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Electrochemically grafted single molecule junctions exploiting a chemical protection strategy

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ABSTRACT

Diazonium grafted oligo(phenylene ethynylene) (OPE) monolayers suitable for single molecule conductance studies have been prepared. The surface-bound OPE is prepared from the amino tolan, 4-(2-(4-(2-(triisopropylsilyl)ethynyl)phenyl)ethynyl)benzamine, which is converted to the diazonium derivative *in situ*, and subsequently attached to a gold substrate using conventional cathodic electrochemical grafting. Multilayer formation is avoided by the presence of the bulky triisopropylsilyl (TIPS) protected ethynyl group. After removal of the TIPS group by treatment with fluoride, the film, now bearing exposed terminal acetylene moieties, is further functionalised by reaction with 1-iodo-4-acetylthiobenzene using Sonogashira coupling chemistry, to create sites bearing a strongly aurophilic top-contacting group. The success of these surface reactions is confirmed using Raman spectroscopy (gap-mode and SHINERS, employing gold nanoparticles and SiO_2 coated gold nanoparticles, respectively). It is shown that such thiolate-modified, diazonium-grafted monolayers are suitable for STM-based molecular junction conductance measurements.

1. INTRODUCTION

The field of molecular electronics has attracted a great deal of interest over the past two decades, driven by the development of methods for reliably characterising the electrical properties of molecules within large area planar and even single molecule junctions. As well as the basic conductance and current-voltage characteristics, topics of on-going research include molecular rectification, conductance switching, electrochemical gating, negative differential resistance, transistor-like behaviour and thermoelectric properties. However, obtaining reliable contacting of molecules within the electrical junctions remains an overriding theme that can impact significantly on all of these phenomena. Gold has featured as by far the most common material for making electrical contacts to molecules. This is due to (i) its lack of surface oxide under standard ambient conditions, (ii) favourable electrical properties of gold and (ii) the ease of preparation of electrode structures that take the form, for instance, of atomically flat surfaces and STM tips, nano-fabricated contacts or mechanically controlled and STM-based break junctions. However, equally importantly, there is also an extensive variety of versatile chemistry for forming gold-molecule contacts. Chemisorbed anchor groups have featured most prominently with key examples including thiol, thiomethyl ether, pyridyl, amine, dimethyl phosphine and carboxylate functional groups [1–5]. An attractive alternative to these has been the direct “grafting” of molecules to metal (M) electrodes through the formation of metal-carbon (M-C) linkages, with the expectation that such coupling would increase the electrical transmission of such junctions, which can be a limiting feature in junction conductance.

Direct Au-C anchoring has been achieved through the spontaneous in-situ cleavage of trimethyltin terminal groups on molecular junction targets [6]. In this way, simple polymethylene or aromatic molecular bridges could be linked by gold contacts within an STM break junction configuration [6]. In a related approach, fluoride-induced cleavage of trimethylsilyl (TMS) protecting groups from alkyne groups has also been shown to

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promote the in-situ formation of Au-C-linked molecular junctions [7]. Direct Au-C bonds are strong [8], and such junctions have produced junction conductance values up to 100 times greater than those with more conventional anchoring groups such as thiols [6]. Another popular method for achieving direct M-C linkage of adsorbates to metal, semiconductor or carbon electrodes involves diazonium chemistry. Surface attachment can be achieved by *in-situ* electrochemical reduction of diazonium-terminated molecular targets, which graft to the cathodically polarised electrode through the resulting radical intermediate ($Ar\text{-}N_2^+ + e^- \rightarrow Ar\cdot + N_2(g)$). This approach was pioneered by Pinson and co-workers in 1992 for the direct attachment of aryl groups to carbon electrodes [9]. Such attachment methodologies based on electrografting of diazonium derivatives have found wide application in electrochemistry and beyond, including, for example, the formation of molecular films for surface functionalisation and polymer growth, electron transfer studies, solubilisation of carbon nanotubes, corrosion protection, surfaces for the immobilisation of nanoparticles, bio- and chemo-sensing systems and surfaces with chemically controlled wettability (see [10] and references therein). Diazonium grafting has also been used for forming carbon-aryl-metal [11–13] and silicon-molecule junctions [14,15] for planar molecular electronics junctions and also in commercial electronic applications [16]. Electrochemical scanning tunnelling spectroscopy has been used to investigate charge transport through redox-active molecules bound to the surface through direct Au-C linkage achieved through diazonium chemistry [17]. More recently, single molecule junctions have been formed through the electrochemical reduction of molecules with diazonium termini at both ends [8]. Although these Au-C-anchored molecular junctions did not have appreciably higher conductance than equivalent junctions anchored with amine termini, they did exhibit greater stability and could be stretched to greater lengths in STM-tip retraction experiments [8].

It is well recognised that diazonium compounds have potential for grafting onto a wide variety of contacts for molecular electronics [11–16], however without protection of the starting diazonium salts multilayers can form, and oligomer chains with a complex stoichiometry are likely to result. Grafting of well-defined monolayers would then be difficult to achieve for either applications in large area molecular electronics or for single molecule measurements. Defined stoichiometry is of course necessary for a robust understanding of the transport properties of metal-carbon junctions. This well-known issue with diazonium grafting arises because of the high reactivity of the electro-generated radicals, which then show a propensity to react with existing surface-grafted materials [10,18,19]. The use of sterically-hindered diazonium salts [20] or protection-deprotection chemistry [21] has proven to be effective in suppressing multilayer formation in the electrografting of aryldiazonium salts. Notably Leroux et al. have employed aryldiazonium salts with protecting groups at the other terminus (trimethylsilyl, triethylsilyl, and triisopropylsilyl were evaluated) in their grafting to carbon substrates [21]. The size of the protecting-head group controlled the spacing of the electrochemically grafted molecules and, once the protecting group was removed, an ethynylaryl monolayer was revealed which could be subsequently functionalised using “click chemistry” [22]. Other protecting group chemistry, for instance *tert*-butyloxycarbonyl (BOC) protection of amine termini [23], have also been employed in diazonium grafting. The triisopropylsilyl (TIPS) protecting group has also been examined previously to make large-area molecular junctions [24].

In this study, diazonium grafting to gold substrates, accompanied by protection-deprotection chemistry, has been deployed in the fabrication of metal-molecule-metal junctions for single molecule electronics. Such junctions were linked to the gold electrode through a direct Au-C bond, while the attachment at the other molecular terminus was through a conventional thiol link to the gold STM probe tip. In this way, the thiol link to the gold STM tip could be repeatedly made, broken and remade in STM evaluation of the molecular junction conductance. Cyclic voltammetry and Raman spectroscopy has also been used to characterise the formation of the molecular layers.

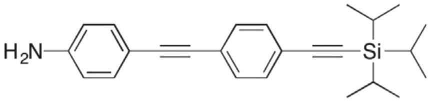
2. EXPERIMENTAL DETAILS

2.1. General synthetic details

NMR spectra were recorded in deuterated solvent solutions on a Varian VNMRS-600 spectrometer and referenced against solvent resonances (^1H, ^{13}C). MS(ASAP) data were recorded on a Xevo QTOF (Waters) high resolution, accurate mass tandem mass spectrometer equipped with Atmospheric Pressure Gas Chromatography (APGC) and Atmospheric Solids Analysis Probe (ASAP). NMR spectra are shown on the supporting information. Microanalyses were performed by Elemental Analysis Service, London Metropolitan University, UK. Analytical grades of solvents were used. ((4-Bromo phenyl)ethynyl)triisopropylsilane [25] and 4-ethynylaniline [26] were synthesised according to literature methods. All other chemicals were sourced from standard suppliers.

2.1.1. Synthesis of 4-(2-(4-(2-(triisopropylsilyl)ethynyl)phenyl) ethynyl)benzamine (1)

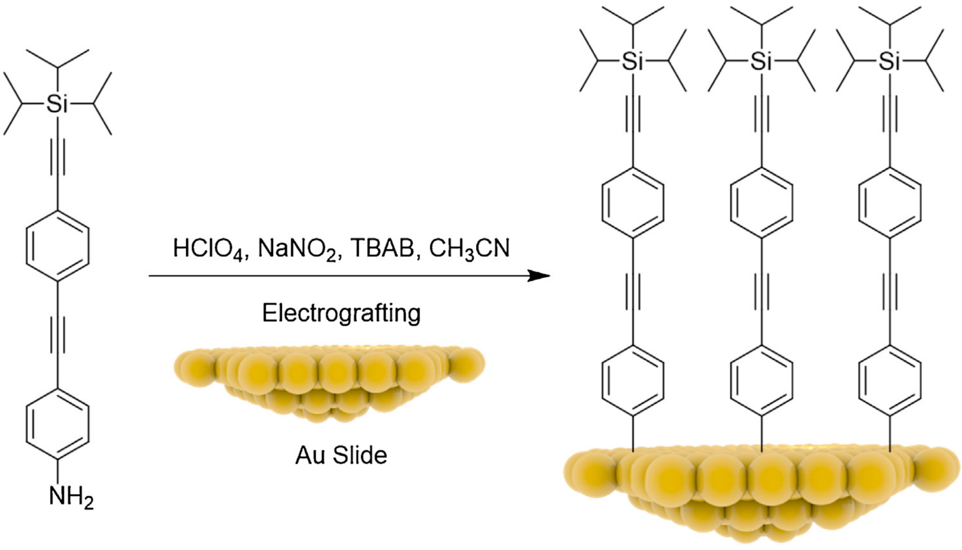
((4-Bromophenyl)ethynyl)triisopropylsilane (2.00 g, 5.95 mmol) and 4-ethynylaniline (0.70 g, 6.00 mmol) were added to a round bottom flask that was degassed and filled with dry THF (50 mL) and Et_3N (10 mL). The solution was degassed by three freeze-pump-thaw cycles before the addition of CuI (0.11 g, 0.59 mmol) and $PdCl_2(PPh_3)_2$ (0.41 g, 0.59 mmol). The solution was heated to reflux for 16 hours under nitrogen, and the solvent was then removed in vacuo. The remaining solid was dissolved in hexane and filtered, the filtrate was eluted on a silica column with CH_2Cl_2:hexane (1:1), collecting the yellow band. The solvent was removed to give a yellow oil. Yield: 1.57 g (71%). ^1H NMR (CD_2Cl_2) δ: 7.45 (s, 4H), 7.34 (d, J = 8 Hz, 2H), 6.65 (d, J = 8 Hz, 2H), 3.94 (s, 2H), 1.14 ppm (s, 21H, assigned to unresolved multiplet from the TIPS group hydrogens). ^{13}C NMR (CD_2Cl_2) δ: 147.3, 132.9, 131.8, 130.9, 123.9, 122.5, 114.5, 106.7, 92.4, 92.2, 18.4, 11.3 ppm. MS(ASAP): m/z 373.220 $[M]^+$, 374.213 $[M+H]^+$. Anal. Calc. For $C_{25}H_{31}NSi$: C, 80.37; H, 8.36; N, 3.75%. Found: C, 80.27; H, 8.16; N, 3.85%.



Compound 1 used to form **Layer-1** (see Scheme 1).

2.1.2. Synthesis of S-(4-iodophenyl)ethanethioate)

A solution of 1,4-diiodobenzene (1.65 g, 5 mmol) in dry toluene (40 mL) was degassed by bubbling Ar through for 30 minutes in a Schlenk flask. CuI (95 mg, 0.5 mmol), KSAc (0.685 g, 6 mmol) and 1,10-phenanthroline (180 mg, 0.1 mmol) were added while keeping the flask in a gentle stream of dry argon and the resulting suspension was stirred for 24 h at 100 °C, after which time the colour changed to deep brown. Upon cooling, 50 mL of H_2O was added and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL), the combined organics washed with brine and dried over $MgSO_4$. The solvent was removed to yield a red crude product that was purified by flash column chromatography on silica (20% CH_2Cl_2 in hexanes as eluent) to give the title compound as a pale yellow solid (0.581 g, 42%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 8.3 Hz, 2H, Ph), 7.03 (d, J = 8.5 Hz, 2H, Ph), 2.32



Scheme 1. Cathodic electrochemical grafting of compound **1** (left) to form **Layer-1** (right).

(s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 193.2, 138.3, 135.9, 127.6, 95.9, 30.3$. *m/z* (HRMS, CI, NH_3) 295.9609 $[M+NH_4]^+$, $C_8H_{11}NIOS$ calc. 284.9606.

2.2. Surface Functionalisation

2.2.1. Layer-1 preparation

The formation of **Layer-1** by cathodic electrografting is described in the Results and Discussion section (see Scheme 1 and accompanying text).

2.2.2. Layer-1 Desilylation

A gold slide with the electrografted **Layer-1** was immersed in 5 mL 1.0 M TBAF in THF solution under Ar atmosphere, and sonicated for 10 minutes at room temperature. The sample was then rinsed with copious ethanol and acetone, and used in the following step.

2.2.3. General procedure for Sonogashira surface functionalisation to form Layer-2

The desilylated **Layer-1** on Au was put in a solution of bis(acetonitrile)dichloropalladium(II) (0.013 g, 0.05 mmol), triphenylphosphine (0.039 g, 0.15 mmol), cuprous iodide (CuI, 0.005 g, 0.026 mmol) and *S*-(4-iodophenyl)ethanethioate (0.139 g, 0.5 mmol) in 20 mL of redistilled and degassed diisopropylamine and sonicated for 1 h under argon, over which time the temperature increased to 45 °C. The sample was then rinsed with copious ethanol and acetone, and used in the STM and Raman characterisation.

Using this surface functionalisation scheme it is possible that the *S*-(4-iodophenyl)ethanethioate might react directly with the bare gold surface if the base layer was pin-holed or poorly packed, but the data (for instance the cyclic voltammograms with ferrocyanide shown in Fig. 2) show this not to be the case. Even in the eventuality of small pinholes and even if the reagent were to in-fill the 'deprotected' monolayer it would be unable to react further in the Sonogashira reaction and would be buried too deeply to interact with the gold nanoparticles.

For the STM imaging of **Layer-2** it was immersed into a dilute Au NPs solution overnight, and then thoroughly rinsed and dried in a nitrogen flow, before being imaged with STM.

2.3. STM Conductance Measurements

Measurements of single molecule conductance were performed using the *I*(*s*) method (where *I* = current and *s* = distance) which has been described in detail previously [27]. In brief, the gold STM tip is taken to high tip-substrate current values (e.g. 30 nA) so that the STM tip approaches close to the metal surface. From this position of close approach the STM tip was then rapidly retracted 2 nm with a scan duration of 10 ms. This process of approaching close to the substrate and then rapidly retracting is repeated many times and the resulting *I*(*s*) scans which show successful metal-molecule-metal junction formation are recorded and analysed. These junction formation traces are collected together in histograms to determine the most probable conductance value of a single molecule at a given bias voltage (U).

All the STM experiments and molecular conductance determinations were performed with a 'Molecular Imaging' (Keysight) STM. STM tips were prepared by cutting a ϕ0.25 mm gold wire (Goldfellow, 99.99%) for each experiment. The molecules were used as received from Sigma-Aldrich (reagent grade) and the synthesis and characterization of **1** is as described in Section 2.1.1. Commercial gold on glass plates (from Arrandee®) were used for all measurements. These samples were used as the working electrode for diazonium grafting by connecting with a gold wire. After flame annealing they were immediately immersed in an electrochemical cell with 5 mM compound **1** + 5 mM $NaNO_2$ + 10 mM $HClO_4$ + 0.1 M TBAB in acetonitrile solution and surface functionalisation was achieved as described in the "Results and Discussion" section.

2.4. Raman spectroscopy

We employed SHINERS in Au(111)|Molecular Layer|Au@SiO_2-NP sandwich structures. The 55 nm Au NPs obtained by a citrate reduction method were further coated with a pinhole-free thin silica film (thickness 2–3 nm) prepared as described in the literature [28]. Gap-mode Raman spectroscopy is also used to characterise the monolayers with the aid of gold nanoparticles not coated with a SiO_2 shell. Some differences in spectra between gap-mode Raman and SHINERS, such as band shifts, may be expected

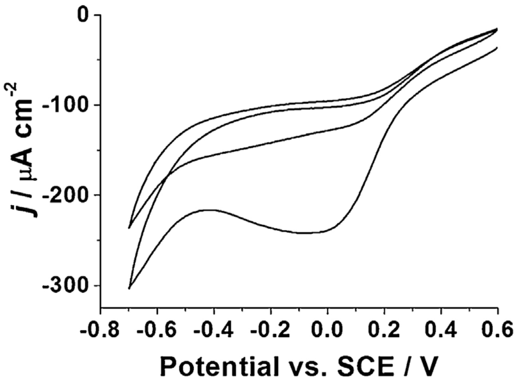


Fig. 1. Cyclic voltammograms for the grafting of diazonium salts of **1** onto the gold surface at a scan rate of 50 mV/s in an acetonitrile solution containing 5 mM **1** + 5 mM $NaNO_2$ + 10 mM aq. $HClO_4$ + 0.1 M TBAB. TBAB served as the supporting electrolyte, a platinum mesh as the counter electrode, and SCE as the reference electrode.

since the former case employs "bare" gold nanoparticles while the latter uses SiO_2 capped nanoparticles.

Raman measurements were performed with a HR800 confocal Raman spectrometer (Horiba JY, France). The excitation wavelength was 632.8 nm from a He–Ne laser. A 50-times magnification long-working-distance (8 mm) objective was used to focus the laser on the sample surface and to collect the scattered light in a backscattering geometry. A laser power of 0.15 mW was used for recording conventional Raman spectra of 1 and also gap-mode Raman experiments, while a power of 1.5 mW was used for SHINERS measurements. In all cases spectra were acquired over a 10 second period and the resolution used in spectra acquisition was ca. 3 cm^{-1}.

3. RESULTS AND DISCUSSION

Scheme 1 shows the initial stage of the surface grafting. The gold samples were flame-annealed and immediately immersed in an electrochemical cell containing compound **1** (5 mM), $NaNO_2$ (5 mM) and aq. $HClO_4$ (70%, 50 μL) in a solution of *tetra*-n-butylammonium bromide (TBAB, 0.1 M) in acetonitrile. Cathodic electrochemical grafting was achieved by running a cyclic voltammogram (CV) at 50 mV/s between 0.6 and −0.7 V (vs. SCE). Fig. 1 shows the first and second CV cycles during the electrografting progress, with the current falling dramatically after the first cathodic cycle indicating rapid passivation of the electrode surface and signifying grafting of the surface layer. The significant cathodic current starting at −0.5 V is also observed in our other studies of diazonium grafting, and we attribute this to the reduction of water. The reduction wave between 0.2 and −0.4 V is mostly likely to arise from the reduction of oxygen dissolved in solution. Obviously, for these reactions to appear in the second cycles, the oxygen as well as H_2O molecules have to be penetrate the molecular layer, even if the layer can prohibit the redox reactions of large ferrocyanide molecules in the electrolyte (see later).

After grafting, the **Layer-1** functionalized samples were thoroughly washed by ultrasonication in ethanol, dried under a nitrogen flow and then transferred into a sealed flask. Cyclic voltammetry can be used as an effective method for assessing the barrier properties of diazonium-grafted organic monolayers on surfaces [29]. Cyclic voltammograms in aqueous potassium ferrocyanide were used to ascertain the formation of a blocked monolayer and these are shown in Fig. 2. A clear voltammetric wave is seen on the bare gold electrode and this is totally suppressed on the electrografted surface. The peak-to-peak separation on the bare gold electrode in these experiments was found to be larger than expected, and surface preparation-dependent. Similar observations for this particular couple on graphite electrodes have been made previously, and attributed to an inner sphere-type mechanism operating, in contrast to other familiar anionic couples such as $[IrCl_6]^{3-/2-}$ [30–32].

Layer-1 features a terminal triisopropylsilyl (TIPS) protecting group that needs to be removed prior to the introduction of a suitable group for forming robust metal-molecule-metal electrical junctions. The deprotection is achieved by treatment of the modified electrodes with *tetra*-n-butylammonium fluoride (TBAF) in THF (Scheme 2). In a subsequent step, the Sonogashira reaction was used to introduce a benzenethiolate terminus to the monolayer (protected as the thioacetate) and it was these modified monolayers (**Layer-2**) that were used for the formation of metal-molecule-metal junctions in the subsequently-described STM conductance measurements.

It has been shown that thioacetate groups can bind to gold in ambient conditions with spontaneous deprotection [33]. With this in mind, the modified thioacetate terminated surfaces of **Layer-2** have been exposed to solutions of ~20 nm diameter gold nanoparticles. STM images (Fig. 3) show the decoration of such surfaces with gold nanoparticles. Such a partial surface coverage with gold nanoparticles is beneficial for the gap-mode Raman characterisation (see below), which would have been more difficult to interpret for densely packed or multilayer gold nanoparticle coverage.

Molecular characterisation of the surface functionalisation steps was achieved with Raman spectroscopy. Fig. 4 shows a cartoon illustration of the gap-mode and SHINERS (shell-isolated nanoparticle-enhanced Raman spectroscopy) methods used. The gap-mode method relies on the adsorption of gold nanoparticles directly onto the top of the monolayer under investigation, while SHINERS [34–36] employs gold nanoparticles coated with a thin SiO_2 shell. Control experiments were also undertaken for the gold nanoparticles on a clean gold substrate. Gap-mode Raman uses bare Au NPs, which can induce charge transport between the NPs and target molecules, which may also shift the frequency or intensity, giving a strong Raman signal as for surface enhanced Raman spectroscopy (SERS). SHINERS uses "insulated" NPs, which are not expected to promote charge transport between the NP and the molecules. Consequently, the SHINERS spectrum is weaker than comparable gap-mode Raman spectra, however the SHINERS signal can be simpler and clearer to interpret. For these reasons we use both techniques.

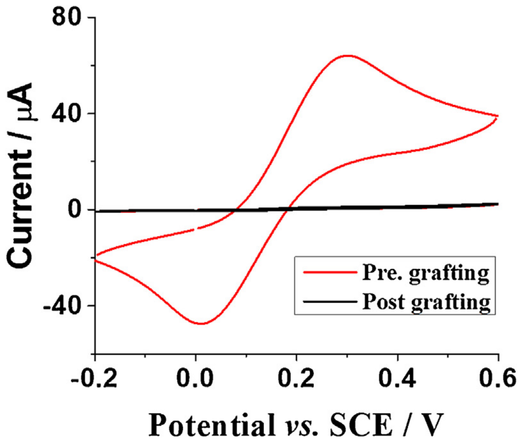
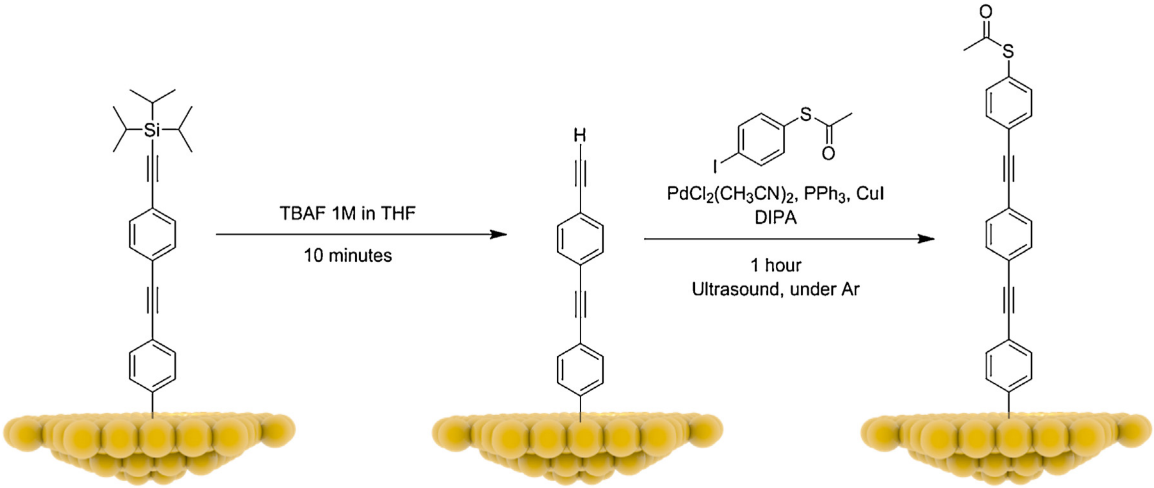


Fig. 2. Cyclic voltammograms of a Au(111) electrode in 1 mM $K_4Fe(CN)_6$ + 0.1 M KCl before (red line) and after (black line) electrografting, scan rate at 50 mV/s.



Scheme 2. Desilylation chemistry and Sonogashira coupling chemistry to synthesise **Layer-2**.

Fig. 5 shows normal Raman spectra of **1** and gap-mode Raman spectra of **Layer-1** and **Layer-2**, alongside a control experiment for the gold nanoparticles adsorbed on a blank gold substrate. Key spectral bands are summarized in Table 1. **Layer-1** shows spectral bands that agree well with those of pure compound **1**. Importantly **Layer-1** features in addition a band at ~400 cm^{-1} which corresponds to the Au-carbon bond stretch of the surface-attached compound. [37,38] **Layer-2**, on the other hand, features additional bands associated with the terminal thioacetate moiety, confirming success of the Sonogashira post-grafting step. SHINER spectra further confirm the success of the surface molecular functionalisation reactions, with new spectral bands apparent after addition of the thioacetate moiety (Fig. 6 and Table 2). Band assignments follow those given in references [39–41].

Layer-2 was used for single molecule electrical measurements recorded with an STM. The metal-molecule contacts here are the direct Au-C bond formed at the substrate and the thiol group at the other terminus. Note that Au-S covalent binding has been shown to spontaneously occur for thioacetate termini upon contact with gold even without the use of base [33]. The so-called $I(s)$ method has been used to generate molecular junctions and measure their conductance [27]. In this method the gold STM tip is lowered into the molecular layer, to high values of set-point current (I_0). The STM tip is then rapidly retracted and current decay (I) as a function of tip retraction distance (s) is recorded. A proportion of these retraction events lead to the formation of gold-molecule-gold junctions and these are recognised as plateaus in the $I(s)$ traces characteristic of current flow through intact molecular bridges [27]. As the junction is extended the plateaus rapidly decay as the molecular junction is cleaved. This presumably occurs at the Au (STM tip)-S interface, as the gold-thiol chemisorption bond will be weaker than the Au-C linkage at the substrate. In this respect we note that gold-thiol bonds have been quoted by Pensa et al. as having bond energies of 40–50 kcal mol^{-1} (1.7–2.2 eV) [42]. On the other hand Cheng et al. [6] find that the energy required to rupture the Au–C bond in Au-(CH$_2$)$_6$-Au molecular single junctions (bound to a single gold atom as a model of the electrode) is 3.0 eV. This highlights the strength of the Au-C bond.

Many plateau containing $I(s)$ traces are represented in histograms of all-current points, with the histogram peak taken as the single molecule conductance. A histogram of such junctions formed from **Layer-2** is shown in Fig. 7. A clear peak is seen at 3.0 nS. Examples of individual $I(s)$ traces and break-off distance analysis is given in the supporting information. By comparison with the 3 nS conductance recorded here, a similar OPE molecular wire with three phenylene rings (1,4-bis[4-(acetylsulphanyl) phenylethynyl]-2,6-dimethoxybenzene), which differs by having thiol groups at both termini and two solubilising methoxy substituents on the central phenyl ring, showed a conductance of slightly less than 2 nS with gold contacts [43]. Comparable amine terminated OPE analogues with three phenylene rings also give comparable conductance values centred around 2.5 nS, but with broad conductance histogram distributions [44]. These comparisons show that the single Au-C anchoring in **Layer-1** does not give appreciably higher junction transmission when compared to similar length OPE analogues with either thiol or amine anchoring groups. The influence of contacting groups on molecular

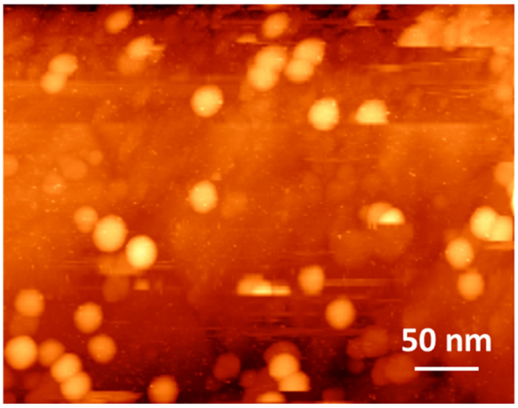


Fig. 3. An STM image of **Layer-2** decorated with 20 nm gold nanoparticles.

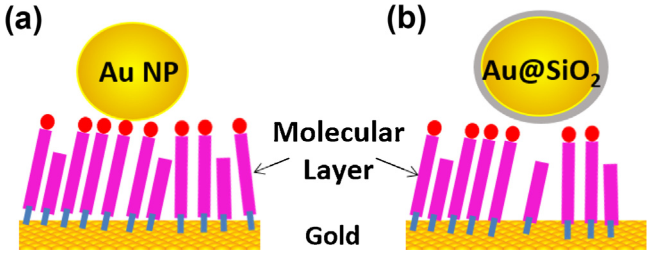


Fig. 4. (a) Schematic diagram of gap-mode SERS (Au(111)/Molecular layer/Au NP) and (b) SHINERS (Au(111)/Molecular layer/Au@SiO$_2$ NP) on the Sonogashira-modified surfaces. Colour code: blue line = Au-C surface contact, red circle = thiol or thioacetate molecular headgroup, grey shell = SiO$_2$ coating of SHINERS particle and pink rectangle = molecular backbone (with and without headgroup).

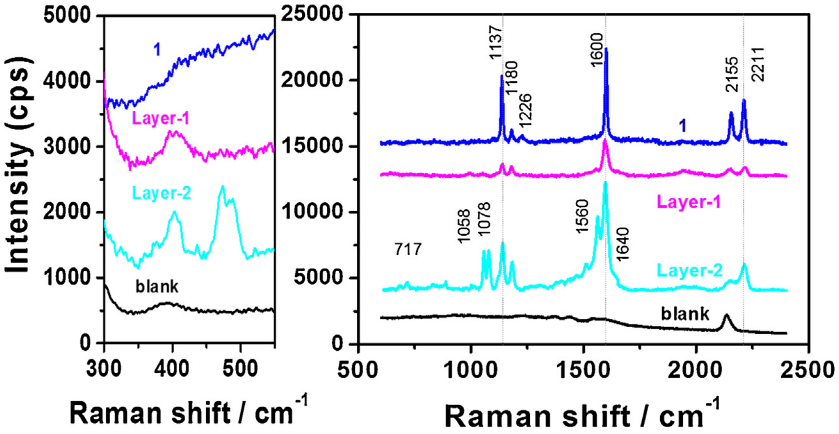


Fig. 5. Gap-mode Raman spectra of **Layer-1**, **Layer-2** on gold substrates and a control spectrum of gold nanoparticles on a blank gold substrate. The upper curve is a normal Raman spectrum of **1**.

Table 1
Summary of key Raman spectral bands of compound **1** and in gap-mode spectra of **Layer-1** and **Layer-2**. Band assignments follows those given in references [39–41]. Also see the supporting information for assignment of the 481 cm^{-1} band.

Mode/cm^{-1}	1	Layer-1	Layer-2
v(C≡C)	2211	2214	2214
	2155	2148	2148
Benzene ring stretching	1600	1592	1597
			1560
=C—NH$_2$ stretching	1226		
Ring modes	1180	1180	1180
	1137	1137	1139
Ring modes			1078
			1058
S—C—O bending mode of terminal thioacetate (see supporting information).			481
v(Au—C)		404	402

junction conductance has been a popular topic of investigation in single molecule electronics [2,45,46]. In general, contact chemistry that alters electronic coupling between molecular bridges and their contacts, and/or alters energy spacing between the contact Fermi energies and the HOMO or LUMO frontier orbitals may be expected to impact on the conductance. The similar conductance we report here between the Au-C terminated **Layer-1** and similar length OPE analogues with either thiol or amine anchoring groups may be related to **Layer-1** possessing a non-symmetrical contacting with Au-C at one end and Au-S at the other. Indeed, in agreement with our current observation, Hines et al. have found that gold-biphenyl-gold molecular junctions with direct Au-C bonding formed by in-situ diazonium grafting do not give appreciably higher conductance than analogous junctions with amine surface contacts [8], although the former junctions were found to be significantly more stable. Nevertheless, this recognised high stability of diazonium grafted monolayers would be expected to confer advantages to the metal-molecule junctions compared to the more fluxional contacts formed by amines or thiols [8].

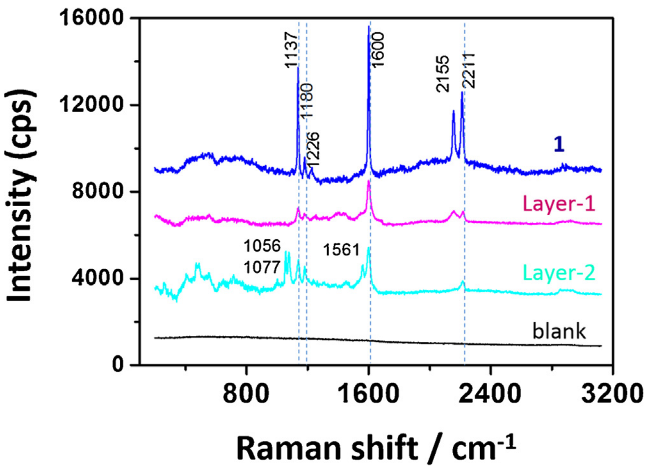


Fig. 6. SHINERS spectra of **Layer-1** and **Layer-2** on gold substrates and a control spectrum of gold nanoparticles on blank gold substrates. The upper curve is a normal Raman spectrum of **1**.

4. CONCLUSIONS

In summary, diazonium grafted oligo(phenylene ethynylene) (OPE) monolayers have been prepared from an amine terminated molecular wire using cathodic electrochemical grafting and protecting group chemistry to avoid multilayer formation.

Table 2
Summary of key Raman spectral bands of compound **1** and in SHINERS spectra of **Layer-1** and **Layer-2**. Band assignments follow those given in references [39–41].

Band/cm^{-1}	1	Layer-1	Layer-2
v(C≡C)	2211	2216	2214
	2155	2157	
Benzene ring stretching	1600	1600	1600
			1561
=C—NH$_2$ stretch	1226		
Ring modes	1180	1182	1178
	1137	1140	1139
Ring modes			1077
			1056

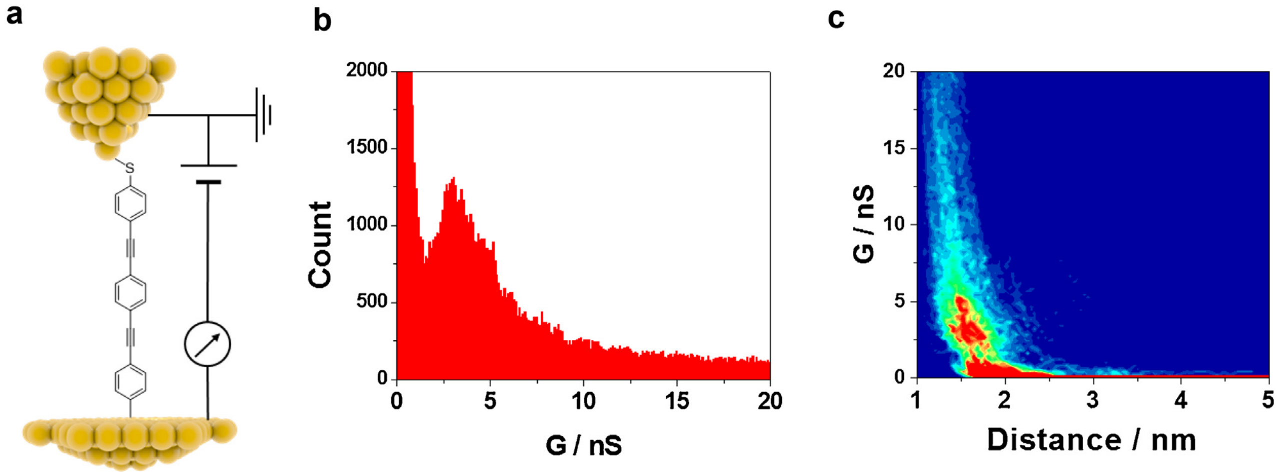


Fig. 7. (a) A schematic diagram of the STM conductance measurements, (b) conductance histograms and (c) 2D conductance and distance histograms of **Layer-2** (3.0 nS). The 2D histogram shows the break-off distance around 1.7 nm (**Layer-2**). The histogram consists of 336 traces. The setpoint current used was 30 nA (giving an initial calibrated tip-substrate distance, $s_0 \approx 1$ nm) and the STM tip retraction rate was 20 nm/s.

Following monolayer electrografting deprotection is achieved by desilylation chemistry and then Sonogashira coupling chemistry is used to append a phenyl-thioacetate terminal group to the monolayer. The success of these surface reactions is confirmed using Raman spectroscopy (gap-mode and SHINERS). It is shown that such monolayers are suitable for STM based molecular junction conductance measurements.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2016.10.095.

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