY IN ORGANIC-SOLVENTS WITHOUT SUPPORTING ELECTROLYTE USING PLATINUM MICROELECTRODES. Journal of Electroanalytical Chemistry 1984, 168 (1-2), 299-312.

2.   Clavilier, J.; Faure, R.; Guinet, G.; Durand, R., PREPARATION OF MONO-CRYSTALLINE PT MICROELECTRODES AND ELECTROCHEMICAL STUDY OF THE PLANE SURFACES CUT IN THE DIRECTION OF THE (111) AND (110) PLANES. Journal of Electroanalytical Chemistry 1980, 107 (1), 205-209.

3.   Kolb, D. M., Electrochemical surface science. Angewandte Chemie-International Edition 2001, 40 (7), 1162-1181.

4.   Long, Y. T.; Unwin, P. R.; Baker, L. A., Single-Entity Electrochemistry: Fundamentals and Applications. Chemelectrochem 2018, 5 (20), 2918-2919.

5.   Baker, L. A., Perspective and Prospectus on Single-Entity Electrochemistry. Journal of the American Chemical Society 2018, 140 (46), 15549-15559.

6.   Crooks, R. M., Concluding remarks: single entity electrochemistry one step at a time. Faraday Discussions 2016, 193, 533-547.

7.   Fan, F. R. F.; Bard, A. J., Electrochemical Detection of Single Molecules. Science 1995, 267 (5199), 871-874.

8.   Haiss, W.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Hobenreich, H.; Schiffrin, D. J.; Nichols, R. J., Redox state dependence of single molecule conductivity. Journal of the American Chemical Society 2003, 125 (50), 15294-15295.

9.   Xu, B. Q.; Tao, N. J. J., Measurement of single-molecule resistance by repeated formation of molecular junctions. Science 2003, 301, 1221-1223.

10.   Guo, S.; Manuel Artes, J.; Diez-Perez, I., Electrochemically-gated single-molecule electrical devices. Electrochimica Acta 2013, 110, 741-753.

11.   Diez-Perez, I.; Li, Z.; Guo, S.; Madden, C.; Huang, H.; Che, Y.; Yang, X.; Zang, L.; Tao, N., Ambipolar Transport in an Electrochemically Gated Single-Molecule Field-Effect Transistor. ACS Nano 2012, 6 (8), 7044-7052.

12.   Darwish, N.; Diez-Perez, I.; Guo, S. Y.; Tao, N. J.; Gooding, J. J.; Paddon-Row, M. N., Single Molecular Switches: Electrochemical Gating of a Single Anthraquinone-Based Norbornylogous Bridge Molecule. Journal of Physical Chemistry C 2012, 116 (39), 21093-21097.

13.   Darwish, N.; Diez-Perez, I.; Da Silva, P.; Tao, N. J.; Gooding, J. J.; Paddon-Row, M. N., Observation of Electrochemically Controlled Quantum Interference in a Single Anthraquinone-Based Norbornylogous Bridge Molecule. Angewandte Chemie-International Edition 2012, 51 (13), 3203-3206.

14.   Li, Z.; Li, H.; Chen, S.; Froehlich, T.; Yi, C.; Schoenenberger, C.; Calame, M.; Decurtins, S.; Liu, S.-X.; Borguet, E., Regulating a Benzodifuran Single Molecule Redox Switch via Electrochemical Gating and Optimization of Molecule/Electrode Coupling. Journal of the American Chemical Society 2014, 136 (25), 8867-8870.

15.   Li, C.; Stepanenko, V.; Lin, M.-J.; Hong, W.; Wuerthner, F.; Wandlowski, T., Charge transport through perylene bisimide molecular junctions: An electrochemical approach. Physica Status Solidi B-Basic Solid State Physics 2013, 250 (11), 2458-2467.

16.   Diez-Perez, I.; Li, Z.; Hihath, J.; Li, J.; Zhang, C.; Yang, X.; Zang, L.; Dai, Y.; Feng, X.; Muellen, K.; Tao, N., Gate-controlled electron transport in coronenes as a bottom-up approach towards graphene transistors. Nature Communications 2010, 1.

17.   Brooke, R. J.; Jin, C.; Szumski, D. S.; Nichols, R. J.; Mao, B.-W.; Thygesen, K. S.; Schwarzacher, W., Single-Molecule Electrochemical Transistor Utilizing a Nickel-Pyridyl Spinterface. Nano Letters 2015, 15 (1), 275-280.

18.   Zhou, X.-S.; Liu, L.; Fortgang, P.; Lefevre, A.-S.; Serra-Muns, A.; Raouafi, N.; Amatore, C.; Mao, B.-W.; Maisonhaute, E.; Schoellhorn, B., Do Molecular Conductances Correlate with Electrochemical Rate Constants? Experimental Insights. Journal of the American Chemical Society 2011, 133 (19), 7509-7516.

19.   Chen, F.; He, J.; Nuckolls, C.; Roberts, T.; Klare, J. E.; Lindsay, S., A molecular switch based on potential-induced changes of oxidation state. Nano Letters 2005, 5 (3), 503-506.

20.   Nichols, R. J.; Higgins, S. J., Single molecule electrochemistry in nanoscale junctions. Current Opinion in Electrochemistry 2017, 4 (1), 98-104.

21.   Nichols, R. J.; Higgins, S. J., Single Molecule Nanoelectrochemistry in Electrical Junctions. Accounts of Chemical Research 2016, 49 (11), 2640-2648.

22.   Shu, C.; Li, C. Z.; He, H. X.; Bogozi, A.; Bunch, J. S.; Tao, N. J., Fractional conductance quantization in metallic nanoconstrictions under electrochemical potential control. Physical Review Letters 2000, 84 (22), 5196-5199.

23.   Tian, J.-H.; Yang, Y.; Zhou, X.-S.; Schoellhorn, B.; Maisonhaute, E.; Chen, Z.-B.; Yang, F.-Z.; Chen, Y.; Amatore, C.; Mao, B.-W.; Tian, Z.-Q., Electrochemically Assisted Fabrication of Metal Atomic Wires and Molecular Junctions by MCBJ and STM-BJ Methods. Chemphyschem 2010, 11 (13), 2745-2755.

24.   Tao, N. J., Probing potential-tuned resonant tunneling through redox molecules with scanning tunneling microscopy. Physical Review Letters 1996, 76 (21), 4066-4069.

25.   Zhang, J.; Kuznetsov, A. M.; Medvedev, I. G.; Chi, Q.; Albrecht, T.; Jensen, P. S.; Ulstrup, J., Single-molecule electron transfer in electrochemical environments. Chemical Reviews 2008, 108 (7), 2737-2791.

26.   Albrecht, T.; Moth-Poulsen, K.; Christensen, J. B.; Hjelm, J.; Bjornholm, T.; Ulstrup, J., Scanning tunneling spectroscopy in an ionic liquid. Journal of the American Chemical Society 2006, 128 (20), 6574-6575.

27.   Albrecht, T.; Moth-Poulsen, K.; Christensen, J. B.; Guckian, A.; Bjornholm, T.; Vos, J. G.; Ulstrup, J., In situ scanning tunnelling spectroscopy of inorganic transition metal complexes. Faraday Discussions 2006, 131, 265-279.

28.   Albrecht, T.; Guckian, A.; Kuznetsov, A. M.; Vos, J. G.; Ulstrup, J., Mechanism of electrochemical charge transport in individual transition metal complexes. Journal of the American Chemical Society 2006, 128 (51), 17132-17138.

29.   Albrecht, T.; Guckian, A.; Ulstrup, J.; Vos, J. G., Transistor-like behavior of transition metal complexes. Nano Letters 2005, 5 (7), 1451-1455.

30.   Nichols, R. J.; Higgins, S. J., Single-Molecule Electronics: Chemical and Analytical Perspectives. In Annual Review of Analytical Chemistry, Vol 8, Cooks, R. G.; Pemberton, J. E., Eds. 2015; Vol. 8, pp 389-417.

31.   Zhang, W.; Gan, S.; Vezzoli, A.; Davidson, R. J.; Milan, D. C.; Luzyanin, K. V.; Higgins, S. J.; Nichols, R. J.; Beeby, A.; Low, P. J.; Li, B.; Niu, L., Single-Molecule Conductance of Viologen–Cucurbit[8]uril Host–Guest Complexes. ACS Nano 2016, 10 (5), 5212-5220.

32.   Osorio, H. M.; Catarelli, S.; Cea, P.; Gluyas, J. B. G.; Hartl, F.; Higgins, S. J.; Leary, E.; Low, P. J.; Martin, S.; Nichols, R. J.; Tory, J.; Ulstrup, J.; Vezzoli, A.; Milan, D. C.; Zeng, Q., Electrochemical Single-Molecule Transistors with Optimized Gate Coupling. Journal of the American Chemical Society 2015, 137 (45), 14319-14328.

** This study of viologen single molecular wires shows how molecular electronics at electrode-electrolyte interfaces can be used to analyse mechanisms of electron transfer, to distinguish electrolyte effects and to provide details not readily available from large ensemble measurements.

33.   Kolivoska, V.; Valasek, M.; Gal, M.; Sokolova, R.; Bulickova, J.; Pospisil, L.; Meszaros, G.; Hromadova, M., Single-Molecule Conductance in a Series of Extended Viologen Molecules. Journal of Physical Chemistry Letters 2013, 4 (4), 589-595.

34.   Pobelovt, I. V.; Li, Z. H.; Wandlowski, T., Electrolyte Gating in Redox-Active Tunneling Junctions-An Electrochemical STM Approach. Journal of the American Chemical Society 2008, 130 (47), 16045-16054.

35.   Leary, E.; Higgins, S. J.; van Zalinge, H.; Haiss, W.; Nichols, R. J.; Nygaard, S.; Jeppesen, J. O.; Ulstrup, J., Structure-property relationships in redox-gated single molecule junctions - A comparison of pyrrolo-tetrathiafulvalene and viologen redox groups. Journal of the American Chemical Society 2008, 130 (37), 12204-12205.

36.   Li, Z. H.; Pobelov, I.; Han, B.; Wandlowski, T.; Blaszczyk, A.; Mayor, M., Conductance of redox-active single molecular junctions: an electrochemical approach. Nanotechnology 2007, 18 (4).

37.   Haiss, W.; Albrecht, T.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Hoebenreich, H.; Schiffrin, D. J.; Nichols, R. J.; Kuznetsov, A. M.; Zhang, J.; Chi, Q.; Ulstrup, J., Single-molecule conductance of redox molecules in electrochemical scanning tunneling microscopy. Journal of Physical Chemistry B 2007, 111 (24), 6703-6712.

38.   Kay, N. J.; Higgins, S. J.; Jeppesen, J. O.; Leary, E.; Lycoops, J.; Ulstrup, J.; Nichols, R. J., Single-Molecule Electrochemical Gating in Ionic Liquids. Journal of the American Chemical Society 2012, 134 (40), 16817-16826.

39.   Li, Y. Q.; Wang, H.; Wang, Z. X.; Qiao, Y. J.; Ulstrup, J.; Chen, H. Y.; Zhou, G.; Tao, N. J., Transition from stochastic events to deterministic ensemble average in electron transfer reactions revealed by single-molecule conductance measurement. Proceedings of the National Academy of Sciences of the United States of America 2019, 116 (9), 3407-3412.

** This study shows that the fluctuations of molecular conductance of a redox active molecular wire can be followed as a function of electrode potential. This shows how the stochastic kinetics of individual reaction events at an electrode-electrolyte interface can be followed.

40.   Manrique, D. Z.; Huang, C.; Baghernejad, M.; Zhao, X. T.; Al-Owaedi, O. A.; Sadeghi, H.; Kaliginedi, V.; Hong, W. J.; Gulcur, M.; Wandlowski, T.; Bryce, M. R.; Lambert, C. J., A quantum circuit rule for interference effects in single-molecule electrical junctions. Nature Communications 2015, 6.

41.   Solomon, G. C.; Herrmann, C.; Hansen, T.; Mujica, V.; Ratner, M. A., Exploring local currents in molecular junctions. Nature Chemistry 2010, 2 (3), 223-228.

42.   Bai, J.; Daaoub, A.; Sangtarash, S.; Li, X.; Tang, Y.; Zou, Q.; Sadeghi, H.; Liu, S.; Huang, X.; Tan, Z.; Liu, J.; Yang, Y.; Shi, J.; Mészáros, G.; Chen, W.; Lambert, C.; Hong, W., Anti-resonance features of destructive quantum interference in single-molecule thiophene junctions achieved by electrochemical gating. Nature Materials 2019, 18 (4), 364-369.

** This study, which includes theory and single molecule conductance measurements using an electrochemically gated mechanically controlled break junctions, demonstrates how electrochemistry can be used to control quantum interference (QI) in single molecular wires. It

shows the electrode potential tuning the molecular conductance towards a minimum of an anti-resonance arising from destructive QI

43.   Baghernejad, M.; Zhao, X. T.; Ornso, K. B.; Fueg, M.; Moreno-Garcia, P.; Rudnev, A. V.; Kaliginedi, V.; Vesztergom, S.; Huang, C. C.; Hong, W. J.; Broekmann, P.; Wandlowski, T.; Thygesen, K. S.; Bryce, M. R., Electrochemical Control of Single-Molecule Conductance by Fermi Level Tuning and Conjugation Switching. Journal of the American Chemical Society 2014, 136 (52), 17922-17925.

44.   Li, X.; Tan, Z.; Huang, X.; Bai, J.; Liu, J.; Hong, W., Experimental investigation of quantum interference in charge transport through molecular architectures. Journal of Materials Chemistry C 2019, 7 (41), 12790-12808.

45.   Li, Y.; Buerkle, M.; Li, G.; Rostamian, A.; Wang, H.; Wang, Z.; Bowler, D. R.; Miyazaki, T.; Xiang, L.; Asai, Y.; Zhou, G.; Tao, N., Gate controlling of quantum interference and direct observation of anti-resonances in single molecule charge transport. Nature Materials 2019, 18 (4), 357-363.

* Electrochemical gating is used in this study to tune the quantum interference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a single molecule bridge. An anti-resonance, attributed to destructive interference, becomes apparent with the electrochemical gate response and this is used to tune the conductance by over two orders of magnitude.

46.   Huang, B.; Liu, X.; Yuan, Y.; Hong, Z.-W.; Zheng, J.-F.; Pei, L.-Q.; Shao, Y.; Li, J.-F.; Zhou, X.-S.; Chen, J.-Z.; Jin, S.; Mao, B.-W., Controlling and Observing Sharp-Valleyed Quantum Interference Effect in Single Molecular Junctions. Journal of the American Chemical Society 2018, 140 (50), 17685-17690.

* This study shows how electrode potential can be used to tune the conductance of a molecular bridge to a conductance valley resulting from destructive quantum interference.

47.   Liu, J.; Huang, X.; Wang, F.; Hong, W., Quantum Interference Effects in Charge Transport through Single-Molecule Junctions: Detection, Manipulation, and Application. Accounts of Chemical Research 2019, 52 (1), 151-160.

48.   Wu, C. L.; Qiao, X. H.; Robertson, C. M.; Higgins, S. J.; Cai, C. X.; Nichols, R. J.; Vezzoli, A., A Chemically Soldered Polyoxometalate Single-Molecule Transistor. Angewandte Chemie-International Edition 2020, 59, 2.

** This study shows a single molecule electrochemical transistor concept for well-defined metal cluster containing molecular wires. The 3-state conductance switching electrochemically gates current flow across the junction by over one order of magnitude.

49.   Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger, R., ''Coulomb staircase'' at room temperature in a self-assembled molecular nanostructure. Science 1996, 272 (5266), 1323-1325.

50.   Zhou, X. S.; Wei, Y. M.; Liu, L.; Chen, Z. B.; Tang, J.; Mao, B. W., Extending the capability of STM break junction for conductance measurement of atomic-size nanowires: An electrochemical strategy. Journal of the American Chemical Society 2008, 130 (40), 13228-13230.

51.   Brooke, R. J.; Szumski, D. S.; Vezzoli, A.; Higgins, S. J.; Nichols, R. J.; Schwarzacher, W., Dual Control of Molecular Conductance through pH and Potential in Single-Molecule Devices. Nano Letters 2018, 18 (2), 1317-1322.

* This work, which uses the STM break junction technique and nickel contacts, shows that the conductance of a molecular bridge (4,4'-vinylenedipyridine) can depend on both the electrochemically applied gate voltage and the pH of the electrolyte. Insights into the acid–base

reaction and discrete proton transfer to the molecular junction, are attained through simultaneous control of pH and the electrode potential.

52.   Catarelli, S. R.; Higgins, S. J.; Schwarzacher, W.; Mao, B.-W.; Yan, J.-W.; Nichols, R. J., Ionic Liquid Based Approach for Single-Molecule Electronics with Cobalt Contacts. Langmuir 2014, 30 (47), 14329-14336.