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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.

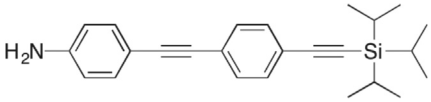
2. EXPERIMENTAL DETAILS

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