



University of Jaffna

**Professor Sivapathasuntharam Mageswaran
Memorial Lecture - 2016**

**"Gone Fishing': Studying Metal |
Molecule | Metal Junctions with
Scanning Probe Microscopy '**

by

Professor Simon Higgins

Department of Chemistry
University of Liverpool
United Kingdom

on

**Monday 7th November 2016
at 3.00 p.m**

at

**Kailasapathy Auditorum
University of Jaffna**





University of Jaffna

Professor Sivapathasunthram Mageswaran

Memorial Lecture - 2016

**“Gone Fishing’: Studying Metal |
Molecule | Metal Junctions with
Scanning Probe Microscopy’**

by

Professor Simon Higgins

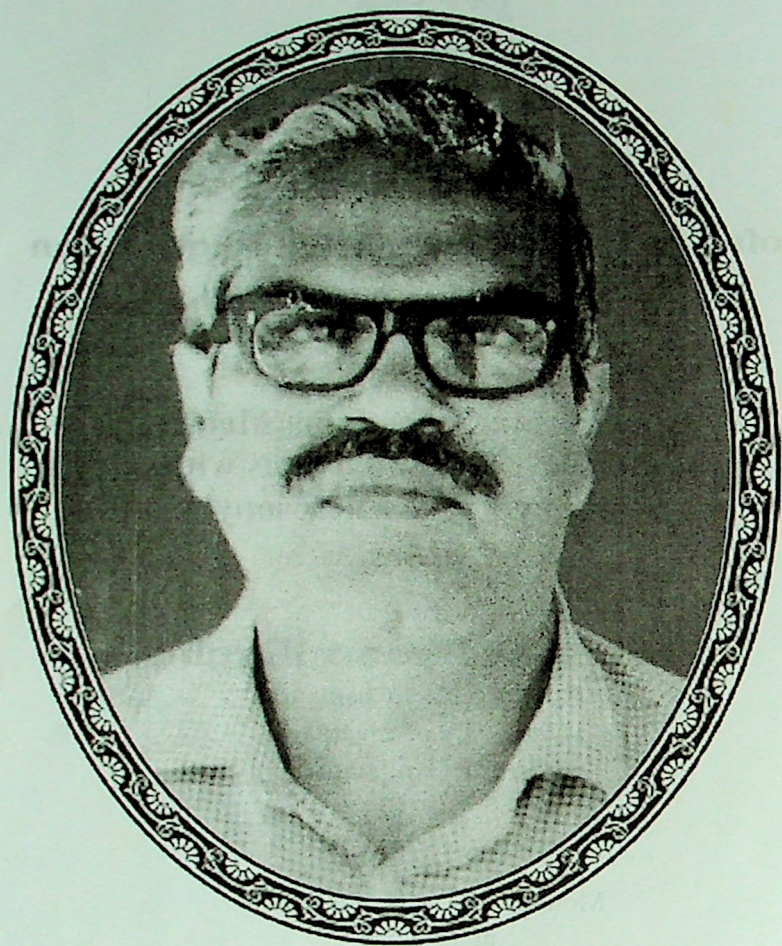
Department of Chemistry
University of Liverpool
United Kingdom

on

Monday 7th November 2016
at 3.00 p.m

at

Kailasapathy Auditorum
University of Jaffna



Professor Sivapathasuntharam Mageswaran

MESSAGE FROM THE VICE-CHANCELLOR



It is my distinct honour and pleasure to welcome each of you to Professor Sivapathasundaram Mageswaran Memorial Lecture.

Late Professor Mageswaran was a well recognized and respected academic who contributed immensely to the development of the University of Jaffna especially to the Faculty of Science.

He has taken keen interest and devoted his time for the improvement and upgrading the standard of the Faculty of Science and Department of Chemistry. Prof. Mageswaran has taken appropriate action to maintain the student discipline during his tenure as Dean of the Faculty of Science and had been the role model to many academic staff.

To honour his memory, the Members of the Faculty of Science and wellwishers established the Prof. Mageswaran Memorial Fund, which supports this annual lecture.

This evening, we have invited Professor Simon Higgins from Department of Chemistry, University of Liverpool, United Kingdom, to deliver the Lecture. He will speak to us on the topic, "Gone Fishing': Studying Metal | Molecule | Metal Junctions with Scanning Probe Microscopy'

I thank Professor Simon Higgins for accepting our invitation and delivering this lecture.

Prof. (Miss.) V. Arasaratnam
Vice-Chancellor
University of Jaffna, Jaffna

'Gone Fishing': Studying Metal | Molecule | Metal Junctions With Scanning Probe Microscopy'

Simon J. Higgins

Department of Chemistry, University of Liverpool, Crown Street,
LIVERPOOL L69 7ZD, U.K.

Ladies and Gentlemen

First of all, I am honoured to be invited to give this S. Mageswaran Memorial Lecture. It is interesting to note that Prof. Mageswaran did his PhD in synthetic organic chemistry in Sheffield, and in the same research group was Ian Sutherland, who was later Professor and Head of the Organic Chemistry Department at Liverpool. He was Head of the Organic Chemistry section when I arrived at Liverpool, following the merger of the two Chemistry Departments (Organic, and Inorganic, Physical and Industrial) shortly before I arrived. What is more, Prof. Mageswaran's wife I believe did some postdoctoral work with Prof. Brian Heaton, who was my boss when I arrived in Liverpool (and my predecessor as External Examiner in Inorganic Chemistry at Jaffna). So I can claim an indirect connection with Prof. Mageswaran.

I should begin by acknowledging the people who have done the work I will talk about today, in particular two very talented PhD students Ed Leary and Andrea Vezzoli. I have collaborated with my colleague at

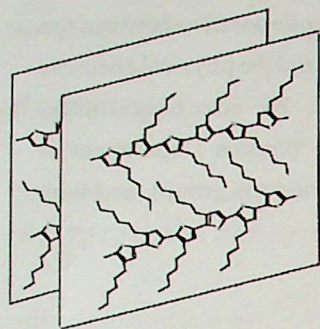
Liverpool Prof. Richard Nichols on this topic for about 15 years; as this is a highly multidisciplinary area, close collaboration between the synthetic chemists who make the molecules, and the physical chemists who make the measurements, is essential. We also have fruitful collaborations with theoreticians from the Physics Department at Lancaster University (Prof. Colin Lambert and his group), and with other international groups too.

Preamble

In this lecture, I will begin by introducing the field of 'molecular electronics', and I will distinguish it from the better-known area of 'organic electronics'. I will explain how our measurements are made, and analysed, and the importance and significance of using electrochemistry to 'gate' or 'switch' the electrical properties of molecular junctions. The lecture will focus on two areas where our group has made distinctive advances, namely the electrical properties of redox-active molecules sandwiched between two electrodes, and the effect of the environment on the electrical properties of some conjugated molecules bridging two metallic contacts, and how this might ultimately be of use in sensing.

Introduction

I guess many of you will have heard of 'organic electronics'. In this field, the solid-state properties of certain conjugated small molecules and polymers are being exploited to perform various electronic functions, taking advantage of the conjugated π -electrons. For instance *regioregular polyalkylthiophenes* and their derivatives can



adopt a sufficiently ordered, π -stacked, structure in the solid state that they have quite high field effect mobility, *i.e.* they can transmit charge carriers (holes, in this case) effectively upon application of a voltage (see *left*). They can be used as the semiconductor in thin-film transistors, for example to drive the pixels in a flexible display device.

In a famous Nature paper from 1989, the Friend and Holmes groups at Cambridge University described a Schottky diode made using a ITO-coated glass electrode as a anode, an aluminium top contact as the cathode, and a different conjugated polymer, polyphenylene-vinylene (PPV), as the semiconductor. On applying a forward bias, the device emitted a yellow-green light. This discovery sparked a huge research effort in both academia and industry, and in recent years such Organic Light-Emitting Diodes (OLEDs) have found their way into commercial products, such as mobile telephone screens, and other applications such as large-area displays, flexible displays and ambient white lighting are in prospect.

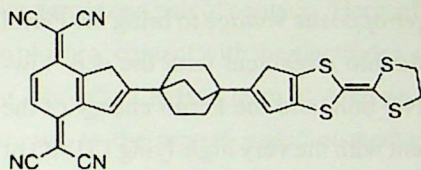
The opposite process, absorption of light and its conversion into electricity, is also possible, again using regioregular polyalkylthiophenes and their derivatives, along with fullerenes in so-called heterojunction organic photovoltaic devices (OPVs).

In all of these areas, although the properties of the polymers can certainly be tuned using synthetic chemistry, the most significant aspect of device operation is the solid-state structures of the materials involved. It is the *bulk material* properties that give rise to the electronic applications.

The fundamental discoveries that are the foundations of organic electronics were first made in the 1950's, and the area has benefitted from enormous investment. It is therefore at quite an advanced state, now reaching commercialisation.

The origins and challenges of 'molecular electronics'

The terms *organic electronics* and *molecular electronics* were originally used almost interchangeably. However, in this lecture, by 'molecular electronics' I mean the idea of using a *single* molecule, or perhaps a small assembly of a few molecules, to perform some electronic function. Clearly, in this case the ability to perform the function depends upon the structure of the individual molecule. The



idea that this might be possible dates back to a theoretical paper from 1974 by Aviram and Ratner (Chem. Phys. Letts. 1974 **29** 277). They

envisaged what would happen if the molecule (*left*) was sandwiched between two metal contacts. Back in the 1960s-1970's there was much

interest in so-called 'charge transfer complexes', where an electron-rich conjugated system interacts with an electron-deficient one, often with the appearance of a strong colour due to the resulting charge transfer band in the visible spectrum, and the Aviram-Ratner molecule reflects this; it consists of a highly electron-deficient system on the left of the molecule (a tetracyanoquinodimethane or TCNQ unit), and a highly electron-rich system (a tetrathiafulvalene or TTF unit) on the right, separated by a saturated 'spacer' group. If this molecule was placed between two metallic electrodes of the same metal, the Fermi energy (E_f) of the metal contact on the left would be nearest in energy to the LUMO of the TCNQ unit, whereas the contact on the right would be closest in energy to the HOMO of the TTF unit. There would be a small tunneling barrier between metal and molecule in both cases, and there would be a larger tunneling barrier between the two halves of the molecule, caused by the saturated 'spacer' unit. It would only require a small bias voltage, making the left-hand electrode more negative (raising E_f) and the right-hand one more positive (lowering E_f) to align the two electrode E_f 's with the respective molecular orbitals so that electrons could tunnel across the central barrier from cathode to anode. But it would require a *much larger opposite voltage* to bring the Fermi energy of the left-hand electrode into alignment with the very low-lying HOMO orbital of the TCNQ unit, and the Fermi energy of the right hand electrode into alignment with the very high-lying LUMO of the TTF unit, if one wanted charge to flow in the opposite direction across the molecule. So *the molecule would act as a diode by virtue of its structure.*

Since that paper appeared, there have been many attempts to make 'molecular diodes' using this general idea (although the original Aviram-Ratner molecule would be far too challenging to synthesise!). Up to about a decade ago, it was very difficult in practice to make electronic devices incorporating a single molecule, or even small assemblies of molecules, and most of the experiments claiming 'molecular diodes' turned out to be unreliable and/or irreproducible. However, in the last 15 years, techniques for making and measuring metal | molecule | metal devices with a few, or even single, molecules have been developed. We will now examine some of these.

Techniques for making metal | molecule | metal junctions

Using the highest resolution electron beam lithography then available, the Dekker team developed *nanofabricated contacts*; two parallel gold contacts less than 10 nm apart, in 2000. This is a distance that can be spanned by a single (very long!) molecule, such as double-stranded DNA. A single chip can be made with several dozen such contacts, and then DNA can be deposited from solution; in fortunate instances (imaged by atomic force microscopy, AFM), a single DNA molecule lies across one pair of contacts. Here, of course, the molecule is simply in physical contact with the electrodes, and this can be a problem (q.v.). In 2002 the Lindsay team at Arizona State developed what became known as the *matrix isolation method*. Here, a close-packed, self-assembled monolayer of an alkanethiol is deposited on a flat gold substrate. A functional di-thiol molecule is then adsorbed, such that a very few (about 1 in 1000 alkanethiols) molecules adsorb at defect

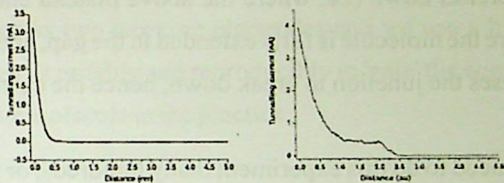
sites, standing upright with the remaining thiol group free. The monolayer is then treated with citrate-coated gold nanoparticles. These covalently bind to the free thiol, attaching the nanoparticle to the surface. The nanoparticles can then be individually located by a gold-coated conducting AFM tip, and hence a metal | molecule | metal junction can form. Note: a molecule covalently bound to the metal is over 100 times as 'conductive' as a molecule (such as an alkanethiol matrix molecule) that is not covalently bound, so the properties of the resulting junctions are dominated by the single alkanedithiol that bridges the substrate to the tip.

At about the same time, physicists were developing the break junction technique, initially for testing the properties of single-atom chains of metal atoms and superconductors (e.g. niobium). Here, a fine metal wire is suspended over a hollow in an oxide substrate, all fabricated using electron beam lithography. The device is built upon a flexible support. This is then bent by the application of a force from a screw mechanism, such that the metal wire breaks leaving a nanometre-size gap. By relaxing the bending force, the two metal contacts can be brought together again. If they are broken in the presence of a molecule that can covalently bind to the metal, again, it is possible to make a metal | molecule | metal junction.

It is also possible to use localised plasma oxidation to cut a metallic C nanotube, leaving the terminal C atoms as -COOH functional groups. Conventional amide bond-forming chemistry can then be used to attach diamine molecules across the gap.

Scanning tunnelling microscopy for metal | molecule | metal junctions

Binnig and Rohrer of IBM Zurich won the Physics Nobel Prize in 1986 for their invention of scanning tunnelling microscopy (STM). The best-known applications of this are in the imaging of conducting surfaces. It relies on the phenomenon of quantum tunnelling (*q.v.*). Piezoelectric controllers accurately determine the position of a metallic tip in 3-D above a conducting surface. A small voltage is applied, and when the tip-surface distance (z) is sufficiently small (of the order of nanometres), a tunnelling current flows. Because this varies exponentially as a function of tip-surface distance z , a feedback loop can be used to control the height of the tip above the surface, and this can therefore be used to image the surface with atomic resolution. The tip can also be used to push atoms or molecules around on the surface, or to lift them off and re-deposit them elsewhere (see the work of Donald Eiger, IBM Almaden labs, for instance).



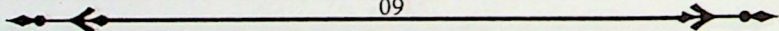
(Left) current-distance relation with no molecule in the gap; (right) with 1,8-octanedithiol bridging the gap. Notice the plateau in the latter case.

Around 2003, we, and a team led by Nonjiang Tao of Arizona State, simultaneously developed STM into techniques for making metal | molecule | metal junctions. In the Liverpool approach, we typically

take a gold substrate (flame-annealed gold on glass slide, mainly Au(111) surface), and coat it with a sub-monolayer coverage of a molecule bearing two contact groups (typically, thiols). We use the STM's feedback mechanism to position a gold STM tip a short distance above the substrate. We then disable the feedback mechanism to allow us to measure the tunnelling current, and we retract the tip vertically. Sometimes, a di-thiol will spontaneously bridge between the tip and substrate, so when we retract the tip, the current-distance curve looks rather different from cases where there is no molecule in the gap (see the picture *above*).

As the molecule is lifted up, and typically slides along the tip, the tunneling current is dominated by through-bond tunneling via the molecule, so *a plateau current is observed, characteristic of the molecule*. We can hence determine the conductance of the metal | molecule | metal junction. We can also determine the distance at which the junction breaks down (*i.e.* where the above plateau ends). This is the point where the molecule is fully extended in the gap, and further tip retraction causes the junction to break down, hence the current rapidly decays.

However, we need to do this experiment many hundreds, or thousands, of times, and analyse the results statistically, because we do not know the details of any individual junction. For example, we don't know the binding geometries of the thiolates on the gold surface at either end of the molecule. We don't know, for any given experiment, if there are one, two or more molecules in the gap. These are things that cannot be



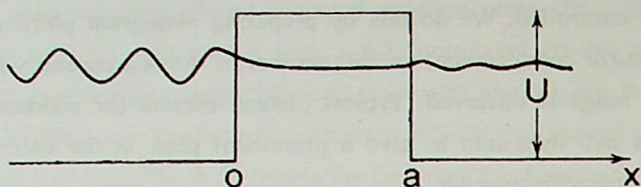
easily controlled. We do this by preparing histogram plots, of the current (or conductance) vs. the number of times a current within a given range is observed. Typical plateau current (or conductance) values will then sum to give a prominent peak in the current (or conductance) histogram.

Electrochemical experiments using the STM

The above STM experiment can be performed in a variety of conditions. In our early work, we simply used ambient conditions. Subsequently, we carried out the experiments under an inert liquid (e.g. mesitylene or a high-boiling perfluorocarbon) under nitrogen or argon, to minimise the effect of variable humidity or organic contaminants. However, an advantage of the STM experiment is that we can also perform it using an electrolyte medium such as an aqueous buffer, or an ionic liquid. This enables us to carry out experiments under electrochemical potential control. Here, both the tip and substrate act as two working electrodes and we use a bipotentiostat. This enables us reliably and reproducibly to 'gate' the conductance of a redox-active molecule in the junction.

How do single molecules conduct in metal | molecule | metal junctions?

Before discussing the results of our studies, it is worth reviewing the different mechanisms by which a molecule might conduct charge.



Electron tunnelling through a rectangular barrier.

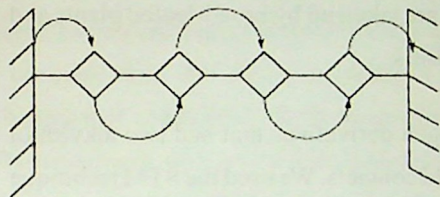
For short (<3 nm) molecules, of any structure, it was predicted that tunnelling will be the dominant mechanism, since this is a short-range phenomenon (conductance decays exponentially with distance).

Owing to wave-particle duality, particles with very small mass such as an electron can *tunnel* through sufficiently narrow barriers, for instance from one metal surface to another through a narrow vacuum gap as in the above diagram. In this case, the conductance decays exponentially with the width of such a barrier. Any molecule, regardless of its structure, will present a barrier of lesser height to a tunnelling electron, owing to the presence of filled and empty orbitals in the molecule. Therefore, even an alkanedithiol is more 'conductive' than a vacuum barrier of the same length. The metal Fermi energies must lie between the filled (HOMO) and empty (LUMO) orbitals of the molecule, and the width of the barrier in the above picture is now controlled by the length of the molecule. A conjugated molecule will have a narrower HOMO-LUMO separation than a non-conjugated molecule, and so the conductance of conjugated molecules will decay less steeply than a non-conjugated molecule as a function of molecular length. We can write an equation $I = Ae^{-\beta L}$ for molecular conductance,

where I is the tunneling current, A is a pre-factor that is largely determined by the contact chemistry (in this case, a thiolate bound to gold) and β is called the decay constant and is mainly a property of the nature of the molecular backbone. It has the units

of reciprocal length. For instance, β for alkanedithiols is about 10 nm^{-1} , for oligophenyls ($1,4\text{-S}(\text{C}_6\text{H}_4)_n\text{S-}$) it is about 4 nm^{-1} and for the highly-conjugated oligothiophenes, it is about 1 nm^{-1} . Another important consideration is that tunnelling is a temperature-independent and coherent process.

Over longer distances (typically $> 3 \text{ nm}$), conjugated molecules in particular will often show significant hopping conductance. This is essentially a redox mechanism, represented by the cartoon (left), in which charge carriers are driven by a potential gradient from one redox



site along the molecule to the next. This can be distinguished from tunnelling because (i) the conductance decays only linearly with the length of the molecule, (ii) it is an

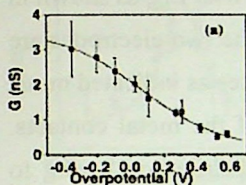
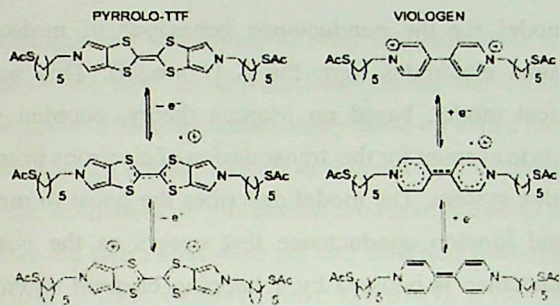
activated process, so tunnelling conductance increases with temperature. It is an incoherent process; the electron (or hole) spends long enough on a given redox site for the molecule to reorganise to accommodate the new redox state. In a long, continuously-conjugated molecule, each 'redox site' arises as a consequence of defects in the

conjugation caused by, for example, torsion of the molecular backbone.

Redox-active molecules as 'molecular switches' or 'single molecule transistors'.

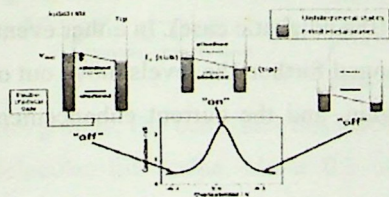
Clearly, molecules that will switch their electronic properties in response to some external stimulus will be of interest in molecular electronics. From the outset, our group was interested in making and studying such single molecule switches. Our early work used the 'viologen' molecule shown below. 'Viologens' (dialkyl-4,4'-bipyridinium salts) have been widely-studied since they were first prepared in the 1950's, owing to their redox- and photo-activity. They are highly electron-deficient aromatic systems, and they can be reduced in two successive, reversible one-electron steps as shown in the scheme below. Commercially, such compounds have been widely-used as weedkillers, since they are taken up by broad-leafed plants and can act as singlet oxygen sensitisers.

In our case, we prepared viologen derivatives that had two alkylthiol chains, for strong binding to gold contacts. We used the STM technique to make and characterise metal | molecule | metal junctions with these molecules, in an aqueous electrolyte under electrochemical potential control (See *J. Am. Chem. Soc.*, 2003, **125**, 15294).



In these experiments, we could only access the first one-electron reduction process, to the viologen radical cation, because at more negative potentials in water, thiols are reductively desorbed from gold electrodes. So the second reduction, indicated below in red, could not be studied

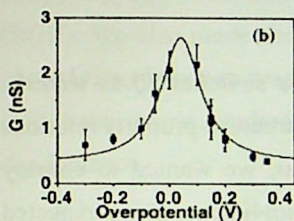
in water. The conductance-overpotential relationship is shown (*left*). It can be seen that the viologen dication forms junctions with a conductance of around 0.5 nS (in other words, a resistance of around 2000 megaohms), and over a wide potential window around the first reduction process, about a volt in total, it slowly rises to a conductance of about 3 nS (or a resistance of 333 megaohms).



At first sight, this behaviour was puzzling. Renowned theoreticians Kuznetsov and Ulstrup had earlier

published a model for the conductance behaviour of molecules adsorbed to metal electrodes (*left*; the K-U model). This was a phenomenological model, based on Marcus theory, coupled with tunneling aspects to account for the transmission of electrons from the metal to the redox system. The model describes the boost in metal | molecule | metal junction conductance that occurs as the normal tunnelling conductance is boosted by a hopping element when the appropriate frontier orbital (in the case of viologens, the LUMO) approaches resonance with the metal contacts. The model predicts a peak in the current enhancement, that coincides with $E_{1/2}$, as shown in the cartoon. In this model, as the potentials of the two electrodes are changed, the energy levels for the two redox states as indicated move into near-resonance with the Fermi energies of the metal contacts. These 'energy levels' are in fact a Gaussian distribution owing to solvent (external) and bond length (internal) fluctuations of the molecule. At some point the energies become correct for an electron to tunnel from one electrode to the molecule. The molecule and its solvation shell will then start to relax to accommodate the new redox state. If there is then another fluctuation that aligns the molecular level with the Fermi energy of the second metal, the electron can then tunnel from the redox site to the second electrode. This can either happen after full molecular relaxation (the diabatic case), or it could happen before complete relaxation has occurred (the adiabatic case). In either event, as the electrode potentials are changed further, the levels move out of resonance with the electrodes again, and the current enhancement declines as shown.

The viologen did not appear to obey this behaviour with its broad, sigmoidal increase in conductance across the redox wave, and Kuznetsov and Ulstrup subsequently came up with a modified picture (called the 'soft gating' model) to account for our observations. This took into account 'soft' vibrational modes of the alkyl chains and the fact that the two redox partners had different inter-ring angles (see Haiss *et al.*, *J. Phys. Chem. C*, 2007, **111**, 6703).



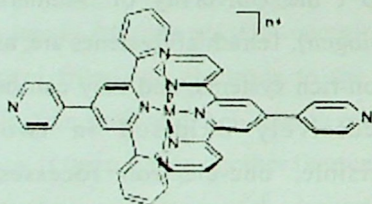
We wondered if this was a general picture for redox molecules 'wired' to two metal contacts. We widened our studies to a structurally-related pyrrolo-tetrathiafulvalene olecule 6PTTF6 (made for us by Jan Jeppesen's group at the University of Southern Denmark; pictured above with the viologen). Tetrathiafulvalenes are, as previously noted, extremely electron-rich systems, and they can be successively oxidised in two, reversible, one-electron processes. However, once again, in aqueous electrolytes we were only able to study the first process because, at more positive potentials, we would encounter anodic desorption of the thiol groups. The behaviour this olecule showed is seen (*left*). Here, the molecular low value, about 0.5 nS, to a high value (2.5 nS) at

Graph showing Conductance / nS versus Potential / V vs. Pt quasi. The plot shows two distinct peaks in conductance. The first peak is centered around -0.2 V with a maximum conductance of approximately 2.2 nS. The second peak is centered around 0.1 V with a maximum conductance of approximately 2.0 nS. The conductance is low (around 0.5 nS) at potentials more negative than -0.4 V and more positive than 0.4 V. Data points are shown with error bars and a smooth curve is fitted to the data.

approximately the half-wave potential for the redox process, and then falls again at more positive potentials. In other words, the 'soft gating' model is *not* needed for this molecule although it has nearly the same structural features as the viologen. It obeys the original K-U model (see E. Leary *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 12204). Moreover later, we studied this molecule in an ionic liquid (BMIM-N(Tf)₂), and here, we could study *both* redox waves (*left*). Again, *both* redox processes showed the K-U 'off-on-off' switching behaviour (see N.J. Kay *et al.*, *J. Am. Chem. Soc.*, 2012, **134**, 16817).

Metal-terpyridyl complexes as 'wires' and as 'switches' (i) As 'wires'.

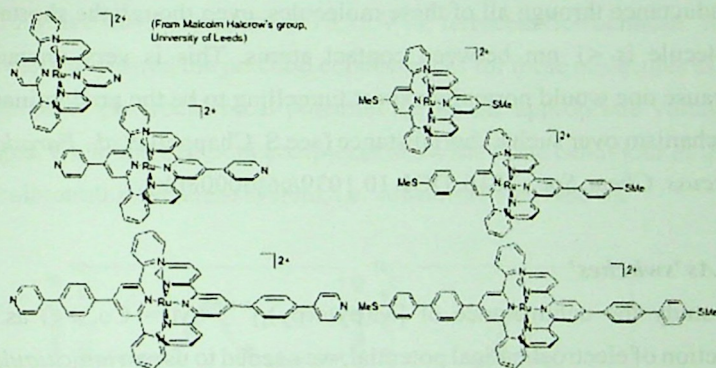
We wanted to widen our studies to explore structure-property relations more thoroughly in this area. In particular, we wanted to employ molecules that did not have flexible alkylthiol linkers, as we expected



that these would be less affected by 'soft gating'. We therefore turned our attention to transition metal-terpyridyl complexes. These have a number of advantages for our

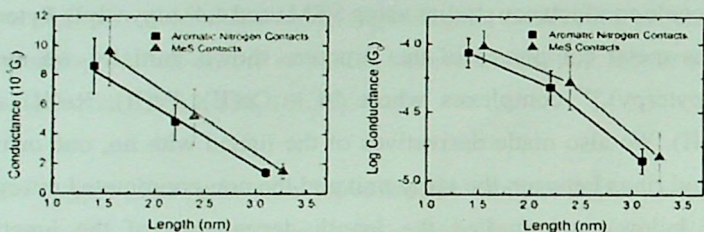
purpose. Firstly, terpyridyls are good ligands for a wide cross-section of transition and other metal centres. Secondly, their complexes are often reversibly redox-active. Thirdly, terpyridyl ligands generally favour *mer* octahedral coordination geometry in [M(terpy)₂]ⁿ⁺ complexes, giving a defined 'linear' geometry as long as a suitable contacting group can be attached to the central pyridine ring. Finally

an important consideration for students undertaking multidisciplinary projects who are not specialist synthetic chemists, the ligands often straightforward to synthesise by condensation reactions from cheap precursors. We chose the ligand 'pyterpy' (left) for our initial studies; the pendant 4-pyridyl group is able to coordinate reliably to gold surfaces and has been widely studied (one of the earliest single molecule conductance studies using STM used 4,4'-bipyridyl). Pyterpy forms metal complexes of the structure shown. Initially, we made $[M(\text{pyterpy})_2]^{2+}$ complexes where $M = \text{Co(II)}, \text{Fe(II)}, \text{Ru(II)}$ and Cr(III) . We also made derivatives of the ligand with no, one or two phenyl rings between the terpy unit and the non-coordinated nitrogen (see below) and studied the length dependence of the junction conductance.



As shown in the picture above, we also made similar ligands with pendant thioether groups. These are also good ligands for gold surfaces, and we examined the conductances of these molecules. We found that the conductance-length relations in these systems were

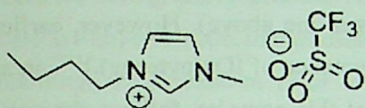
unusual in two ways. Firstly, the conductances fell with length much more slowly than one would expect for an oligophenyl system; β was around 1 nm^{-1} for both of these families of molecules, rather than 4 nm^{-1} as expected for tunneling through an oligophenyl series. Secondly, in fact a linear fit to the conductance- length data was better than a log fit for both series, as shown below.



Both of these facts argue in favour of a hopping mechanism for conductance through all of these molecules, even though the shortest molecule is $<1 \text{ nm}$ between contact atoms. This is very unusual because one would normally expect tunnelling to be the predominant mechanism over such a short distance (see S. Chappell *et al.*, *Faraday Discuss. Chem. Soc.*, 2016, DOI: 10.1039/c6fd00080k).

(ii) As 'switches'

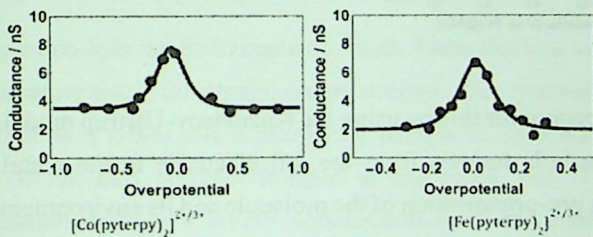
To study the conductance of $[\text{M}(\text{pyterpy})_2]^{2+/3+}$ ($\text{M} = \text{Co}, \text{Fe}$) as a function of electrochemical potential, we needed to use an *ionic liquid*; the Fe(II)/(III) redox process in particular occurs at too positive a potential for us to be able to use an aqueous electrolyte. Ionic liquids are simply salts that are molten at room temperature. There is much current interest in these as electrochemical media. For our purposes,



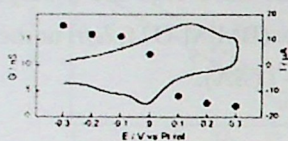
their main advantages are that they are chemically inert, have a wide potential 'window', and are non-volatile. The latter is an important consideration

because we cannot use volatile nonaqueous electrolytes in our STM kit because they tend to attack the glues and circuit board components in the STM scanners etc. The ionic liquids we have used are *n*-butyl methylimidazolium trifluoromethylsulfonate (BMIM-OTf; *left*) or the corresponding bis(triflyl)amide salt (BMIM-TFSA).

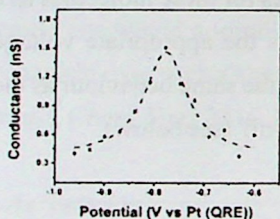
Both the Fe and Co complexes showed chemically-reversible M(II)/M(III) redox processes in BMIM-TFSA, the Co complex at -0.15 V and the Fe complex at $+0.75$ V vs. ferrocene/ferrocinium. We therefore measured the junction conductances for these molecules as a function of electrochemical potential across the appropriate voltage ranges. We found that both complexes show the same behaviour as the pyrrolotetrathiafulvalene system, i.e. 'off-on-off' (see below).



Therefore, clearly, these molecules follow the original Kuznetsov-Ulstrup model (the fit is shown as a line above). However, earlier, another team had studied the conductance of $[\text{Os}(\text{pyterpy})_2]^{2+/3+}$ in an aqueous buffer, and had shown that this complex follows the same pattern as our viologen system, i.e. a broad, sigmoidal increase in conductance across the Os(III)-Os(II) redox process (*left*).



Since the Os complexes are isoelectronic with the Fe complexes, it was hard to explain why the different molecules should show such different behaviour. Therefore, we wondered whether it might be the *medium*, not the *molecule*, that controls which behaviour is seen.



Accordingly, we then re-examined the viologen molecule in ionic liquid electrolyte. Sure enough, in ionic liquid, the viologen shows 'off-on-off' behaviour! (see *left*).

We can account for this by using the Kuznetsov-Ulstrup model. In this model the hole tunnels from the left electrode to the metal centre following pre-organisation of the molecule and its environment so that charge transfer can follow a Frank-Condon type transition. The molecule and its environment then relax, with the hole losing

coherence during this relaxation. The hole then tunnels from the metal centre to right electrode. In the adiabatic limit, which is used here in the modelling, the relaxation prior to the second hole transfer step is partial. Following the first hole transfer the M(II) centre is oxidised and then subsequently reduced following charge transfer to other electrode. In the limit of strong electronic interactions between the redox centre and the electrodes the steady state current flow through the molecular junction is given by:

$$i = 2en \frac{\tilde{k}_1 k_2}{k_1 + k_2}$$

Where n represents the number of holes or electrons that can transfer in a "cascade" while the redox centre and its environment relaxes, and e is the electronic charge. k_1 and k_2 are electrochemical rate constant expressions.

The equation for the two-step adiabatic model of Kuznetsov and Ulstrup is:

$$J_{enh} \approx J_0 \exp\left(-\lambda/4k_B T\right) \frac{\exp\left(\frac{e|V_{bias}|}{4k_B T}\right)}{\cosh\left(\frac{e(0.5-\gamma)V_{bias} - e\xi\eta}{2k_B T}\right)}$$

In this equation k_B is the Boltzmann constant, V_{bias} the bias voltage, T the temperature and e the charge on an electron. The overpotential is represented as η while γ is a modelling parameter representing the fraction of the bias voltage dropped at the redox site. The total reorganization energy is λ , which includes both inner and outer-sphere contributions. ξ The fraction of the electrochemical potential experienced at the redox site is ξ .

The additional terms here are as follows: κ is the electron transmission coefficient, ρ is the density of electronic states in the metal electrodes near the Fermi level and ω_{eff} is the effective nuclear vibrational frequencies. The subscripts L and R refer to the left and right electrodes, respectively. Using these equations a numerical form for the enhanced current flowing across the molecular junction (*jenh*) can be obtained and single molecule conductance data vs. electrochemical potential can then be quantitatively analysed with respect to this model.

In this case, the fitting parameters for the cobalt complex are $\lambda = 0.80$ eV, $\xi = 0.5$ and $\gamma = 0.40$, while those for the iron complex are $\lambda = 0.77$ eV, $\xi = 0.8$ and $\gamma = 0.55$. The reorganisation energies of the pyterpy complexes are considerably less than a similar analysis for both the first and second redox transitions for the pyrrolo-tetrathiafulvalene bridge in ionic liquid environment, which gave values of $\lambda = \sim 1.2$ eV. It is also noteworthy that for both the viologen and pyrrolo-TTF examples $\xi = \sim 1$ was obtained. This value corresponds to the full electrochemical potential being experienced at the redox centre, indicative of the short Debye screening lengths of the ionic liquids and effective structuring of the ionic liquid in the nano-gap junction. In the case of the pyterpy complexes, ξ is lower indicating that the screening is not so effective. This may be due to the more “voluminous” redox centre with the metal ion redox centre being surrounded by a bulky ligand shell.

Part 2: Towards Molecular Scale Sensors. (i) A Molecular Water Sensor.

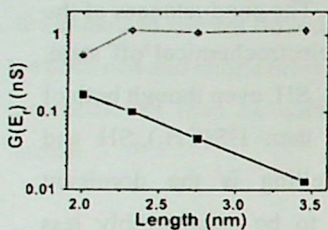
During our work with the viologen molecule and the pyrrolo-tetrathiafulvalene molecule, we also carried out a study of the conductances of single alkanedithiol molecules, $\text{HS}(\text{CH}_2)_n\text{SH}$, and this led to an interesting and unexpected finding. The conductances of the viologen and the pyrrolo-TTF, even in their electrochemical 'off' state, were both much higher than that of $\text{HS}(\text{CH}_2)_{12}\text{SH}$, even though both of these molecules are considerably longer than $\text{HS}(\text{CH}_2)_{12}\text{SH}$ and therefore, on the expectation that tunnelling is the dominant mechanism in the 'off' state, they ought to be considerably less conductive (since conductance decays exponentially with length).

Molecule	Conductance (nS)
6V6	0.49
6PTTF6	0.81
6Ph6	0.68
$\text{HS}(\text{CH}_2)_6\text{SH}$	2.5
$\text{HS}(\text{CH}_2)_{12}\text{SH}$	0.012

We made the molecule 1,4- $\text{HS}(\text{CH}_2)_6\text{C}_6\text{H}_4(\text{CH}_2)_6\text{SH}$ ('6Ph6') and showed that even though this is not redox-active (and hence its conductance is not electrochemically 'gated'), it still has a conductance similar to that of the viologen 6V6 and the pyrrolo-TTF molecule 6PTTF6 in their 'off' state (see Table above). We then made some similar molecules with different substituents on the phenyl ring, and showed that the conductance significantly varied, with electron-

donating groups (Me, MeO) giving higher conductances and electron-withdrawing groups (C_6F_4) a lower value (see E. Leary *et al.*, *Chem. Comm.* 2007, 3939).

Our initial model for this behavior was that the conjugated group acts



as a 'well' in a molecular analogue of an inorganic double tunneling barrier.

We decided to explore this idea further with a family of oligothiophene molecules, $HS(CH_2)_6(C_4H_2S)_n(CH_2)_6SH$ ($n = 1, 2, 3, 5$).

Making the molecule longer (by increasing the number of thiophene rings) should decrease conductance, but on the other hand, it will make the central oligothiophene unit more conjugated, which should increase its effectiveness as a 'well', just as putting electron-donating groups onto the phenyl ring in 6Ph6 also makes it more effective as a 'well'.

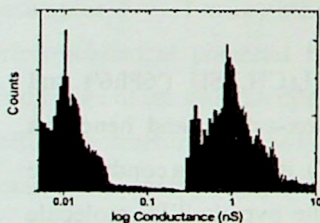
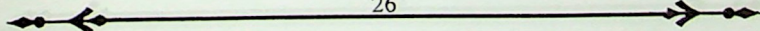


Figure 1 Showing conductance histogram obtained for the terthiophene molecule in the presence of water (right hand peak) and its absence (left hand peak). Note the log scale!

In fact, when we measured the single molecule conductances of these molecules, we found that they *increased* somewhat from $n = 1$ to $n = 2$, then remained almost unchanged for $n = 3$ and $n = 5$ (see upper line in plot left). Initially, we thought

that this might indicate that the two opposing factors (increasing length; increasing conjugation) were simply cancelling each other out. However, our theoretician co-workers at Lancaster University calculated the conductances of the molecules and found that they should, in fact decrease exponentially with length (the lower line in the previous plot). After some considerable discussion of what might account for this difference, we discovered that the presence of water is an essential factor in determining the experimental conductances; the measurements were made at room temperature in ambient laboratory conditions, and it is known that under these conditions, several monolayers of water are present on 'bare' gold surfaces. When the calculations were repeated with water molecules interacting with the thiophene rings, the calculated values of conductance were in much better agreement with experiment, because the relatively small shifts in frontier orbital energies caused by arene...H interactions significantly increase junction conductance by slightly shifting the transmission resonances for the system towards the contact Fermi energy, and the effect is more substantial for the longer, more conjugated molecules.

We then repeated the conductance measurements using a home-built inert atmosphere chamber purged with dry argon. We saw a dramatic decrease in conductance for the terthiophene molecule in argon (*see histogram plot, previous page*). Furthermore, in argon containing water vapour, the conductance was restored, proving that it is indeed water (and not oxygen) that is responsible for the effect.



(ii) Charge transfer complexes

Charge transfer complexes form when an electron-rich conjugated system interacts with an electron-deficient conjugated system. For instance, when tetracyanoethylene (TCNE), a pale yellow strongly electron-deficient compound, is dissolved in toluene, an intensely orange solution forms. The orange colour arises because of a charge transfer absorption in the visible spectrum owing to the interaction of TCNE with the donor toluene π -system. With much stronger donors, like tetrathiafulvalene, complete charge transfer and the formation of $\text{TTF}^+\text{TCNQ}^-$ salts can occur. These can have unusual solid-state properties, for example TTF.TCNQ was the first organic metal (Ferraris *et al.*, *J. Am. Chem. Soc.*, 1973 95 948).

We reasoned that if water can boost the conductance of our terthiophene molecule, then the formation of a charge transfer complex should also have an effect upon molecular conductance. Accordingly, we investigated the effect of TCNE binding upon the conductances of the above terthiophene, and also of the corresponding phenyl compound 6Ph6. First, we characterized the formation of the TCNE complexes in solution in CH_2Cl_2 . Linear regression analysis of the charge transfer band responsible for the orange colour of the 6Ph6:TCNE complex was analysed using commercial 1,4-diethylbenzene as a surrogate. This procedure yields both the extinction coefficient for the CT band, and the equilibrium constant for formation of the donor:acceptor complex. The latter was *ca.* 1 for 1,4-diethylbenzene. For the terthiophene:TCNE complex, it was estimated

at *ca.* 20. As expected, the more conjugated and more electron-rich terthiophene unit gives the stronger TCNE complex.

Next, the conductances of the molecules were measured using the STM break junction technique. We found that the conductance of the terthiophene molecule was boosted by a factor of about 25 when complexed to TCNE, while the phenyl molecule had its conductance boosted by about a factor of 15.

How can we account for this? How can TCNE complexation increase the conductance of a single molecule?

According to the calculations of our colleagues in Lancaster, the answer is that the TCNE introduces an alternative conductance pathway in the system, and because there is now a partially-occupied orbital in the system in the TCNE unit, this must by definition occur at the Fermi energy of the metal contacts. A resonance close to the Fermi energy in a molecular junction will necessarily induce a very high conductance in the system, almost regardless of the detailed molecular structure (see A. Vezzoli *et al.*, *Nanoscale* 2015 7 18949).

Future prospects

In our electrochemical studies of 'molecular redox switches', we have seen that so far, we can only achieve a relatively small boost in junction conductances by controlling the redox potential (and hence, to a degree, the Fermi energies of the contacts). About the largest factor

increase in conductance we have seen is 6-fold (for 6V6 in aqueous solutions).

In contrast, for 6-terthiophene-6, we observed a factor of about 100-fold increase in its conductance upon introducing water into the nanogap, and then about another 25-fold by forming a charge transfer complex with TCNE. These observations could ultimately give rise to 'designer' molecules that could act as selective sensors. For instance, we could envisage making a crown ether derivative that could selectively bind to a particular alkali metal cation, changing its conductance.

In the future, we shall widen our work to encompass molecules bearing unpaired electrons (metal complexes, free radicals) for 'spintronics' applications, and we have already begun using alternative ferromagnetic metals as contacts for this purpose (mainly cobalt and nickel). We have also started work on semiconductor substrates, in particular GaAs, for photonics applications.

There are many challenges to overcome before molecules can perform electronic functions in circuits. But in establishing techniques for fabricating and measuring single molecule junctions, we have uncovered some unexpected and remarkable results and we are beginning to learn to control these effects.



Prof. Simon Higgins graduated with First Class Honours (1981) from the University of Southampton, United Kingdom and remained there for his Ph.D. studies with Bill Levason, on the coordination chemistry of nickel and iron in higher oxidation states, before postdoctoral work in Leeds with Bernard Shaw on diphosphine-bridged bimetallic complexes, and then Oxford with Andrew Hamnett on the electrochemistry and properties of conducting polymer films. He moved to Liverpool as a Lecturer in 1989 and was promoted to Senior Lecturer in 2003, Reader in 2007 and was appointed to a Chair in 2011. Prof. Simon has published over two hundred research articles in international refereed journals. Over the years in Liverpool, U.K his research interests have encompassed conducting polymers functionalised with metal complexes and other moieties for electrocatalysis and sensing, the synthesis of organic semiconductors for organic electronics, and (with his colleague at Liverpool, U.K., Prof. Richard Nichols) structure-property relations in single molecule electronics. Currently he is working as an external examiner for the Department of Chemistry, University of Jaffna, Sri Lanka.

