According to Moore’s Law, in 2012, silicon may not be able to meet the requirements of modern technology — therefore alternatives must be contemplated.

A computer filled a room.

A microprocessor — small enough to pass through the eye of a needle.

Devices on the molecular scale?

Molecules that can be electrically switched between two states provide the possibility of molecular computing.

Oxidation Reduction

Catenanes

Rotaxanes
What is the Story About?

- A crosspoint random access memory circuit utilizing a two-station [2]rotaxane as a switching molecule is presented in this poster.


- 16- And 36-bit memory circuits have been fabricated from [2]rotaxane molecular monolayers sandwiched in a crossbar structure.

- The room temperature performance characteristics of the [2]rotaxane-based device and circuits are discussed in the poster and device-scaling to sub-100 nanometers dimensions is reported.

- **A SYSTEMS-ORIENTED APPROACH** is likely to be critical for the development of any **ADVANCED TECHNOLOGY** that emerges out of **FUNDAMENTAL NANOSCIENCE**.
The [2]Catenane from Solution...

...can be transformed onto a Langmuir–Blodgett trough...

...using hydrophobic DMPA− counterions.

A molecular film formed on polysilicon, followed by evaporation of titanium...

...gives a molecular junction that can be electrically addressed.

...to Devices
Artificial Molecular Devices Based on Tetrathiafulvalene

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From Catenanes...

In the **catenane** device, the electroactive species is closed to one of the electrodes.

![Catenane Diagram]

Ideally, the electroactive units should span the molecular junction, and opening the catenane loop to form a **pseudorotaxane** allows this.

![Pseudorotaxane Diagram]

The **pseudorotaxane** must be amphiphilic in order to allow deposition on a surface by Langmuir–Blodgett techniques...

...but another important consideration is the spacing of the molecules in a junction – a **rotaxane** has a bulky groups on both ends of the dumbbell, helping to separate the molecules, which allows the cyclophane to shuttle more freely between the stations.

...to Rotaxanes
Synthesis of an Amphiphilic Dumbbell

Asymmetric TTF Building Block


Synthesis of a Two-Station [2]Rotaxane

[2]Rotaxane was isolated as a 1:1 mixture of two translational isomers, isolable on the laboratory timescale.
Isolating the Translational Isomers

GREEN Isomer
805 nm

RED Isomer
540 nm


Preparative TLC
RED isomer was isolated and allowed to equilibrate to a 1:1 mixture.

\[ \Delta G^+ \]

24 kcal mol\(^{-1}\) in (CD\(_3\))\(_2\)CO
22 kcal mol\(^{-1}\) in (CD\(_3\))\(_2\)SO

1:1 Mixture shows to sets of signals

\[ ^1H \text{ NMR } (\text{CD}_3)_2\text{CO} \]

235 K
0 h
300 K
1 h
300 K
3 h
300 K
5 h
300 K
8 h
300 K
21 h

1:1 Mixture shows to sets of signals
Device Performance is Poor...

The SMe group acts as a "slippage" stopper and restricts the shuttling of the tetracationic cyclophane in solution. This slow shuttling is also reflected in the poor device performance.

...So Improvements were Made
Synthesis...

SMe group on the TTF unit now points away from the naphthalene unit – there should be no barrier to the movement of the cyclophane.

...of an Amphiphilic [2]Rotaxane With...
...a Much Lower Shuttling Barrier

The translational isomers cannot be isolated because the barrier to shuttling is too small – however, the relative population of the two isomers can be controlled by changing the temperature.

\[ \text{1H NMR / 500 MHz / CD}_3\text{CN} \]

\[ \begin{align*}
\text{345 K} \\
\text{330 K} \\
\text{315 K} \\
\text{300 K} \\
\text{285 K} \\
\text{270 K} \\
\text{255 K} \\
\text{240 K}
\end{align*} \]

\[ \text{6.3} \quad \text{6.2} \quad \text{6.1} \quad \text{6.0} \quad \text{4.9} \quad \text{4.8} \quad \text{4.7} \quad \text{4.6} \]
Constructing a Molecular Switch Tunnel Junction...

A scanning electron micrograph showing a circuit of molecular switch tunnel junctions.

Self-organize ~7000 nm²

Transfer

Ti/Al Deposition

~ 70 nm

~ 100 nm

~ 7000 nm²

~ 5000 Molecules
In the device setting, the [2]rotaxane exhibits excellent switching and cycling properties, and the Remnant Molecular Signature begins to resemble that of a close competitor – the conventional magnetic bit. A sharp switching voltage and a large ON / OFF ratio are desirable characteristics for molecular memory.
Proposed NanoElectroMechanical Switching Mechanism

Apply Bias (+2 V) → Mechanical Movement I → Remove Bias

Ground State Switch-OFF

Mechanical Movement II → Thermally (15 min) or Reversed Bias (–2 V) → Metastable State Switch-ON

Solution 14.5 Kcal mol\(^{-1}\)
Surface 17.7 Kcal mol\(^{-1}\)
Device 21
A Molecular Electronics-Based Random Access Memory Circuit in Operation

Testing the Memory

- Initially, all switches are OFF
- Current of 2 - 5 pA recorded for each bit
  - Number ‘1’ or ‘0’ is stored
    - ‘1’ ≡ ON Switch
    - ‘0’ ≡ OFF Switch
- Memory was read out
- Signals for ‘1’ bits ≈ 75-200 pA
- Each bit could be opened selectively
- Three plots over a few minutes

We have Molecular RAM!
Conclusions

- An electronically addressable, reconfigurable, molecular-based, solid-state switching device capable of ambient operation has been fabricated.

- The devices exhibit robust operation under ambient conditions and can be cycled many times.

- The Remnant Molecular Signature of the molecular device has improved on going from catenanes (via pseudorotaxanes) to rotaxanes.

- The change in the junction resistance (for a rotaxane) between the ON and OFF states of the device is approximately a factor of 10.

IMPLYING THAT THEY ARE USEFUL AS MEMORY AND LOGIC DEVICES
Where Can You Find Our Chemistry?

**B R E A K T H R O U G H O F T H E Y E A R**

In 2001, scientists assembled molecules into basic circuits, raising hopes for a new world of nanoelectronics.

**Molecules Get Wired**

Good connections. Molecules can now be crafted into working circuits. Constructing real molecular chips will be a big challenge.

*Science 2001, 294, 2442–2443*

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**C O V E R S T O R Y**

**C H E M I C A L**

& Engineering News

TEAM EFFORT Molecular electronics research at UCLA brings together organic synthesis and device measurements through the efforts of (standing, from left) Jeppesen, Stoddart, Heath, and Luo, and (kneeling, from left) Tseng, Beverly, and Celestre.

*Chem. Eng. News 2002, 80 (39), 38–43*

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**The Economist**

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