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13. ABSTRACT *(Maximum 200 words)*

A nanostructured material consisting of a superlattice of metallic dots separated by uniform tunnel barriers is expected to exhibit interesting electronic properties. One route to the synthesis of such a material is to self-assemble it from nanometer-size, crystalline, metal clusters interconnected by rigid organic molecules. In this project techniques were developed that permit (i) the synthesis of organic molecular wires that provide uniform tunnel barriers between adjacent clusters, (ii) the synthesis of metal clusters of sufficient uniformity to allow the assembly of a periodic network and, (iii) the self-assembly of these elements to form a uniform 2-D network of interconnected metal clusters, a linked cluster network (LCN). An important step in predicting the electronic properties of a cluster-based, nanostructured material is a theory for understanding the factors that influence electronic conduction through a single organic molecule connecting two metal surfaces. A theoretical treatment of this problem was developed and the calculated current-voltage characteristics show good quantitative agreement with experimental measurements on individual molecules using scanning tunneling microscopy.

14. SUBJECT TERMS
Linked Cluster Network, Molecular Wire, Self-Assembly, Single-Electron Tunneling, Scanning Tunneling Microscope

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ELECTRONIC CONDUCTION IN MOLECULAR NANOSTRUCTURES

Final Progress Report

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I. Statement of the problem

The problem is best summarized by quoting from our original proposal which began with a statement of our objective:

> "..... to develop the knowledge base necessary to design and fabricate what we call a 'coupled cluster device' consisting of an array of metallic clusters connected to each other and to external contact pads through conducting organometallic wires."

At the time the proposal was submitted (June 1991), the linked cluster network (see Fig.1 which is taken from our original proposal) was an unknown concept. No one to our knowledge had even tried to demonstrate anything like it. In course of this project we have successfully demonstrated such structures and measured their current-voltage characteristics, thus opening up new possibilities for both basic and applied sciences.

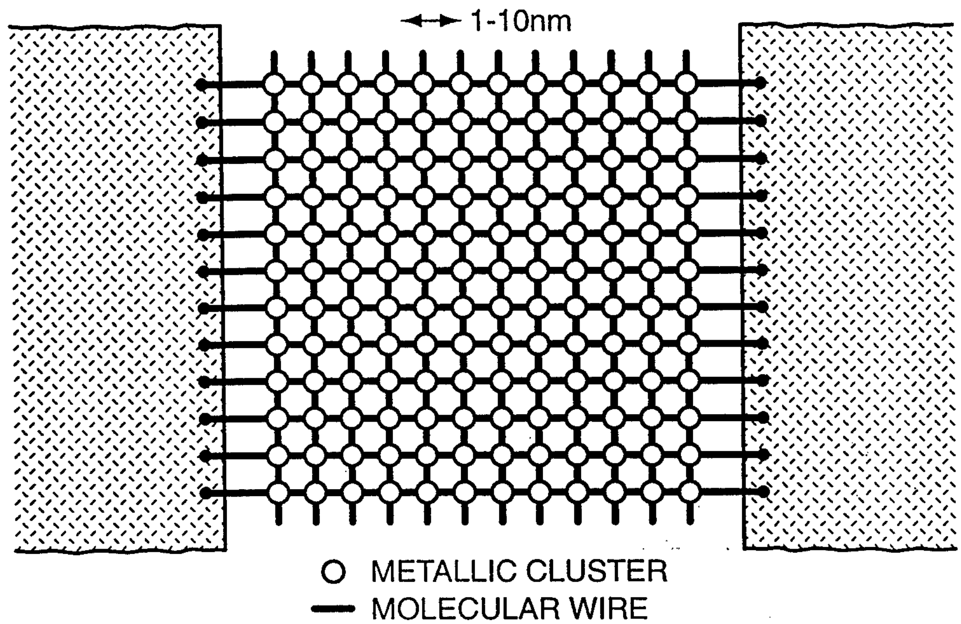

Fig.1. Schematic representation of a generic coupled cluster device (taken from the original proposal) . We now refer to this as a linked cluster network or LCN.

II. Summary of the most important results

The appendix provides a detailed technical description of the results achieved in this project. Here we will simply summarize the most important ones. Metallic nanoclusters and molecular wires have been studied for some time as two active but distinct fields of research. In this interdisciplinary project we have been able to combine the expertise from these two fields to fabricate what we call a Linked Cluster Network (LCN) : a two-dimensional superlattice consisting of nanometer-sized gold clusters electronically linked by pi-conjugated organic molecules (Fig.1). We have fabricated uniform LCN's of upto 1μm x 1μm in area using gold clusters and dithiol linking molecules, deposited them between two contacts and measured the current-voltage characteristics at different temperatures. These measurements correlate well with the theoretical model that we have developed giving us confidence that we understand the factors that influence the resistance of LCN's. This pioneering work is documented in a number of recent publications, of which the most notable ones are

- "Coulomb Staircase at Room Temperature in a Self Assembled Molecular Nanostructure" R.P. Andres, T. Bein, M. Dorogi, S. Feng, J.I. Henderson, C.P. Kubiak, W. Mahoney, R.G. Osifchin, R.G. Reifenberger, ***Science*, *272***, 1323 (1996).

  This paper describes the first observation of the Coulomb staircase at room temperature. The measurements were made using metallic clusters tethered to a substrate by a self-assembled monolayer (SAM) of thiol molecules. Both the clusters and the SAM were well-characterized from other measurements, allowing us to deduce the resistance of an individual molecule from this experiment. This is one of the first reliable estimates for molecular resistance.

- "Self-Assembly of a Two-Dimensional Superlattice of Molecularly Linked Metal Clusters", R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W. Mahoney, R.G. Osifchin, ***Science*, *273***, 1690 (1996).

  This paper describes the first synthesis of an LCN between two metallic contacts and the measured current-voltage characteristics. We have shown that the linking molecules provide tight mechanical and electronic binding leading to stable and reproducible structures that can carry large current densities (~ 10^6 A / cm^2).

- "Current-Voltage Characteristics of Self-Assembled Monolayers by Scanning Tunneling Microscopy," S. Datta, W. Tian, S. Hong, R. Reifenberger, J.I. Henderson and C.P. Kubiak, ***Phys. Rev. Lett.* *79***, 2530 (1997).

  This paper presents a comparison of the theoretical and experimental current-voltage characteristics of self-assembled monolayers of different molecules attached to gold substrates by thiol groups. Good quantitative agreement is obtained providing support for the basic conceptual picture for conduction through individual molecules.

This achievement was made possible by the combined efforts of the interdisciplinary team of researchers who were brought together in 1992 under this University Research Initiative:

	Department	***Expertise***
Andres	Chemical Engineering	Synthesis of nanoparticles
Datta	Electrical Engineering	Theory of current flow in nanostructures
Janes	Electrical Engineering	Processing and characterization of nanoscale electronic devices
Kubiak	Chemistry	Synthesis of molecular "wires"
Reifenberger	Physics	Scanning probe microscopy of nanostructures

These five co-PI's representing four different academic disciplines provided the broad range of expertise necessary for the success of this truly interdisciplinary project: the expertise to form passivated nanoclusters of high crystalline quality (Andres), the expertise to synthesize sophisticated organic molecules having the appropriate functional groups at the ends needed to bond to the clusters (Kubiak), the expertise to characterize nanostructures electrically with scanning probes (Reifenberger) as well as with metallic contacts fabricated by lithographic techniques (Janes) and finally the tools of modern mesoscopic physics to model electronic transport at the atomic level in order to interpret and guide the experiments (Datta).

III. Publications and technical reports

Book Chapter

R.P. Andres, S. Datta, D.B. Janes, C.P. Kubiak and R. G. Reifenberger, "The Design, Fabrication and Electronic Properties of Self-Assembled Molecular Nanostructures" to appear in The Handbook of Nanostructured Materials and Nanotechnology, H.S. Nalwa (Editor), Academic Press (1998).

Journal Papers

1. S. Datta, D.B. Janes, R.P. Andres, C.P. Kubiak and R. Reifenberger, "Molecular Ribbons", submitted for publication.

2. W. Tian, S. Datta, S. Hong, R. Reifenberger, J.I. Henderson and C.P. Kubiak, "Conductance Spectra of Molecular Wires", submitted for publication.

3. W. Tian, S. Datta, S. Hong, R. Reifenberger, J.I. Henderson and C.P. Kubiak, "Resistance of Molecular Nanostructures", Physica E (to appear).

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1. S. Datta, W. Tian and C.P. Kubiak, "Resistance of Molecular Nanostructures", ***Proc. 4th Intl. Symp. on Quant. Confinement***, The Electrochemical Society Inc. PV 97-11.

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IV. Scientific Personnel

Senior Personnel :

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Research Associates :

J. Gomez, R. Lake

Graduate Students :

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V. Inventions

None

VI. Appendix

"The Design, Fabrication and Electronic Properties of Self-Assembled Molecular Nanostructures" by R.P. Andres, S. Datta, D.B. Janes, C.P. Kubiak and R. G. Reifenberger, to appear in The Handbook of Nanostructured Materials and Nanotechnology, H.S. Nalwa (Editor), Academic Press (1998).

This article provides a detailed technical description of the research accomplished under the present project and also includes an extensive bibliography.