CAMBRIDGE

Cambridge University Press
978-1-107-40833-3 - Concepts in Molecular and Organic Electronics: Materials Research Society Symposium Proceedings: Volume 1154
Editors: Norbert Koch, Egbert Zojer, Saw-Wai Hla and Xiaoyang Zhu
Excerpt
More information

Molecular Scale Electronics

Mater. Res. Soc. Symp. Proc. Vol. 1154 © 2009 Materials Research Society 1154-B04-02

A Dramatic Effect of Water on Single Molecule Conductance

Edmund Leary[1], Horst Höbenreich[1], Simon J. Higgins[1], Harm van Zalinge[1], Wolfgang Haiss[1], Richard J. Nichols[1], Christopher Finch,[2] Iain Grace[2] and Colin J. Lambert[2]
1. Department of Chemistry, University of Liverpool, L69 7ZD, U.K.
2. Department of Physics, Lancaster University, Lancaster, LA1 4YB, U.K.

ABSTRACT

Simple alkanedithiols exhibit the same molecular conductance whether measured in air, under vacuum or under liquids of different polarity[1]. Here, we show that the presence of water 'gates' the conductance of a family of oligothiophene–containing molecular wires, and that the longer the oligothiophene, the larger is the effect; for the longest example studied, the molecular conductance is over *two orders of magnitude larger* in the presence of water, an unprecedented result suggesting that ambient water is a crucial factor to be taken into account when measuring single molecule conductances (SMC), or in the design of future molecular electronic devices. Theoretical investigation of electron transport through the molecules, using the *ab initio* non-equilibrium Green's function (SMEAGOL) method[2], shows that water molecules interact with the thiophene rings, shifting the transport resonances enough to increase greatly the SMC of the longer, more conjugated examples.

INTRODUCTION

We have examined the electrical properties of molecular junctions in which a π-conjugated, often redox-active, unit is sandwiched between two thiahexyl 'spacers', with gold contacts[3-5]. Since the frontier orbitals of the alkyl groups are far from the Fermi energy of the contacts, while the frontier orbitals of the π–conjugated unit are closer to the Fermi energy, these molecules may be thought of as molecular analogs of double tunnelling barriers[6]. To examine the effect of varying the length (and hence degree of conjugation) of the π-conjugated unit, oligothiophenes were selected. Oligothiophenes, polythiophenes and their derivatives have been extensively investigated as semiconductors in organic thin film transistors and photovoltaic devices[7, 8]. We have found a remarkable effect of water on the SMC of longer oligothiophene molecules, and we report these results here.

EXPERIMENT AND THEORY

Low-coverage phases of **1**–**4** (as dithiolates) on clean, atomically–flat gold surfaces were prepared; X-Ray photoelectron spectra were consistent with the intact molecules 'lying down' and binding to Au through both thiol sulfurs. We employed the scanning tunnelling microscopy (STM)-based I(s) technique of Haiss *et al*[3] to determine the single molecule conductances of **1**–**4**. Au STM tip is brought close to the surface (without making contact), the feedback loop is switched off and the tip is retracted while the tunneling current is monitored. In experiments where a molecule bridges between tip and substrate, the current at a given retraction distance is greater than in the absence of a molecule, and characteristic current plateaux are observed; see Figure 1B.

In the theoretical calculations, the relaxed geometry of the oligothiophenes was found using the density functional code SIESTA[9]. A double-zeta plus polarization basis set, Troullier-Martins pseudopotentials to remove core electrons and the Ceperley-Alder Local Density Approximation description of the exchange correlation, were used and the atomic positions were relaxed until all force components were smaller than 0.02 eV/Å. The molecule was then extended to include the surface layers of the gold leads; a layer comprising 14 atoms was chosen and the extended region included 8 layers of gold to allow a suitable representation of charge transfer effects at a molecule-gold interface. A fixed geometry corresponding to the fully-extended, all–*trans* molecule in the junction was assumed. The location of the thiols was taken to be a top site (*i.e.* directly above a surface gold atom), although the alkane chains limit any dependence on the contact geometry.

RESULTS

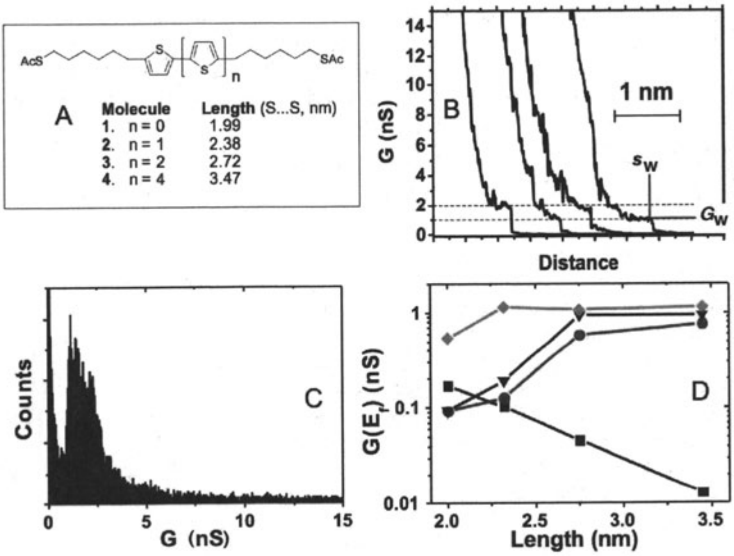

Figure 1. (A) Structures of **1-4**, and S…S distances for the fully-extended molecules, calculated using molecular mechanics. (B) Current-distance relations for several I(s) determinations on **3**. (C) Histogram of all of the characteristic conductance plateaux (G_w) observed for **2** measured in ambient air (setpoint current I_w = 4 nA, tip-sample bias 200 mV; 300 measurements, of which 72 produced plateaux as in B). (D) Experimentally-determined single molecule conductance values (*vs.* molecular length) for **1–4**, measured in ambient conditions (light blue diamonds), computed zero-bias conductance in the absence of water (black squares), and in the presence of individual water molecules located at the favoured "side" positions (red circles). The blue triangles show the computed ensemble-averaged conductance in the presence of 'side' molecules together with randomly-positioned background water molecules.

Samples of **1–4** (Figure 1A) were synthesised and fully characterised by standard chemical techniques (details to be published). Since the conduction mechanism in such junctions is superexchange, the molecular conductance of **1–4** was expected to decrease exponentially with the length of the molecule[10]. Remarkably, however, the experimental molecular conductances of **1–4** are almost length-independent (Figure 1D). It is clear from the experimental data in Figure 1D that all of the oligothiophene units are acting as tunnelling barrier indentations, because the conductances are all larger than that of $HS(CH_2)_8SH$, although **1–4** are all much longer than $HS(CH_2)_8SH$ (S…S = 1.19 nm)[11]. To understand this unusual behavior, we have carried out a detailed theoretical investigation of electron transport through these molecules, using the recently–developed *ab initio* non-equilibrium Green's function (SMEAGOL) method[12].

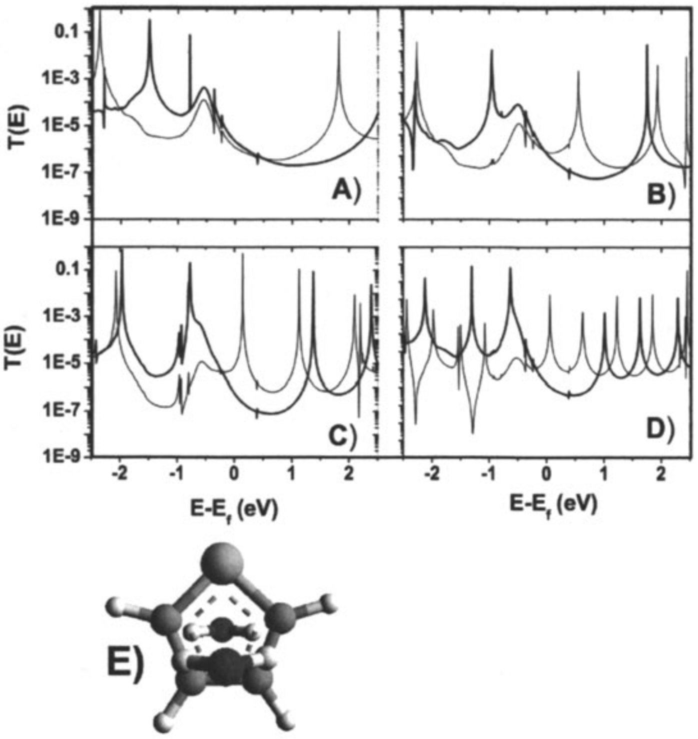

Figure 2. Zero bias transmission coefficient versus energy for **1** (A), **2** (B), **3** (C) and **4** (D). The blue curves are obtained in the absence of water and the black curves in the presence of two water molecules located at the lowest energy "side" positions as illustrated in (E).

The black curves in Figure 2(A-D) shows the electron transmission coefficient T(E) for electrons of energy E for **1–4**. These molecules exhibit the expected behavior of a decrease in the gap between the HOMO and LUMO resonances as the molecule becomes longer. Figure 1D (black squares) shows a plot of the conductance at the Fermi energy against the molecule length and shows that the conductance of **1–4** decreases exponentially with length, in spite of the decrease in HOMO-LUMO gap with increasing number of thiophene rings. The apparent discrepancy between theory and experiment was resolved by realizing that the calculations leading to Figure 1D (black squares) assume a vacuum environment, whereas the experiments were conducted in ambient air, containing water vapor, and gold electrodes under such conditions are coated with a film of water. We therefore undertook detailed *ab initio* calculations in the presence of surrounding water molecules. We examined both the relative effects of water molecules in the first solvation shell of the oligothiophene units, occupying favored local energy minima positions, and the effects of randomly-positioned water molecules beyond the first solvation shell.

First we performed molecular dynamics simulations to find the optimum location of a water molecule in the vicinity of the thiophene units. For molecule **1**, Figure 2 shows the location of the lowest energy position (in qualitative agreement with previous work[13]) and it also produces the most dramatic change in the conductance, and therefore we initially recalculated the conductance in the presence of these 'side' water molecules alone. For **1–4**, we include two 'side' water molecules per thiophene ring. Figure 2 (a-d) shows that in the presence of these 'side' molecules, the transmission resonances are significantly shifted with respect to their vacuum positions. In particular, the LUMO resonance shifts towards the Fermi energy in all molecules, thus causing an increase in the zero-bias conductances. Crucially, the longer molecules exhibit greater shifts, due to the presence of a larger number of water molecules, which in turn compensates for the reduction in conductance as a function of length. Figure 1D (red circles) shows the zero-bias conductance in the presence of water molecules in the 'side' configuration. Clearly, the exponential length dependence is removed and, in agreement with experiment, after an initial rise for small n the conductance is predicted to be almost independent of length.

We also examined the effect of a homogeneously-disordered cloud of water molecules surrounding the molecules, and we find that this alone does not remove the exponential length dependence. However, when included together with the 'side'-bound water, additional homogeneously-disordered water does have a small but significant additional effect upon the calculated conductances (Figure 1D, blue triangles). Random water also leads to a smearing of transmission resonances, so that negative differential resistance behaviour (which might be expected from a brief inspection of Figure 2C or 2D, for example) is not observed.

The remarkable results from the theoretical calculations of molecular conductance in the presence of water prompted us to perform I(s) conductance measurements on molecules **1** and **3** under water-free conditions. Figure 3 compares the conductance histograms for **3** measured after purging the STM sample chamber with dry argon for 24 h (right), and subsequently after re-admitting ambient air (left).

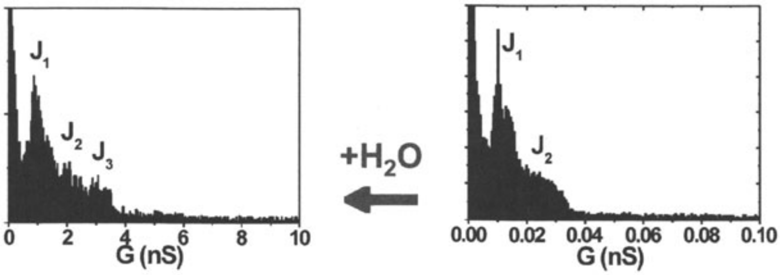

Figure 3. Histogram of the characteristic current plateaux ($I(w)$) observed for molecule **3** measured under: (right) dry argon, $U_{tip} = +1$ V, setpoint current = 7 nA; 60 I(s) scans with plateaux selected from 350 total; (left) after subsequent re-admission of ambient (wet) air to the STM chamber, same conditions, 48 I(s) scans with plateaux selected from 250 total.

The conductance of **3** determined under argon is (0.012 ± 0.006) nS *almost two orders of magnitude smaller* than the conductance in air. When ambient air was re-admitted to displace the argon in the ambient pressure STM chamber, the conductance returned to the value previously found under ambient conditions (within experimental error), (1.0 ± 0.2) nS. Crucially, this also occurred when the experiment was conducted under Ar in the presence of water vapour, excluding the possibility that atmospheric O_2 might be involved in the effect. This result is reproducible. It is important to note, however, that the conductance of **3** after argon purging for 24 h is much larger than would be predicted for an α,ω–dithiaalkane of length (2.74 nm) comparable with **3** (*i.e.* $HS(CH_2)_{20}SH$, S…S distance 2.69 nm; calc. conductance 1.37×10^{-5} nS), and that therefore, the terthiophene unit is still acting as an indentation in the tunnelling barrier. We tried to measure the conductance of junctions with molecule **4** under dry Ar, but we could not measure meaningful I(s) data; the conductance of **4** under Ar was too low for the current follower on our STM even with $U_{tip} = 1.0$ V. This puts an upper limit of the conductance of **4** in the absence of water of 0.006 nS, over two orders of magnitude smaller than in the presence of water. In contrast, and again in agreement with the theoretical calculations, the molecular conductance of **1** did not change significantly under argon compared with ambient air.

DISCUSSION

The observation that water, by weakly interacting with the π–system of a molecule, can drastically alter the molecular conductance of the gold|molecule|gold junction, has wider implications in other important electron transfer processes. Water is known significantly to affect rates of electron transfer (ET) reactions in biological systems by mediating ET coupling pathways and changing activation free energies[14]. Unusual 'structured' water molecules near redox cofactors have been found to accelerate ET kinetics when the cofactors are close together; such water appears to show anomalously weak distance decay for electron tunneling[15]. In this instance, it is believed that water is involved in the electron tunneling pathway, whereas in **3** and **4** it "gates" the electron tunnelling pathway through the molecule. It has been suggested that water could interact strongly with thiol–gold contacts[16], leading to a length-independent *lowering* of the conductance of gold|molecule|gold junctions, for simple alkanethiols and alkanedithiols. Our results represent the first examples of a length-dependent water-induced "gating" of electron transport through a synthetic molecular wire. They will have implications for molecular electronics, and it may also provide a new paradigm for the construction of single molecule sensors. It also emphasizes that solvent effects must be taken into account in laboratory studies of single molecule electronics.

REFERENCES

1. X. L. Li, J. He, J. Hihath, B. Q. Xu, S. M. Lindsay and N. J. Tao, J. Am. Chem. Soc. **128**, 2135-2141 (2006).
2. A. R. Rocha, V. M. Garcia-Suarez, S. Bailey, C. Lambert, J. Ferrer and S. Sanvito, Phys. Rev. B **73**, 085414 (2006).
3. W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Höbenreich, D. J. Schiffrin and R. J. Nichols, *J. Am. Chem. Soc.* **125**, 15294-15295 (2003).
4. E. Leary, S. J. Higgins, H. van Zalinge, W. Haiss, R. J. Nichols, J. O. Jeppesen, S. Nygaard and J. Ulstrup, J. Am. Chem. Soc. **130**, 12204-12205 (2008).
5. E. Leary, S. J. Higgins, H. van Zalinge, W. Haiss and R. J. Nichols, Chem. Comm. 3939-3942 (2007).
6. L. L. Chang, L. Esaki and R. Tsu, *Appl. Phys. Lett.*, **24**, 593-595 (1974).
7. T. A. Skotheim and J. R. Reynolds, eds., Handbook of Conducting Polymers Third Edition, Taylor and Francis Group, Boca Raton, 2007.
8. I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. M. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee and M. F. Toney, Nature Materials **5**, 328 (2006).
9. J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon and D. Sanchez-Portal, *J. Phys-Condens. Mat.* **14**, 2745-2779 (2002).
10. A. M. Kuznetsov and J. Ulstrup, Electron Transfer in Chemistry and Biology: An Introduction to the Theory, John Wiley, Chichester, U.K., 1999.
11. W. Haiss, S. Martín, E. Leary, H. van Zalinge, S. J. Higgins, L. Bouffier and R. J. Nichols, *J. Phys. Chem. C*, 2009, **113**, 5823-5833.
12. A. R. Rocha, V. M. Garcia-Suarez, S. W. Bailey, C. J. Lambert, J. Ferrer and S. Sanvito, Nature Materials **4**, 335-339 (2005).
13. S. C. Meng, J. Ma and Y. S. Jiang, J. Phys. Chem. B **111**, 4128-4136 (2007).
14. H. B. Gray and J. R. Winckler, Q. Rev. Biophys. **36**, 341 (2003).
15. J. P. Lin, I. A. Balabin and D. N. Beratan, Science **310**, 131 (2005).
16. D. P. Long, J. L. Lazorcik, B. A. Mantooth, M. H. Moore, M. A. Ratner, A. Troisi, Y. Yao, J. W. Ciszek, J. M. Tour and R. Shashidhar, Nature Materials **5**, 901-908 (2006).

Poster Session I

Cambridge University Press
978-1-107-40833-3 - Concepts in Molecular and Organic Electronics: Materials Research Society Symposium Proceedings: Volume 1154
Editors: Norbert Koch, Egbert Zojer, Saw-Wai Hla and Xiaoyang Zhu
Excerpt
More information