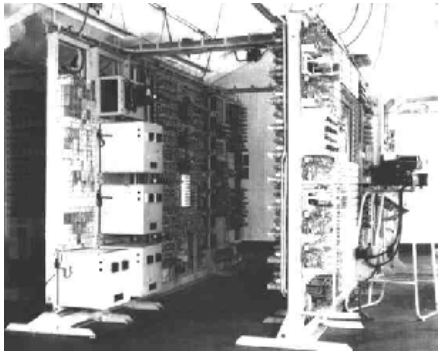
The Future of Technology — NanoElectronics?

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

1942

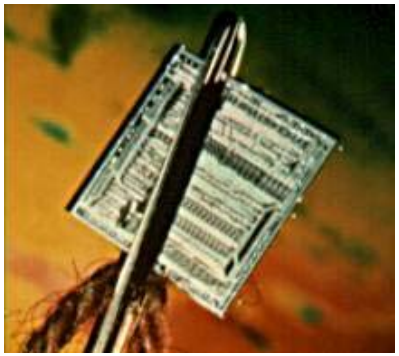
m



A computer filled a room.

2000

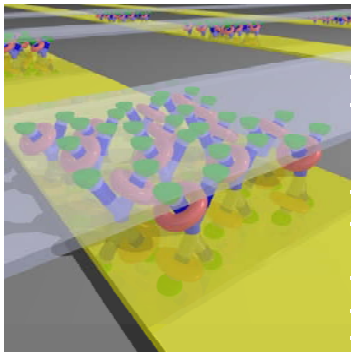
cm



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

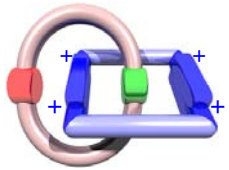
2010?

nm

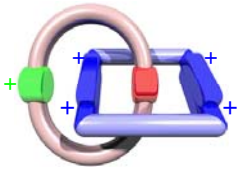


Devices on the molecular scale?

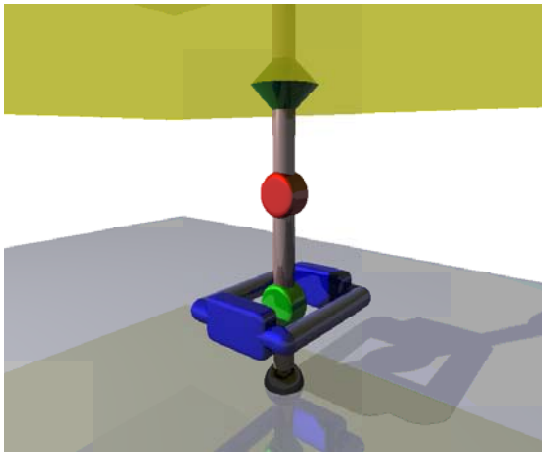
Molecules that can be electrically switched between two states provide the possibility of molecular computing.



Oxidation ⇅ Reduction

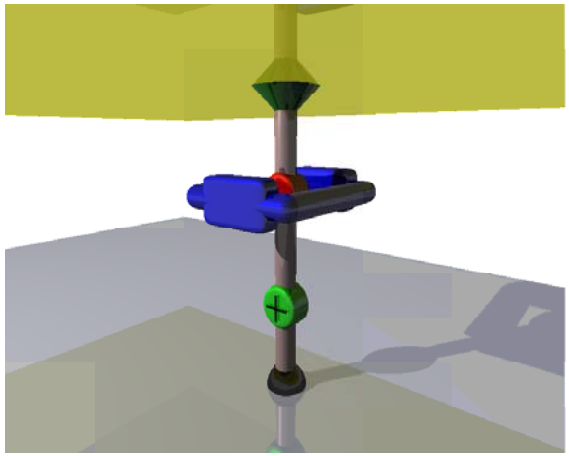


Catenanes



Oxidation ⟶

⟵ Reduction



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.

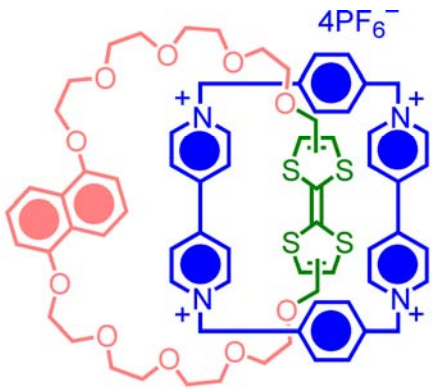
- The [2]rotaxane-based device operates as an electrochemically addressable molecular switch tunnel junction.

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

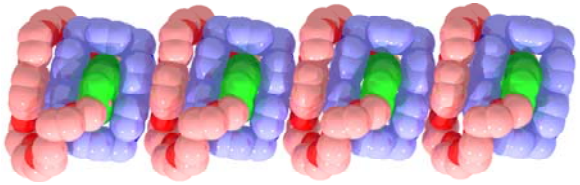
- The room temperature performance characteristics of the [2]rotaxane-based device and circuits are discussed in the poster and device-scaling to sub-100 nanometers dimensions is reported.

- **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...

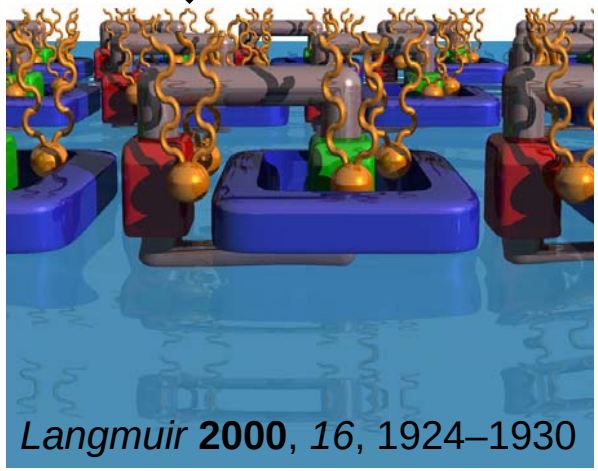


Solid state structure of a repeating ***DADA*** stack...

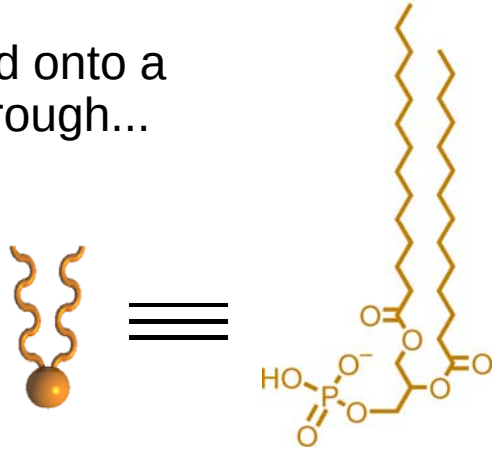


DADA DADA DADA DADA

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

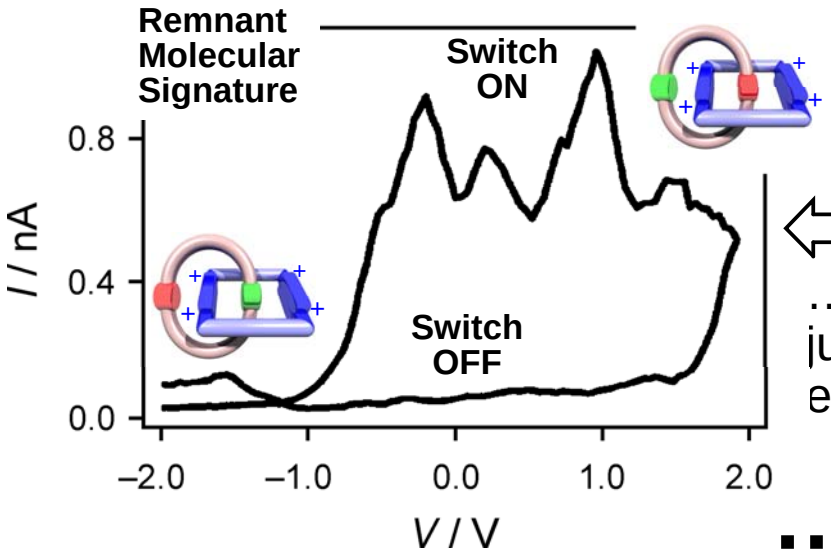


Langmuir **2000**, *16*, 1924–1930

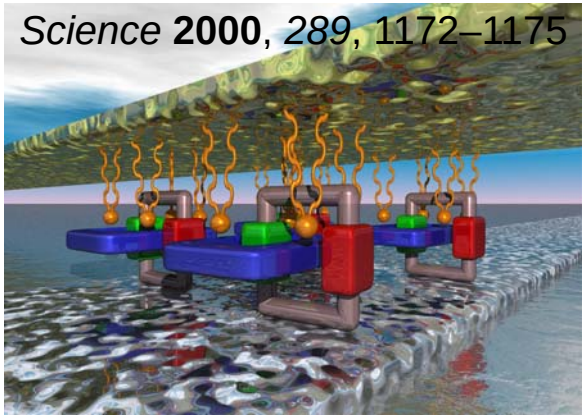


…using hydrophobic DMPA⁻ counterions.

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

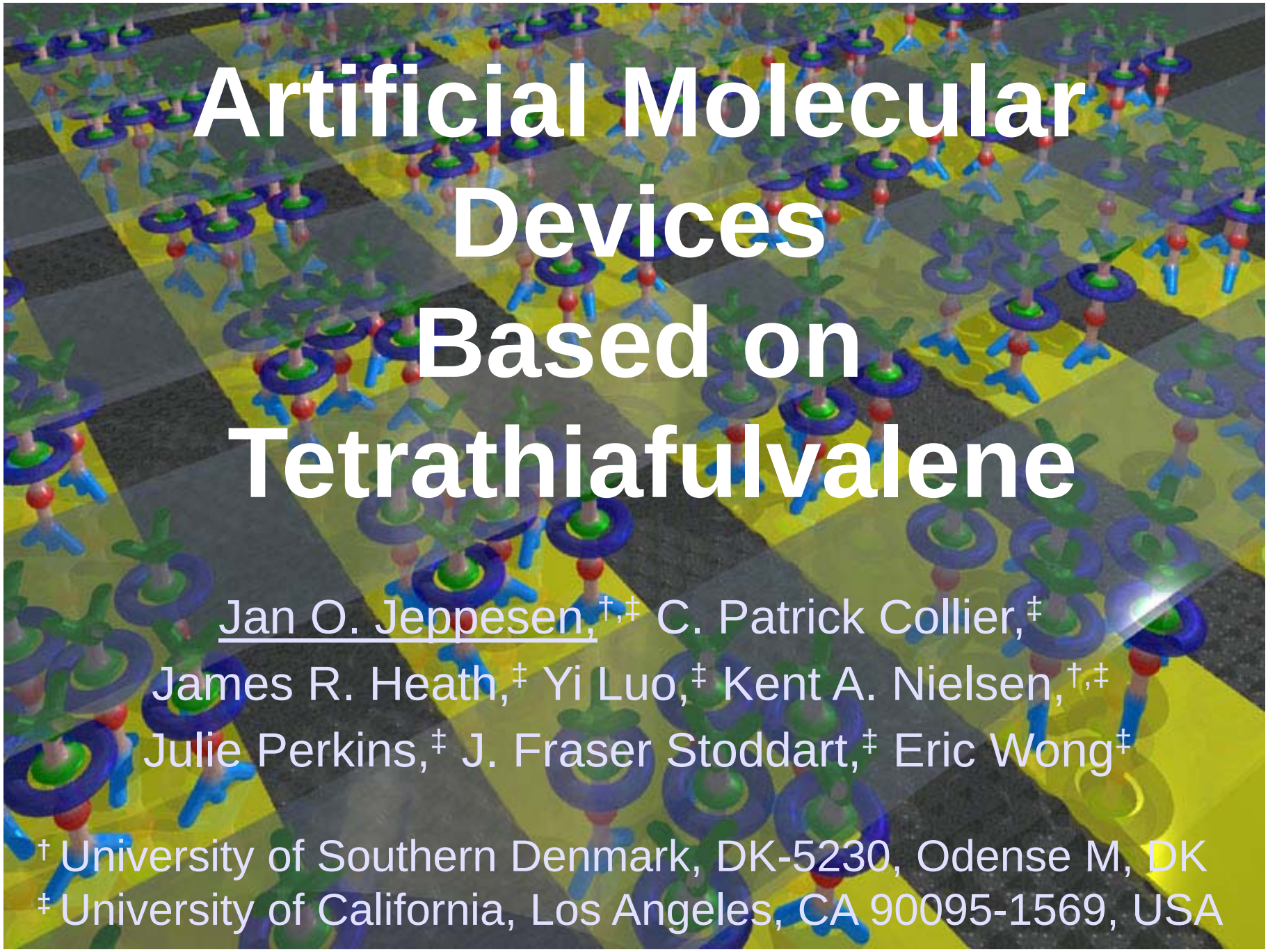


…gives a molecular junction that can be electrically addressed.



Science **2000**, *289*, 1172–1175

…to Devices



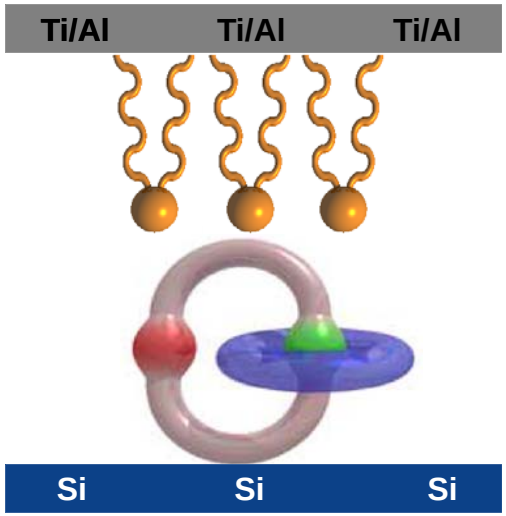
Artificial Molecular Devices Based on Tetrathiafulvalene

Jan O. Jeppesen,[†,‡] C. Patrick Collier,[‡]
James R. Heath,[‡] Yi Luo,[‡] Kent A. Nielsen,[†,‡]
Julie Perkins,[‡] J. Fraser Stoddart,[‡] Eric Wong[‡]

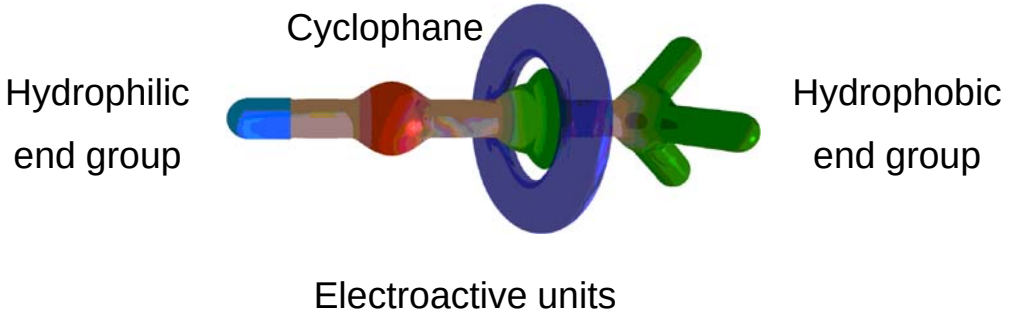
[†] University of Southern Denmark, DK-5230, Odense M, DK
[‡] University of California, Los Angeles, CA 90095-1569, USA

From Catenanes...

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

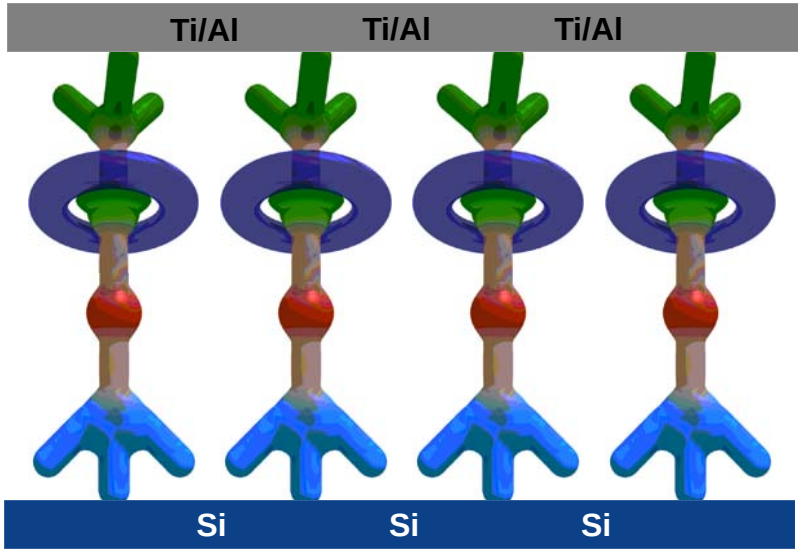


Ideally, the electroactive units should span the molecular junction, and opening the catenane loop to form a pseudorotaxane allows this.



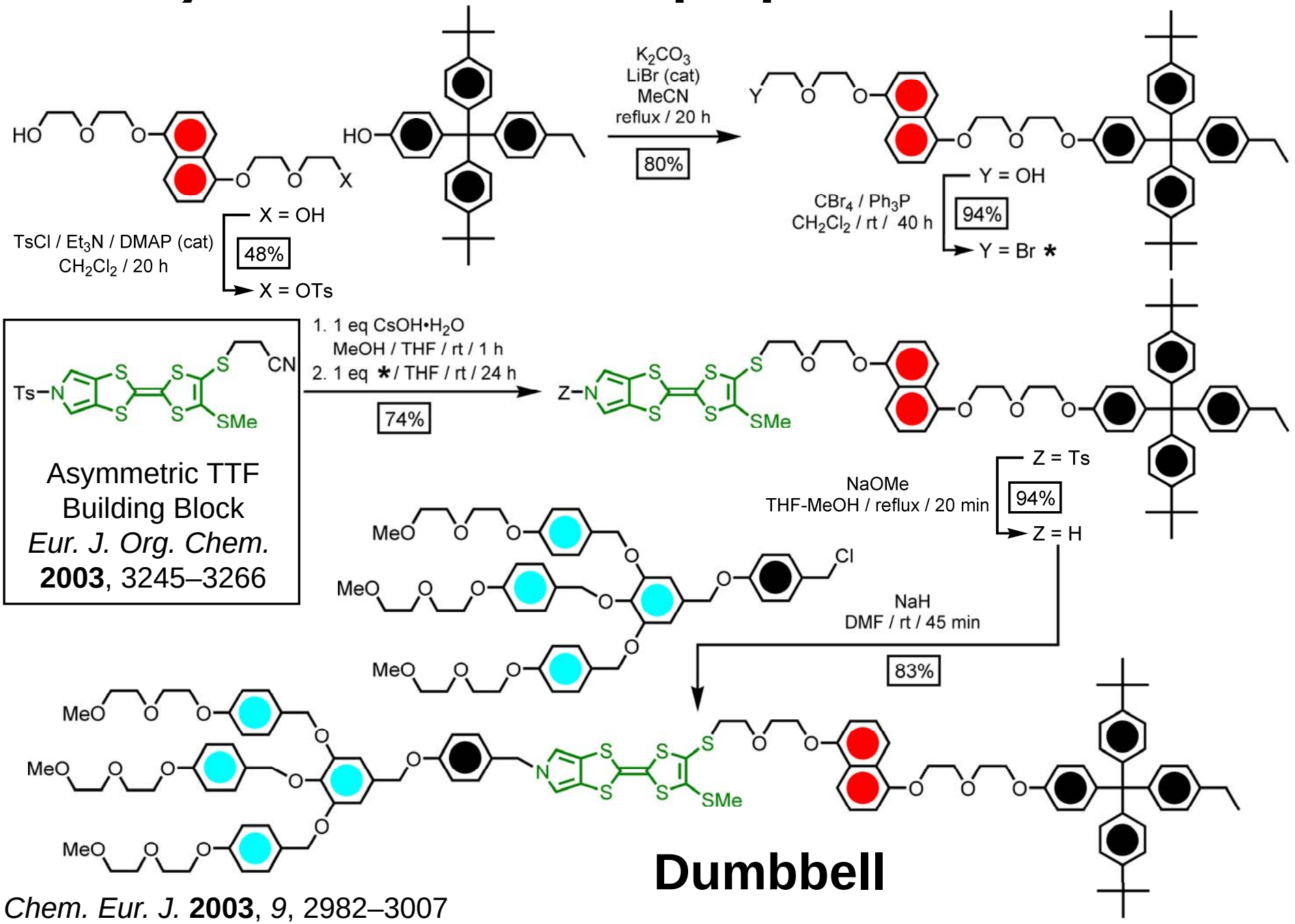
The pseudorotaxane must be amphiphilic in order to allow deposition on a surface by Langmuir–Blodgett techniques...

...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.



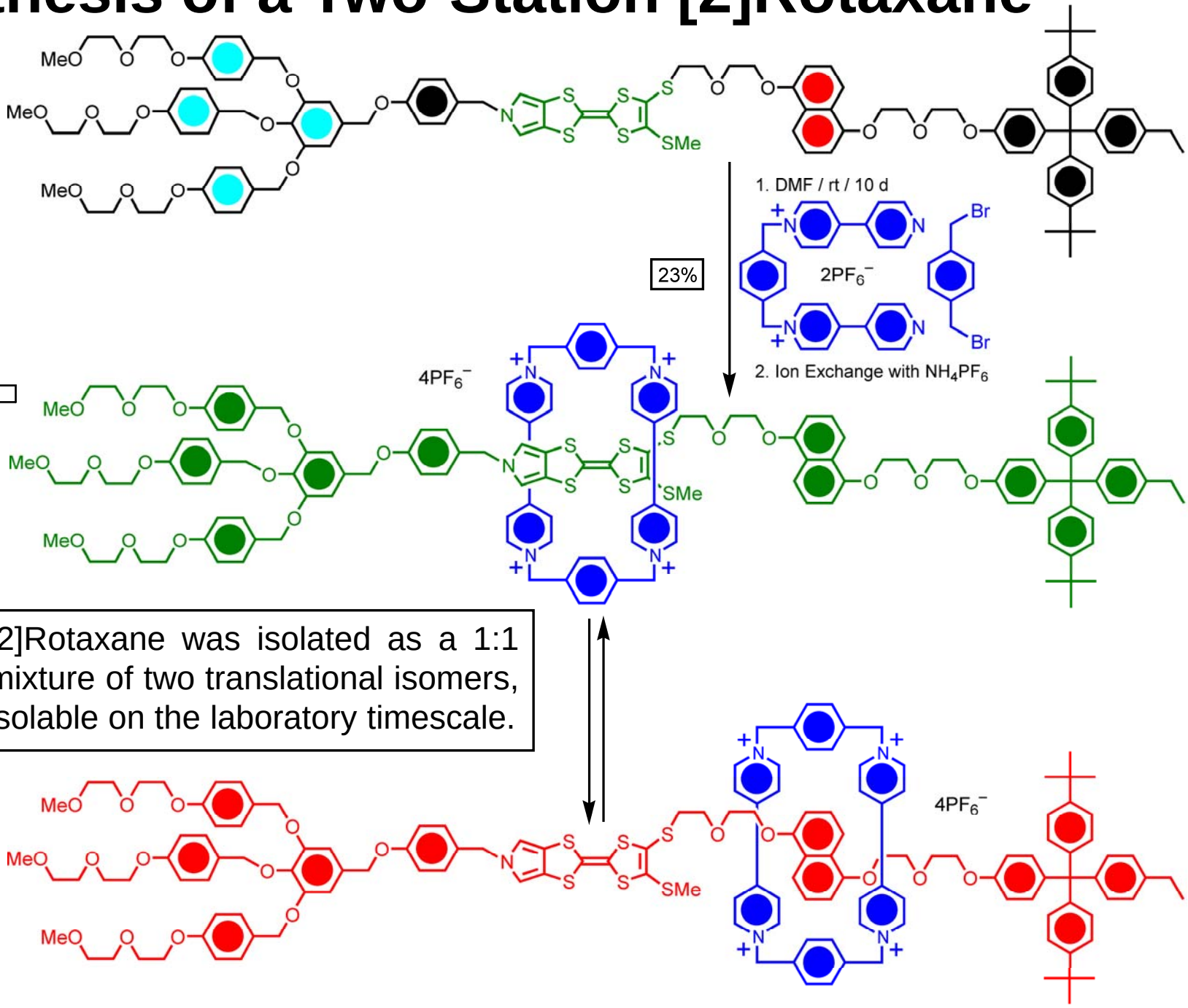
...to Rotaxanes

Synthesis of an Amphiphilic Dumbbell

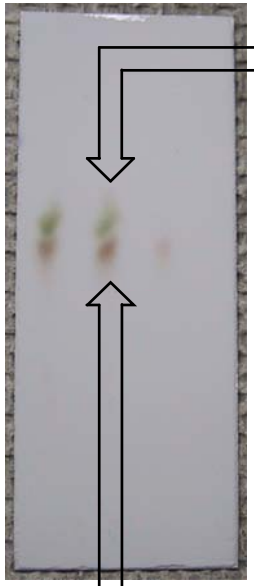


Chem. Eur. J. **2003**, *9*, 2982–3007

Synthesis of a Two-Station [2]Rotaxane

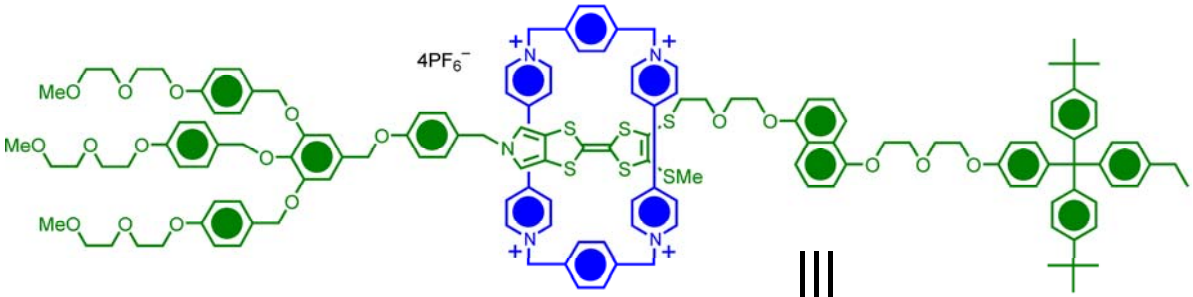


TLC



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

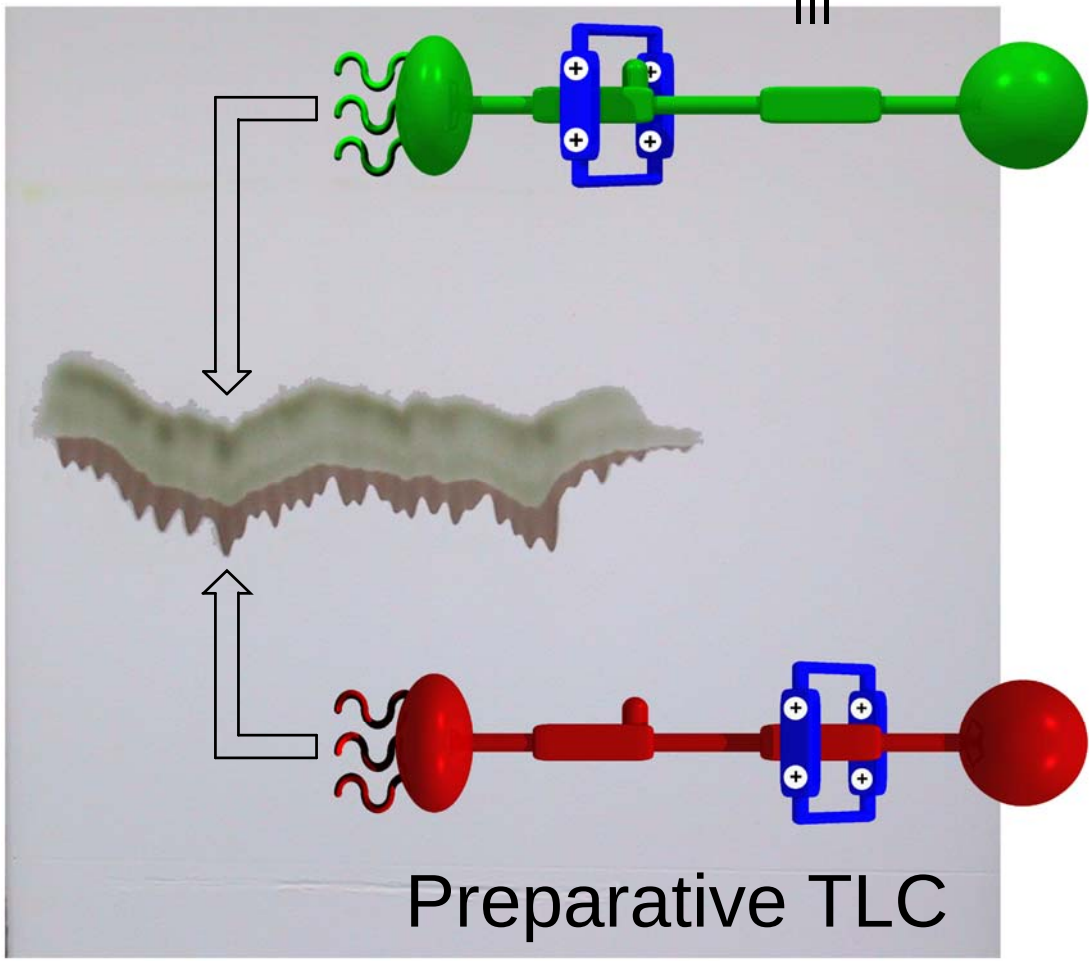
Isolating the Translational Isomers

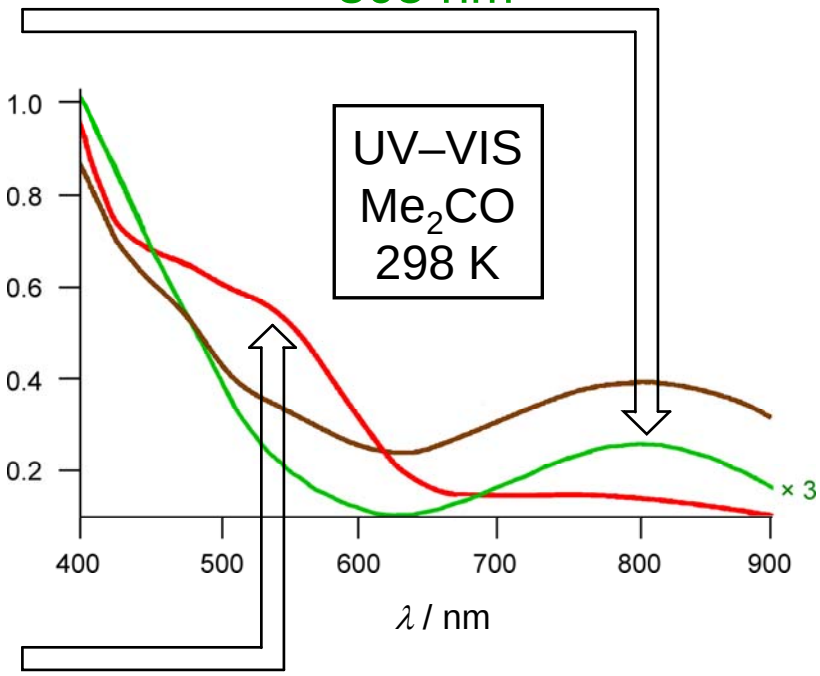


Angew. Chem. Int. Ed.
2001, *40*, 1216–1221

GREEN Isomer

805 nm

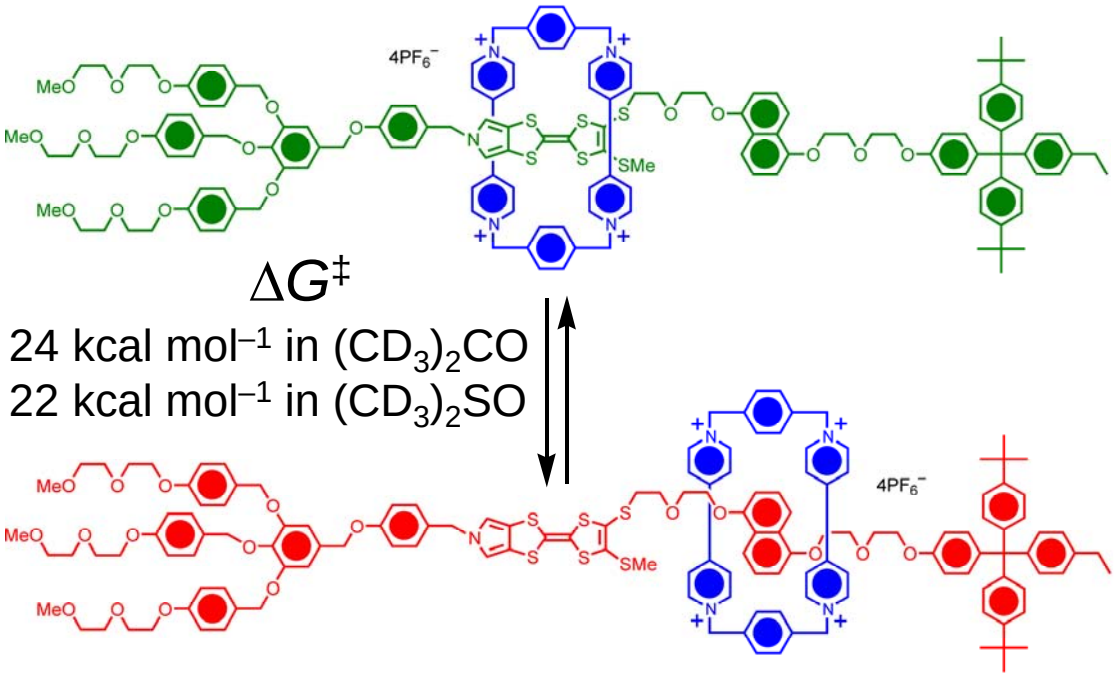


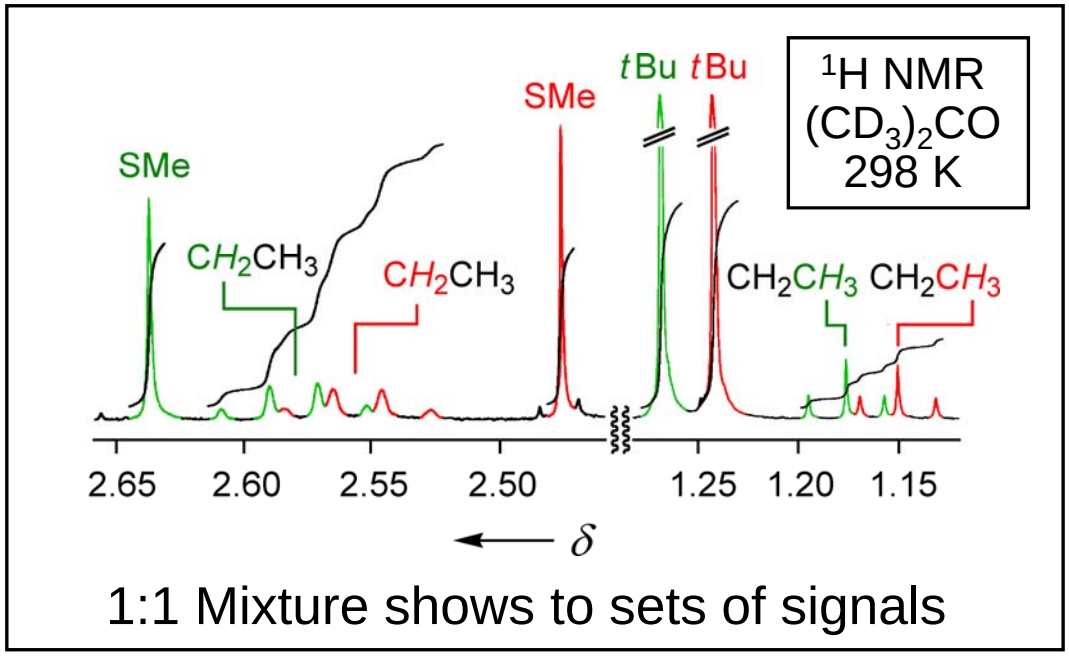


RED Isomer

540 nm

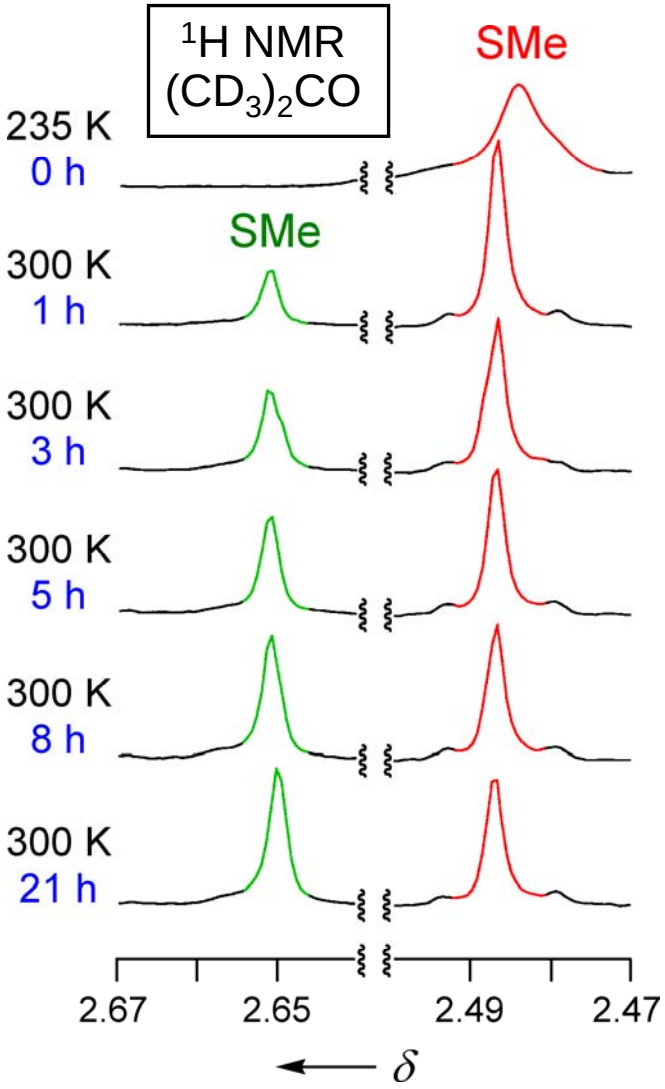
NMR Investigations of the Two-Station [2]Rotaxane



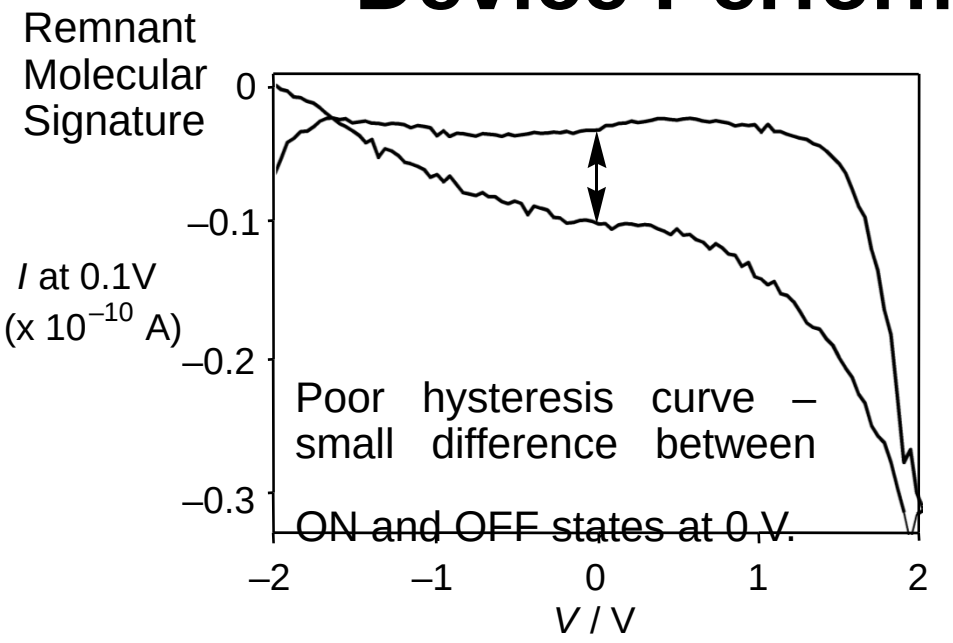


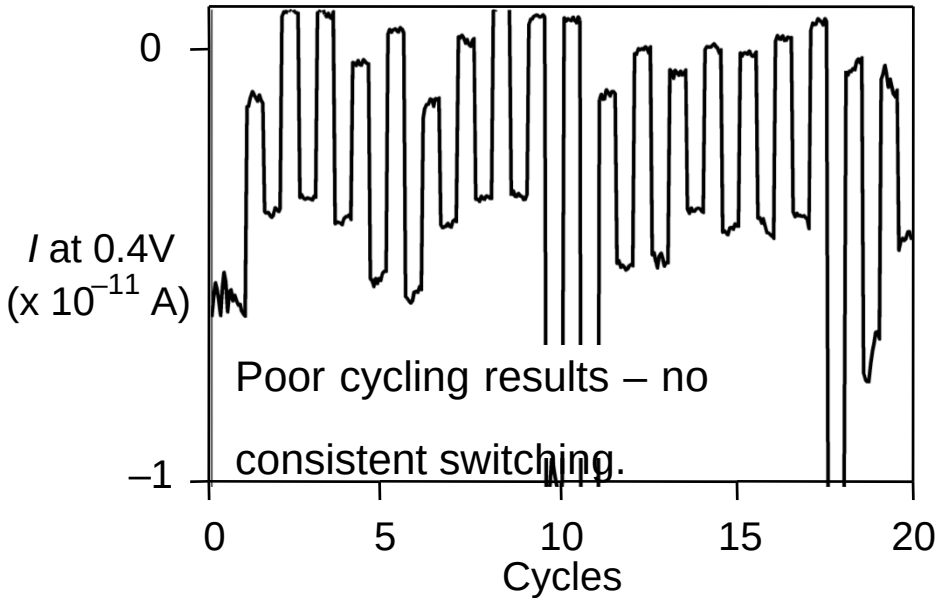
1:1 Mixture shows to sets of signals

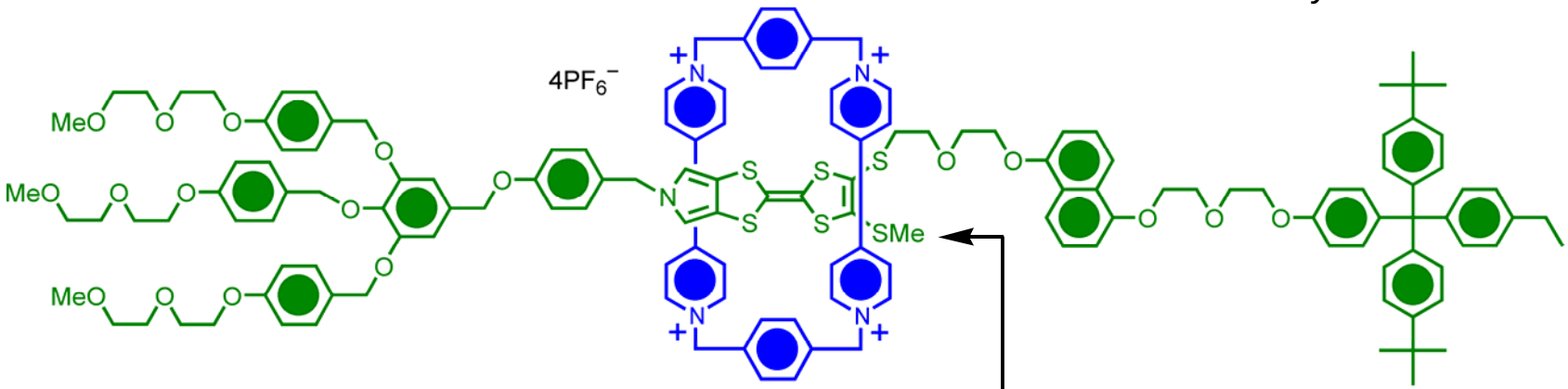
RED isomer was isolated and allowed to equilibrate to a 1:1 mixture.



Device Performance is Poor...



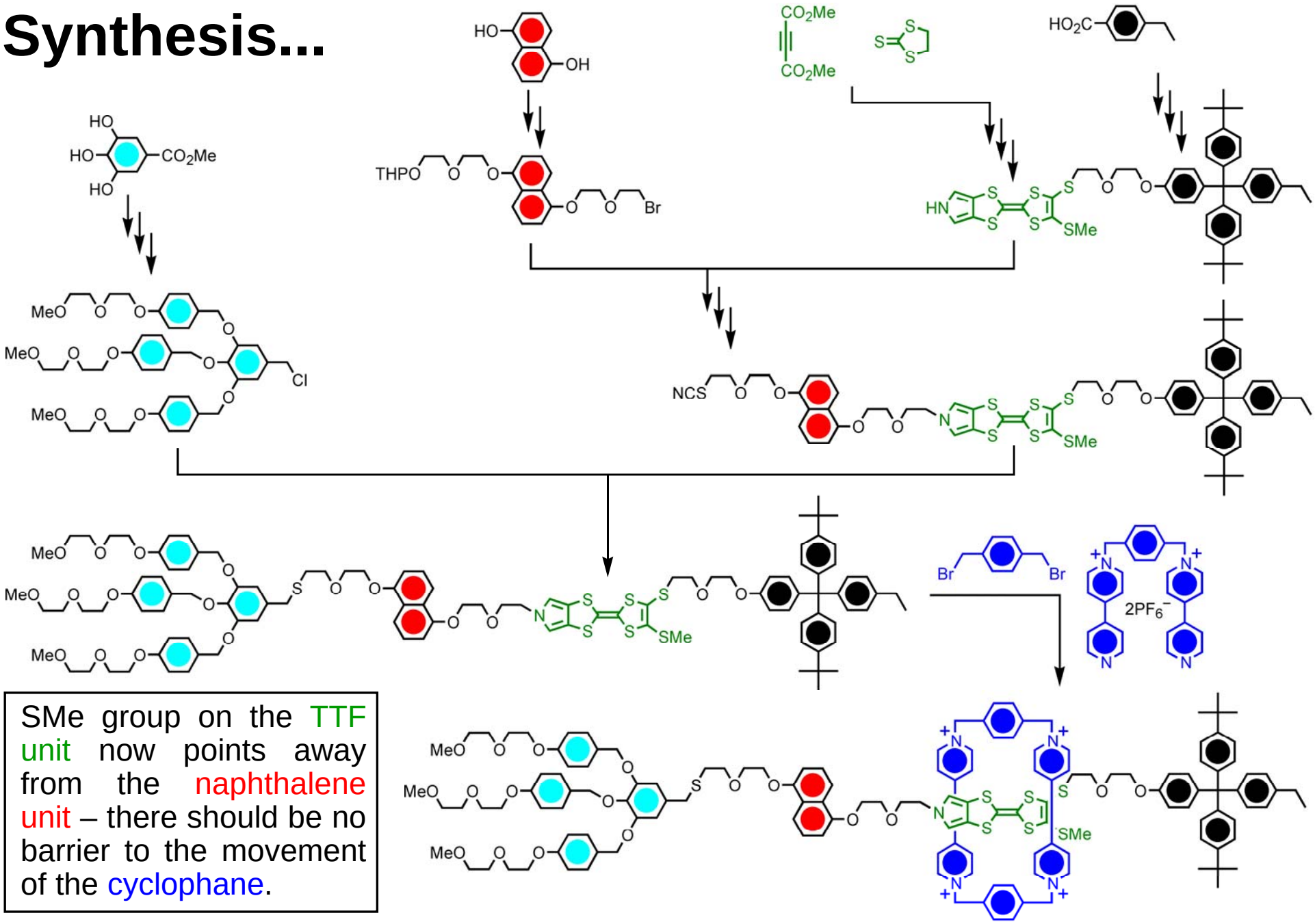




The SMe group acts as a "slippage" stopper and restricts the shuttling of the tetracationic cyclophane in solution. This slow shuttling is also reflected in the poor device performance.

…So Improvements were Made

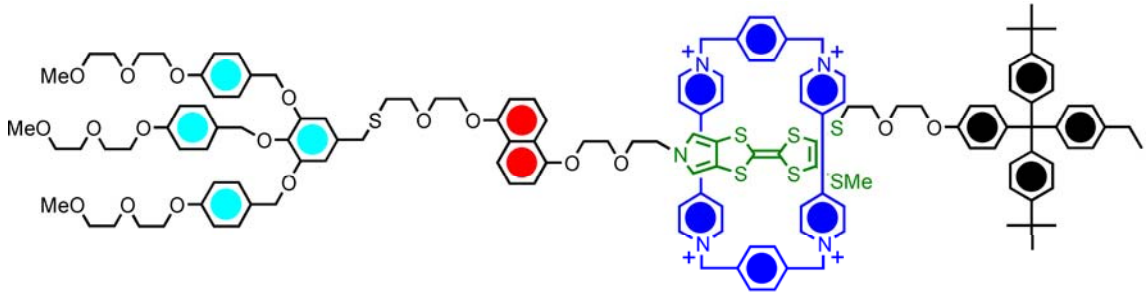
Synthesis...



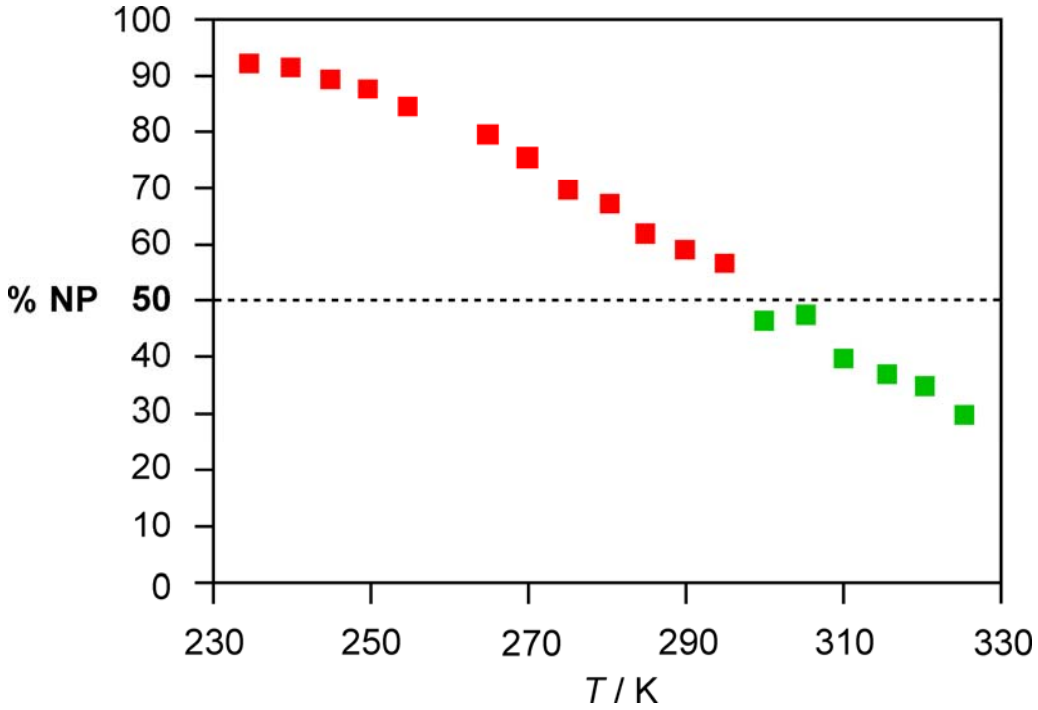
SMe group on the TTF unit now points away from the naphthalene unit – there should be no barrier to the movement of the cyclophane.

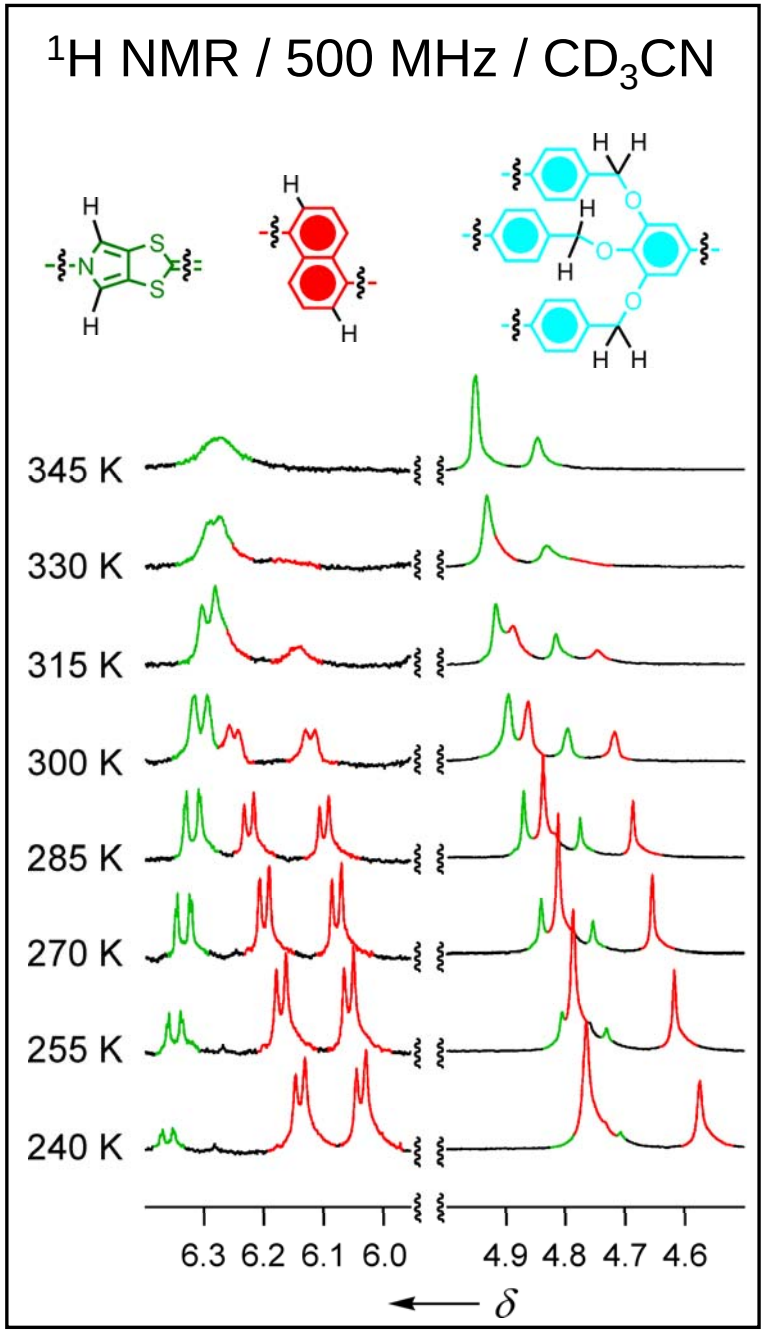
…of an Amphiphilic [2]Rotaxane With...

…a Much Lower Shuttling Barrier

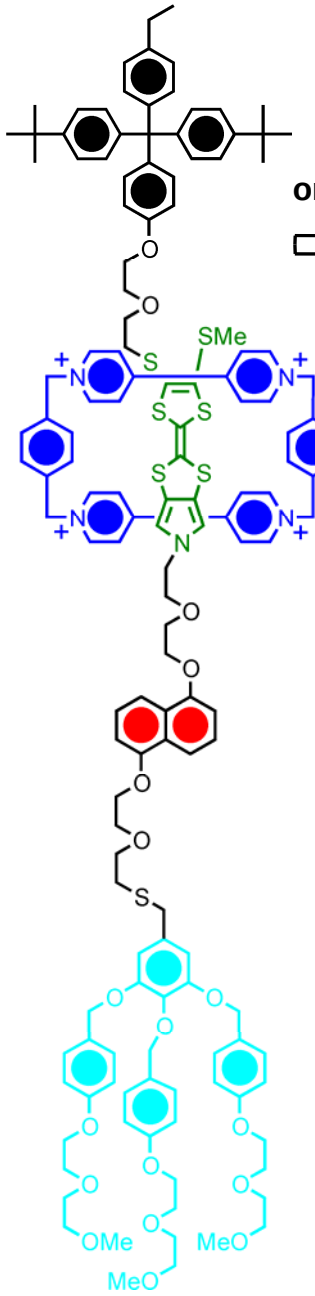


The translational isomers cannot be isolated because the barrier to shuttling is to small – however, the relative population of the two isomers can be controlled by changing the temperature.

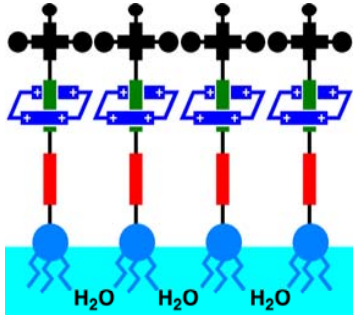




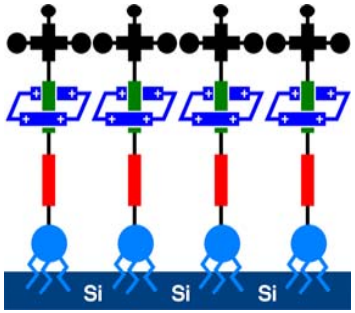
Constructing a Molecular Switch Tunnel Junction...



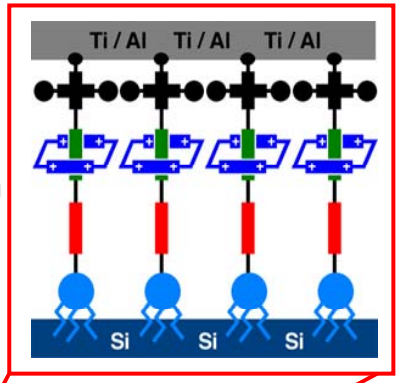
Self-organize

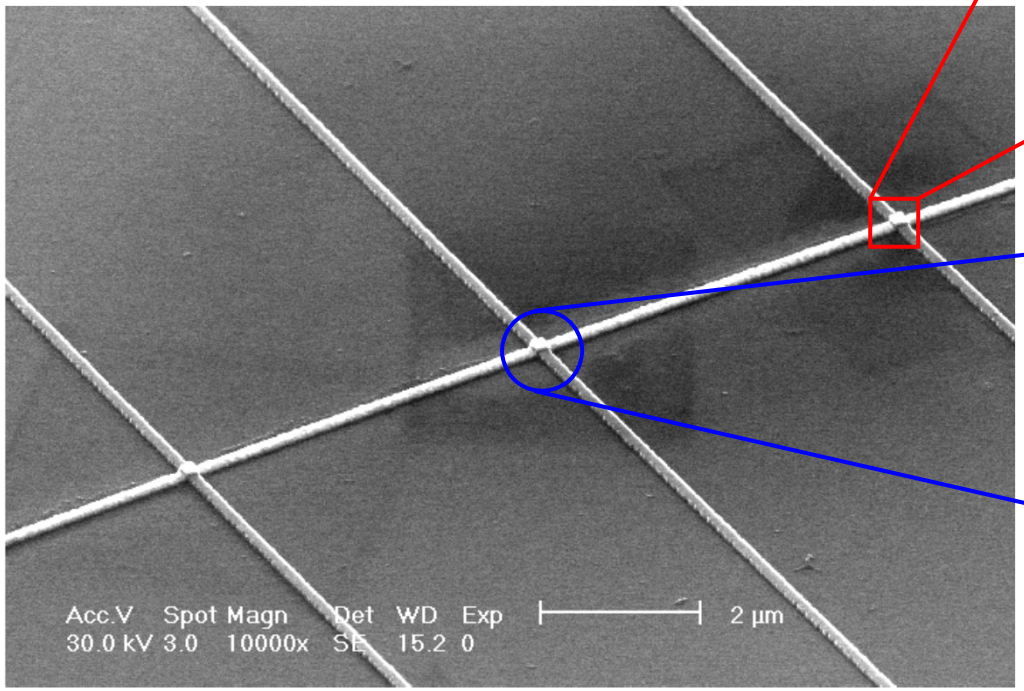


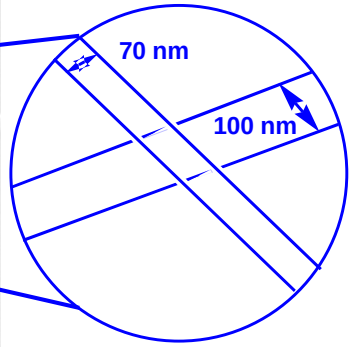
Transfer



Ti/Al Deposition





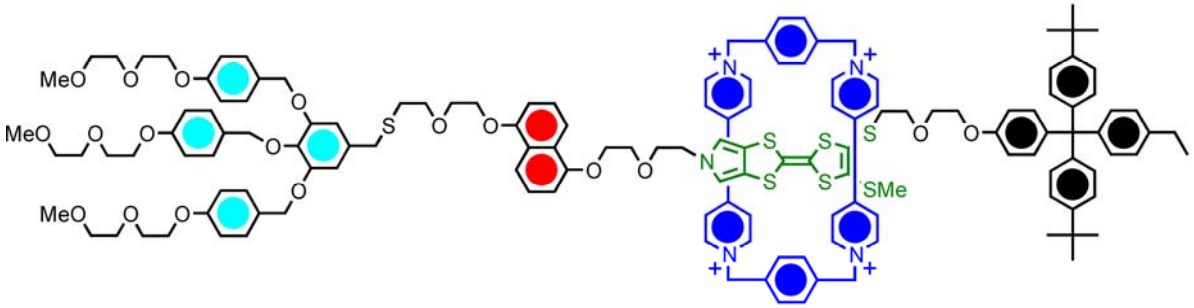


~ 7000 nm^2

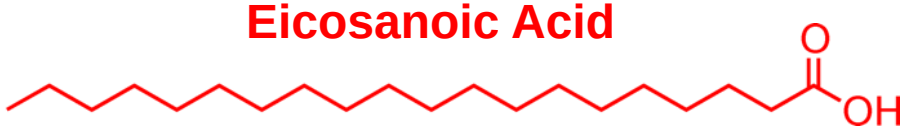
~ 5000 Molecules

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

…and Comparing Switchable and Control Molecules in a Device Setting

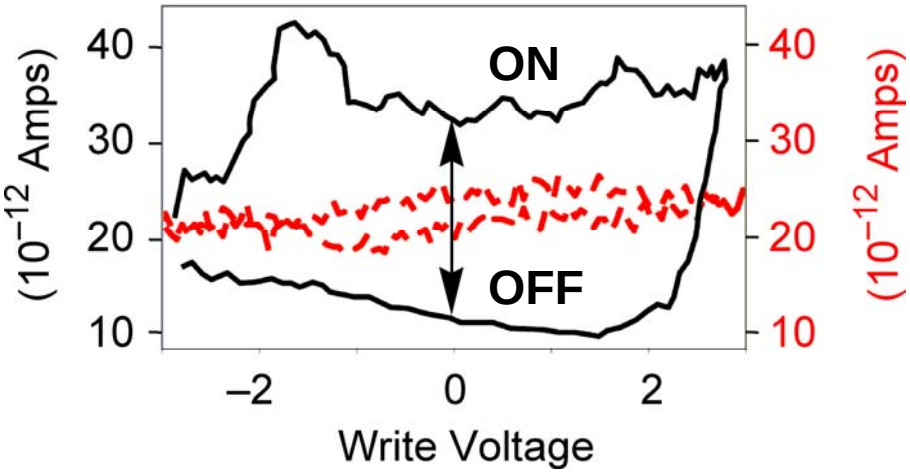


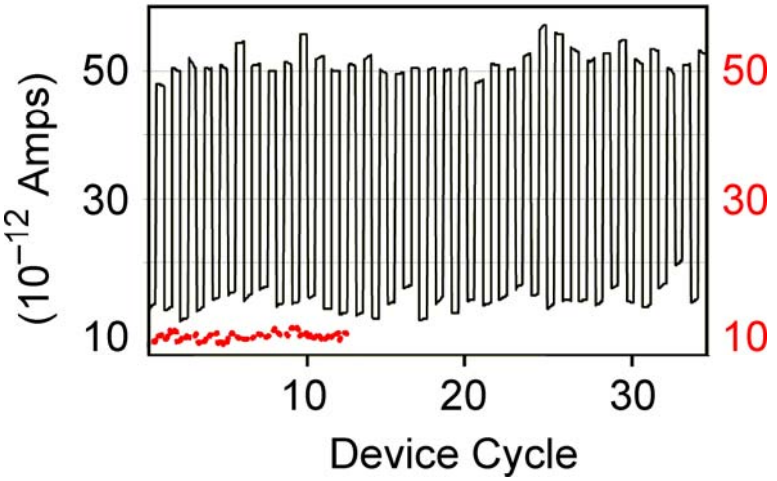
Eicosanoic Acid



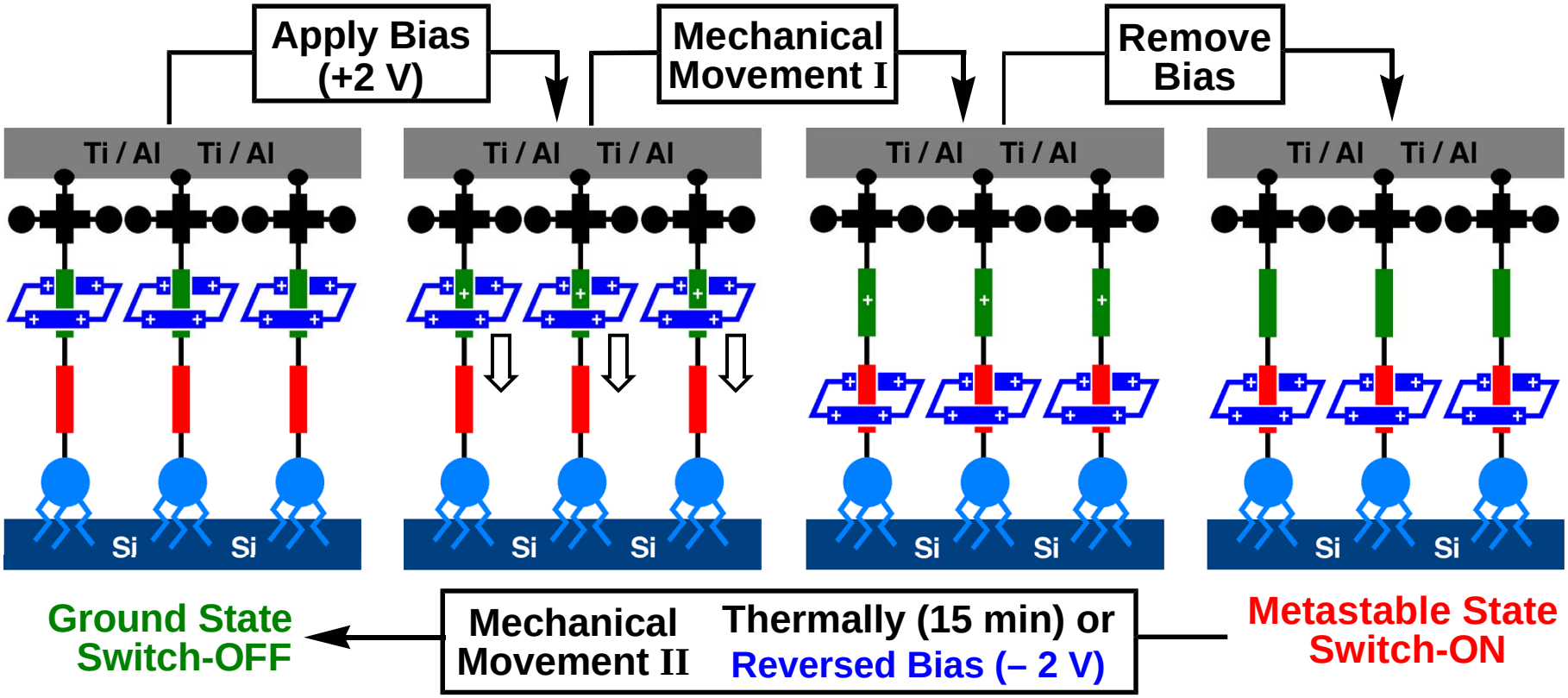
In the device setting, the [2]rotaxane exhibits excellent switching and cycling properties, and the Remnant Molecular Signature begins to resemble that of a close competitor – the conventional magnetic bit. A sharp switching voltage and a large ON / OFF ratio are desirable characteristics for molecular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

Remnant Molecular Signature





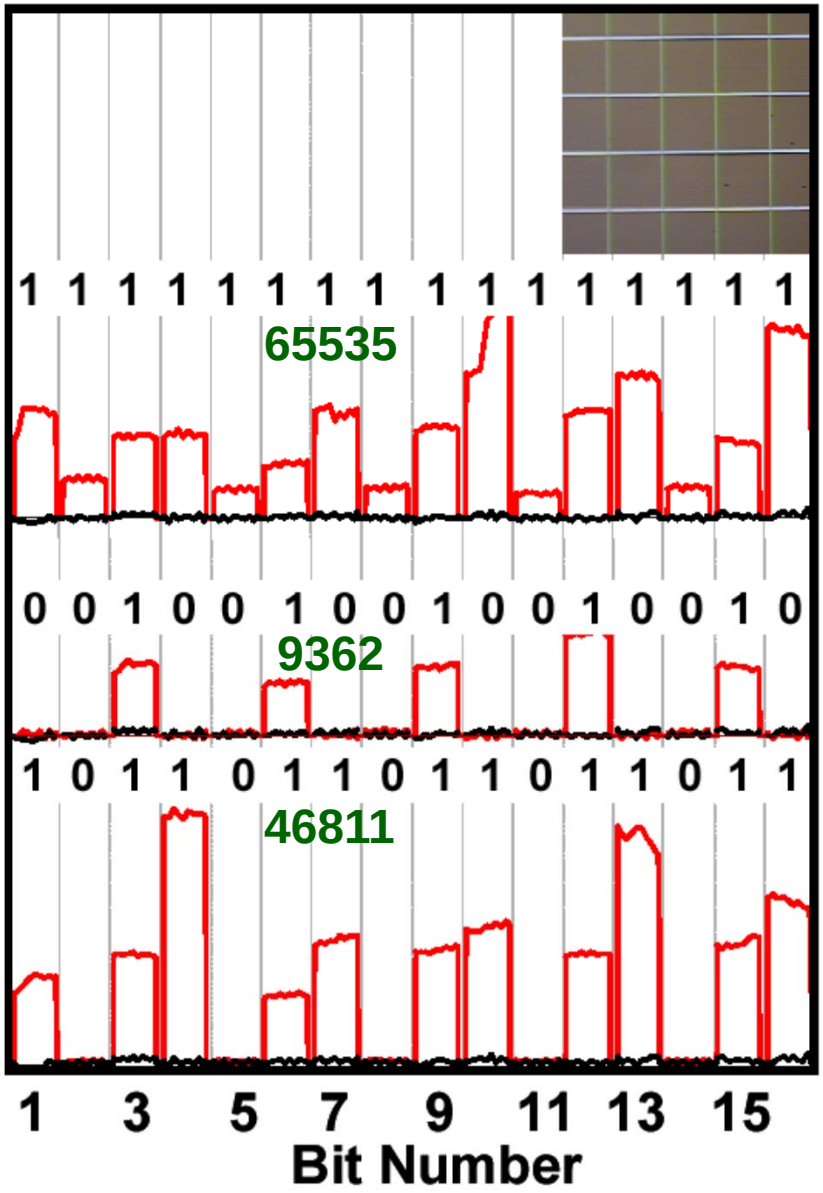
Proposed
NanoElectroMechanical Switching Mechanism



Solution	Surface	Device
14.5	17.7	21

Kcal mol^{-1}

A Molecular Electronics-Based Random Access Memory Circuit in Operation



Demonstrate Memory Circuit Performance of 16 of these 25 Bits

25 Bits were Operational

6 × 6 Crosspoint Structure
36 Molecular Switch Tunnel Junctions
Containing the Two-Station Fast [2]Rotaxane

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.

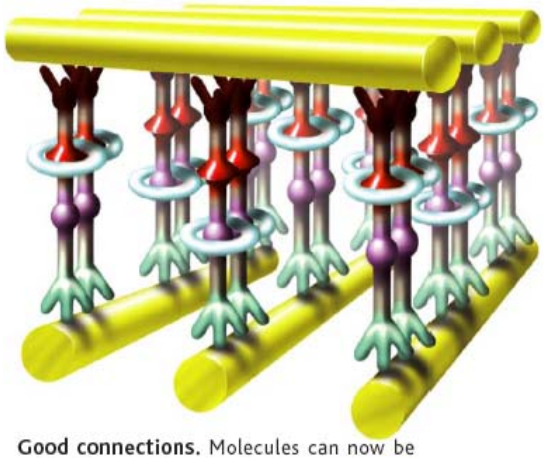
IMPLYING THAT THEY ARE USEFUL AS MEMORY AND LOGIC DEVICES

Where Can You Find Our Chemistry?

BREAKTHROUGH OF THE YEAR

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

COVER STORY

CHEMICAL & 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

The Economist

SEPTEMBER 14TH - 20TH 2002