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Metal / molecule / metal junction studies of organometallic and coordination complexes; what can transition metals do for molecular electronics?

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Abstract

The science of 'molecular' electronics has been stimulated by the evolution of reliable techniques for fabricating and testing metal / single molecule / metal junctions over the last fifteen years. Transition metals offer the possibilities of redox activity, stable paramagnetic states and, in some cases, relatively narrow HOMO-LUMO separation, factors that make them of interest for incorporation into such junctions. In this short review, we describe our progress to develop reliable contacts for organometallic molecular wires, to test the effects of incorporating metal centres into molecular wires, and to examine the electrochemical gating of redox-active coordination complexes.

Introduction: the techniques.

The evolution of techniques permitting the creation and electrical characterisation of metal / single molecule / metal (MSMM) junctions over the last two decades has greatly stimulated molecular electronics and molecular devices. Although most early studies focussed on organic molecules, a very early landmark from this field was a study in which $[Co(terpy)_2]^{2+/3+}$ (terpy = 2,2':6',2''-terpyridine) moieties with pendant thiol binding groups were used to form gold / single molecule / gold junctions using the electromigration break junction technique (see later).[1] The metal-centred redox activity of the molecules enabled the demonstration of 'single molecule transistor' behaviour, gated by a third electrode, and the paramagnetism of the low spin Co(II) form was crucial for making a second observation, the operation of the Kondo effect under cryogenic conditions. This illustrates two of the most important properties transition metal complexes can bring to the field of molecular devices, namely redox activity and the possibility of stable paramagnetic states.

The field of single molecule junctions involving transition metal complexes has been very recently reviewed.[2] Accordingly, this short review focuses on the work of our group and that of our collaborators on single molecule conductance measurements involving transition metal complexes, made using scanning probe microscopy methods. We begin with a brief introduction to the techniques employed.

Here, we focus on specifically *single* molecule techniques. Methods in which metal / molecules / metal junctions are made using self-assembled monolayers on flat metallic surfaces (e.g. mercury or template-stripped silver or gold) onto which a probe microelectrode (e.g. a mercury drop, or more recently, a GaIn eutectic electrode) is lowered to electrical contact have a longer history[3] and can be regarded as complementary to MSMM junction techniques. The former methods have the advantage that they are amenable to the 'bottom-up' construction of complex molecules using surface chemical synthesis methods, including metal complexation reactions.[4-7] Moreover, with the current state of the art it is difficult to envisage the incorporation of truly single molecule junctions into working electronic circuits, whereas it is conceivable that self-assembled monolayers could form the basis for a suitable technology.

However, (i) it is not possible to know how precisely many molecules are involved in any given junction in monolayer microelectrode junction experiments, making individual molecular conductances hard to determine and making molecule to molecule comparisons in structure:property studies less reliable, and (ii) cooperative effects can occur between molecules in self-assembled monolayers; it has been theoretically shown that conductance does not necessarily scale linearly with the number of molecules in a metal / molecule / metal junction with more than a single molecule.[8-10] In addition, single molecule conductance measurements are invaluable for probing conduction mechanisms and new molecular electronics phenomena, for instance negative differential resistance, new mechanisms for rectification[11] and gating,[12] thermoelectric effects, quantum interference phenomena and spintronics.[13] Importantly, it also enables the testing of novel binding groups that would not support the formation of conventional self-assembled monolayers on gold, yet are capable of forming MSMM junctions with interesting properties, such as 4-pyridyl or thioethers.[14]

The earliest studies of MSMM junctions typically used so-called break junction (BJ) methods.[15-17] Classical solid-state electronics techniques are used to fabricate a very thin metallic wire. This can be deposited on a thin insulator film. Various methods can then be used to break the wire, for example electromigration (EMBJ) or mechanical

control (MCBJ). In the latter case, the device is poised on a flexible substrate that can be bent by turning a screw from below, giving very fine (of the order pm) control over the distance between the resulting broken ends of the wire. Suitable molecules, having contact groups at either extremity, may bridge the broken wire, and if the insulator film is on top of a third metallic contact, it is also possible to gate such junctions electrically. Progress in this method means that it is now possible alternately to open and close the metallic contacts by bending and relaxing such a device multiple times, to obtain statistical data.[18-20] This is important because in some of the early work, very low success rates meant that only a very few junctions (sometimes only one or two) could be studied,[17] so that it was not possible definitively to establish that single molecules were involved in the junctions.

The demonstration that the scanning tunnelling microscope could be used to make and characterise MSMM junctions was an important development that enabled many more groups to enter this field. The most commonly-used implementation of this technique is the so-called STM break junction (STMBJ) method, first described by Xu and Tao in 2003.[21] Here, a metal tip is first held at tunnelling distance above a metal substrate in the presence of suitable molecules, either in solution or adsorbed to the substrate. The molecules are designed to have binding groups (e.g. thiol, thioether, pyridine, amine) at each end. The feedback loop is disabled and the tip is pushed into the substrate while a bias voltage is maintained and the resulting current is measured. The tip is then retracted. As the gold filament this creates thins, steps down in current are observed in the resulting current-distance plot, until the last gold atomic point contact breaks; these steps down in current correspond to the quantum unit of conductance G_0 (= $2e^2/h$ where e is the electron charge and h is Planck's constant; 77.48 nS) because in the case of gold, a single point contact has a single quantum conductance channel. After the final point contact has broken it is possible for a molecule to bridge between the substrate and tip. In this case, the tunnelling current at a given vertical distance will be larger than in the absence of a molecule and as the tip retraction is continued, the molecule may re-orient itself within the junction. This typically leads to a plateau in the current-distance plot, where the current does not significantly change as a function of distance. However, as retraction continues, at some point the junction must break down, and this is marked by a significant decrease in tunnelling current, typically down

to a level below the noise limit for the measurement. In any measurement of this kind, there is little or no control over such factors as the precise nature of the gold-substrate interaction, the orientation of the molecule(s) in the gap, and sometimes even the exact number of molecules in the junction. It is therefore accepted practice to repeat the measurements many hundreds or thousands of times, and to analyse the results statistically.[22, 23]

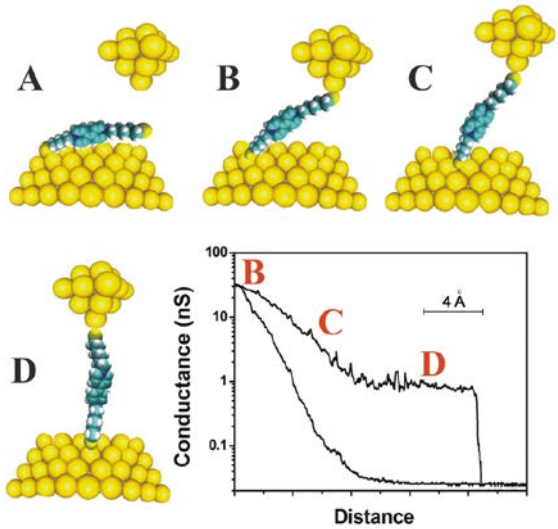


Figure 1 An illustration of the STM $I(z)$ method for creation and electrical characterisation of MSMM junctions . Inset: junction conduction as a function of retraction distance (z) for a MSMM junction during events labelled B-D (upper trace) compared with exponential conductance decay for an empty junction (lower trace). From reference [23] reproduced by permission of the PCCP owner societies.

A variation on this method is the *I(z)* technique first described by Haiss et al in 2003.[24] Here, the STM tip is not pushed into the substrate, but is held above the substrate at an initial vertical height (z) that is less than the molecular length (Figure 1). It is possible once again for a molecule spontaneously to bridge between the tip and substrate. The tip is retracted with the feedback mechanism disabled while the tunnelling current is monitored. In the same manner as for the STMBJ method, this experiment is repeated many times and the results are analysed statistically. The starting position of the tip is controlled by the set point current and tip bias prior to the retraction event, so the initial z can be calibrated by analysis of those current –distance events in which pure exponential decay occurs with no molecule bridging the gap. Importantly, both contact and non-contact variations of the STM method can be implemented in electrolyte solution, provided that the tip is coated first with an

insulator to minimise Faradaic currents, and that a bipotentiostat is used since this constitutes a four-electrode electrochemical setup where the two working electrodes are the tip and substrate. Further details of these and related experimental techniques and of the statistical approaches to data analysis have been given in recent reviews.[22, 23, 25]

One issue that is often addressed in MSMM junction studies is the mechanism by which conductance occurs. The consensus view is that typically, for molecules shorter than 3-4 nm, a coherent resonant tunnelling mechanism dominates. For such systems, conductance decays exponentially with distance, and it is expected to be temperature-independent since tunnelling is activationless. If a molecule is placed in a MSMM junction at zero bias, since the Fermi energy E_F of the system is constant this means that E_F must lie between the HOMO and LUMO of the molecule. If it lies closer to the HOMO then hole transport via the HOMO level dominates the conductance. If it lies closer to the LUMO, electron transport via the LUMO orbital dominates. Whether it lies energetically closer to the HOMO or to the LUMO is determined partly by the nature of the molecular backbone, but mainly by the nature of the contact groups.

For small biases, the tunnelling barrier can be regarded as rectangular, and the tunnelling current is then given by the expression $I_T = Ae^{-\beta L}$ where A is a prefactor that is mainly (but not exclusively) controlled by the nature of the metal-molecule contact chemistry, β is the decay factor, which is governed mainly by the nature of the molecular backbone, in particular the HOMO-LUMO gap, and L is the molecular length. The decay factor β has units of reciprocal length, and varies from *ca.* 10 nm^{-1} for alkane backbones, to 3-4 nm^{-1} for para-$[-C_6H_4-]_n$ and *ca*. 1 nm^{-1} for the more conjugated oligo-2,5-thienyls. The lowest values of β yet found are *ca*. 0.19 nm^{-1} for fused porphyrin tapes,[26] between *ca*. 1.0-0.1 nm^{-1} for oligoynes (the β values in the latter case proved to be significantly solvent-dependent),[27, 28] and 0.06 ± 0.004 nm^{-1} for a series of extended viologen molecules.[29]

For larger biases, the barrier can become effectively triangular and then conductance occurs by the field emission (sometimes called Fowler-Nordheim tunnelling) process.

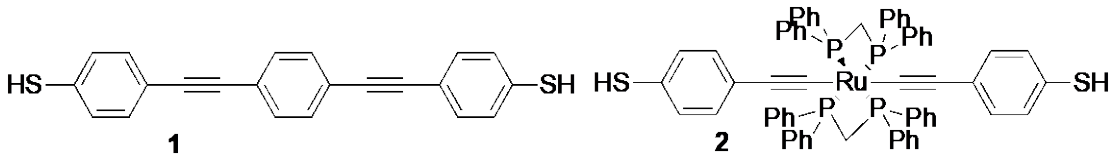
The onset of this behaviour can be determined by measuring the current-voltage relationship for MSMM junctions and then plotting $\ln(I/V^2)$ *vs*. $\ln(1/V)$, a so-called Fowler-Nordheim plot; for biases where the barrier is still effectively rectangular, the slope of such a plot is positive, and it becomes negative once field emission occurs, giving rise to a minimum, which is therefore a measure of the barrier height at zero bias.

Because hopping mechanisms involve a linear decrease of conductance with distance, hopping becomes important for molecules longer than 3-4 nm. A consequence of this linear relation is that it can be difficult to distinguish between a tunnelling mechanism with a very low value of β, and a hopping mechanism, particularly since many highly-conjugated systems are also redox-active. Temperature-dependent conductance measurements can help here, since tunnelling is an activated process, but this is not without complications. For instance, the temperature-dependent conductance observed for a non-conjugated, thioether-contacted tercyclohexylidene has been attributed to the temperature-dependent Fermi distribution function of the leads, within a simple resonant tunnelling model.[30]

Metal-alkyne complexes as wires; single molecule measurements.

Among families of conjugated organic oligomers, oligophenyleneethynylene (OPE) systems have been extensively explored in molecular electronics for over 20 years.[31, 32] Their syntheses are generally straightforward, they are structurally rigid rod-like molecules making them conformationally simple and they have comparatively low β values (*ca*. 0.2 nm^{-1}) in MSMM junction experiments.[33] Terminal aryl alkynyl species are good ligands for transition metals, and there has been much interest in developing mono- and poly-metallic wire-like molecules for molecular electronics in which oligophenyleneethynylene-based contact groups act as ligands to metal centres, particularly *trans*-$[Ru(PR_3)_4(C{\equiv}CAr)_2]$ and *trans*-$[Pt(PR_3)_2(C{\equiv}CAr)_2]$ (where PR_3 denotes any phosphine, including chelating examples in the case of the Ru(II) complexes); to date, the great majority of such studies have involved self-assembled monolayer-based microelectrode contact or scanning probe spectroscopy (non-contact) based methods. For example, Liu *et al*.[34] compared the OPE **1** with the similar Ru-containing molecule **2** (structures in Scheme 1). Scanning tunnelling

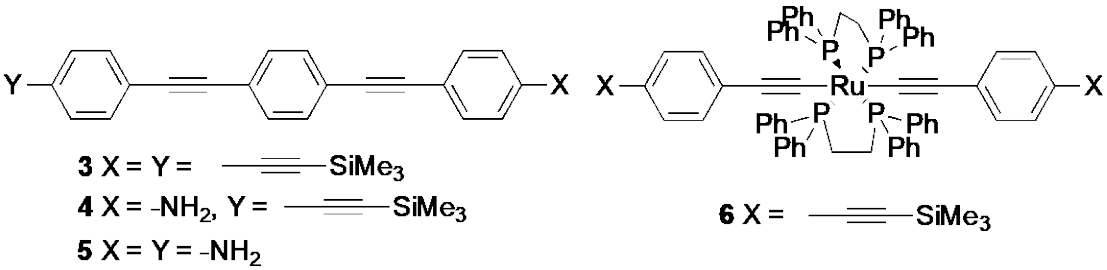
spectroscopy (STS) on the conjugated molecules diluted into an alkanethiol layer on a Au substrate was used to determine apparent heights of the conjugated molecules and from this, an approximation of relative decay constants for **1** and **2** could be obtained; **2** had a smaller decay constant than **1**. STMBJ single molecule conductance determinations on **1** and **2** gave values of $(4.7\pm2.6) \times 10^{-5}G_0$ and $(2.5 \pm 0.9) \times 10^{-4}G_0$ (3.6 ± 2.0 and 19 ± 7 nS), respectively. Barrier heights for **1** and **2** were determined using Fowler-Nordheim analyses of current–voltage behavior obtained with conducting probe atomic force microscopy (CP-AFM) experiments; these were 0.66 ± 0.11 and 0.25 ± 0.03 eV, respectively. It was postulated that the larger conductance and lower barrier height for the metal complex **2** were related to the HOMO energy being closer to the metal contact Fermi energy than the purely organic OPE **1** (thiol contact groups almost invariably give rise to HOMO-dominated conductance[35, 36]).



Scheme 1 Structures of molecules **1** and **2**.

Although thiols have a very high binding energy to gold electrodes, their use in MSMM junctions is not without complications. Molecules with thiol contact groups can give different MSMM conductance values depending upon the exact nature of the thiol coordination to the gold surface.[37, 38] It has been suggested that weaker binding groups such as amines give sharper peaks in STM-BJ histograms because such groups exclusively bind to under-coordinated gold atoms.[39] However, we[40] and others[38] have found evidence that amines can also give multiple conductance values in STM conductance experiments. STM imaging and other techniques previously established that $Me_3SiC{\equiv}C$- (TMSE-) terminated molecules form stable self-assembled monolayers on gold. Since this group is relatively unreactive towards transition metal centres (in contrast to many other potential contact groups, particularly thiols or isocyanides), it was reasoned that it could be a useful contact group for metal complexes. A simple OPE with TMSE contact groups (**3**; Scheme 2) gave only a single conductance value in STM *I(s)* experiments, whereas analogous amine-contacted OPEs (**4** and **5**; Scheme 2) gave more than one value.[40] This, and earlier studies,[41]

supported the idea that the bulky, weakly-binding TMSE group uniquely binds only to defect sites on gold surfaces, thus giving only one conductance value for a given molecule. The latter is an advantage, but the weak binding to defect sites also results in rather low conductance values owing to weak coupling.[42] That TMSE is a weak contact group is suggested by the fact that in all these experiments, the 'hit rate' (the proportion of individual STM tip withdrawal experiments that result in a current-distance profile characteristic of the presence of a molecule in the tip-substrate gap) is small, 10-15% in the case of the metal complexes.



Scheme 2 Structures of molecules **3–6**.

Quartz crystal microbalance and XPS measurements on gold surfaces treated with both **4** and **6** were consistent with monolayer formation with the TMS groups intact,[42] ruling out the possibility that junctions form under these conditions by cleavage of the Me_3Si- groups, in a manner analogous to the use of Me_3Sn- groups to form direct Au-C bonds in MSMM experiments.[43] Direct interaction of TMSE with gold is also supported by the fact that neither stable monolayers on Au surfaces, nor junctions in attempted MSMM experiments, form when the Me_3Si- groups are replaced with Me_3C-.[42] Bulkier examples such as triisopropylsilylethynyl also fail to give junctions. The conductance value measured for **6** (Scheme 2; $(5.10 \pm 0.99) \times 10^{-5}\ G_0$ (3.9 ± 0.76 nS); see data in Figure 2[42] is a little smaller than that found earlier for thiol-contacted **2**,[34] but **2** is somewhat shorter than **6** as a result of the two additional carbyne units in the latter; **6** was also significantly more conductive than its 'all-organic' analogue, **4** $(2.75 \pm 0.56) \times 10^{-5}\ G_0$ (2.1 ± 0.43 nS) (Figure 2).

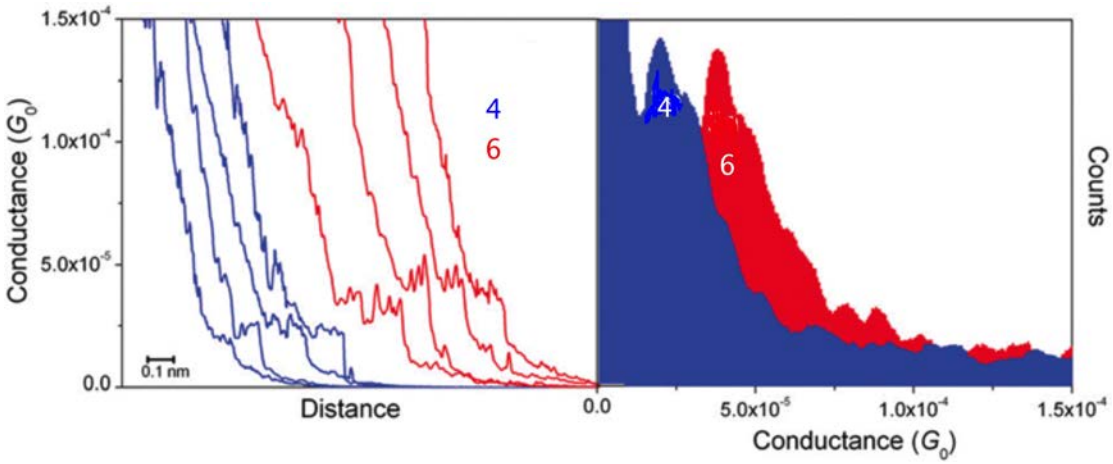
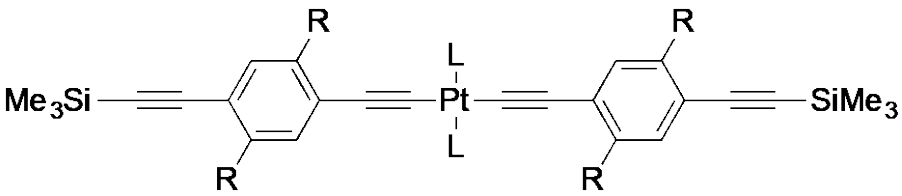
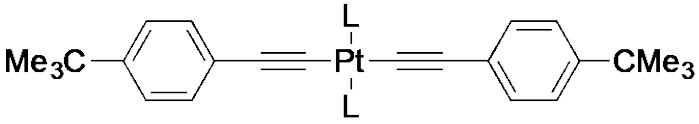


Figure 2 Typical conductance traces from **4** and **6** using the *I(z)* method and conductance histograms derived from *I(z)* measurements. The curves are shifted horizontally for clarity. Conductance data are presented in units of the conductance quantum $G_0 = 2e^2/h$ = 77.5 μS. Setpoint current = 20 nA and tip bias = 0.6 V. The one-dimensional histograms here are constructed by binning of the data from those conductance traces containing a plateau characteristic of molecular junction formation. From ref., [42] used by permission of the Dalton Transactions owner society.

The use of the weakly-binding TMSE contacts in this work revealed some additional unexpected and interesting findings regarding the formation of molecular junctions with structurally-complex molecules and sounded a cautionary note for the design of more sophisticated molecules for molecular electronics studies. In a wider study of the conductance of Pt(II)-alkynyl complexes contacted by TMSE groups, we observed an interesting difference between the behavior of molecules. Thus, while molecules **7a** and **7b** (Scheme 3) bearing solubilizing hexyloxy groups had very similar conductances, ((3.1 ± 0.9) × 10^{-5} G_0 or 2.4 ± 0.7 nS) and ((3.2 ± 0.8) × 10^{-5} G_0 or 2.5 ± 0.6 nS) respectively, suggesting no influence of the supporting phosphine on conductance as also found earlier for thiol-contacted analogues,[44] complexes **8a** and **8b** (Scheme 3) showed significant differences. Complex **8b** had a conductance of (3.2 ± 1.3) × 10^{-5} G_0 (2.5 ± 1.0 nS), similar to complexes **7**, and like them, it gave a mean break-off distance (2.1 ± 0.15 nm) reasonably consistent with its molecular length (2.4 nm Si…Si). But complex **8a** gave a broader, less well-defined conductance peak at a significantly higher value, (7.9 ± 1.1) × 10^{-5} G_0 or 6.1 ± 0.85 nS) and a mean break-off distance of only 1.70 ± 0.1 nm.



R = OC_6H_{13}; L = PPh_3 (**7a**) or PEt_3 (**7b**)
R = H; L = PPh_3 (**8a**) or PEt_3 (**8b**)



L = PPh_3 (**9a**) or PEt_3 (**9b**)

Scheme 3 Structures of molecules **7**–**9**.

Extensive junction modeling using DFT and NEGF calculations suggested that the results could be rationalised as due to the phenyl rings of the PPh_3 supporting ligands giving an alternative weak contact group in the case of **8a**, such that a significant proportion of junctions are formed in which **8a** bridges substrate and tip via one PPh_3 and one TMSE, accounting for both the higher conductance and shorter break-off distance. For **7a**, this alternative junction geometry is presumably inhibited by the long pendant –OR groups, and in the case of PEt_3 supporting ligands, alkyl group interactions with Au would not be expected to compete with TMSE. Strong supporting evidence for this concept was provided by attempts to measure junction conductances for molecules **9**. These complexes were selected to be as similar as possible to **8a** but with no TMSE contact groups; the bulky Bu^t groups were included to inhibit any possible contact to the aryl rings of the alkynyl ligands.[45] While *I(z)* studies of **9a** (Scheme 3) resulted in a peak in the conductance histogram at $(4.1 \pm 0.6) \times 10^{-5}$ G_0 or 3.17 ± 0.46 nS, with a break-off distance (1.46 ± 0.21 nm) consistent with the dimensions across the aryl rings of the two *trans* phosphine ligands (*ca*. 1.4 nm), *I(z)* experiments on complex **9b** gave no discernable plateaus consistent with any metal | single molecule | metal junctions being formed.[45] Figure 3 shows the relevant histograms.

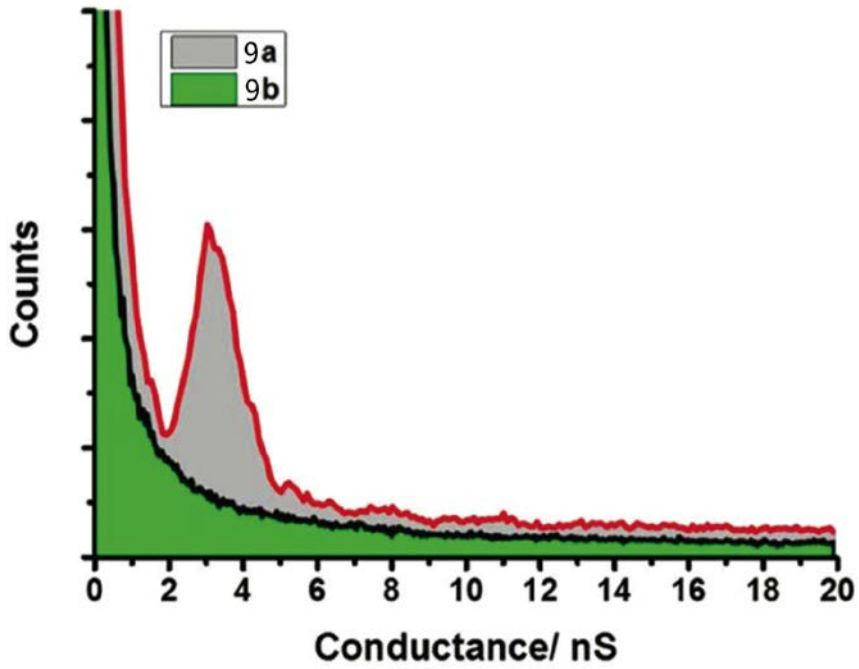
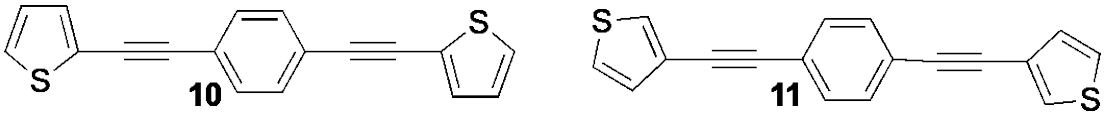


Figure 3 *I(z)* conductance histograms of **9a** and **9b**, constructed from 500 traces. While data from molecule **9b** produces no histogram peak because **9b** has no potential contact groups, **9a** produces a peak because, in the absence of any stronger contact groups, junctions can form from molecules contacted via the aryl rings of the two PPh_3 ligands. From reference [45], edited with appropriate numbering for the present article.

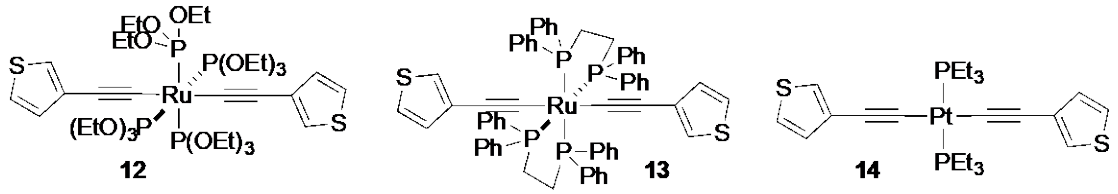
Thiophenes have been demonstrated to work as contact groups in mechanically-controlled break junction (MCBJ) MSMM experiments with organic molecules.[46, 47] For the OPE isomers **10** and **11** (Scheme 4), the 3-thienyl-connected **11** gave a slightly sloped histogram plateau with a marginally higher junction conductance than **10**, which it was suggested was most likely due to slight differences in the gold-thiophene binding for the two isomers. [46]



Scheme 4 Structures of molecules **10** and **11**.

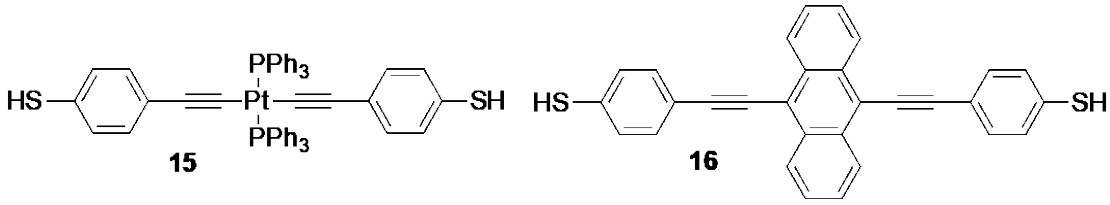
That thiophenes work as contact groups at all is at first sight surprising since thiophenes are generally poor ligands towards transition metals,[48] but it did suggest that they could also prove useful as contact groups for metal-alkynyl and other complexes because thiophenes are, like TMS groups, unlikely to complicate the synthetic chemistry by competing as ligands at the metal centres. Accordingly, 3-

thienyl moieties were used in assessing the conductances of molecules **12-14** (Scheme 5) in MSMM junctions, using both the STMBJ and *I(z)* methods.[49]



Scheme 5 Structures of molecules **12–14**.

As with the TMSE contact group, we found that both the STMBJ and the *I(z)* STM-based methods for junction formation gave very low 'hit rates' for these 3-thienyl-contacted molecules,[49] consistent with the previously-observed poor ligand behavior of thiophenes,[48] and to extract single molecule junction conductance vales, recourse to data selection was necessary. An unsupervised, automated multi-parameter vector classification (MPVC) method, previously verified using data from experiments with an alkanedithiol,[50] allowed the extraction of conductance values from the data. It was found that molecules **11-14** gave quite similar conductance values, (2.70±0.66–3.18±1.04) × 10^{-4} G_0 (STMBJ data), although the purely organic molecule **11** had the lowest value.[49]



Scheme 6 Structures of molecules **15** and **16**.

A very early MCBJ study had compared the conductance of the Pt(II)-alkynyl **15** with analogous organic molecules such as **16** (Scheme 6) and found that **15** had a conductance some 3 orders of magnitude smaller than its organic counterparts (albeit with extremely high bias voltages, ±5 V).[51] This was rationalized as being due to the lack of significant d(π)-p(π) overlap between Pt(II) centres and alkynyl ligands, making the Pt(II) centre effectively 'insulating'. Our results with the thienyl-contacted molecules are obviously not in agreement with this, and we probed possible reasons for the discrepancy by using density functional theory (DFT) in conjunction with transport (non-equilibrium Green's function, NEGF) calculations. We found that for these molecules there was surprisingly little difference in the degree of metal d-orbital character in the frontier orbitals of the Ru(II) and Pt(II) complexes (Figure 4 shows the

HOMOs), and since the Fermi level lies close to the centre of the HOMO–LUMO gap, but shifted slightly towards the HOMO resonance, a HOMO-mediated hole tunnelling mechanism is anticipated in each case.

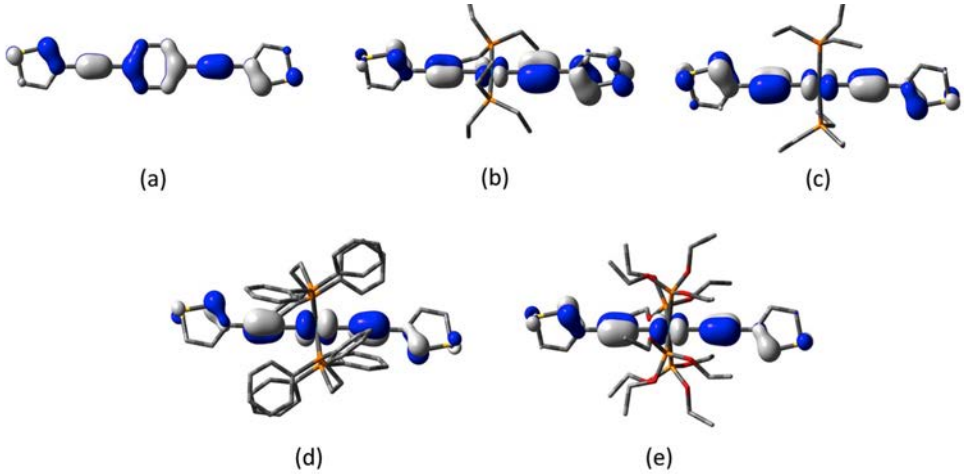
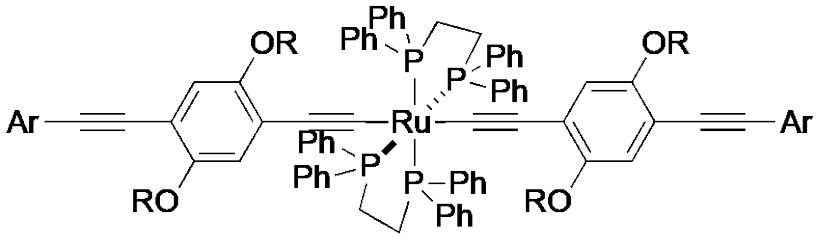


Figure 4 The isosurfaces (±0.04 (e bohr^{-3})$^{1/2}$) of the HOMOs for: (a) **11**, (b) **14** with the thienyl groups perpendicular to the Pt(II) square plane, (c) **14** with the thienyl groups and the Pt(II) coplanar, (d) **13**, and (e) **12**. From reference [49], reproduced by permission of the owner society.

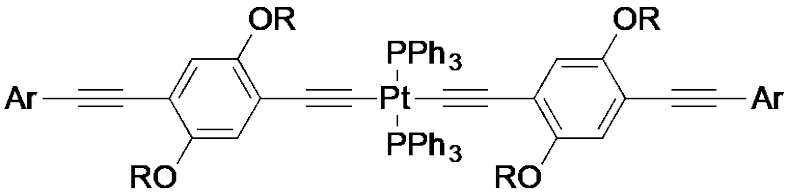
The relative lack of variation in conductance values for **11**-**14** occurs because although the HOMO and LUMO transport resonances differ significantly between the molecules, transport in the vicinity of the middle of the HOMO–LUMO gap is similar for all molecules as the HOMO-LUMO resonance separation is large. This is not necessarily the case for thiol–contacted molecules such as **3**–**6**, where there is much stronger covalent interaction between the gold leads and the thiol, leading to so-called 'gateway state' resonances close to the Fermi energy of the contacts which can strongly perturb the resulting molecular conductances. However, it is also worth pointing out that a family of complexes analogous to **15**, but with different phosphine and phosphite ligands, has been tested in monolayer junctions using a 'crossbar' configuration in which a gold filament coated with a monolayer of the molecule under test is brought into physical connection with a second gold filament. Here it was found that there was no significant variation in current/voltage properties as a function of the P(III) ligand and, more interestingly, the conductances were significantly higher than in analogous experiments with the all-organic analogue **4** (X = SH).[44]

To probe the effect of incorporating Ru(II) and Pt(II) centres into longer oligophenyleneethynylene molecules, we reverted to using more conventional contact

groups with higher 'hit rates' (and probably higher binding energies), namely 4–pyridyl and MeS–, and we investigated the conductances of molecules **17**-**20** (Scheme 7).[52] At *ca.* 3 nm between contact groups, these molecules lie at the border between tunneling and hopping mechanisms of conduction noted earlier for a series of all-organic OPE 'wires' with 4-pyridyl contact groups.[53]



17: Ar = 4-pyridyl R = $-C_6H_{13}$
18: Ar = 4-$MeSC_6H_4$



19: Ar = 4-pyridyl R = $-C_6H_{13}$
20: Ar = 4-$MeSC_6H_4$

Scheme 7 Structures of molecules **17**–**20**.

While (4-pyridyl)-[C≡C-$C_6H_2(OC_6H_{13})_2$)]$_3$C≡C-4-pyridyl was previously shown to have a conductance of $2.0 \times 10^{-7}G_0$ (0.015 nS), [53] the pyridyl-contacted complexes **17** and **19** had conductances of $4.5 \times 10^{-6}G_0$ (0.35 nS) and $9.8 \times 10^{-6}G_0$ (0.75 nS) respectively, while the MeS- contacted molecules **18** and **20** both had conductances of $1.8 \times 10^{-5}G_0$ (1.4 nS). Two notable observations here are the considerably higher conductances of the metal complexes than the purely organic analogue and the fact that the two Pt(II) complexes had conductances similar to, or even higher than, the Ru(II) analogues in this case. The stronger binding groups meant that the observed break-off distances for the molecules in the *I(z)* experiments roughly tallied with the calculated molecular lengths. DFT combined with NEGF transport calculations suggested that for these molecules, transport is LUMO-based, as already precedented for pyridyl-[54] and some MeS- contacted[55] all-organic molecules, and this may help rationalize why the Pt(II) complexes had such high relative conductances; their LUMOs have some metal d-character, whereas the LUMOs of the Ru(II) complexes do not. The higher

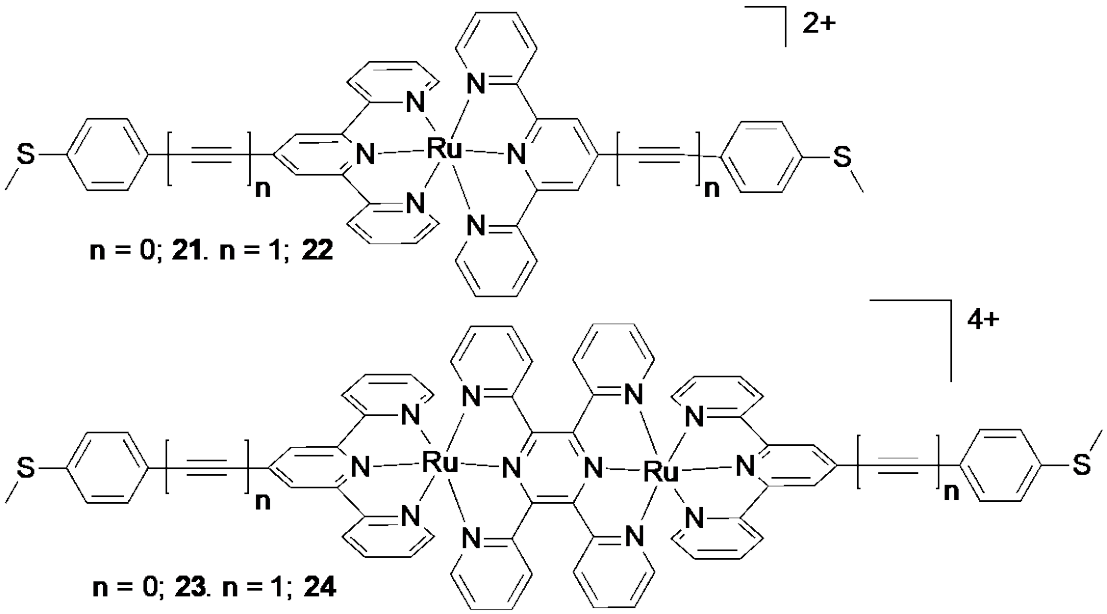
conductances of the MeS- contacted molecules is probably a consequence of stronger covalent interaction of the gold electrodes with the MeS- contacts, resulting in broadening of the LUMO resonance and a consequent larger degree of transmittance at the contact Fermi energy.[52]

Ongoing challenges in this area are to extend the single molecule studies to multimetallic examples and to take advantage of the redox activity of the Ru(II)-alkynyl complexes to study electrochemical gating in an appropriate medium, such as an ionic liquid. As the 17-electron oxidized species may not have sufficient long-term stability for the kind of steady-state measurements at fixed electrochemical potentials we have previously employed with other redox systems,[56, 57] we are developing dynamic methods for studying electrochemical gating *in situ* with pre-formed single molecule junctions as a potential method for overcoming this issue.

Single molecule junction conductance studies of $[Ru(terpy)_2]^{2+}$ derivatives and related complexes; electrochemical 'gating' of conductance.

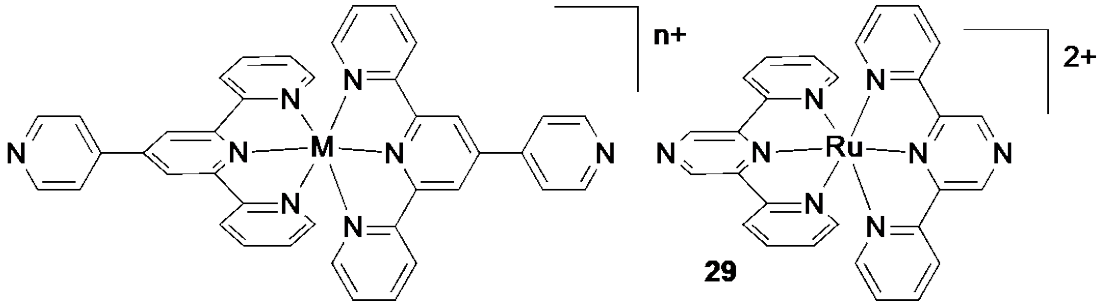
Increasingly sophisticated methods of assembling multimetallic complexes, including very long 'molecular wires', at conducting surfaces are being devised.[4, 58, 59] Extremely low (and metal ion-dependent) β values have been claimed for some of the multimetallic wire-like complexes, made from transition metal ions and 'back to back' terpyridyl and analogous ligands.[4, 59] This is strongly suggestive of a hopping-type mechanism, at least for the longer molecules. Accordingly, we were interested in examining MSMM junctions with related complexes.

Initially, robust Ru(II) mono- and binuclear complexes were prepared using both 4–$MeSC_6H_4$- and 4-$MeSC_6H_4$-C≡C- functionalised terpyridine derivatives, together with the 'back to back' terpyridine analogue 2,3,5,6-tetra(pyridine-2-yl)pyrazine, to afford a family of mono- and binuclear Ru(II) complexes with lengths ranging from 2.16 to 3.20 nm between the contact S atoms, **21**-**24** (Scheme 8).[60]

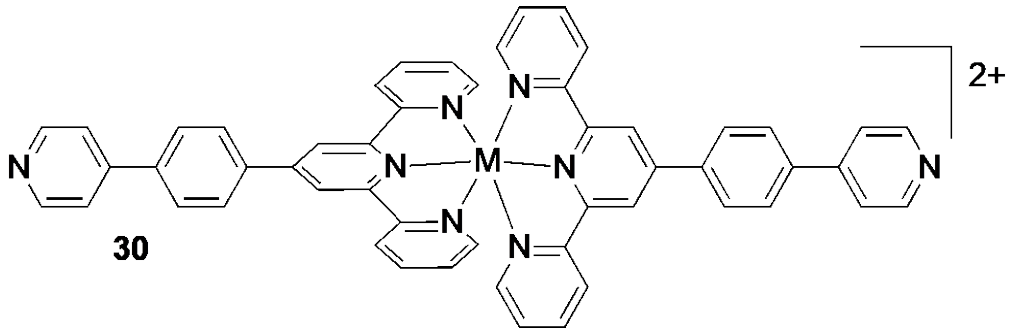


Scheme 8 Structures of molecules **21–24**.

The conductance of MSMM junctions with these molecules was determined using the non-contact *I(z)* method, and was found to range from 2.7×10^{-5} G_0 (2.1 nS) for **21**, to 5.6×10^{-6} G_0 (0.43 nS) for **24**. A roughly linear correlation was found for a log(conductance) vs. length plot for the four molecules, with a slope (β value) of 1.5 nm^{-1}.[60] This compares with a value of *ca* 2 nm^{-1} found for all-organic OPEs.[33] Although this is not a true β value since these molecules do not form a homologous series, the reasonable linear correlation, and the relatively large value of β, both suggested a conventional tunnelling mechanism for conduction through these junctions, at least as measured in ambient conditions in a nonpolar medium without electrochemical potential control. [60] Efforts are ongoing to extend these studies to measure MSMM junction conductances as a function of redox potential. This should be particularly interesting for the binuclear examples since related Ru(II) complexes of this back-to-back ligand show two successive reversible one-electron oxidations and, depending upon the co-ligands, the one-electron oxidation product can show Robin and Day class III mixed valence behavior.[61, 62]

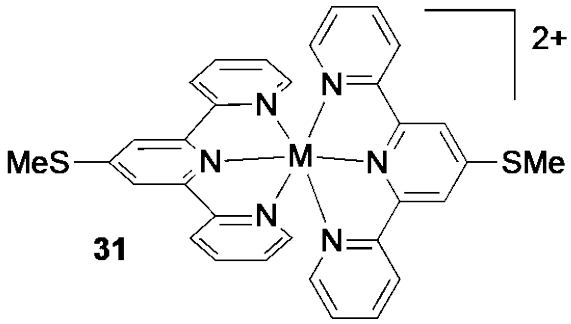


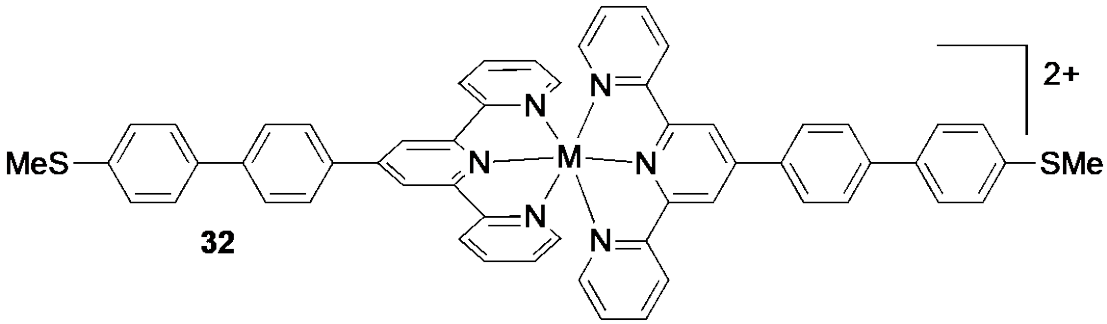
n = 2, M = Ru: **25**. M = Fe: **26** M = Co: **27**
n = 3, M = Cr: **28**



Scheme 9 Structures of molecules **25–30**.

The ligand 4'-(4-pyridyl)-2,2':6',2''-terpyridine (pyterpy) has been widely used in supramolecular coordination chemistry since its introduction by Constable *et al*,[63] and since 4-pyridyl units have been quite widely used as contact groups in MSMM studies,[14, 25] we have used it (and its variants) in the family of complexes **25-30** (Scheme 9).[57] The Ru(II) complexes **25**, **29** and **30** had conductances ranging from $(8.6 \pm 1.9) \times 10^{-5} G_0$ for **25** to $(1.4 \pm 0.3) \times 10^{-5} G_0$ for **30**. Plotting log(conductance) vs. molecular length for these three complexes revealed a significant deviation from linearity, whereas a linear plot of conductance *vs* molecular length was evidently closer to linearity. The value of β calculated from the best linear fit of the log plot was 1.03 nm^{-1}. This compares with values of *ca*. 4.3 nm^{-1} previously observed for all-organic oligophenyls with both amine and direct carbon-gold contacts.[64] It was not possible to synthesise complexes with longer ligands because the ligand used to make complex **30** was already at the limit of solubility for synthesis. Accordingly, to obtain additional data on these oligophenyls with a central $[Ru(terpy)_2]^{2+}$ unit, we also prepared complexes **21** and **31-32** (Scheme 10) for comparison.[57] This series showed similar behavior to **25**, **29** and **30** (Figure 5).





Scheme 10 Structures of molecules **31** and **32**.

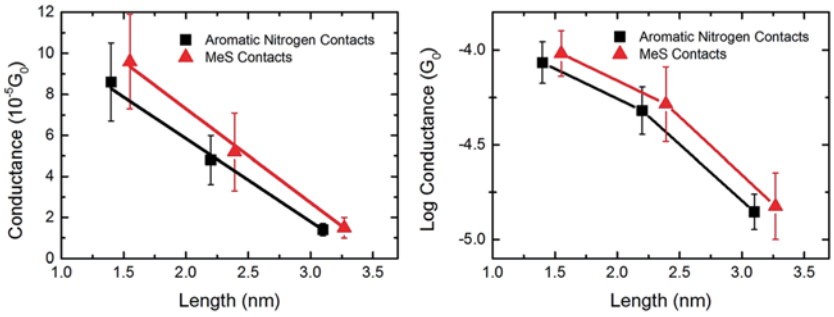


Figure 5 Plots of molecular junction conductance *vs*. length and log(conductance) *vs*. length for 4-pyridyl-contacted and MeS-contacted oligophenyl Ru(II) complexes. From reference [57] reproduced by permission of the owner society.

The fact that the β value for these complexes is much lower than for all-organic oligophenyls is strongly suggestive of a substantial hopping element in the conductance of these junctions. For the pyterpy ligand, we also synthesised complexes **26-28** of Fe(II), Co(II) and Cr(III).[57] The conductances of these molecules measured in ambient conditions were, within experimental error, independent of the identity of the metal ion (*ca*. 3.4 ± 1.0 nS; [4.4 ± 1.3] × 10^{-5} G_0), apart from the Cr(III) complex which was somewhat lower (2.5 ± 0.5 nS; [3.3 ± 0.6] × 10^{-5} G_0). The conductances of **26** and **27** were additionally measured in ionic liquid (1-(n-butyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, BMIM-TFSI) under electrochemical potential

control, as a function of electrochemical potential across the potential range corresponding to the electrochemically reversible Fe(II)/Fe(III) and Co(II)/Co(III) redox waves respectively. As previously found for organic redox-active molecules in ionic liquid,[56, 65] the conductance-overpotential relationships for **26** and **27** both showed a peak in conductance that almost coincided with the redox potential (Figure 6).[57]

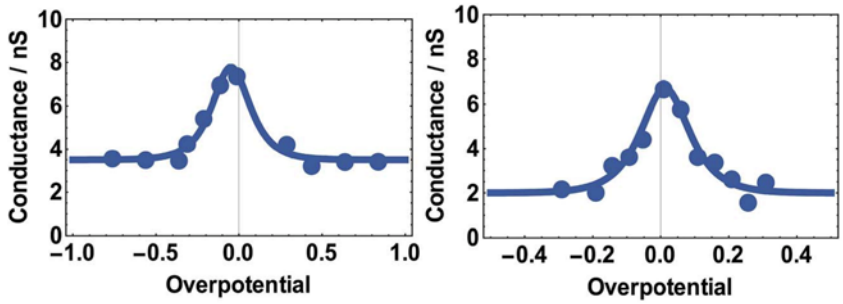


Figure 6 Conductance *vs*. overpotential plots for (left) $[Co(pyterpy)_2]^{2+/3+}$ redox process and (right) $[Fe(pyterpy)_2]^{2+/3+}$ process. Dots show experimental data; line shown is fitting to Kuznetsov-Ulstrup model (see main text). From reference [57], reproduced by permission of the owner society.

This behaviour is in agreement with the two-step charge transfer model of Kuznetsov and Ulstrup. This model is illustrated in Figure 7; the molecule bridges between the substrate and STM tip with the metal redox centre tethered in the nano-gap.

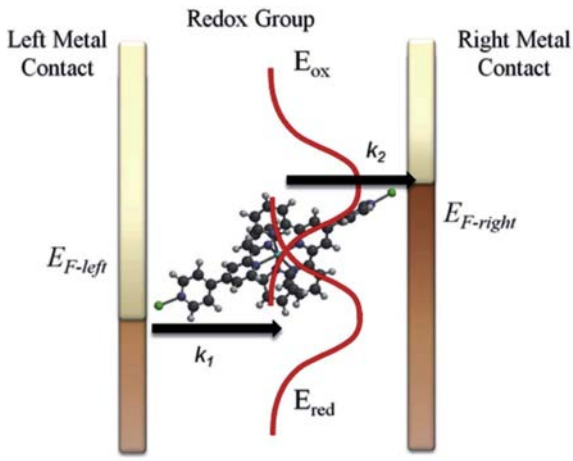


Figure 7. An illustration of the Kuznetsov–Ulstrup model showing $[M(pyterpy)_2]^{2+/3+}$ bound to two gold electrodes denoted left and right respectively. The energies of the two redox states are represented in red; charge transfer occurs sequentially through these by two electron transfer processes with rates labelled k_1 and k_2. From reference [57], reproduced by permission of the owner society.

A hole tunnels from the left electrode to the metal centre following pre-organisation of the molecule and its ionic liquid environment so that charge transfer can follow a

Frank–Condon-type transition. In the adiabatic limit (used in the modeling in this instance), the molecule and its environment then partially relax, with the hole thus losing coherence. The hole then tunnels from the metal centre to the right electrode. The resulting enhancement in junction current is given by Equation 1 (derived in reference [66]), where k_B is the Boltzmann constant, V_{bias} the bias voltage, T the temperature, and e the electron charge. Other important criteria here are the overpotential η, a modeling parameter representing the fraction of the voltage dropped at the redox site (γ) and the total reorganization energy (inner plus outer sphere), λ. The parameter ξ represents the fraction of the electrochemical potential experienced at the redox site.

Equation 1

$$j_{enh} \approx j_0 \exp(-\lambda/4k_B T) \frac{\exp(e|V_{bias}|/4k_B T)}{\cosh\left(\frac{e(0.5-\gamma)V_{bias} - e\xi\eta}{2k_B T}\right)}$$

The fitting parameters for $[Co(pyterpy)_2]^{2+/3+}$ are λ = 0.80 eV, ξ = 0.5 and γ = 0.40, while those for $[Fe(pyterpy)_2]^{2+/3+}$ are λ = 0.77 eV, ξ = 0.8 and γ = 0.55.[57] The reorganization energies for the two complexes were considerably smaller than those previously found for less structurally-rigid organic redox groups with pendant alkylthiolate contacts, and also the parameter ξ is lower for the complexes, indicating that screening is less effective. This may be because the redox centre is surrounded by a bulky ligand 'shell', which was not the case for the organic redox centres (viologen and tetrathiafulvalene) in our earlier work.[56, 65] Interestingly, the conductance of MSMM junctions with $[Os(pyterpy)_2]^{2+}$, isoelectronic with $[Fe(pyterpy)_2]^{2+}$, was previously examined as a function of electrochemical potential over the Os(II)/Os(III) redox wave, and it was found that the conductance decreased in a roughly sigmoidal fashion, from $23.1 \times 10^{-5} G_0$ (17.8 nS) for the Os(II) redox state to $2.70 \times 10^{-5} G_0$ (2.1 nS) in the Os(III) state.[67] However, that study was performed using an aqueous electrolyte. This further supports the idea that the medium is the most important factor in controlling the form of the conductance-overpotential relationship in electrochemical gating studies.[68]

Efforts to prepare bi- and multimetallic examples of pyterpy-terminated Ru(II) and Fe(II) complexes using the 'back to back' ligand 1,4-di([2,2':6',2''-terpyridin]-4'-yl)benzene have so far had limited success owing to inseparable oligomeric impurities evidently caused by ligand scrambling, which is interesting in view of the extensive use of this approach for surface-localised reactions, [4-7] but which has so far precluded us from examining conductance-length relationships for such complexes using MSMM techniques.

Conclusions

To summarise, our MSMM studies to date have shown that the incorporation of Ru(II) and Pt(II) centres into oligophenyleneethynylene molecules using metal-alkynyl coordination has a variable effect upon the conductance of the molecules, that depends upon the nature of the contact groups, but generally the metal complexes are significantly more conductive and, in the case of the longest well-defined examples studied, they are much more conductive (*ca*. 2 orders of magnitude). Although combined DFT and NEGF calculations suggest that the conductances of this family can all be accommodated within a conventional tunneling description, in the case of metal-terpyridyl complexes there is significant evidence for a hopping element, even for relatively short molecules. Further theoretical studies are required to shed more light on the latter. In the future, we hope to use these and related complexes in studies of redox-active spintronic devices, and possibly also for molecular thermoelectric applications.

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