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Organic Molecular WiresPeter Hadley¹ and Murat Durkut

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1. Introduction

One route towards making nanoelectronic circuits is to use single molecules as electronic components. This is appealing because very many molecules can be made simultaneously by chemical synthesis. This fact has motivated researchers to measure the electrical characteristics of many different molecules. One conclusion that can be drawn from all those measurements is that molecules less than one nanometer in size never exhibit signal gain at room temperature. Single molecules are too small to be transistors. There is no space here to go into the reasons why single molecules have no signal gain but the arguments are similar to those that show that silicon transistors with signal gain cannot be made smaller than a few nanometers. Since any complicated circuit will require components with signal gain, it is interesting to look at chemically synthesized structures larger than a few nanometers to see if they can be used as transistors.

It is already known that structures tens of nanometers in size such as carbon nanotubes and semiconducting nanowires can be used to make transistors. These structures have covalent bonds in the direction that current is flowing. Here we consider supermolecular assemblies of organic molecules. Organic molecules are interesting because a great deal of known about how to arrange these molecules into supermolecular assemblies. We focused on systems that were designed to self-assemble into one-dimensional wires. In a typical self-assembled molecular wire, the atoms of the individual molecules are covalently bonded to each other but weaker noncovalent bonds are used to connect the molecules to form a wire. The idea behind this is that during self-assembly the molecules may first come together in some undesirable conformation and when this happens a weak bond between the molecules may form. However, if there is just one weak bond, the molecules will break apart again due to thermal fluctuations. When the molecules come together in the desired conformation, they fit together like a lock and key and several weak bonds are made in parallel. Since there are more bonds holding the molecules together, it is less likely that they will fall apart due to thermal fluctuations. Fibers a few nanometers in diameter and microns long can be made this way.

2. Molecular Wires

In this project we chose to work with organic materials that have already been used to make electronic devices in bulk or

thin film form such as oligo *p*-phenylene vinylene (MOPV) [1], polyisocyanidepeptides [2], and hexabenzocoronene (HBC) [3]. Self-assembled molecular wires of these materials have already been used to make films that were incorporated in devices such as field effect transistors, light emitting diodes, and solar cells. [3-6]

The MOPV's and HBC's are molecules that spontaneously stack to form wires several microns long. The polyisocyanidepeptides use a rigid spiral nonconducting template to arrange perylenes into a wire that should then conduct. It was possible to isolate individual wires of the MOPV's and polyisocyanidepeptides on a substrate but the HBC's tended to form twisted ropes that included several wires in parallel. We suspected that in previous measurements on films of these materials that the conductivity was limited by the interwire transport. We therefore designed experiments to measure the conductivity of individual wires.

Figure 1 shows an AFM image of a set of gold electrodes that were used to measure the conductivity of the MOPV, polyisocyanidepeptide, and HBC molecular wires. The electrodes were produced by electron beam lithography and are 200 nm wide with 200 nm spacings. This electrode spacing is smaller than the length of the self-assembled molecular wires to allow us to perform measurements on individual wires. However, the measured conductivity of the wires prepared this way was lower than the conductivity that was observed in dense films of the molecular wires. The current through the molecular wires was below our noise floor of a 100 fA.

There are two possible explanations for the low conductivity measured in the molecular wires. Either the wires are intrinsically poor conductors or our preparation method produces so many defects and/or such bad contacts that were not able to measure any current. Many modifications of our preparation and measurement procedures were tried in an attempt to improve the conductivity of the wires. Variations in the concentrations and temperatures were made during formation of the wires. The wires were annealed, extra platinum contacts were deposited using a focused ion beam, four terminal measurements were performed, position dependent voltage measurements were made using an AFM with a conducting tip, an electrical probe station in a SEM where the probes can be positioned with a resolution of 5 nm was used to measure the voltage as a function of position, gate voltages of up to +/-80 V were applied to the substrate to induce charge carriers in the wires and a contactless method,

called electrostatic force microscopy was used to evaluate the conductivity of the wires. A measurable current was not observed in any of these cases. One observation that we made was that the wires were easily broken in scanning probe measurements and the wires could typically not be manipulated as a unit. This contrasts with carbon nanotubes and semiconducting nanowires which can be pushed around on the substrate. The mechanical frailty of the molecular wires could lead to more defects in an individual wire than in a crystal of the same molecules possibly explaining why the films conduct better than the individual wires.

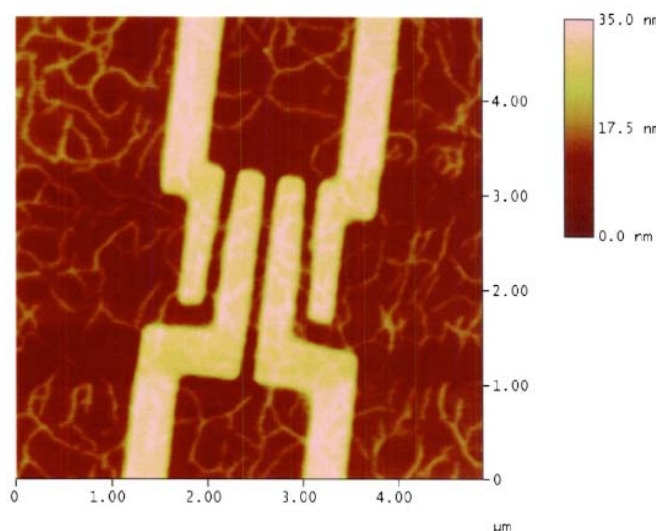


Fig. 1. An AFM image of MOPV molecular wires lying across gold electrodes.

The low conductivity of the wires we measured led us to consider the possibility that molecular wires self-assembled in this manner will never be good conductors. A transition is expected from hopping conductivity to band conductivity as coupling between the molecules increases. Clearly the wires we have prepared were in the hopping conduction regime. To move an electron from one of the molecules and place it on the next molecule, a certain amount of energy ΔE is required. This energy could be provided by a quantum fluctuation for a short period of time $\hbar/\Delta E$. If the average time between tunnel events is much longer than duration of the quantum fluctuation with the required energy, then the electrons will delocalize along the chain. This means that small ΔE and a large overlap between the molecules will promote electron delocalization. The energy ΔE needed to add an electron to a molecule is smaller for large stiff molecules. The HBC's seem to be a very good candidate in this respect. They are large stiff plate-like molecules that have a large overlap area between the molecules when they stack in columns. Nevertheless no band conductivity was observed in those samples. Defects introduce fluctuations in the parameters of the wires. Locally, ΔE can be

increased while the tunneling between molecules is decreased. The overall effect of the defects is to localize the electrons.

3. Conclusions

It would be desirable to be able to make electronic components tens of nanometers in size using supermolecular chemistry. We tested individual molecular wires of various materials but found none that seemed suitable for electronics applications. The conductivity these self-assembled molecular wires was lower than films of similar materials and orders of magnitude lower than covalently bonded structures like semiconducting nanowires and carbon nanotubes. It remains an open question as to whether self-assembled structures that are held together by weak bonds in the direction that current flows can be band conductors. Our experiments show at least it is not trivial to realize band conductors using organic self-assembled molecular wires.

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References

- [1] M. Durkut, M. Mas-Torrent, P. Hadley, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, S. George and A. Ajayaghosh, *J. Chem. Phys.* 124 (2006) 154704.
- [2] J. Hernando, P.A.J. de Witte, E.M.H.P. van Dijk, J. Korterik, R.J. Nolte, A. E. Rowan, M.F. Garcia-Parajo, N.F. van Hulst, *Angew. Chem., Int. Ed.* 43 (2004) 4045.
- [3] C. D. Simpson, J. Wu, M. D. Watson, and K. Müllen, *J. Mater. Chem.* 14 (2004) 494-504.
- [4] P. Jonkheijm, Ph.D. thesis, Eindhoven University of Technology, 2005.
- [5] J. W. Hofstraat, E. W. Meijer, A. P. H. J. Schenning, and F. J. M. Hoeben, The Netherlands PCT International Application No. CT/IB2004/050840_23 December 2004.
- [6] A. El-ghayoury, A. P. H. J. Schenning, P. A. v. Hal, J. K. J. v. Duren, R. A. J. Janssen, and E. W. Meijer, *Angew. Chem., Int. Ed.* 40 (2001) 3660.