Simplifying the conductance profiles of molecular junctions: the use of the trimethylsilylethynyl moiety as a molecule–gold contact†‡

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Conductance across a metal|molecule|metal junction is strongly influenced by the molecule–substrate contacts, and for a given molecular structure, multiple conductance values are frequently observed and ascribed to distinct binding modes of the contact at each of the molecular termini. Conjugated molecules containing a trimethylsilylethynyl terminus, $-C{\equiv}CSiMe_3$ give exclusively a single conductance value in *I*(s) measurements on gold substrates, the value of which is similar to that observed for the same molecular backbone with thiol and amine based contacting groups when bound to under-coordinated surface sites.

Single molecule electronics science has advanced rapidly through the introduction of reliable methods for the measurement of trans-molecule conductance in various metal|molecule|metal configurations, such as mechanically controlled break junction (MCBJ), STM-break-junction (STM-BJ), conducting probe AFM (CP-AFM), nano-pore devices, and STM-based matrix isolation, *I*(s) and *I*(t) methods.[1] Data from a statistically significant number of individual measurements on a junction typically reveal a range of conductance values arising from not only the number of molecules trapped within the junction,[2] but also from variations in the nature of the molecule-substrate contact, the tilt-angle of the molecule to the surface,[3] and the site of binding on flat terraces or step edges[4] and adjacent neighbouring adatoms.[5] The measured conductance of an individual molecular junction is therefore influenced by both the chemical composition of the contacting group and the structure of the local, accessible binding sites on the electrode surfaces. Given the different degrees of surface roughness, and hence range of accessible molecule–surface binding sites, associated with the different measurement platforms (*e.g.* break junction methods *vs.* the use of a pristine STM tip in *I*(s) methods), the measurement method can dictate the range of contact types observed.[5] Low conductance type A contacts are due to molecular binding at low coordination surface sites, whilst the progressively more conductive contacts are due to molecular binding at higher coordinate defect sites at one (type B) or both (type C) contact surfaces. Type C contacts are commonly observed in MCBJ and STM-BJ measurements, but are generally less often observed in junctions formed through the softer *I*(s) and *I*(t) methods.[4] This electrical variability arising from the site of molecule–surface binding may limit the use of molecules as active components within device structures, and contacting groups that permit the assembly of robust, reproducible and stable molecular junctions are to be desired.[6,7]

Trimethylsilylethynyl has emerged as a promising contacting group, able to form stable, and often well-ordered, self-assembled monolayers on Au(111) surfaces.[8] The arrangement of molecules in the SAM is consistent with the silyl moiety either being bound to three-fold hollow sites or a top single metal atoms on the Au(111) surface, whilst the presence of single atom-step deep etch-pits provides evidence for chemisorption similar to thiol on gold interactions.[8] The trimethylsilylethynyl terminated oligophenylene ethynylene (OPE) **1a** (Fig. 1) forms contacts to gold substrates in both Langmuir–

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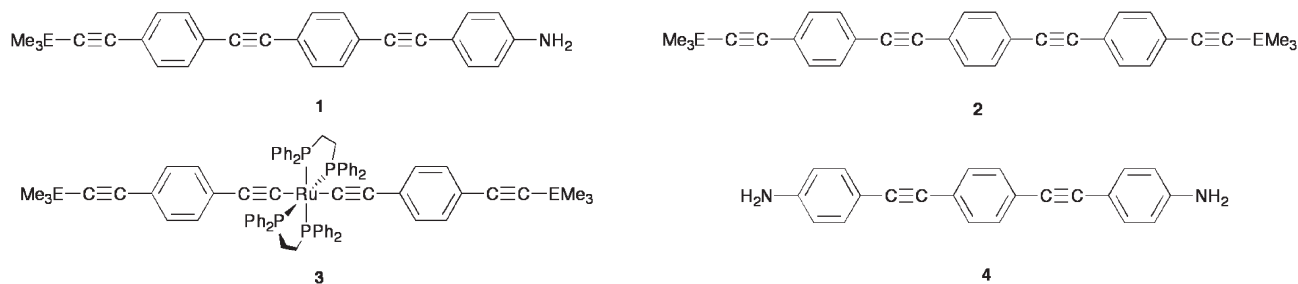
Fig. 1   Complexes used in this work E = Si (**a**), C (**b**).

Blodgett films and in single molecule configurations. Conductance values obtained from $Me_3SiC\equiv C/NH_2$ contacted junctions formed from **1a** are of the same order of magnitude as obtained from thiol–thiol anchored OPEs when measured by the I(s) method.[9] When compared with thiol, –SH, and amine, –NH₂, contacting groups, the additional steric bulk of the SiMe₃ group was thought to be potentially useful in limiting the range of accessible surface binding sites, which in turn could be used to give rise to molecular junctions with more reproducible conductance signatures. To explore the potential of trimethylsilylethynyl contacting groups in more detail we have undertaken a study of a series of molecular junctions formed from OPE and organometallic derivatives featuring $-C\equiv CSiMe_3$ and $-C\equiv CCMe_3$ contacts using the I(s) method.

The compounds **2a** and **3a** (Fig. 1 and 2) offer rigid, linear molecular geometries with estimated Si···Si distances of 24.49 (**2a**)–23.97 (**3a**) Å.§ [10]‡ In contrast to related Pt complexes in which the metal acts as an insulating fragment,[11] these trans-$Ru(C\equiv CR)_2(dppe)_2$-based systems offer a highly delocalised π–d–π electronic structure which spans the length of the molecular backbone.[12] Electrical measurements were performed using low-coverage of the target molecule on a Au(111) gold substrate using an STM operating in the I(s) configuration,[13]‡ with relatively high set point currents (20 nA) although no special care was taken to record data exclusively from flat Au(111) terraces to allow formation of both type A and type B contacts.

Fig. 3 shows typical I(s) curves exhibiting current plateaus from **2a** and **3a**. The plateaus are attributed to the formation of conductive molecular junctions and can be observed in *ca.* 14–16% of the scans. Conductance histograms reveal single conductance values of $(2.75 \pm 0.56) \times 10^{-5}$ G_0 (**2a**) and $(5.10 \pm 0.99) \times 10^{-5}$ G_0 (**3a**) and the exclusive formation of 'type A' contacts (Fig. 3). The higher conductivity of the organometallic molecular junction from **3a** is consistent with the slightly shorter length of the molecule, and the better alignment of the molecular HOMO with the Fermi levels of the gold contacts.[14] Under the same conditions, the reference compound **4**, which contacts to each metallic surface in the junction through an amine moiety, gave rise to two well-resolved conductance peaks due to type A $((3.20 \pm 0.83) \times 10^{-5}$ $G_0)$ and type B $((14.4 \pm 2.78) \times 10^{-5}$ $G_0)$ contacts,‡ the latter in good agreement with data from STM-BJ measurements.[15] Conductance histograms constructed from I(s) measurements with **1a** also
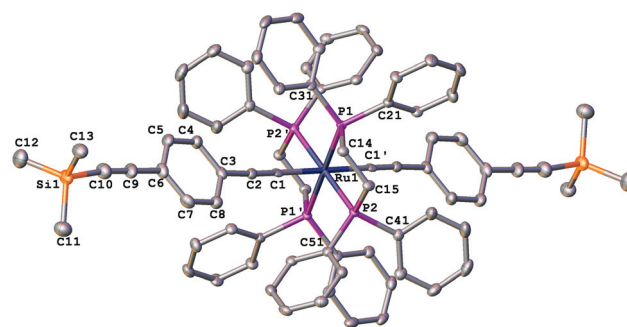

Fig. 2   Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): Ru(1)–P(1, 2) 2.3598(6), 2.3555(7); Ru(1)–C(1) 2.066(3); C(1)–C(2) 1.204(4); C(2)–C(3) 1.438(4); C(6)–C(9) 1.449(4); C(9)–C(10) 1.197 (4); C(10)–Si(1) 1.836(3); P(1)–Ru(1)–P(1') 180.0.
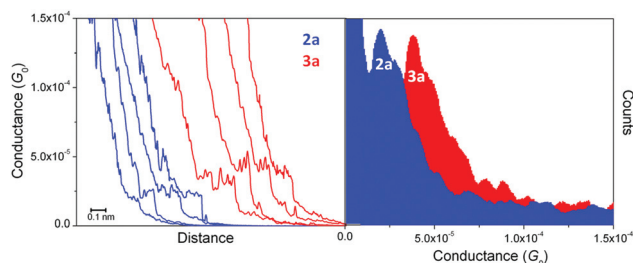

Fig. 3   Typical conductance traces from **2a** and **3a** using the I(s) method and conductance histograms derived from I(s) measurements. The curves are shifted horizontally for clarity. Conductance data are presented in units of the conductance quantum $G_0 = 2e^2/h = 77.5$ μS. $I_0 = 20$ nA and $U_t = 0.6$ V.

revealed two conductance peaks for type A $((2.99 \pm 0.43) \times 10^{-5}$ $G_0)$ and B $((7.92 \pm 1.33) \times 10^{-5}$ $G_0)$ contacts.‡ The similarity of the type A conductance values of **2a** and **4** indicates the electrical similarity of the trimethylsilyl and amino contacts to gold. The type B contact from **1a** was less conductive than bis-(amine) contacted **4**, but clearly distinguishable from the type A peak.

Recently, the formation of highly transmissive Au–C contacts from addition of Me₃Sn–alkyl bonds to gold surfaces during STM-BJ measurements has been reported.[16] Although the Si–C bond in trialkylsilyl-ethynyl moieties is sensitive to cleavage following attack at Si by nucleophiles, compounds containing this moiety are rather more environmentally stable than those with trialkyltin functionality and may be less prone

to rupture in the presence of the substrate surface. Chemisorption of the $-C \equiv CSiMe_3$ functionalised molecules on gold was demonstrated by Quartz Crystal Microbalance (QCM) experiments. AT-cut, α-quartz crystals with a resonant frequency of 5 MHz having circular gold electrodes patterned on both sides were incubated in 0.01 mM solutions of **2a** and **3a** in $CHCl_3$ for 24 h. Afterwards the substrates were thoroughly rinsed with $CHCl_3$ and the variation of the resonant frequency of the substrates before and after incubation was determined. High surface coverage of 7.32×10^{-10} and 3.90×10^{-10} mol cm^{-2} were obtained for **2a** and **3a** compounds, respectively. XPS measurements on **2a** and **3a** as both powders and SAMs on Au were also undertaken.‡ The Si $2p_{3/2,1/2}$ doublet appears as a single, asymmetric peak due to the small spin–orbit coupling in Si with BE of 100.86 (**2a**) and 101.26 (**3a**) eV, and 151.94 (**2a**) and 152.59 (**3a**) eV for the 2s peak in the powder samples, consistent with the $Me_3Si-C \equiv C$ moiety.[8,17]

The signal intensity is much lower in the SAMs and resolving the surface bound and free $SiMe_3$ moieties is difficult, with only a single, broad peak shifted with respect to the powders (2p, 2s: **2a** 102.88, 154.31; **3a** 103.19, 154.28 eV). The shift in the 2s peak may be some indication of a change in hybridisation at Si.

To further establish the electronic functionality of the silyl group, molecular junctions featuring $-C \equiv CCMe_3$ terminal groups **1b**, **2b** and **3b** were examined within an identical $I(s)$ configuration, but no conductance plateaus could be detected in any case over 5000 individual measurements per molecule. The physical and electronic differences between *tert*-butyl- and trimethylsilyl-ethynyl groups has also been noted in comparisons of the SAM forming behaviour of molecules bearing these functional groups.[8] The molecular structure of **3b** displays little variation from the silyl analogue,‡ but there are substantial differences in physical/electrical behaviour of junctions formed by trimethylsilylethynyl and *tert*-butyl ethynyl contacted molecules. It has been proposed that given the propensity for Si(IV) to adopt coordination numbers greater than four, that the $-SiMe_3$ groups can adopt a five-coordinate, trigonal bipyramidal geometry with a Au–Si interaction, aided by the presence of the electron-withdrawing ethynyl substituent.[8,18] In this conformation, the steric bulk of the trimethyl groups may restrict binding at higher coordination surface sites, resulting in exclusive A-type contacts. In contrast, the *tert*-butyl contact can only 'bind' to Au *via* weak and longer-range van der Waals contacts, leading to ineffective molecule-surface coupling.

Conclusions

Effective electrical contacts between conjugated molecules and conducting substrates are important for the continued development of molecular electronic technology. The trimethylsilylethynyl moiety forms contacts to gold substrates that have similar electrical characteristics to amine ($-NH_2$) contacts. Given the prevalence of trimethylsilyl as a protecting group in alkynyl chemistry, and the formation of molecular junctions with unique conductance profiles using this contact, the trimethylsilylethynyl moiety holds significant promise as a contacting group. Work is underway to clarify the molecule–substrate interaction and to confirm the role of the methyl groups in restricting access to surface defect sites and adatoms.

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