This article is part of a PCCP themed issue on:

Analysis, manipulation, and simulation on the nanoscale

Guest Editors: Harald Fuchs, Dominik Marx and Ulrich Simon

Other papers in the issue:

Textile electrodes as substrates for the electrodeposition of porous ZnO

Fluorescence resonance energy transfer in conjugated polymer composites for radiation detection

Simulating charge transport in tris(8-hydroxyquinoline) aluminium (Alq3)

Functional molecular wires

Forced imbibition—a tool for separate determination of Laplace pressure and drag force in capillary filling experiments

Assembly of DNA-functionalized gold nanoparticles studied by UV/Vis-spectroscopy and dynamic light scattering

Metal adsorption on oxide polar ultrathin films

Microstructure analysis of monodisperse ferrofluid monolayers: theory and simulation

Molecular simulation study of temperature effect on ionic hydration in carbon nanotubes

Adsorption of small organic molecules on anatase and rutile surfaces: a theoretical study

Electron-induced isomerisation of dichlorobenzene on Cu(111) and Ag(111)

Au–Pd supported nanocrystals prepared by a sol immobilisation technique as catalysts for selective chemical synthesis

Transport effects in the oxygen reduction reaction on nanostructured, planar glassy carbon supported Pt/GC model electrodes

Structure, optical properties and defects in nitride (III–V) nanoscale cage clusters

Adsorption of oxalate on rutile particles in aqueous solutions: a spectroscopic, electron-microscopic and theoretical study

Theoretical evaluation of nano- or microparticulate contact angle at fluid/fluid interfaces: analysis of the excluded area behavior upon compression
Functional molecular wires

Geoffrey J. Ashwell, a,b Piotr Wierczowiec, a,b Laurie J. Phillips, a,b Christopher J. Collins, a,b Joanna Gigon, a,b Benjamin J. Robinson, a,b Christopher M. Finch, c Ian R. Grace, c Colin J. Lambert, c Philip D. Buckle, d Kym Ford, c Barry J. Wood e and Ian R. Gentle e

Received 17th December 2007, Accepted 15th February 2008
First published as an Advance Article on the web 22nd February 2008
DOI: 10.1039/b719417

The properties of self-assembled molecules may be tuned by sequentially coupling components on a gold surface, the molecular electronics toolbox of chemically reactive building blocks yielding molecular wires with diode-like current–voltage (I–V) characteristics. The bias for rectification in each case is dependent upon the sequence of electron-donating and electron-accepting moieties and similar behaviour has been achieved for four different contacting techniques.

Introduction

Current interest in molecular scale electronics focuses upon non-invasive electrical contacting to molecules and ultra-thin films as well as self-assembling molecules that act as wires and diodes, the latter being organic counterparts of the pn junction. In these, a donor and acceptor are linked via a σ-bridge or, if sterically hindered, a π-bridge whereby induced non-planarity breaks the conjugation and safeguards the integrity of the electroactive moieties. There has been some reluctance to accept the concept of molecular rectification but extensive studies now show it to be the rule rather than the exception. For example, it has been verified by the following: (i) rectification in opposite quadrants of the I–V plot when chromophores are respectively linked to the substrate via their acceptors and donors, (ii) symmetrical curves from centric Langmuir–Blodgett bilayers and, as above, rectification in opposite quadrants when amphiphilic isomers with the hydrophobic tail located at the donor or acceptor end are aligned by LB deposition, the films in this case is dependent upon the sequence of electron-donating and electron-accepting moieties and similar behaviour has been achieved for four different contacting techniques.

Step-by-step deposition

Molecular wires were synthesized on gold-coated substrates using a multi-step modular chemistry approach, the surface-based reactions being monitored from the frequency change following deposition on the gold electrodes of 10 MHz quartz crystals and verified by X-ray photoelectron spectroscopy (XPS). For example, symmetrical wires were obtained by immersing plasma-cleaned substrates in a chloroform solution of 4-[(3-mercaptophenylimino)methyl]benzaldehyde (0.1 mg cm⁻²) to yield self-assembled monolayers. The SAM-coated substrates were then immersed in an acetone solution of 2,6-diaminoanthra-9,10-quinone (0.1 mg cm⁻³) to which glacial acetic acid (0.05 cm³) was added to assist the reaction. Finally, they were immersed once more in a chloroform solution of 4-[(3-mercaptophenylimino)methyl]benzaldehyde in the presence of acetic acid. Condensation of the surface-based substituents, for example CHO after the first step and NH₂ after the second, with the solution-based reactants yields molecular wires via imino group formation (Scheme 1).

A Sauerbrey analysis of the frequency change of the 10 MHz quartz crystals following SAM formation provides an area of ca. 0.31 nm² molecule⁻¹ after 3 h, which approximates to the molecular cross-section. Confirmation of chemisorption has been verified by XPS: a doublet at 162.8 eV and 164.2 eV characteristic of the sulfur binding energy of the gold–thiolate link, whereas the parent compound exhibits a sulfur doublet at 164.5 and 165.1 eV that is typical of its thiol group. A symmetrical imino nitrogen peak at 398.6 eV (N 1s), cf. 399.3 eV in the parent self-assembling compound, is also found and quantitative analysis of the areas under the curves, fitted using a Gaussian–Lorentzian function, yields an expected sulfur to nitrogen ratio of ca. 1:1 when corrected for atomic sensitivity factors.

Molecular areas obtained for the initially formed SAM provide the limiting values for all subsequent reaction steps

---

a School of Chemistry, College of Physical and Applied Sciences, Bangor University, Bangor, Gwynedd, UK LL57 2UW. E-mail: g.j.ashwell@bangor.ac.uk; Tel: +44 (0)1248 382386
b Ysgol Cemeg, Coleg Gwyddonau Ffisegol a Chymhwysol, Prifysgol Bangor, Bangor, Gwynedd, UK LL57 2UW
c Department of Physics, Lancaster University, Lancaster, UK LA1 4YB
d QinetiQ PLC, St Andrews Road, Malvern, UK WR14 3PS

e School of Molecular and Microbial Sciences, University of Queensland, St Lucia, Brisbane, QLD 4072, Australia

This journal is © the Owner Societies 2008
where reaction times are ca. 24 h. When reacted with 2,6-diaminoanthra-9,10-quinone, XPS studies on the resultant wire again yield a doublet that corresponds to the bound sulfur with binding energies consistent with those detailed above for the initially formed SAM. However, the nitrogen peak is asymmetric and its profile arises from slightly different N 1s binding energies associated with the imino (N=C=H) and amino (NH$_2$) groups (Fig. 1). A peak-fitting routine has resolved the spectrum into two separate bands with binding energies of 399.3 and 400.7 eV and, although the signal to noise ratio is poor, areas that approximate to the ratio of the different nitrogens in the molecular structure following the second step. The combined areas under the curves also yield a nitrogen to sulfur ratio of ca. 3:1 (cf. 1:1 for the SAM), which is expected following reaction with 2,6-diaminoanthra-9,10-quinone.

Symmetrical wires

$I–V$ characteristics of films following each of the three steps shown in Scheme 1 were investigated by scanning tunnelling spectroscopy (STS), the data each time being obtained using a Veeco Instruments Nanoscope IV Multimode microscope. In excess of 100 curves were obtained at different locations across each of the films and the data averaged for multiple scans on the same spot using contacting gold probes. The behaviour was found to be independent of the set point conditions, which were varied across a broad range of current and voltage. They affect the magnitude of the current by altering the distance between probe and surface but have minimal effect on the shapes of the $I–V$ curves.

The films exhibit almost symmetrical $I–V$ curves for the initially formed SAM, rectifying behaviour for the donor–acceptor structure formed by the surface-based reaction with 2,6-diaminoanthra-9,10-quinone, and symmetrical behaviour for the donor–acceptor–donor sequence formed by subsequent reaction with 4-[(3-mercaptophenylimino)methyl]benzaldehyde (Fig. 2). The rectification is explained in the next section but at this stage we note the reproducible control of different $I–V$ characteristics by sequencing the molecular components. It confirms that the behaviour is molecule-induced and we also note corresponding $I–V$ profiles obtained by electrometer-based methods. Electrical contact was induced by magnetic manipulation of a ferromagnetic cantilever with a gold wire electrode attached. The apparatus is schematically shown in Fig. 3 for SAMs on planar substrates and in Fig. 4 for those assembled on 25 µm diameter gold wire where contacting is via a crossed-wire method.

The theoretical current through the symmetrical molecular wire formed from the third step of the process was calculated by using an $ab$ initio approach with a combination of the DFT code SIESTA$^{22}$ and a Green’s function scattering method, as encapsulated in the non-equilibrium molecular electronics SMEAGOL$^{23}$ code. The relaxed geometry was found using SIESTA and, to describe charge transfer effects at the lead–molecule interface, the structure was extended to include five surface layers of gold with each layer containing fifteen gold atoms. This large surface area is required to fully describe the coupling between the gold surfaces and the molecular wire when it is vertically aligned between the contacts. A mean-field, DFT, tight-binding Hamiltonian describing the extended structure is obtained, from which the scattering matrix and electron transmission coefficient $T(E)$ are computed. We assume that the bonding of the thiol to the gold surface causes the molecular wire to be vertically aligned in the junction with a characteristic Au–S–C angle of 120°. For this configuration, the transmission coefficient $T(E)$ displays a variety of resonant features which may be modified by out-of-plane rotations of the various ring structures. For the relaxed geometry, shown in Fig. 5, LUMO resonances at ca. 0.2 eV and above show typical Lorentzian line shapes that correspond to Breit–Wigner resonances through molecular levels delocalized.

![Fig. 1](image-url)  
**Fig. 1** XPS analysis of the nitrogen regions of the spectrum for films obtained after (a) step 1 and (b) step 2. The latter has been resolved into peaks with binding energies of 399.3 and 400.7 eV.
across the molecule. Our previous studies have demonstrated that the attachment of side groups to a molecular backbone causes Fano resonances in the transmission\textsuperscript{24} and thus, the anti-resonance at \(E_0\) may be attributed to the oxygens of the central anthraquinone moiety of the molecular wire.

The modelled current shown in Fig. 5 has been computed by integrating the transmission coefficient using the equation below, where \(\mu_{L,R} = E_F \pm V/2\): \(I = \frac{\hbar}{2} \int_{E_F}^{E_0} T(E)dE\). The calculated \(I-V\) characteristics are similar to the profile of the STS obtained curve (see Fig. 2) and those obtained from electrometer-based techniques shown schematically in Fig. 3 and 4. They are also consistent with the \(I-V\) plots obtained by assembling the molecules across the nano-sized electrode gaps of preformed device structures\textsuperscript{1} (Fig. 6). The theoretical data

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{\(I-V\) characteristics of a SAM formed from 4-[(3-mercaptophenylimino)methyl]benzaldehyde (left) and normalised data following reaction with 2,6-diaminoanthra-9,10-quinone (red) and 4-[(3-mercapto-phenylimino)methyl]benzaldehyde (blue). The sign corresponds to the substrate electrode and data were collected \textit{via} STS.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{\(I-V\) characteristics of a SAM formed from 4-[(3-mercaptophenylimino)methyl]benzaldehyde (top left) and normalised data following reaction with 2,6-diaminoanthra-9,10-quinone (red) and 4-[(3-mercapto-phenylimino)methyl]benzaldehyde (blue) where the sign corresponds to the substrate electrode. Data were collected using the apparatus shown where movement of a 25 \(\mu\)m diameter gold wire electrode attached to a ferromagnetic cantilever is induced by tuning the current through a solenoid located below.}
\end{figure}
display typical off-resonant currents due to the broadened HOMO and LUMO resonance tails and, significantly, the theoretically predicted current of ca. 0.2 nA at 300 mV is in reasonable agreement with the experimentally measured single molecule current of 0.55 nA at the same bias (Fig. 7). This was obtained using the method of Haiss et al.\textsuperscript{25} and achieved by observing transient current jumps with an STM probe located just above the surface. In their work on films with surface-based thiol groups, such transient behaviour was interpreted as reversible chemisorption of the sulfur to the gold probe. It is, however, more likely that the probe simply contacts the film, for example via diffusion of its gold atoms, and contact is not necessarily with the sulfur. Moreover, we have found that current jumps also occur when the substrate is uncoated (Au,
Si/SiO₂, highly oriented pyrolytic graphite) or has an inert organic surface layer such as CₙH₂ₙ₊₁–S–Au.

I–V profiles of molecular wires formed from the third step of Scheme 1 are similar for four different contacting methods: STS (Fig. 2); magnetically induced contacts (Fig. 3) including crossed-wire arrangements (Fig. 4); and prefabricated devices with the molecules located across nano-sized electrode gaps (Fig. 6). A preliminary communication on these nano-gap structures has reported that the molecular wires assemble as a single strand necklace around the central insulating 6 μm diameter core. This observation was based on the number of participating molecules, estimated from a ratio of the device and single molecule currents, and thereafter from their mean separation around the core circumference. The highest device current so far obtained, 15 μA at 300 mV (cf. 0.55 nA single molecule current at this voltage), yields a mean separation of 0.7 nm which suggests that the molecular wires loosely pack as a necklace arrangement. Significantly, I–V profiles obtained for the molecule-inserted nano-gap device are similar to those obtained from closely packed films where the mean area from a Sauerbrey analysis of the quartz crystal frequency data is typically ca. 0.3 nm² molecule⁻¹. They are similar to profiles determined by STS (Fig. 2) where electrical contact is either to a single molecule or small cluster of molecules. They are also similar to those obtained by the magnetically induced technique (Fig. 4) where the area of the gold wire electrode in contact with the film is ca. 0.05 nm², this value being derived from the number of participating molecules as estimated by comparison with single molecule current.

Rectifying molecular wires

Molecular rectification requires a donor–acceptor sequence and we now focus on rectifying arrangements obtained by reacting components from the chemical toolbox following the chemisorption (molecular self-assembly) of 4-[(4-mercapto-phenylimino)methyl]benzaldehyde on gold-coated substrates (Scheme 2). The initially formed SAM exhibits symmetrical I–V curves similar to those obtained from the 3-mercaptopHENYL isomer and, as before, rectification is observed when the assembled moieties react with 2,6-diaminoanthra-9,10-quinone (Fig. 8). The direction of electron flow at forward bias is from the STM probe to substrate. Electrons tunnel from the cathode to 2-aminoanthra-9,10-quinone acceptor on one side and from the thiolate-connected end of the molecule, which is weakly electron-donating, to the anode on the other side. The direction of forward flow confirms that the surface-based 2-aminoanthra-9,10-quinone moiety is electron-accepting and it suggests that the NH₂ substituent is either resonantly coupled to the acceptor’s ring structure or the electron-donating character of the substituent is otherwise effectively neutralised by adsorption to the contacting gold probe. When the film formed from the second step of Scheme 2 is reacted with 4-dimethylaminonaphthaldehyde, the resultant wire-like structure also rectifies but this time at opposite bias. It is logical as, although this molecular wire has a donor–acceptor–donor (Dₓ–A–Dᵜ) sequence, the electron-donating character of the terminal groups is very different. The dialkylamino moiety is a far stronger donor than the thiolate group and the device may be considered as Au|Au–S–wire–A–π–D|Au.

Other structures formed from surface step-by-step reactions (e.g. Scheme 3) exhibit a corresponding bias for rectification as long as the molecular ordering of the donor–acceptor sequence is the same (Fig. 9). Furthermore, all sequences studied to date exhibit rectifying behaviour when there is a donor–acceptor arrangement and, albeit not shown, the I–V curves are
invariably symmetrical when the first and third components of Scheme 2 and also Scheme 3 are the same. This is clearly demonstrated by the symmetrical derivative obtained from the third step of Scheme 1 (e.g., see Fig. 6). The I–V characteristics are reproducible and, as before, have been verified for multiple film preparations as well as by using different measuring methods: e.g., STS and magnetically induced contacting as shown in Fig. 3 and 4.

Extended molecular wires

The step-by-step technique described here has similarly been used to synthesise functional molecular wires with extended lengths and up to six component parts (Fig. 10) although much longer molecules could be obtained by this method. For example, subsequent to the formation of SAMs from 4-[(3-mercapto-phenylimino)methyl]benzaldehyde on the gold electrodes of 10 MHz quartz crystals (step 1), molecules were lengthened by sequentially reacting each of the following: 1,4-phenylenediamine (step 2), 2,5-bis(hexyloxy)terephthalaldehyde (step 3), 2,6-diaminoanthra-9,10-quinone (step 4), terephthalaldehyde (step 5) and finally 4-nitroaniline (step 6), which is monosubstituted with a reactive group to terminate the sequence. For each of these steps, SAM-coated quartz crystals were immersed in a solution of the reactant for 24 h and the process monitored from the frequency change following rinsing with copious volumes of solvent and drying in air. A Sauerbrey analysis of the frequency data verifies that molecules in the initially assembled layer closely pack with an area of ca. 0.31 nm² molecule⁻¹ and the first reacted species combines in a 1:1 ratio. The substituent groups of the next component, 2,5-bis(hexyloxy)terephthalaldehyde, provide a significantly larger cross-section: consequently, it combines with ca. 50% of molecules and the reactants in all subsequent steps then combine with ca. 80–100% yields (Fig. 11).

XPS studies on the wire as well as other final step wires (Schemes 1–3) provide evidence of the initial self-assembly and subsequent condensation reactions. Their spectra exhibit sulfur doublets at 162.8–163.0 eV (S 2p3/2) and 164.0–164.2 eV (S 2p1/2). Those with terminal dialkylamino groups, for example, as shown in Scheme 3, exhibit slightly asymmetric N 1s peaks at ca. 399.2–399.5 eV (imino) with shoulders on the high energy side that correspond to the surface-based amino substituent. In contrast, wires with the terminal nitro group exhibit non-overlapping N 1s peaks with imino and nitro binding energies at ca. 399.2 and 405.8 eV respectively. The signal to noise ratio from monolayer films is poor and quantitative analysis of the data is challenging when the ratio of the different types of nitrogen is 6:1 as for the molecule shown in Fig. 10. However, when condensation of nitro-terminated substituents is scheduled at an earlier stage, XPS characterisation of these shorter molecular wires yields binding energies for the imino and nitro nitrogens with areas that approximate to the expected ratio.

Films formed after the final step of the six-stage process exhibit rectifying behaviour (Fig. 12) and the forward bias direction of electron flow is consistent with the electron-donating moieties being at the substrate and the electron-accepting moieties at the upper surface. The donor-acceptor sequence in this nitro-terminated wire, relative to the donor-terminated wire obtained from the third step of Scheme 2, is reversed and, significantly, rectification this time occurs in the
Fig. 9  $I-V$ characteristics of a SAM formed from 4-(3-acetylsulfanylpropyloxy)benzaldehyde (left) and normalised data following reaction with 2,6-diaminoanthra-9,10-quinone (red) and 4-dimethylaminobenzaldehyde (blue). The data were collected by STS and the sign corresponds to the substrate electrode.

Fig. 10 Structure of the molecular wire formed in six steps on gold.

Fig. 11 Frequency change from each stage of the process vs. molecular mass of the wire as it is first assembled and then elongated in five subsequent steps on 10 MHz quartz crystals.

Fig. 12  $I-V$ characteristics of the molecular wire from Fig. 10 where the sign corresponds to that of the substrate electrode and data were obtained by STS. Electron flow at forward bias is from the gold probe (cathode) to the electron-accepting nitro group and from the thiolate end of the wire to the gold substrate (anode).

opposite quadrant of the $I-V$ plot. We note a consistency in the $I-V$ characteristics as, even for wires with weak and strong donors on opposite sides of the anthraquinone acceptor (e.g. from the third step of Scheme 3), the forward bias direction of electron flow is from the cathode to the more electron-accepting side of the molecule and from the stronger of the two
donors to the anode on the opposite side of the device. This forward bias direction of flow is consistent with that predicted by Aviram and Ratner\textsuperscript{16} although they considered a $\sigma$-electron bridge between donor and acceptor to be a prerequisite for molecular rectification. In contrast, we have demonstrated electrical asymmetry from \pi-bridged donor–acceptor wires as well as from asymmetric donor–acceptor–donor systems where one of the terminal groups is only weakly donating compared with the other.

**Conclusions**

In summary, the properties of the extended molecular wire formed from the six-stage synthesis and other functional wires reported here confirm the significance of the step-by-step method. It readily provides complex molecular structures by simply using a chemical toolbox of commercially available component units and significantly, detailed understanding of synthetic chemistry is not required. It provides the means to overcome difficulties in precisely controlling the component length to connect across prefabricated nano-sized electrode gaps\textsuperscript{1,2} and permits functional electroactive groups to be readily ordered with a predetermined donor–acceptor sequence for use as molecular diodes.

**Acknowledgements**

We acknowledge the Engineering and Physical Sciences Research Council, Royal Society/Wolfson Foundation, Australian Research Council, Welsh Assembly Government and Centre for Advanced Functional Materials and Devices for support and the Cranfield XPS facility for providing some preliminary data.

**References**