

Organic rectifying junctions from an electron-accepting molecular wire and an electron-donating phthalocyanine†

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Received (in Cambridge, UK) 16th January 2006, Accepted 20th February 2006

First published as an Advance Article on the web 17th March 2006

DOI: 10.1039/b600617e

Self-assembled monolayers (SAMs) of arylene-ethynylene oligomers that incorporate electron-accepting 9-fluorenone and 9-[(4-pyridyl)methylene]fluorene units in the backbone exhibit symmetrical current-voltage (I-V) characteristics, but rectifying junctions with current ratios of 20–80 at ± 1 V have been obtained by protonating these wire-like molecules and ionically coupling with anionic donors.

Molecules that display wire-like behaviour are at the forefront of attention¹ as they facilitate intramolecular electron transport from one site to another under the control of an external electrical, electrochemical or photonic stimulus.² They can be functionalised for self-assembly on metals or semiconductors and synthesis provides precisely-structured nanometre-sized molecular wires.³ Monodisperse π -conjugated oligomers with rod-like backbones are of particular interest from experimental and theoretical viewpoints and, in particular, arylene-ethynylenes are attractive candidates for use in metal-(molecular wire)-metal structures. Coplanar molecular conformations have been observed but the barrier to rotation about the aryl-ethynyl bond is low, estimated at <1 kcal mol⁻¹, and their structures when self-assembled may be less well ordered.⁴ They have rigid π -systems and lack the *Z/E* isomerism of their arylene-vinylene counterparts and, for these reasons, attract attention as potential components of molecular electronic structures. Oligo(phenylene-ethynylene) derivatives, *ca.* 2 nm long, have been investigated in various device architectures⁵ whereas, in this work, we now focus on an extended molecular system.

We discuss the self-assembly and electronic behaviour of an arylene-ethynylene oligomer whose synthesis is reported.^{3a} The molecule has a 7 nm long backbone, hexyloxy side-chains to ensure solubility in organic solvents and its terminal thiol groups for chemisorption are cyanoethyl protected. It also incorporates 9-fluorenone units and a central 9-[(4-pyridyl)methylene]fluorene moiety in its backbone (Fig. 1) and the reduction waves of these, from cyclic voltammetric studies, reveal that the components endow the oligomer with n-doping characteristics. Consequently, organic rectifying junctions may be formed by protonating the self-assembled molecular wires and then by ionically coupling with

anionic donors, in this case with copper phthalocyanine-3,4',4'',4'''-tetrasulfonate, to provide the required donor-acceptor bilayer arrangement. It is one of few reported examples^{6–9} where the donor-acceptor sequence is contacted by non-oxidisable electrodes and we note that this is the first example of a rectifying junction that incorporates a molecular wire.

SAMs were fabricated by immersing gold-coated substrates in a tetrahydrofuran solution of the arylene-ethynylene oligomer (0.1 mg cm⁻³) to which sodium methoxide was added to facilitate removal of the cyanoethyl group(s). Substrates were repeatedly immersed for 15 min intervals and washed each time with THF to remove physisorbed material from the surface. Throughout this process, self-assembly was monitored from the frequency change for deposition on gold-coated 10 MHz quartz crystals, which prior to use were washed with chloroform, methanol and water and then plasma cleaned. The frequency saturated to a constant value after *ca.* 3 h and a Sauerbrey analysis¹⁰ of the data provided a mean area of *ca.* 1.7 nm² molecule⁻¹ for the chemisorbed wire (Fig. 2). Similar data were also obtained by omitting the deprotecting agent, sodium methoxide, but the timescale for assembly is considerably longer. However, the area each time is consistent with the van der Waals dimensions of the molecular wire but only if partial overlap of these highly tilted molecules is assumed.

SAMs on gold-coated highly oriented pyrolytic graphite were investigated by scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) using a Nanoscope IV MultiMode microscope (Veeco Instruments, Cambridge). The film surface was first imaged using Au and PtIr probes and then, for I-V characterisation, the probe was landed at distinct surface features distant from grain boundaries. In each case, the SAMs were investigated at several locations and the recorded I-V data were averaged from ten scans at each of the sites. Significantly, SAMs for the most part exhibit symmetrical I-V characteristics although slight electrical asymmetries have been observed albeit infrequently. These have current ratios of less than 1.2 at ± 1 V and are probably probe-induced whereas the vast majority of scans provide ratios of 1.0. Symmetrical I-V characteristics have also been obtained for both Au and PtIr probes, which is not unexpected as their work functions are similar.^{11,12} Furthermore, although there are subtle differences in the shapes of the I-V curves, the symmetry is unaffected as the conditions to land the probe are varied. For example, the set point current was varied by an order of magnitude, from 0.05 to 0.5 nA, at a constant substrate bias of 1 V and symmetrical or almost symmetrical I-V characteristics were obtained each time (Fig. 3). The rescaled data of Fig. 4 correspond to one of the mid range scans from the previous figure: the plot is symmetrical and the altered set point

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† Electronic supplementary information (ESI) available: Cyclic voltammograms of unprotonated and protonated forms of the wire; uv/visible absorption spectrum of the bilayer on platinum-coated glass substrates. See DOI: 10.1039/b600617e

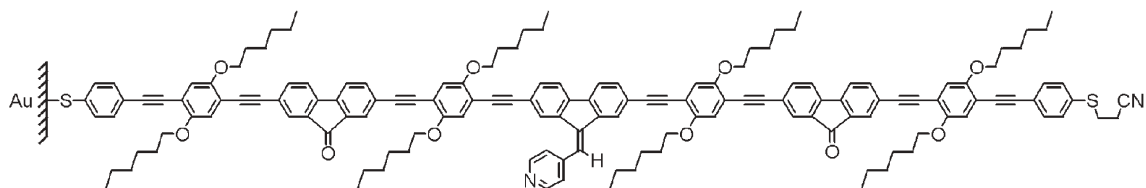


Fig. 1 Molecular structure of the wire with the terminal sulfur showing the cyanoethyl group intact when formed without the deprotecting agent.

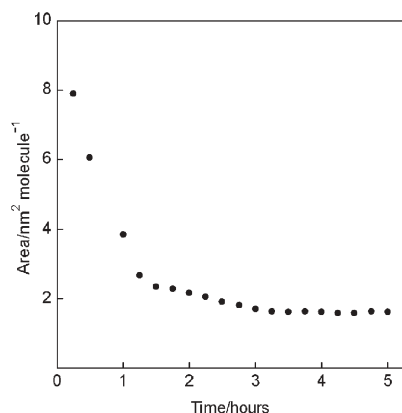


Fig. 2 Variation of the mean molecular area with the combined period of immersion of a gold-coated 10 MHz quartz crystal in a tetrahydrofuran solution of the self-assembling molecular wire (0.1 mg cm^{-3}) to which sodium methoxide was added.

conditions, which influence the distance between probe and surface, only appear to affect the magnitude of the tunnelling current.

Oligomers with 9-fluorenone units in the backbone and lengths that increase progressively from *ca.* 2 to 10 nm are currently under investigation. Their SAMs also exhibit symmetrical I–V characteristics and none shows evidence of negative differential resistance (NDR), which has been extensively reported for *ca.* 2 nm long arylene-ethynylene wires contacted by evaporated electrodes.⁵ There is speculation that the NDR, at least in some instances, arises from gold nanofilaments that penetrate the films. Organic

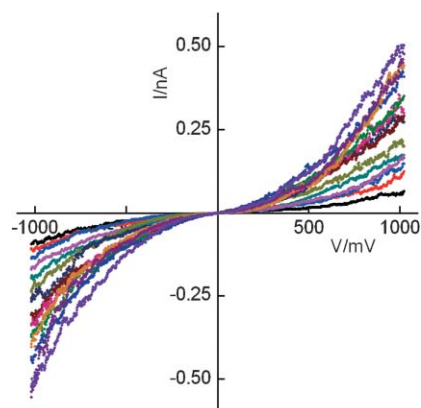


Fig. 3 I–V characteristics of the Au–WIRE structure contacted by an Au probe, the fourteen curves being symmetrical or almost symmetrical in each case and obtained for set point currents of 0.05 to 0.5 nA and bias of 1 V. The data were obtained from the same site and each curve was averaged from ten separate scans.

structures are readily damaged by evaporated contacts and there are reports of molecular wires¹³ and molecular diodes¹⁴ being contacted by titanium, which has a lower sublimation temperature than gold. However, its use is not recommended as ambiguities arise from oxide-induced Schottky barriers which dominate the electrical properties when such devices are exposed to even trace levels of oxygen.¹⁵

Crucial to the development of nanoscale devices are methods of probing ultra-thin films. Equally important are techniques that enable the molecules to be assembled in a controlled manner and, as part of this investigation, we have formed an organic rectifying junction by protonating the 9-[(4-pyridyl)methylene]fluorene unit of the wire by exposure to HCl and exchanging the chloride counterion with an anionic donor (Fig. 5). This was achieved by immersing protonated SAMs in an aqueous acetone solution of the tetrasodium salt of copper phthalocyanine-3,4',4'',4'''-tetrasulfonate, $\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_4$, for 24 h and washing with water to remove NaCl from the lattice. Confirmation of metathesis is provided by the X-ray photoelectron spectrum: it exhibits peaks at, for example, 936 eV (Cu 2p) and 1074 eV (Na 1s) that correspond to the binding energies of atoms unique to the phthalocyanine component. It is also verified by the uv/visible spectrum, this time for bilayer films on platinum-coated glass slides, which exhibits a broad transition with $\lambda_{\text{max}} < 450 \text{ nm}$, indicative of the wire (*cf.* 398.5 nm in CHCl_3), albeit modified by nearby bands of the counterion, and a broad transition at *ca.* 700 nm that is attributed to the Q band of the phthalocyanine.

STM images of $\text{Au-WIRE}^+[\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_n]_{1/(4-n)}$ bilayer structures on gold-coated highly oriented pyrolytic graphite were obtained using a gold probe and, for example, a set point current of 0.5 nA and sample bias of 0.05 V (Fig. 5). The bilayer films

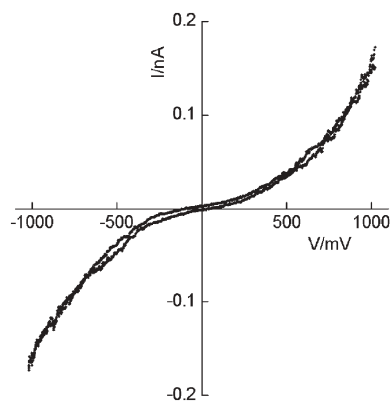


Fig. 4 I–V characteristics of the Au–WIRE structure contacted by an Au probe, the data being obtained for a set point current of 0.2 nA and bias of 1 V. The data are rescaled from Fig. 3 and correspond to one of the mid range curves.

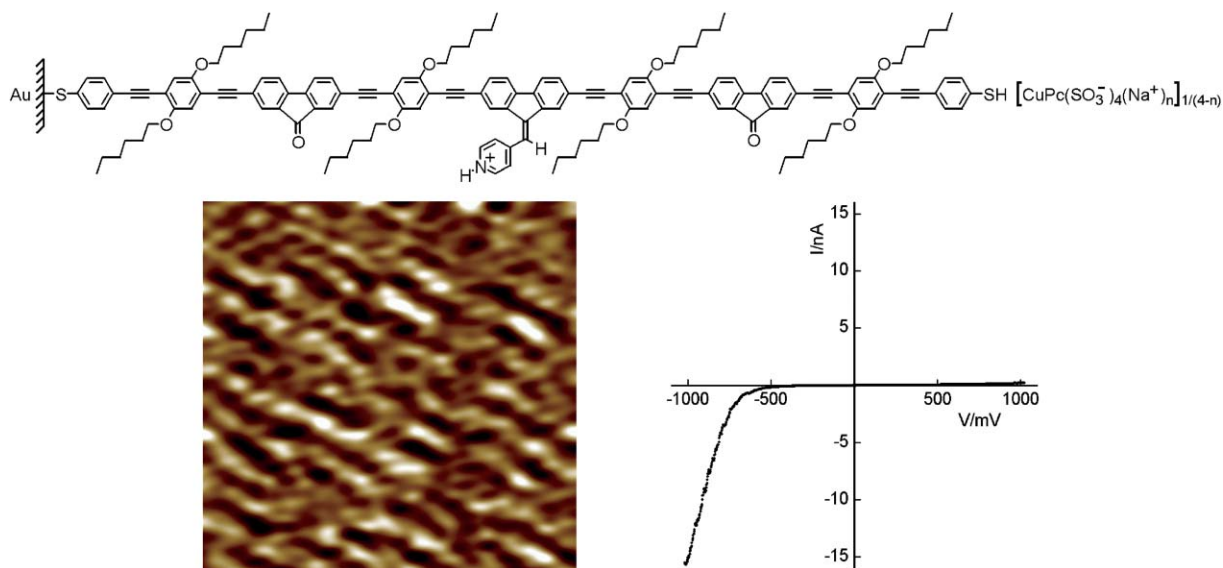


Fig. 5 Protonated wire ionically coupled with $\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_n$; $7.7 \text{ nm} \times 7.7 \text{ nm}$ STM image of the disordered upper surface of the bilayer structure obtained using a set point current of 0.5 nA and sample bias of 0.05 V and I–V characteristics averaged from ten scans on the same site. The STM image differs from that of the underlying substrate and exhibits features, albeit disordered, with dimensions consistent with the edge of the phthalocyanine anion. The polarity for rectification is reproducible across the film but the current ratio differs from 20 to 80 at $\pm 1 \text{ V}$.

exhibit features, albeit highly disordered, with dimensions that probably correspond to an edge-on arrangement of phthalocyanine anions in the upper layer. Consequently, images of the disordered structure compare less favourably than those of phthalocyanine molecules that adsorb face-down on $\text{Au}(111)$.¹⁶

I–V characteristics were obtained as for SAMs of the neutral wire, for example, by using Au and PtIr probes and varying the set point current and voltage throughout a broad range. However, unlike the wire, the curves this time invariably show rectifying behaviour with high current ratios in the range 20–80 at $\pm 1 \text{ V}$. Such properties are not unexpected as the 9-[(4-pyridinium)methylene]fluorene and 9-fluorenone components endow the self-assembled layer with electron-accepting character and, besides, the phthalocyanine donor was specifically chosen to complement it in a rectifying device. The direction of electron flow at forward bias is expectedly from the substrate (cathode) to the lowest unoccupied molecular orbital of the wire on one side of the device and from the highest occupied molecular orbital of the phthalocyanine to the probe (anode) on the other. The rectification simply arises from an energy mismatch between these orbitals and the Fermi levels of the contacting electrodes when the bias is reversed. In contrast, SAMs of protonated wires with chloride counterions exhibit symmetrical I–V characteristics and support the contention that the rectifying behaviour, as shown in Fig. 5, arises from the designated donor–acceptor sequence.

In conclusion, SAMs of the electron-accepting molecular wire, both in its neutral form and when protonated by HCl, invariably show non-rectifying behaviour but asymmetric I–V curves are obtained from bilayer structures with an electron-donating upper layer. There are few examples of organic rectifying junctions^{6–9} and all but one concern layers of donors and acceptors. The junction reported here has monolayers of each and exhibits high rectification ratios in the range 20–80 at $\pm 1 \text{ V}$.

We are grateful to the EPSRC (UK), Department of Trade and Industry, and Royal Society/Wolfson Foundation for support.

Notes and references

- 1 N. Robertson and C. A. McGowan, *Chem. Soc. Rev.*, 2003, **32**, 96.
- 2 (a) G. Maruccio, R. Cingolani and R. Rinaldi, *J. Mater. Chem.*, 2004, **14**, 542; (b) R. A. Wassel and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2004, **43**, 5120.
- 3 (a) C. Wang, A. S. Batsanov and M. R. Bryce, *Faraday Discuss.*, 2006, **131**, 221; (b) C. Wang, A. S. Batsanov, M. R. Bryce and I. Sage, *Org. Lett.*, 2004, **6**, 2181.
- 4 A. Beeby, K. Findlay, P. J. Low and T. B. Marder, *J. Am. Chem. Soc.*, 2002, **124**, 8280.
- 5 (a) J. M. Tour, A. M. Rawlett, M. Kozaki, Y. Yao, R. C. Jagessar, S. M. Dirk, D. W. Price, M. A. Reed, C.-W. Zhou, J. Chen, W. Wang and I. Campbell, *Chem.–Eur. J.*, 2001, **7**, 5118; (b) J. M. Tour, L. Cheng, D. P. Nackashi, Y. Yao, A. K. Flatt, S. K. St. Angelo, T. E. Mallouk and P. D. Franzon, *J. Am. Chem. Soc.*, 2003, **125**, 13279.
- 6 G. J. Ashwell, J. Ewington and B. J. Robinson, *Chem. Commun.*, 2006, 618.
- 7 T. Reda, A. F. Collings, C. Barton and P. Lukins, *J. Phys. Chem. B*, 2003, **107**, 13774.
- 8 C. M. Fischer, M. Burghard, S. Roth and K. von Klitzing, *Europhys. Lett.*, 1994, **28**, 129.
- 9 T. L. Anderson, G. C. Komplin and W. J. Pietro, *J. Phys. Chem.*, 1993, **97**, 6577.
- 10 G. Sauerbrey, *Z. Phys.*, 1959, **155**, 206.
- 11 J. W. G. Wildöer, C. J. P. M. Harmans and H. van Kempen, *Phys. Rev. Lett.*, 1997, **55**, 16013.
- 12 D. R. Lide, *CRC Handbook of Physics and Chemistry*, CRC Press, New York, 83rd edn, 2003.
- 13 C. Zhou, M. R. Deshpande, M. A. Reed, L. Jones and J. M. Tour, *Appl. Phys. Lett.*, 1997, **71**, 611.
- 14 D.-H. Kim, H. Lee and T. Zyung, *Synth. Met.*, 2005, **152**, 293.
- 15 R. L. McCreery, J. Dieringer, A. O. Solak, B. Snyder, A. M. Nowak, W. R. McGovern and S. DuVall, *J. Am. Chem. Soc.*, 2004, **126**, 6200.
- 16 D. E. Barlow and K. W. Hipps, *J. Phys. Chem. B*, 2000, **104**, 5993.