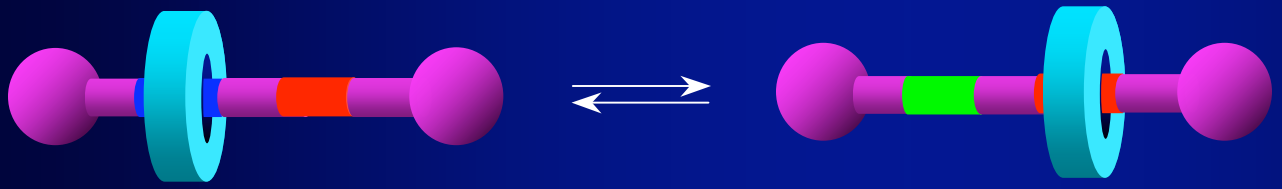
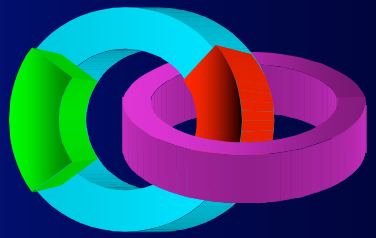
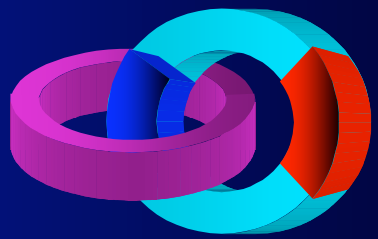
Application of Rotaxanes & Catenanes to Molecular Switches







Michigan State University

Department of Chemistry

SEPT. 8, 2004.

Soong-Hyun Kim

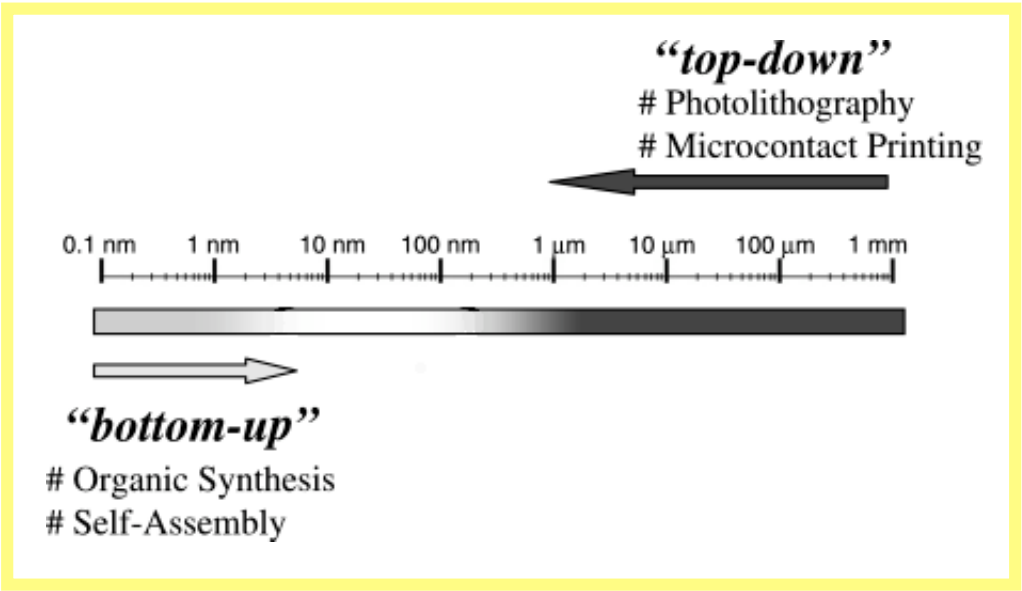
Molecular Machines

What is a molecular machine?

"An assembly of a discrete number of molecular components designed to perform mechanical-like movements as a consequence of appropriate external stimuli"

Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2000**, *39*, 3348-3391.

Electronic Devices (Top-down *vs.* Bottom-up)



Intrinsic Limitations of Top-down Process

- photolithography
- oxide layer
- semiconductor

→ Errors into computation

"There's plenty of room at the bottom"

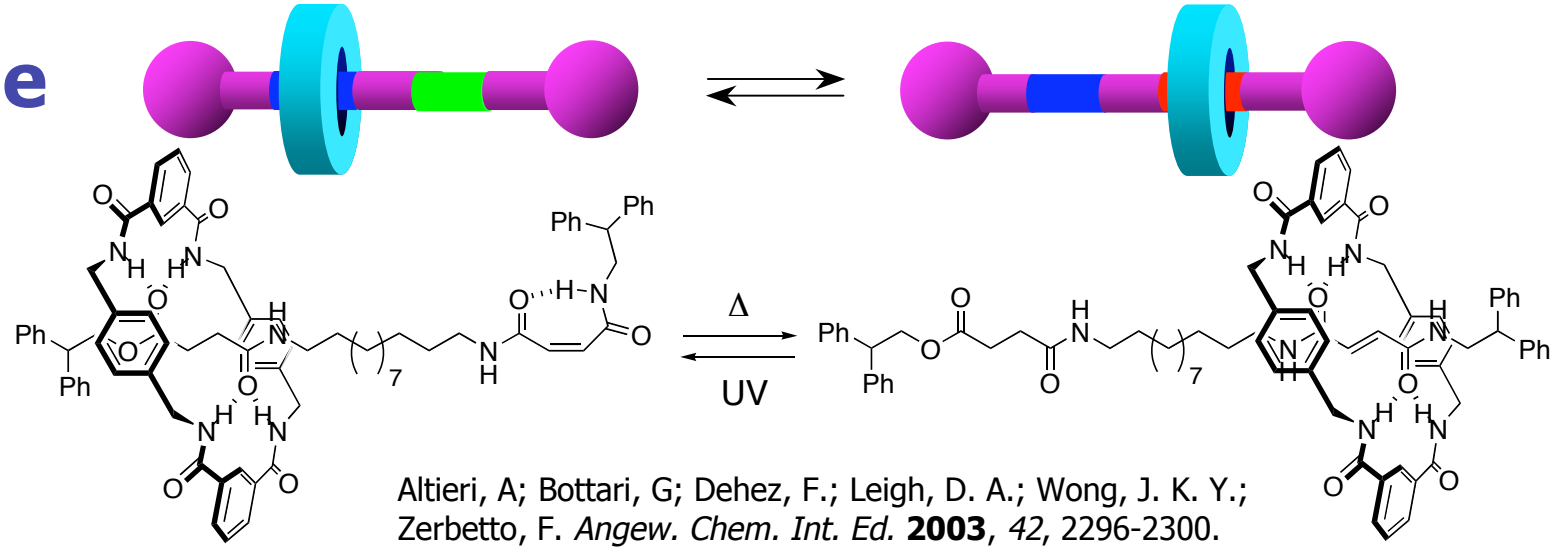
- Richard P. Feynman, 1959, APS talk.

The Genesis of Molecular Electronics (Bottom-up Approach)

Carroll, R. L.; Gorman, C. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 4378-4400.
Niemeyer, C. M. *Angew. Chem. Int. Ed*. **2001**, *40*, 4128-4158.

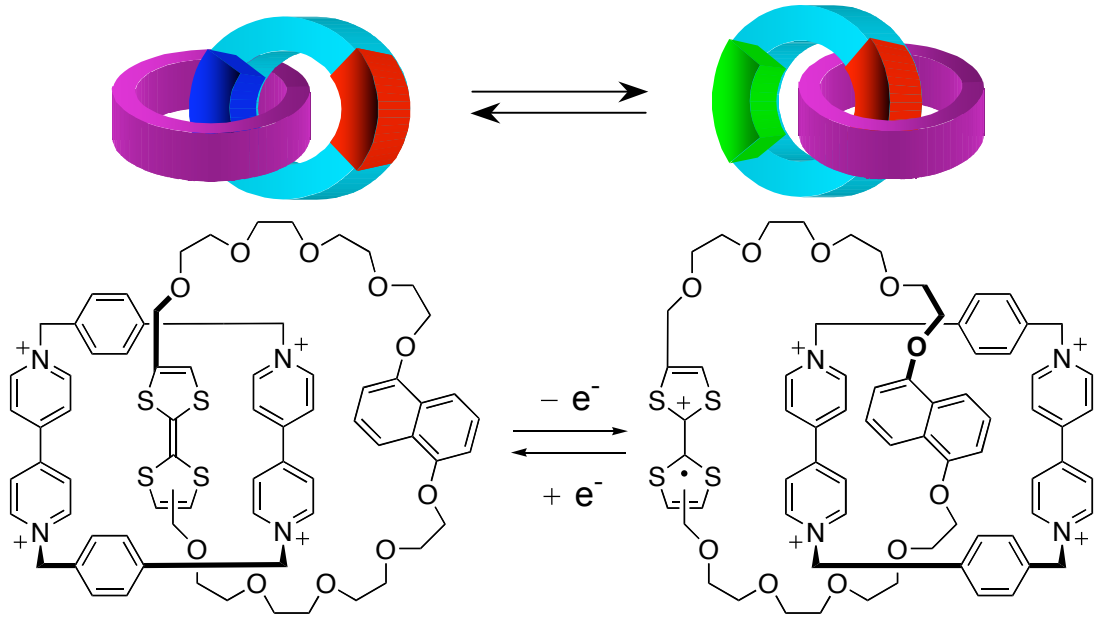
Molecular Switches

Rotaxane



Altieri, A; Bottari, G; Dehez, F.; Leigh, D. A.; Wong, J. K. Y.; Zerbetto, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 2296-2300.

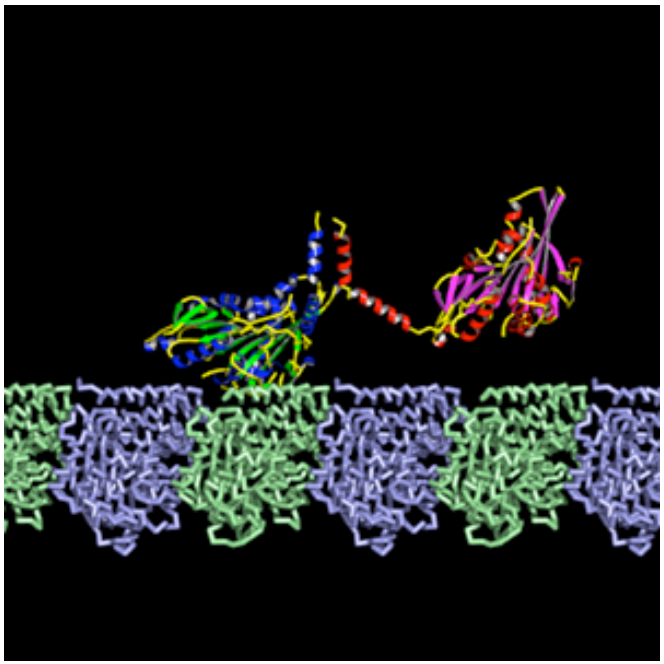
Catenane



Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O. A.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2000**, *65*, 1924-1936.

Natural Molecular Machines - Biomotors

Kinesin - Linear Motor

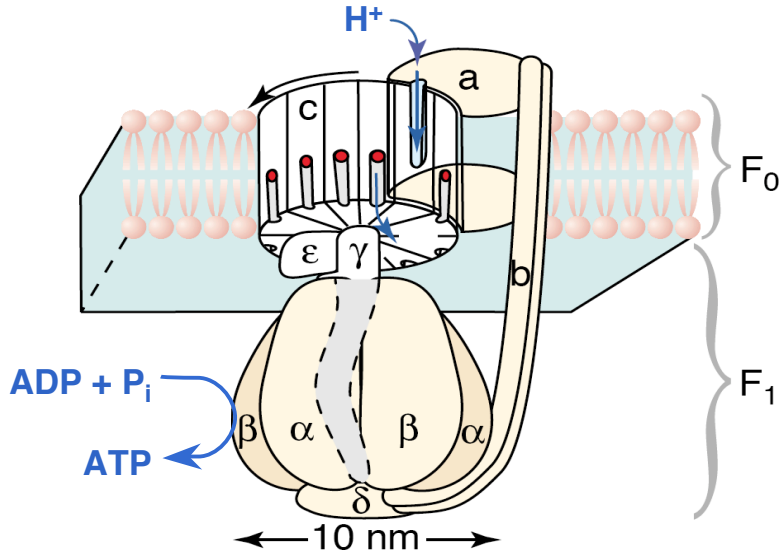


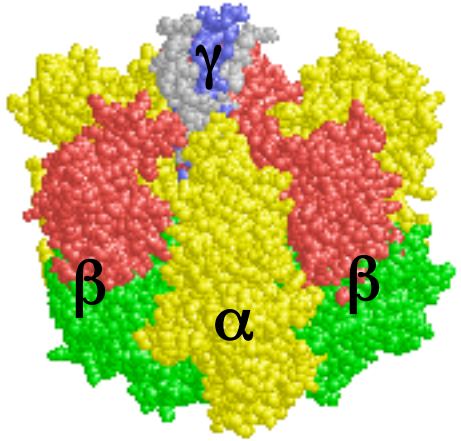
Role: vesicle-transport in the cell along the microtubule in linear fashion

Driving force: ATP hydrolysis

Hoenger, A.; Thormählen, M.; Diaz-Avalos, R.; Doerhoefer, M.; Goldie, K. N.; Müller, J.; Mandelkow, E. *J. Mol Biol* **2000**, *297*, 1087-1103.
http://www.mpasmb-hamburg.mpg.de/ktdock/

ATP synthase - Rotary Motor

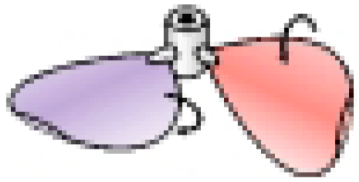


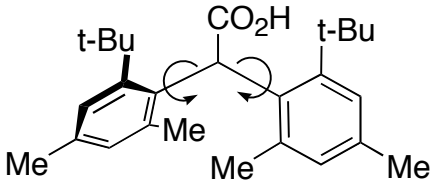


Wang, H.; Oster, G. *Nature* **1998**, *396*, 279-282.
Oster, G.; Wang, H. *Trends Cell Biol.* **2003**, *13*, 114-121.
http://nature.berkeley.edu/~hongwang/Project/ATP_synthase/

Artificial Molecular Motors

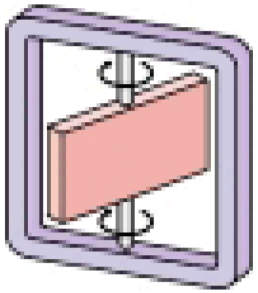
Propeller

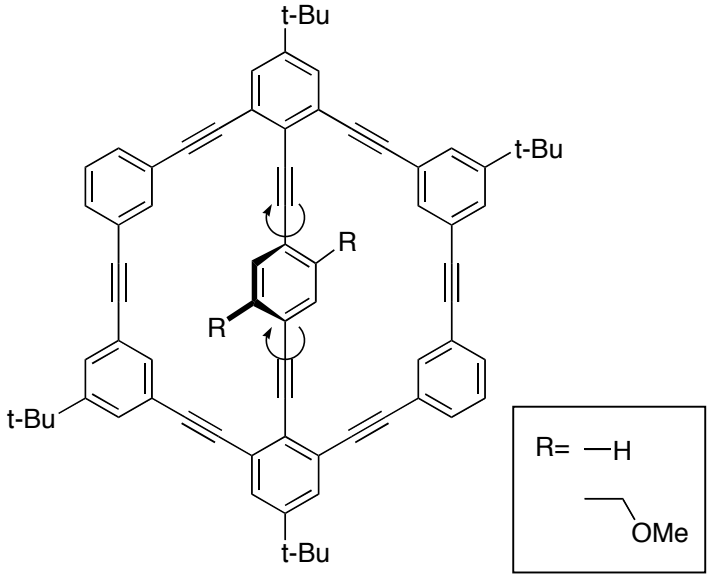




Akkerman, O. S.; Coops, J. *Rec. Trav. Chim. Pays-Bas* **1967**, *86*, 755-761; *ibid.* **1970**, *89*, 673-679.

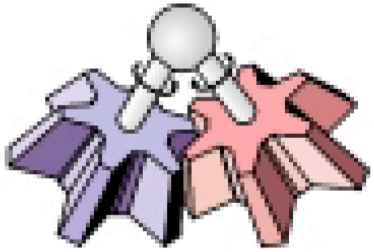
Turnstile

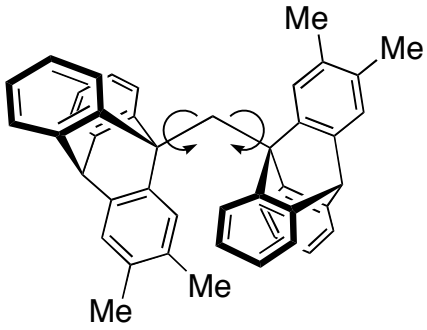




Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662-10671.

Gear

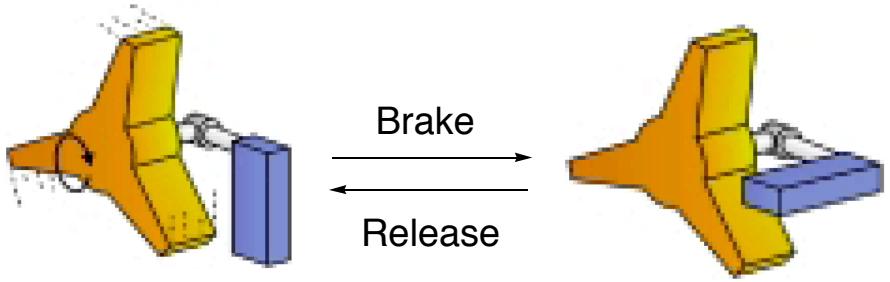


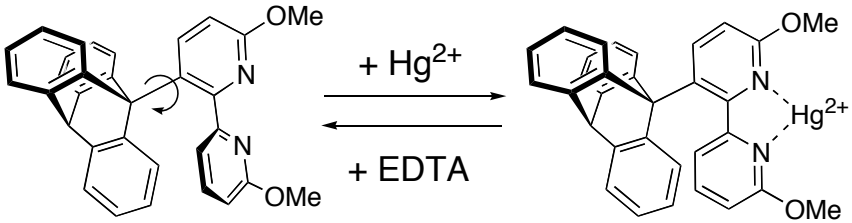


Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957-958.

Artificial Molecular Motors

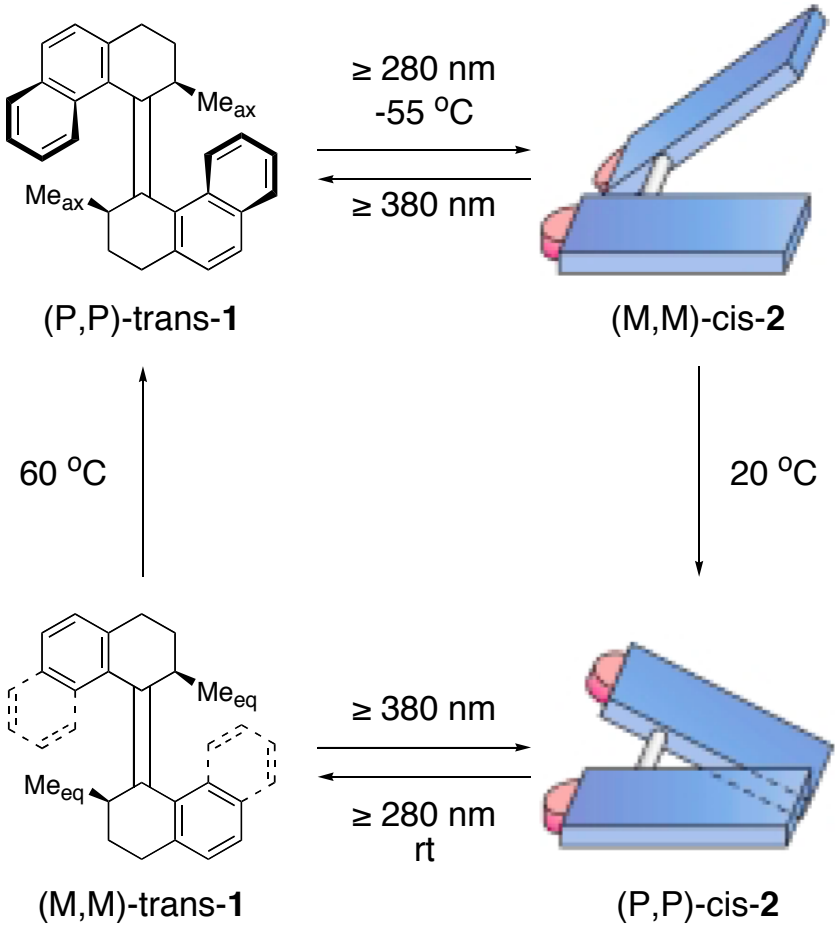
Brake





Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; Garcia, A.; Lang, F.; Kim, M. H. Jette, M. P. *J. Am. Chem. Soc.* **1994**, *116*, 3657-3658.

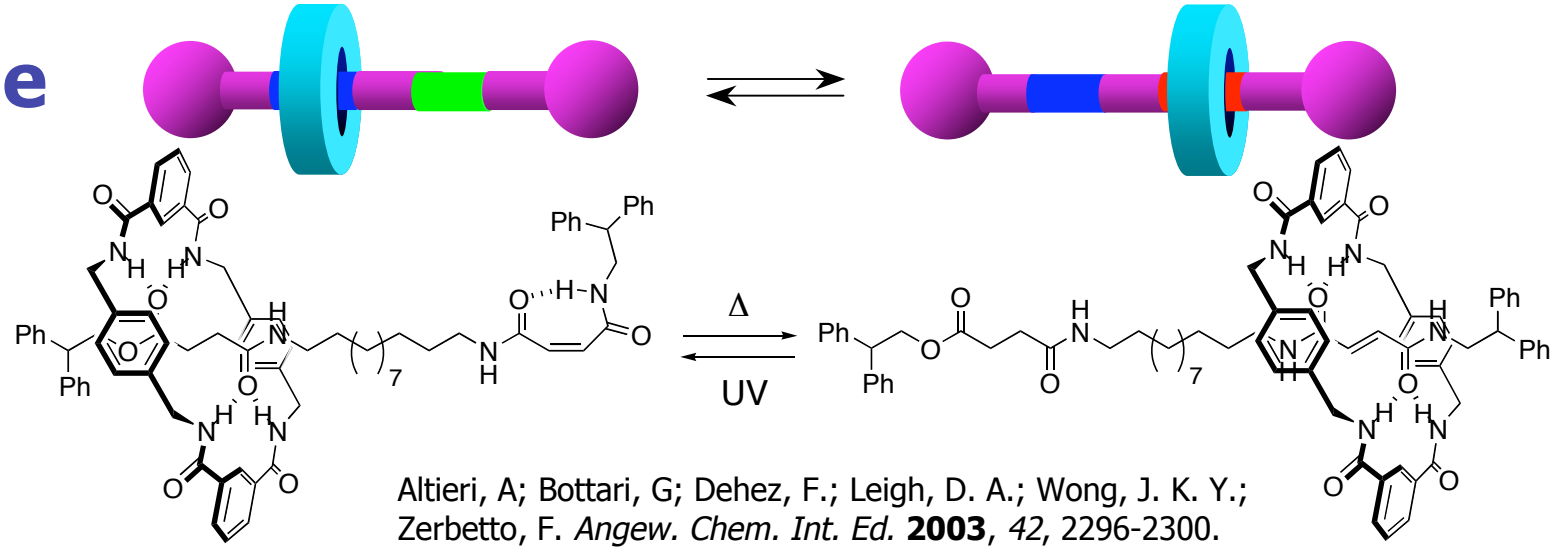
Unidirectional Molecular Rotor



Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152-155.

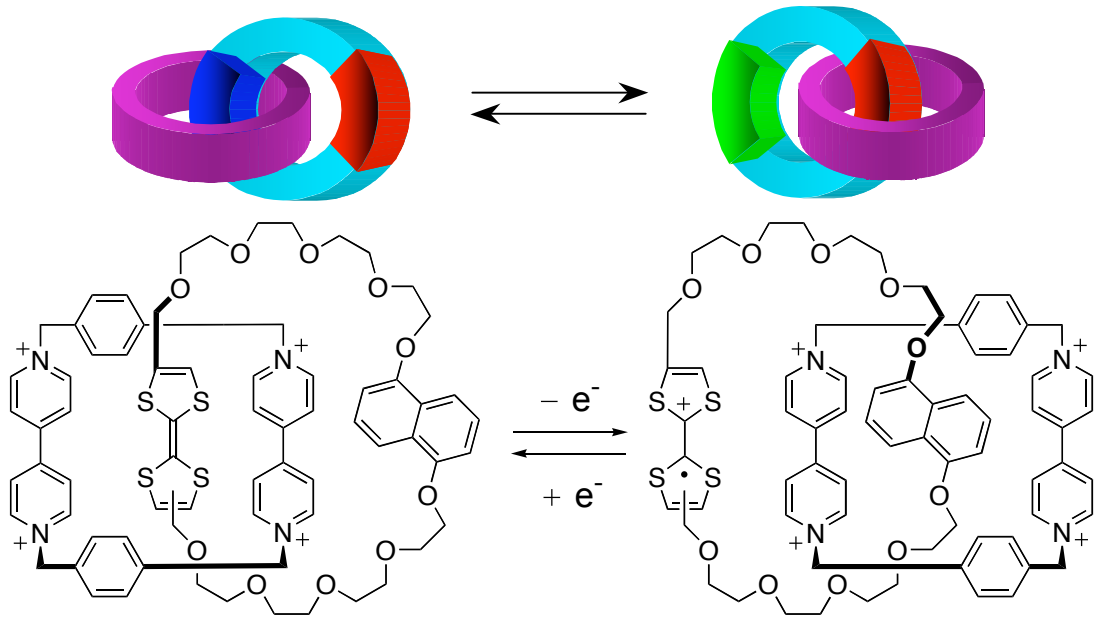
Artificial Molecular Motors

Rotaxane



Altieri, A; Bottari, G; Dehez, F.; Leigh, D. A.; Wong, J. K. Y.; Zerbetto, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 2296-2300.

Catenane

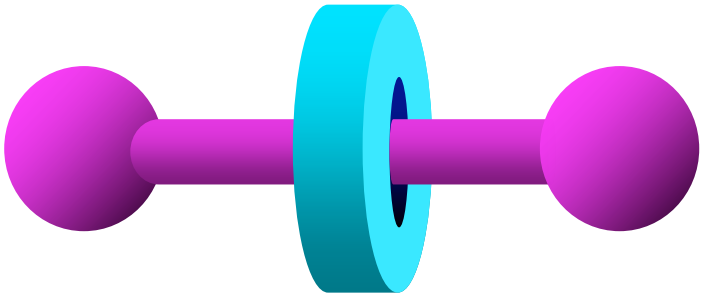


Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O. A.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2000**, *65*, 1924-1936.

What Are Rotaxanes & Catenanes ?

[n]Rotaxanes

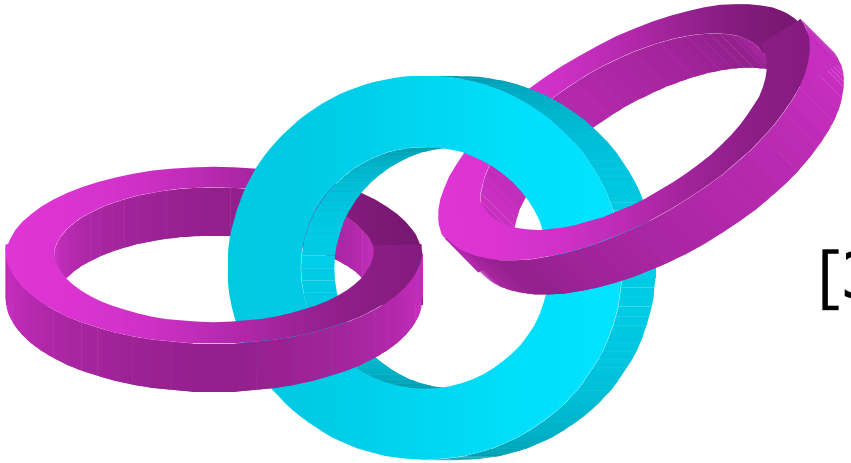
from Latin:
rota = wheel
axis = axle



[2]rotaxane

[n]Catenanes

from Latin:
catena = chain

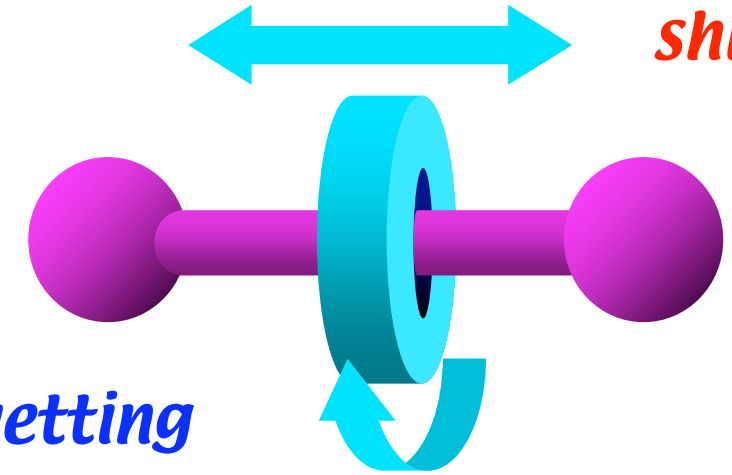


[3]catenane

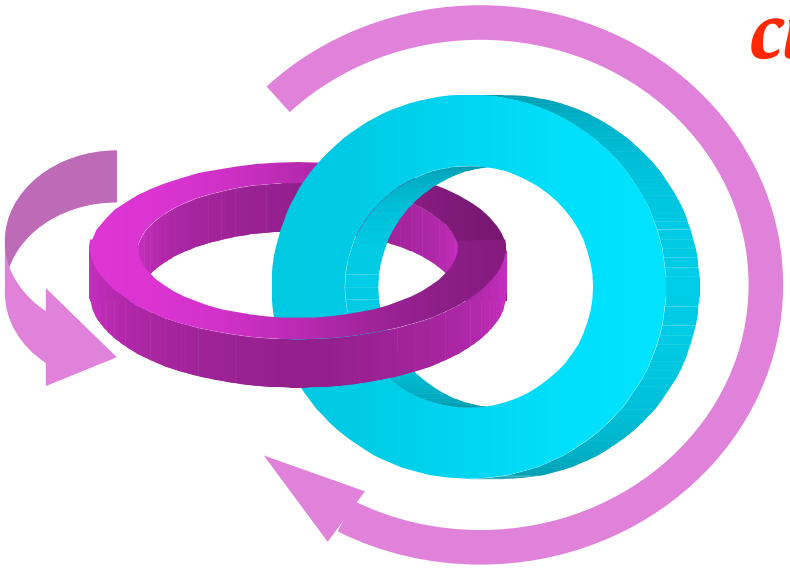
Note: n = the total # of the interlocked components

How Do Rotaxanes & Catenanes Move ?

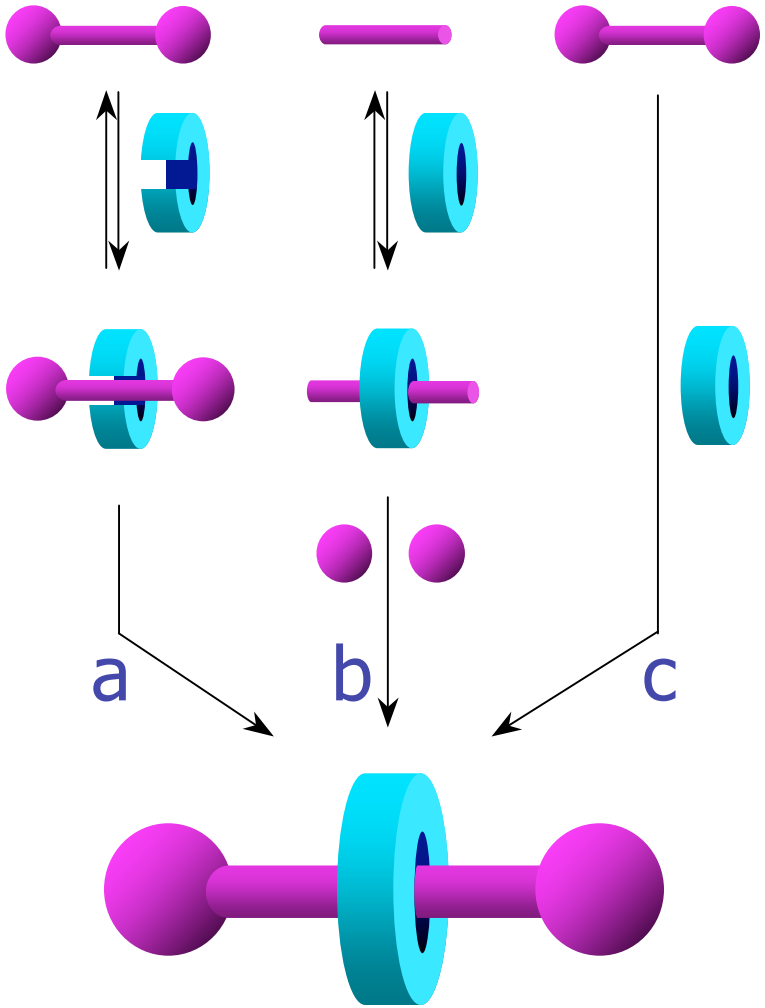
[2]Rotaxanes

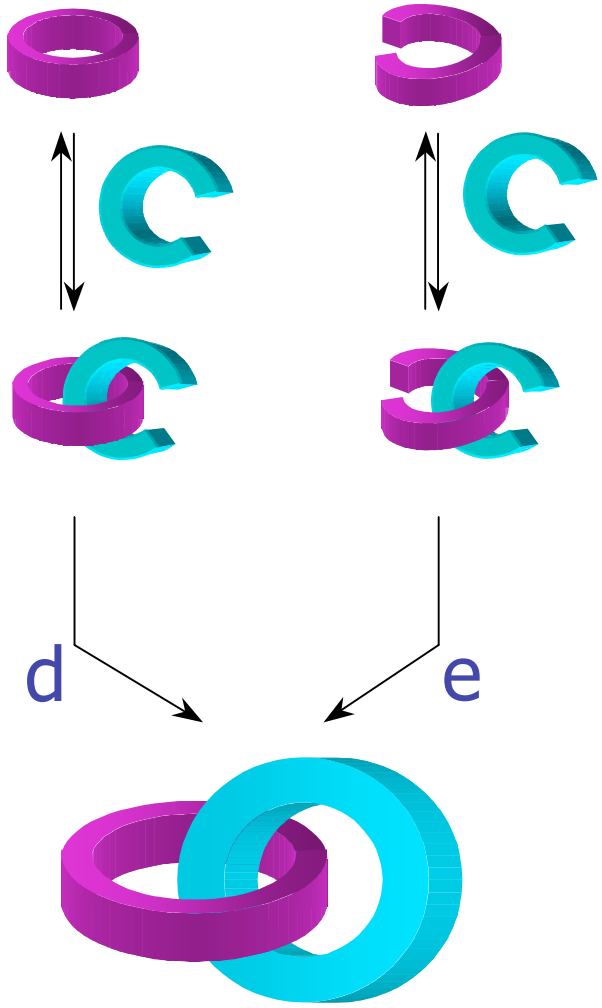


[2]Catenanes



How to Construct Rotaxanes & Catenanes ?

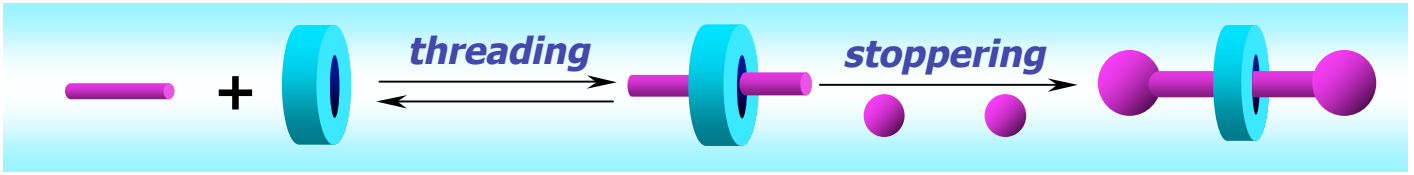


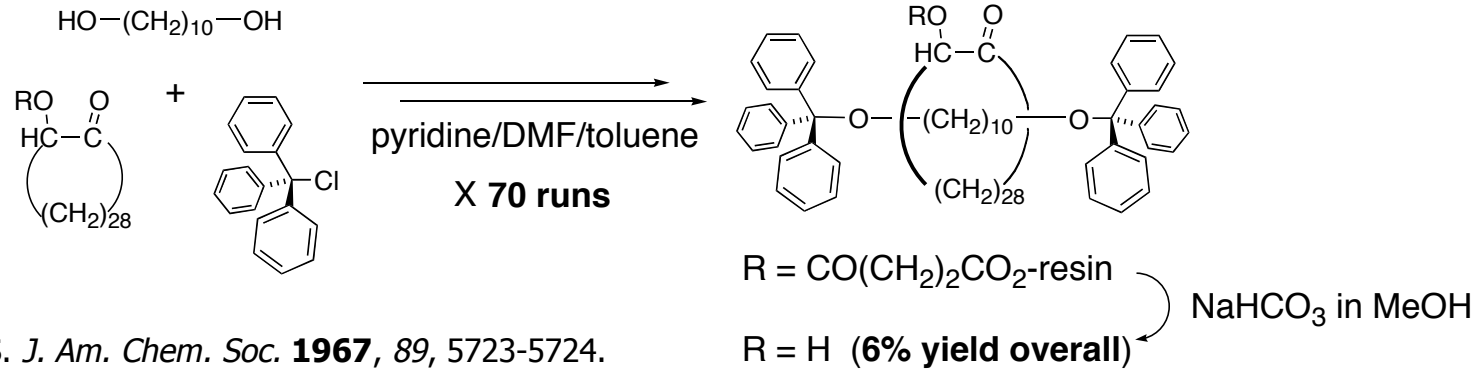


a: **Clipping**
b: **Threading & Stoppering**
c: **Slipping**

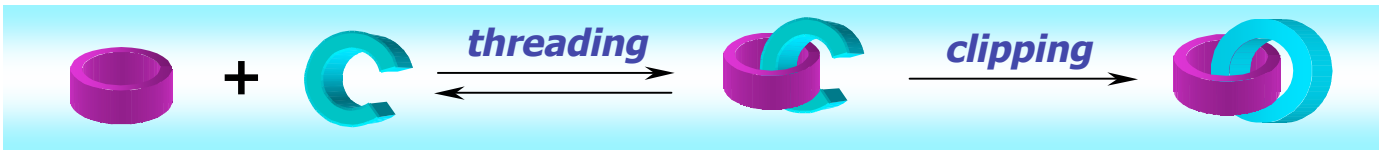
d: **Threading & Clipping**
e: **Double Clipping**

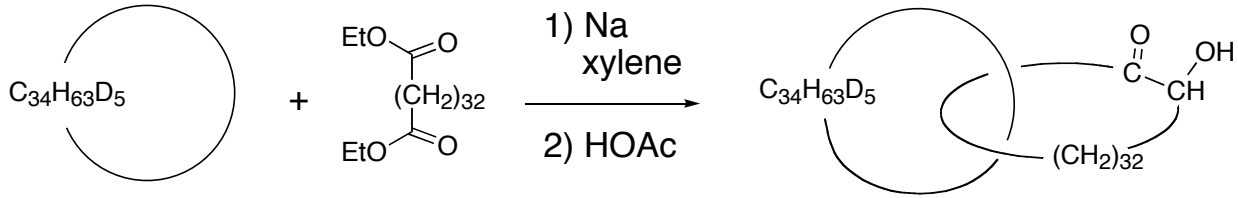
First Synthesis of Rotaxanes & Catenanes





Harrison, I. T.; Harrison, S. *J. Am. Chem. Soc.* **1967**, *89*, 5723-5724.



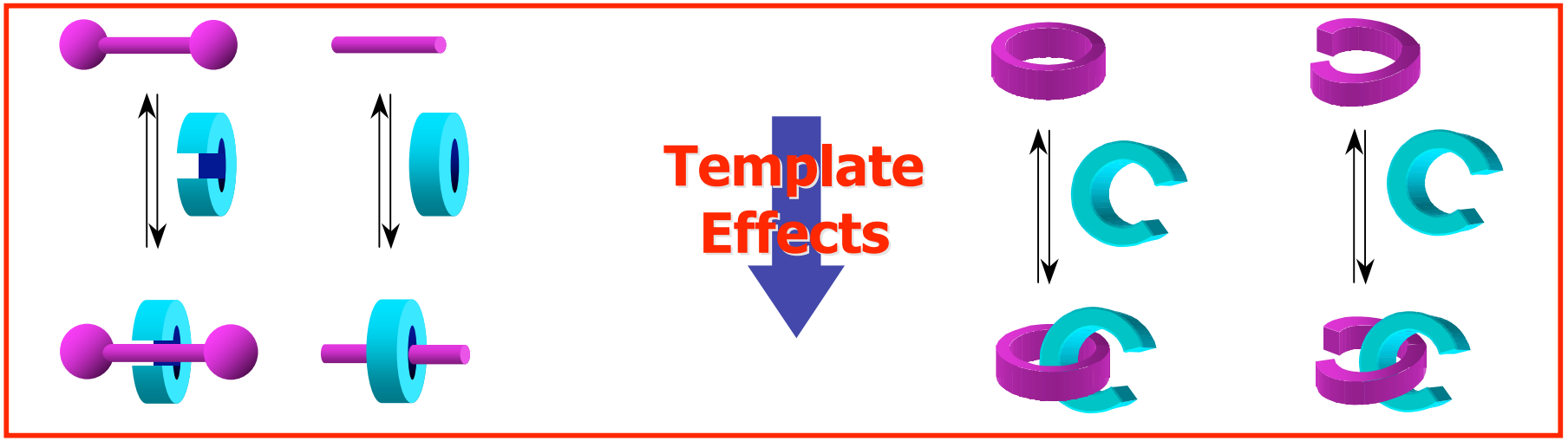


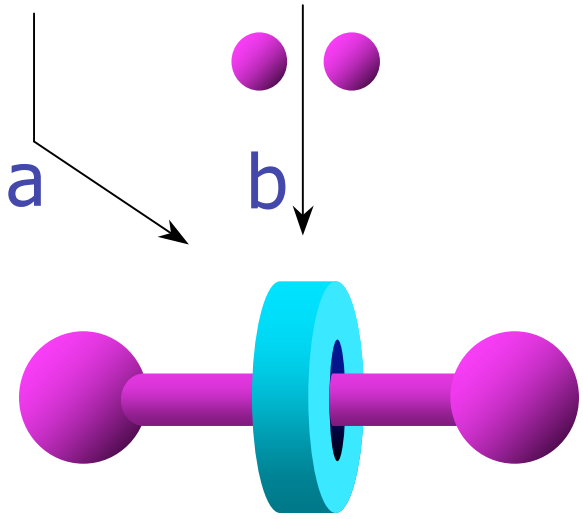
Wasserman. E. *J. Am. Chem. Soc.* **1960**, *82*, 4433-4434.

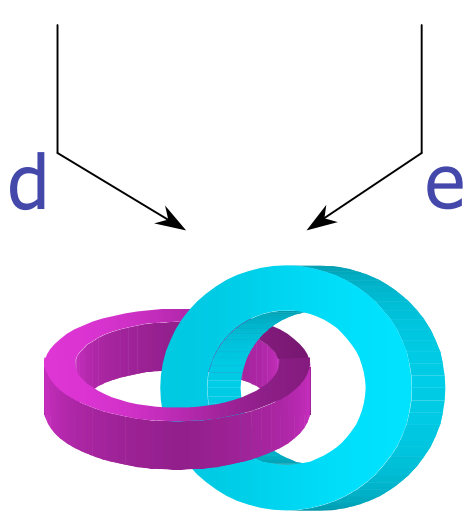
<1% yield

- **First synthesis** of Rotaxane and Catenane was dependent only on **statistical probability**.

How Can We Make Complex Efficiently ?







a: **Clipping**
b: **Threading & Stoppering**

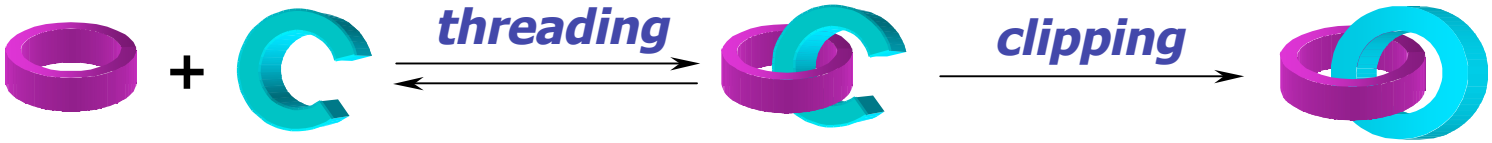
d: **Threading & Clipping**
e: **Double Clipping**

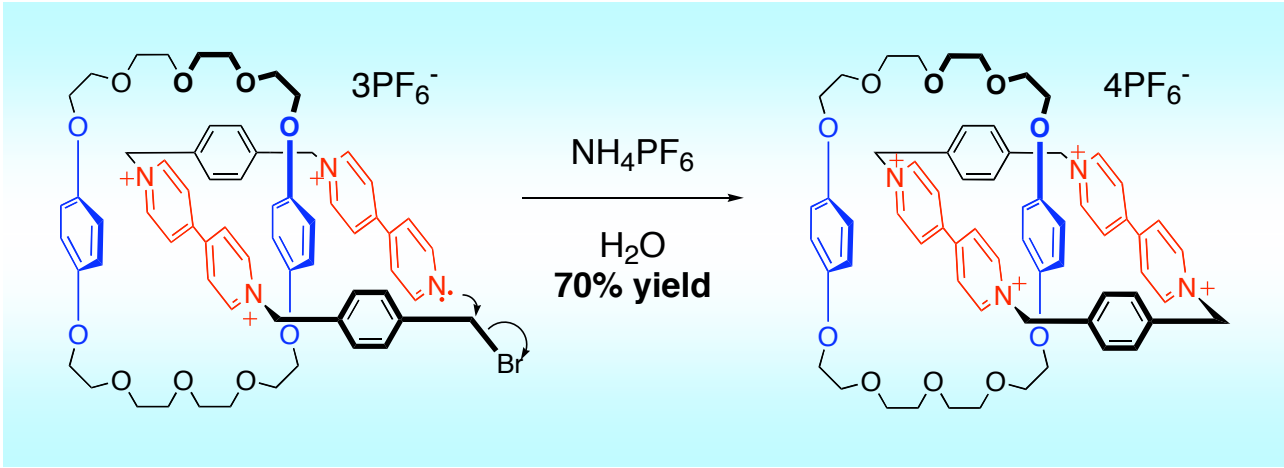
Template Effects to Make Complex Efficiently

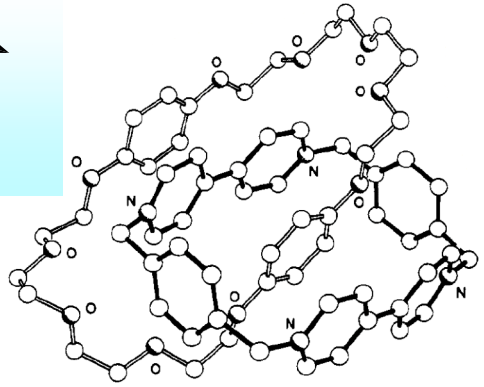
- π Donor - π Acceptor Interaction
- Metal-Ligand Coordination
- Hydrogen Bonding
- Hydrophobic Interactions

Template Effects to Make Complex Efficiently

π Donor - π Acceptor Interaction



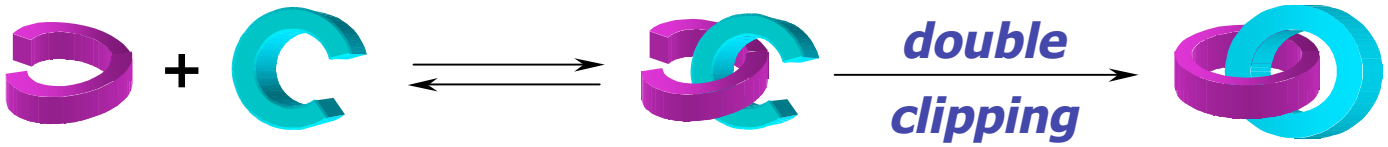


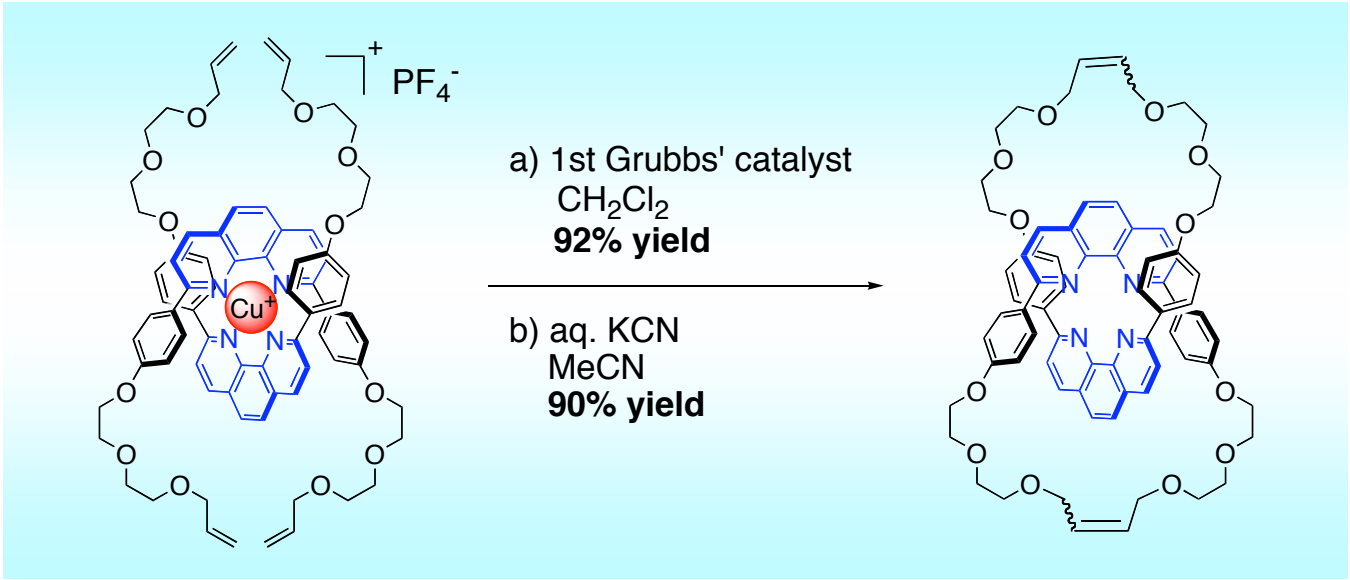


Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193-218.

Template Effects to Make Complex Efficiently

Metal-Ligand Coordination

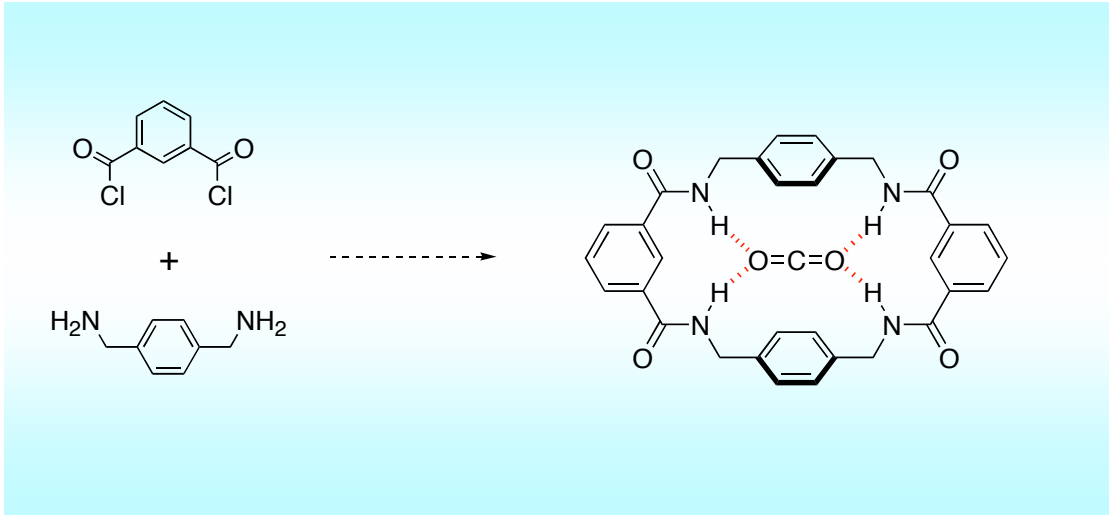




Weck, M.; Mohr, B.; Sauvage, J.-P.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 5463-5471.

Template Effects to Make Complex Efficiently

Hydrogen Bonding

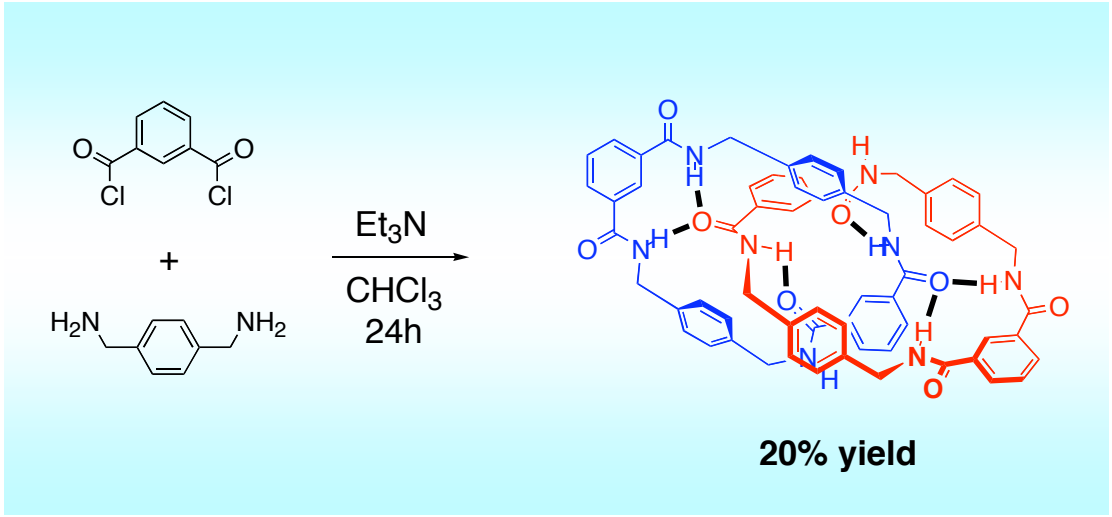


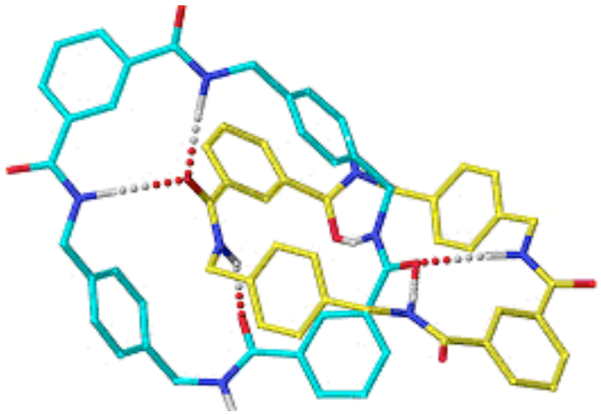
Johnston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem. Int. Ed.* **1995**, *34*, 1209-1212.

Template Effects to Make Complex Efficiently

Hydrogen Bonding

one pot self assembly
(eight-molecule condensation)

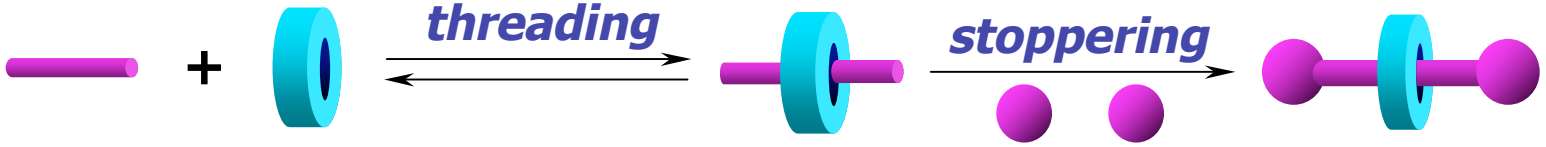


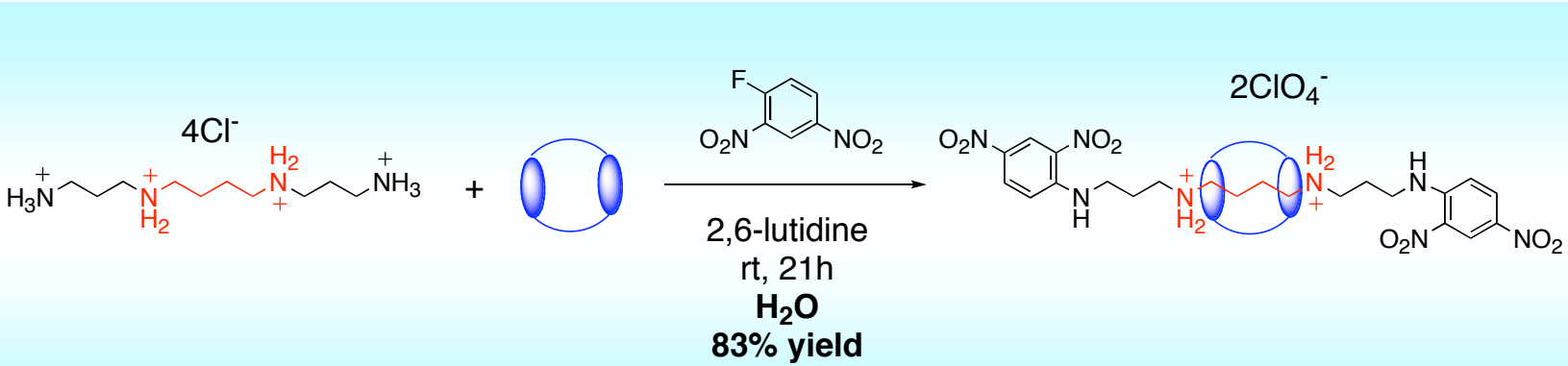


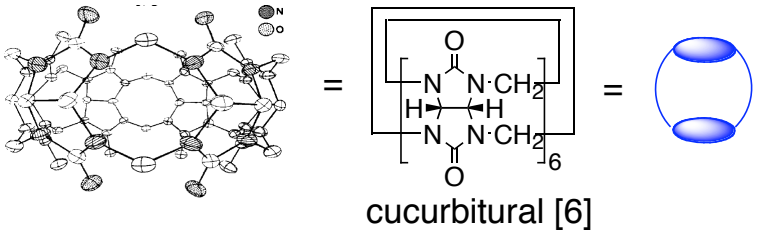
Johnston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem. Int. Ed.* **1995**, *34*, 1209-1212.

Template Effects to Make Complex Efficiently

Hydrophobic Interactions







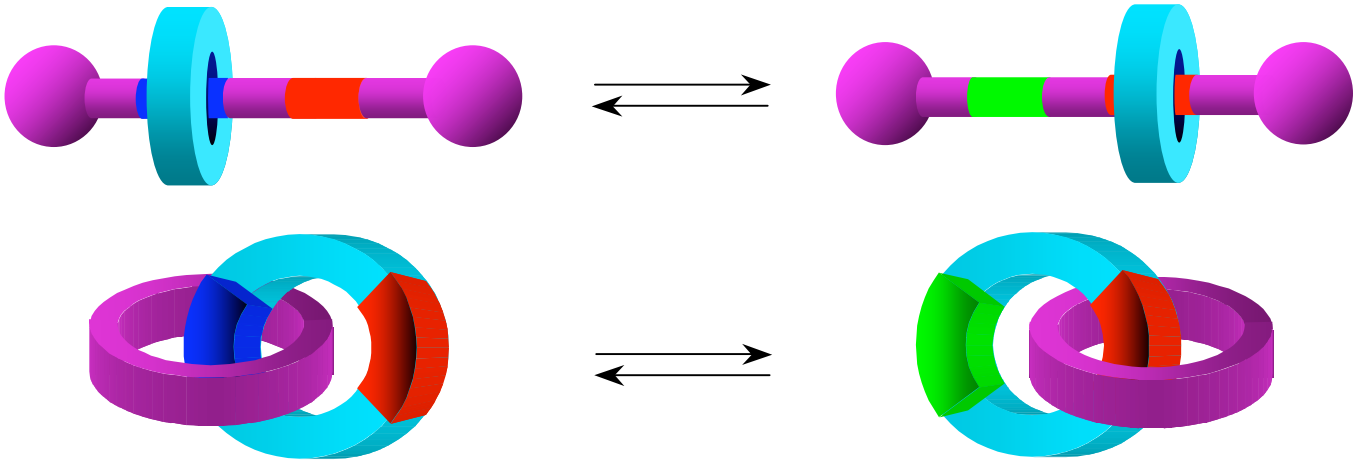
Jeon, Y.-M.; Whang, D.; Kim, J.; Kim, K. *Chem. Lett.* **1996**, 503-504.

Rotaxanes & Catenanes

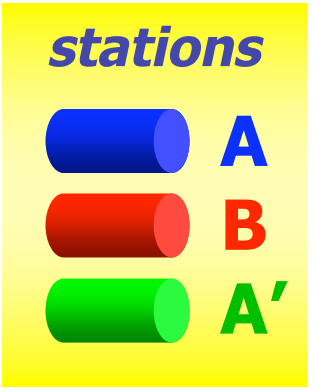
- Rotaxanes & catenanes are structurally **interlocked molecules** in which there is no covalent connection between the components of each system.

- Rotaxanes & catenanes can be synthesized by using various strategies and several effective ways to make complexes have been developed utilizing **template effects**.

Incorporation of Different Stations for Switching



"0" "1"



For the switching system:

- **The binding constants** between the wheel and each station should be in the following order: **A > B > A′**
- The two states should be **reversible** and **cyclable**. ?
- The process should be easily controllable by **external stimuli**.

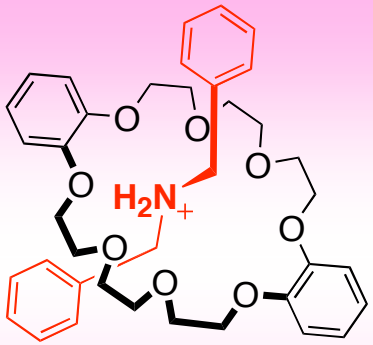
External Stimuli for Switching Systems

- **Chemically Driven Switching Systems**
  - Acid-Base Reaction
- **Photochemically Driven Switching Systems**
  - Olefin Isomerization
- **Electrochemically Driven Switching Systems**
  - Reduction-Oxidation Reaction

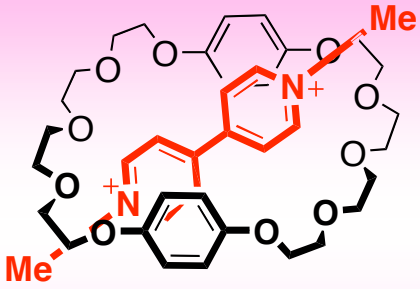
Chemically Driven Switching Systems

Acid-Base Reaction

Host-Guest Chemistry



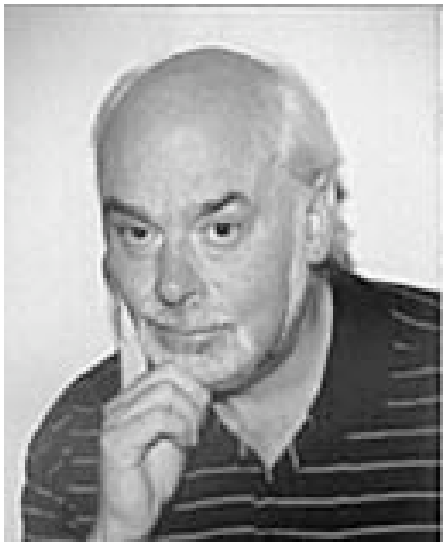
DB24C8
&
dialkylammonium



BPP34C10
&
paraquat

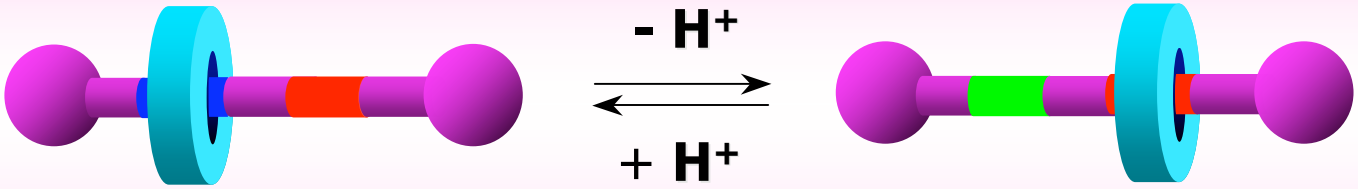
etc…

J. Fraser Stoddart
UCLA
US

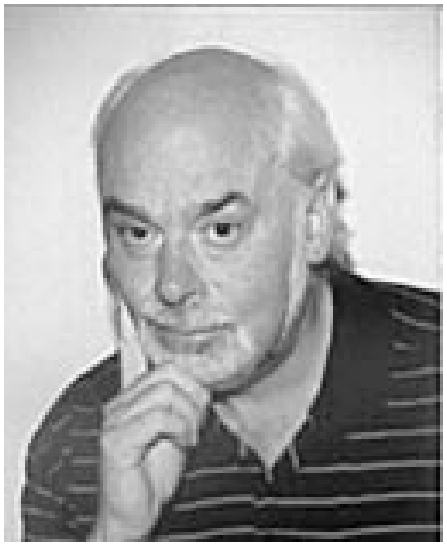


Chemically Driven Switching Systems

Acid-Base Reaction



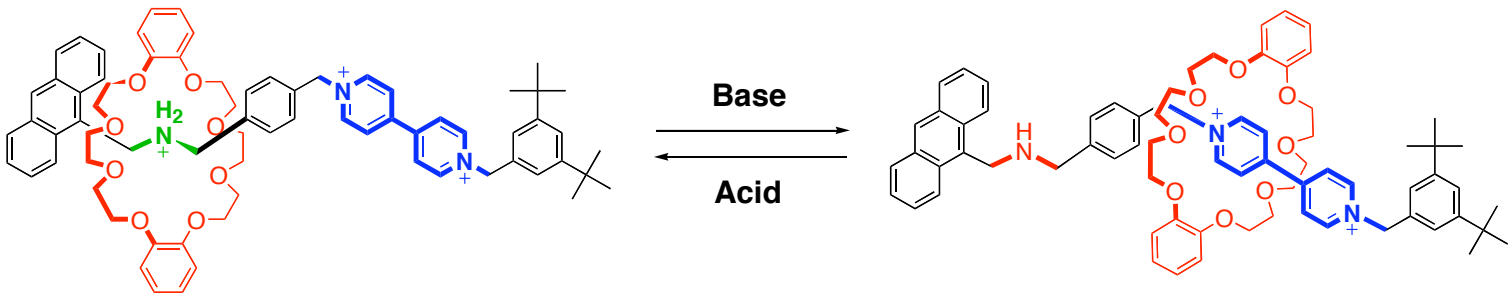
J. Fraser Stoddart
UCLA
US



Chemically Driven Switching Systems

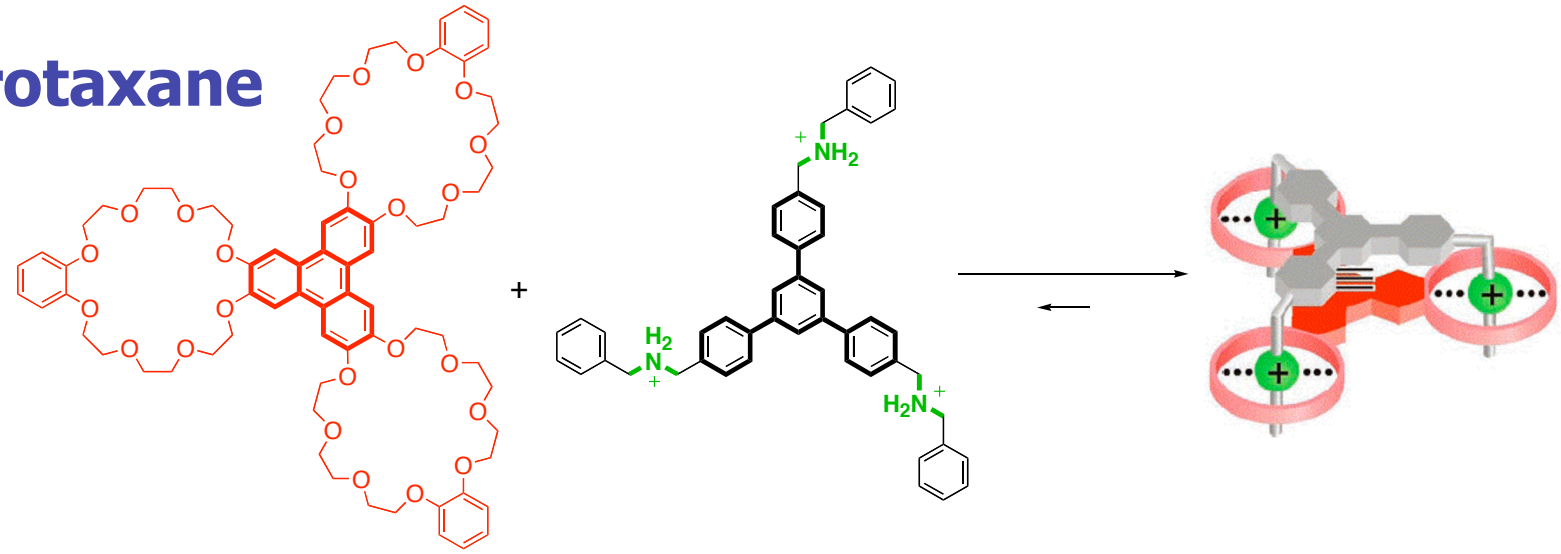
Rotaxane

Ashton, P. R. *et al.*
JACS **1998**, *120*,
11932-11942.



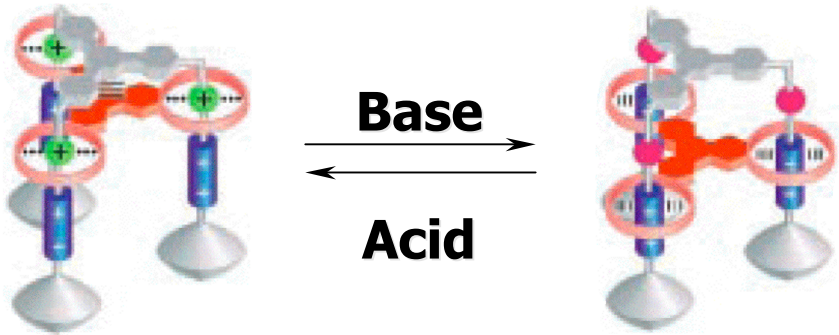
Pseudo-rotaxane

Balzani, V. *et al.*
Chem. Eur. J. **2003**,
9, 5348-5360.



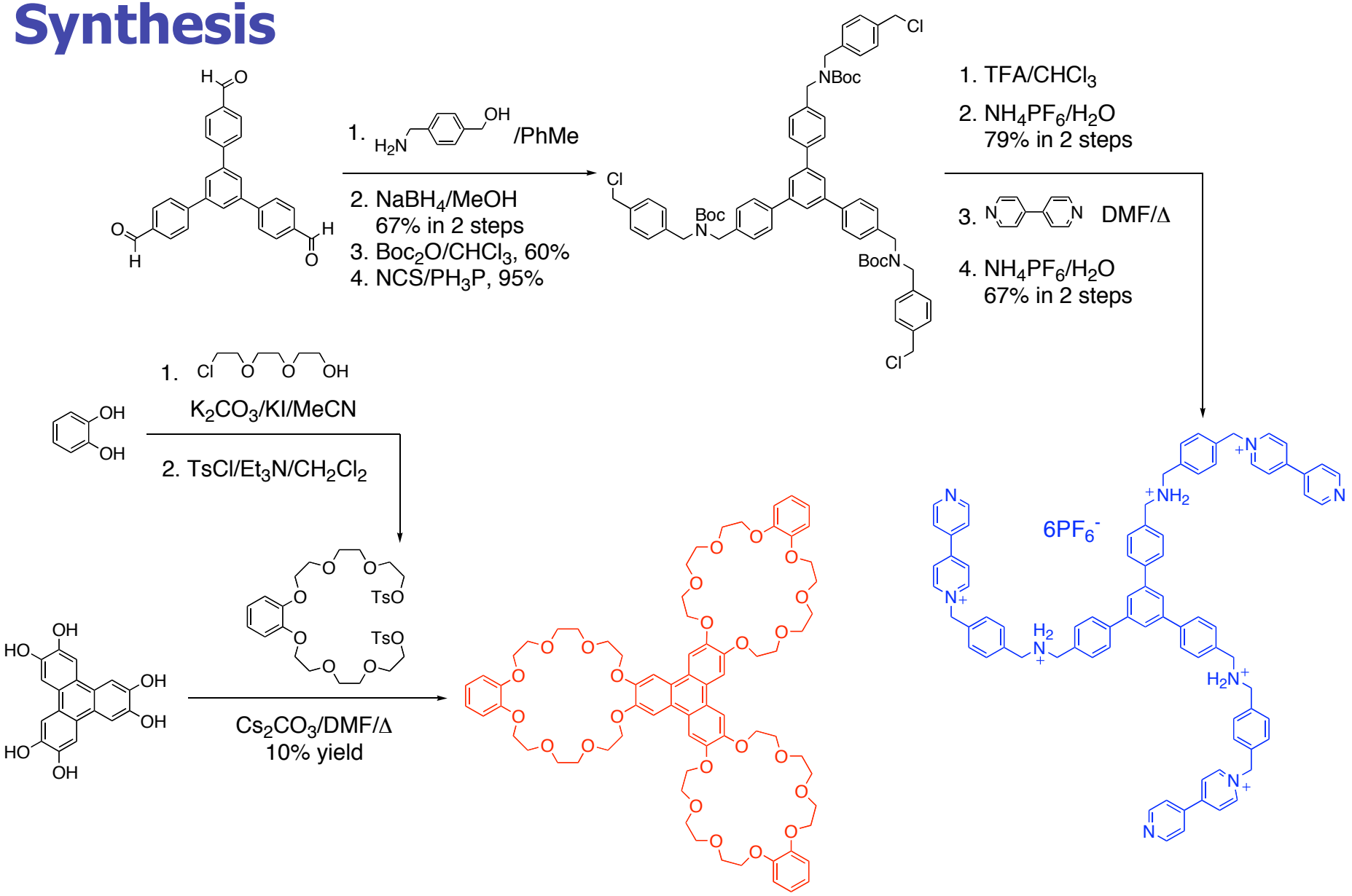
Molecular Elevator

Badjic, J. D.; Balzani, V.; Credi, A.;
Silvi, S.; Stoddart, J. F.
Science **2004**, *303*, 1845-1849.



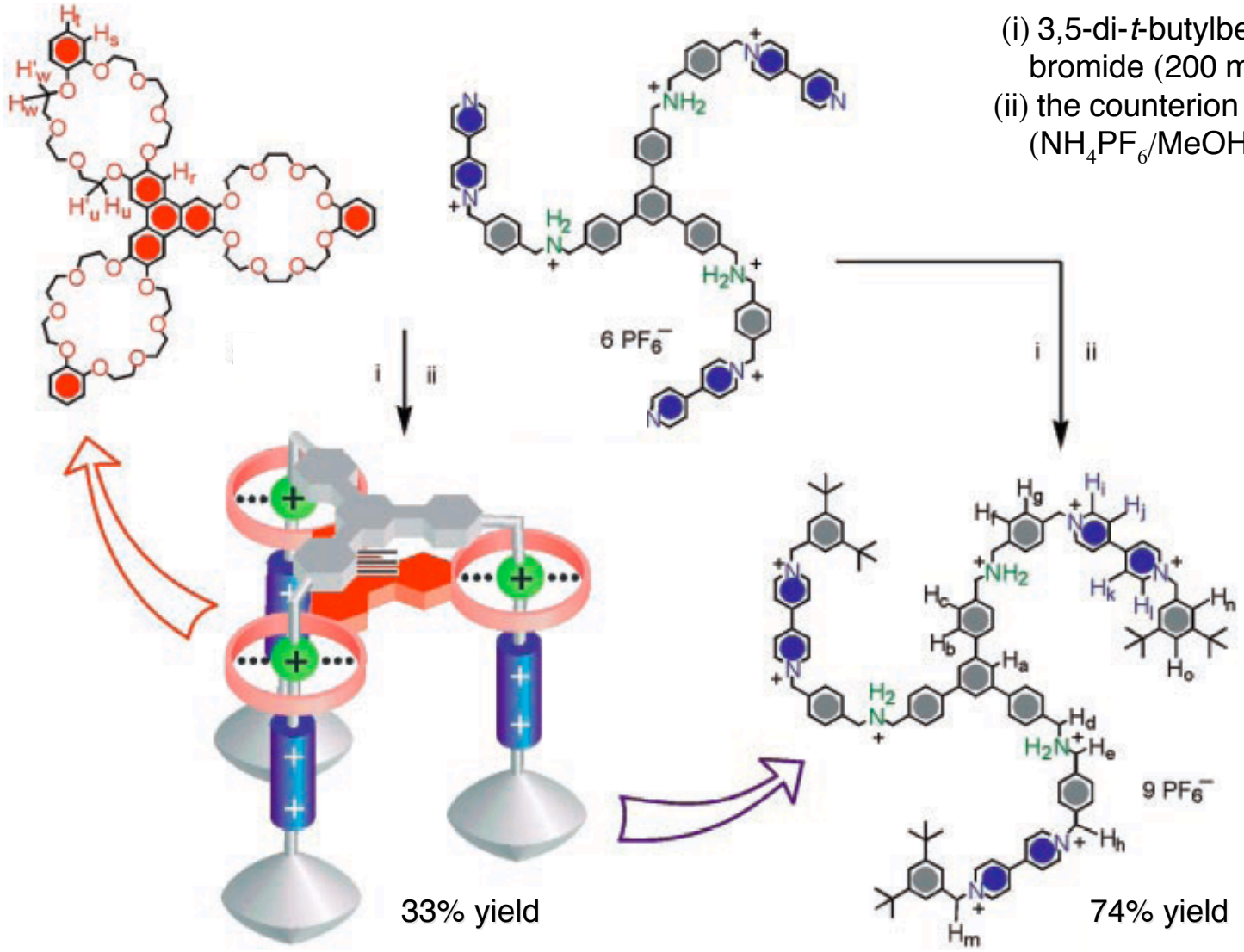
Chemically Driven Switching Systems

Synthesis



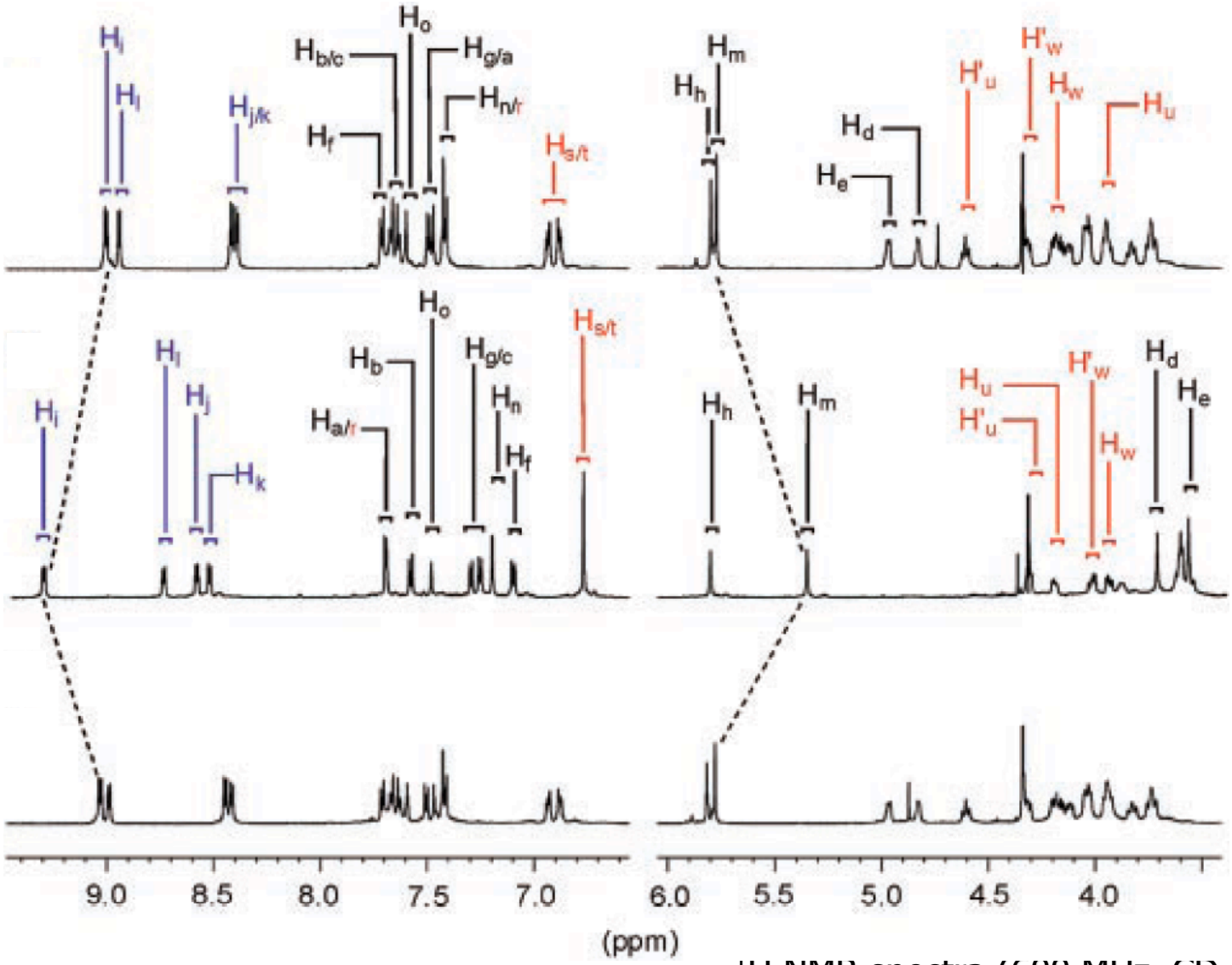
Chemically Driven Switching Systems

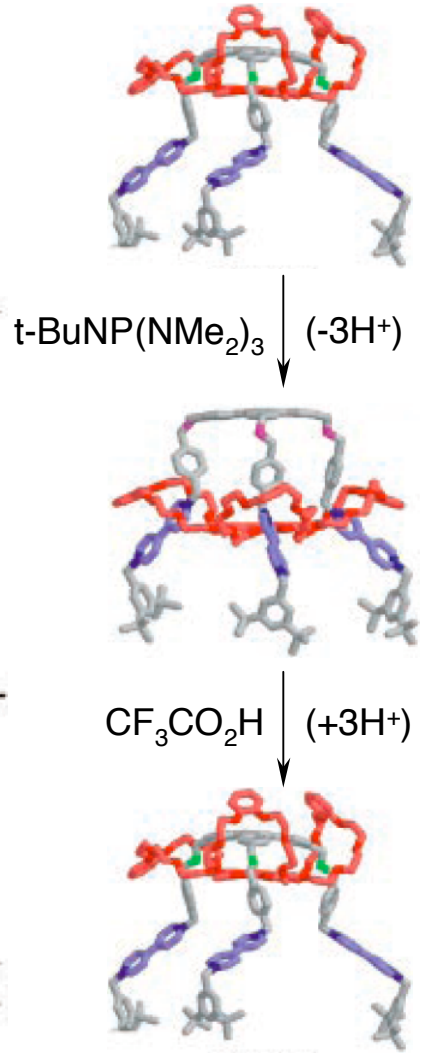
Synthesis



Chemically Driven Switching Systems

Switching Mechanism

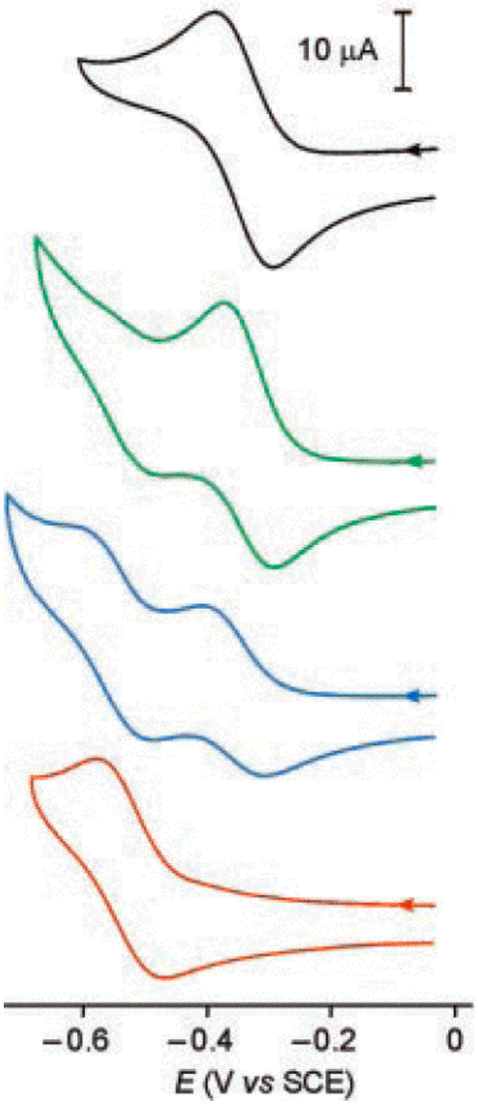


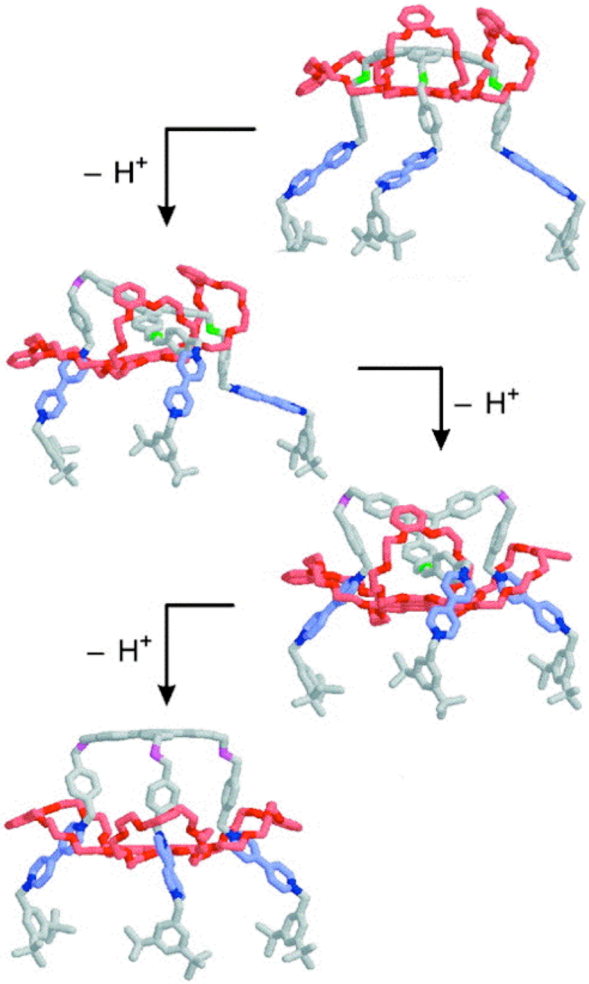


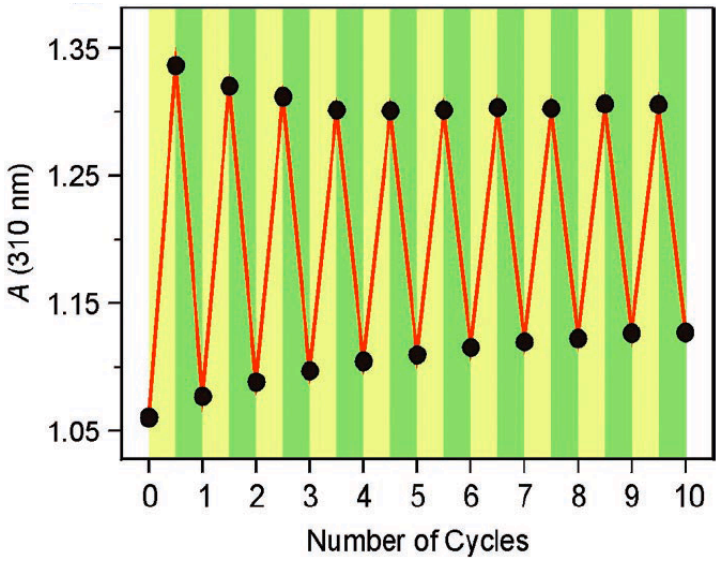
^{1}H NMR spectra (600 MHz, CD_3CN, 4.3 mM, and 298K)

Chemically Driven Switching Systems

Switching Mechanism







- **Disadvantage of Acid-Base Reaction**

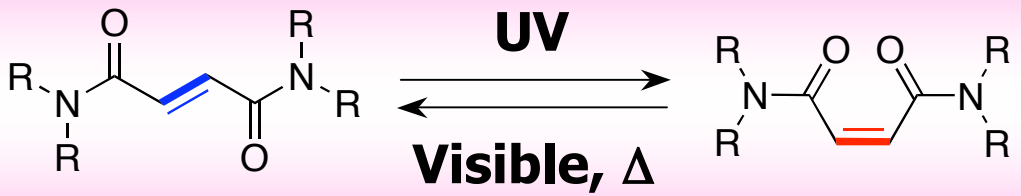
➔ By-product like salts

External Stimuli for Switching Systems

- **Chemically Driven Switching Systems**
  - Acid-Base Reaction
- **Photochemically Driven Switching Systems**
  - Olefin Isomerization
- **Electrochemically Driven Switching Systems**
  - Reduction-Oxidation Reaction

Photochemically Driven Switching Systems

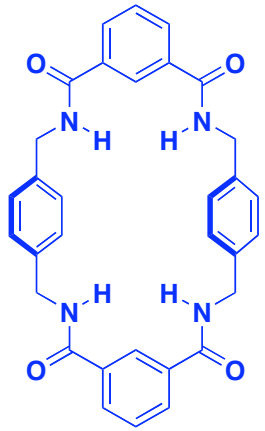
Olefin Isomerization of C=C



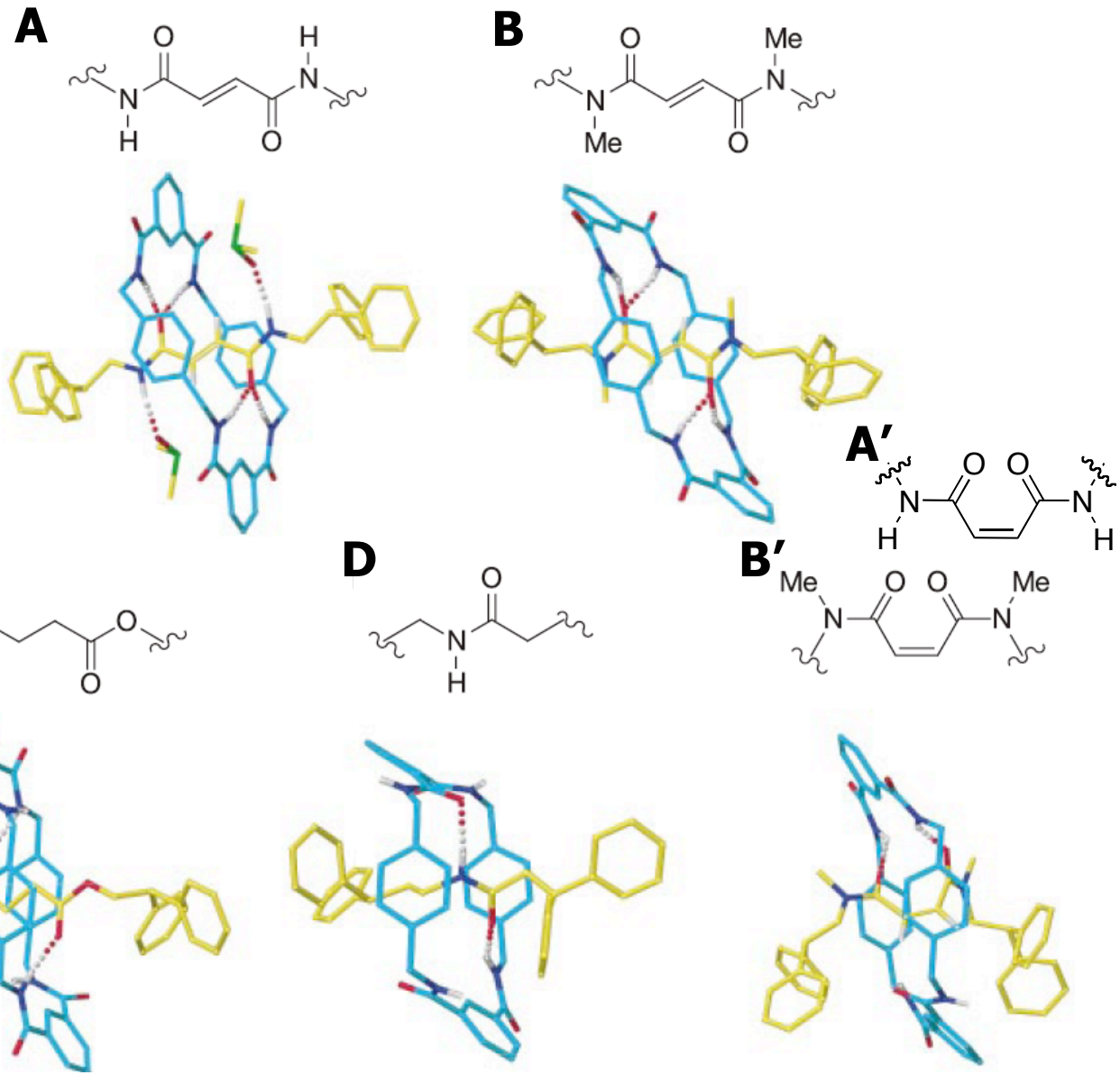
David A. Leigh
The University of Edinburgh
UK

Photochemically Driven Switching Systems

Rotaxanes with Various Stations



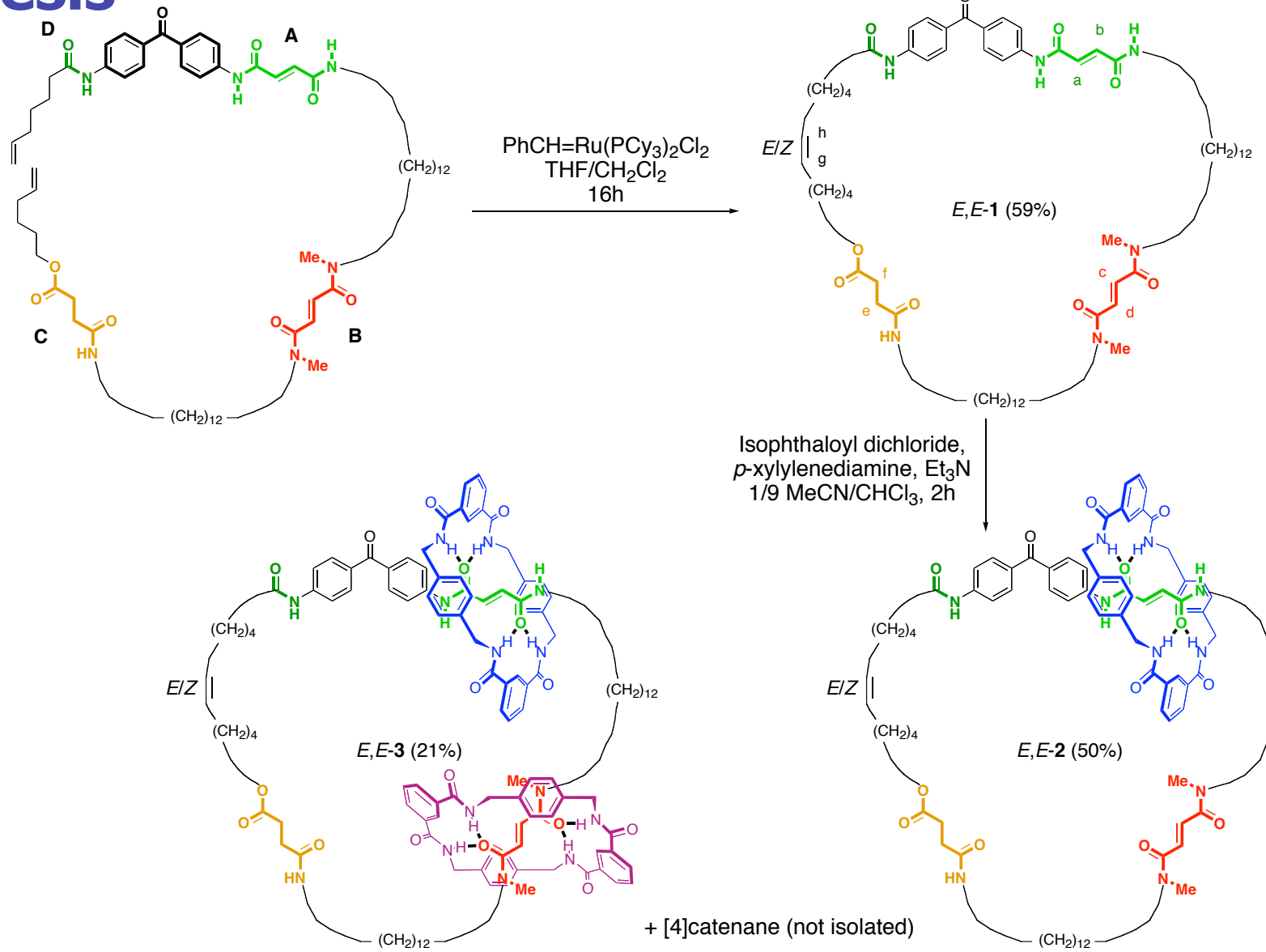
amide-macrocycle



Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174-179.

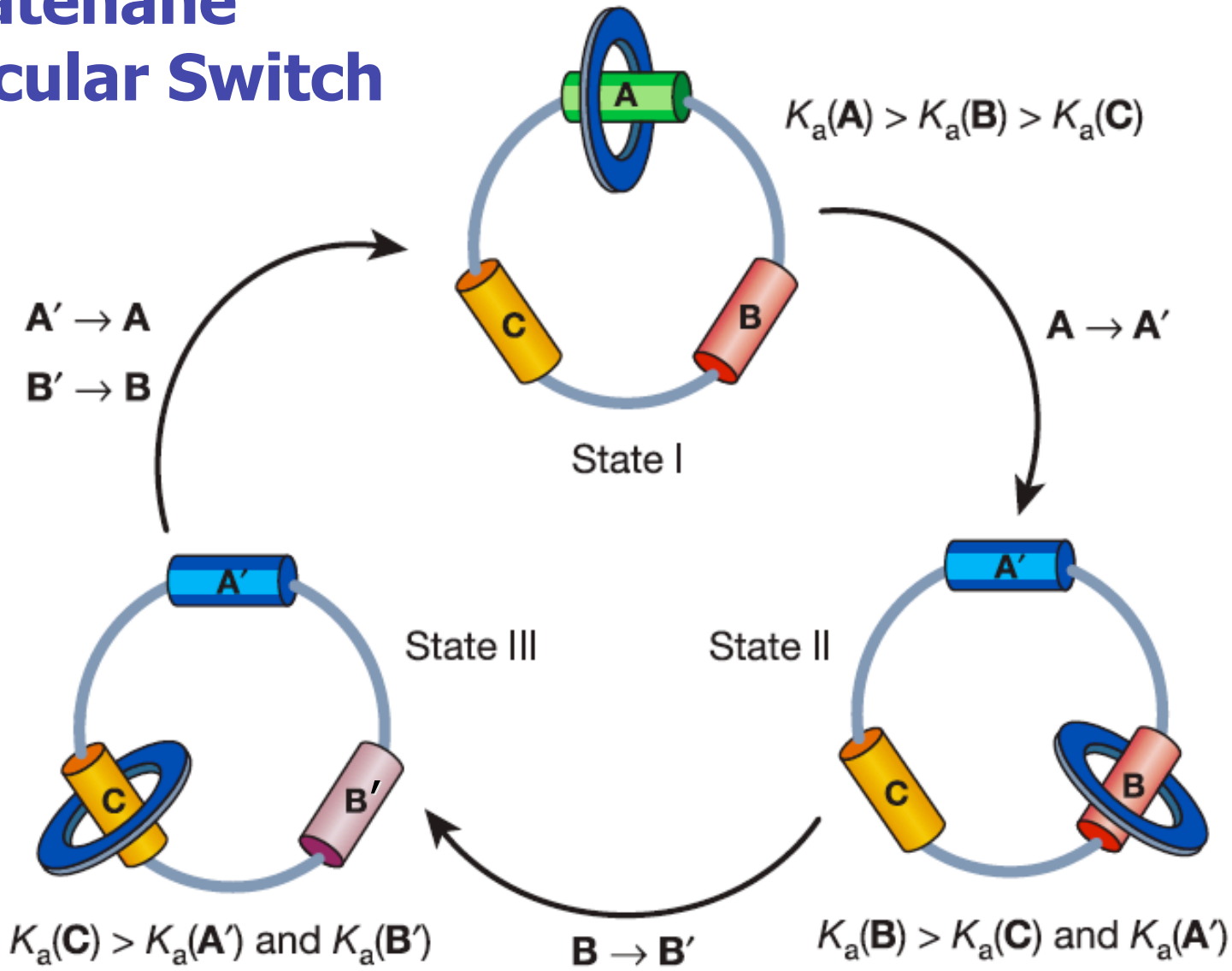
Photochemically Driven Switching Systems

Synthesis



Photochemically Driven Switching Systems

[2]Catenane Molecular Switch



Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174-179.

Photochemically Driven Switching Systems

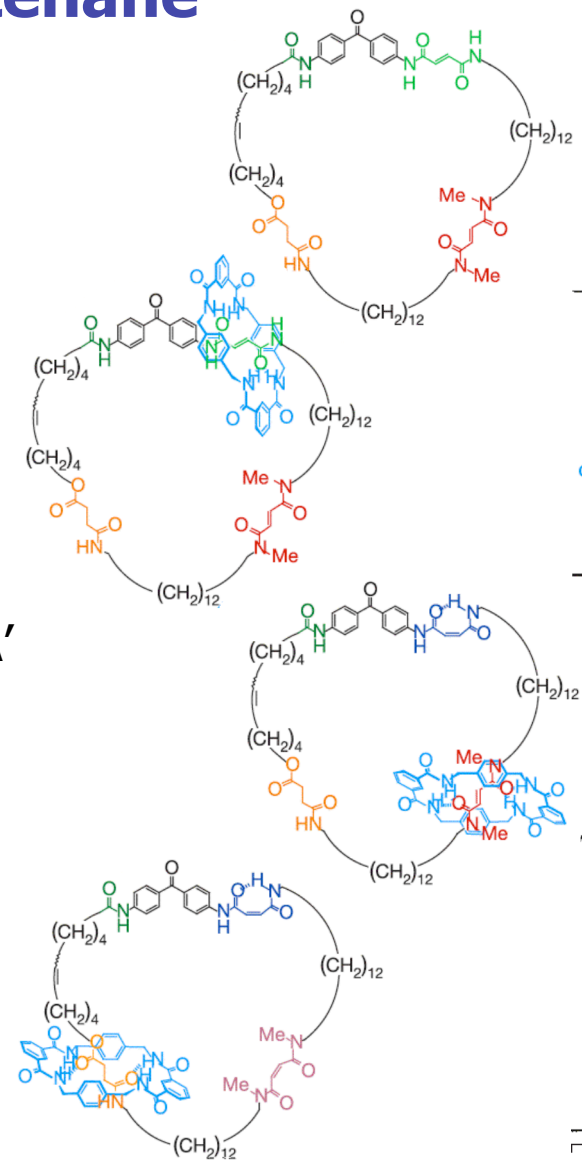
[2]Catenane

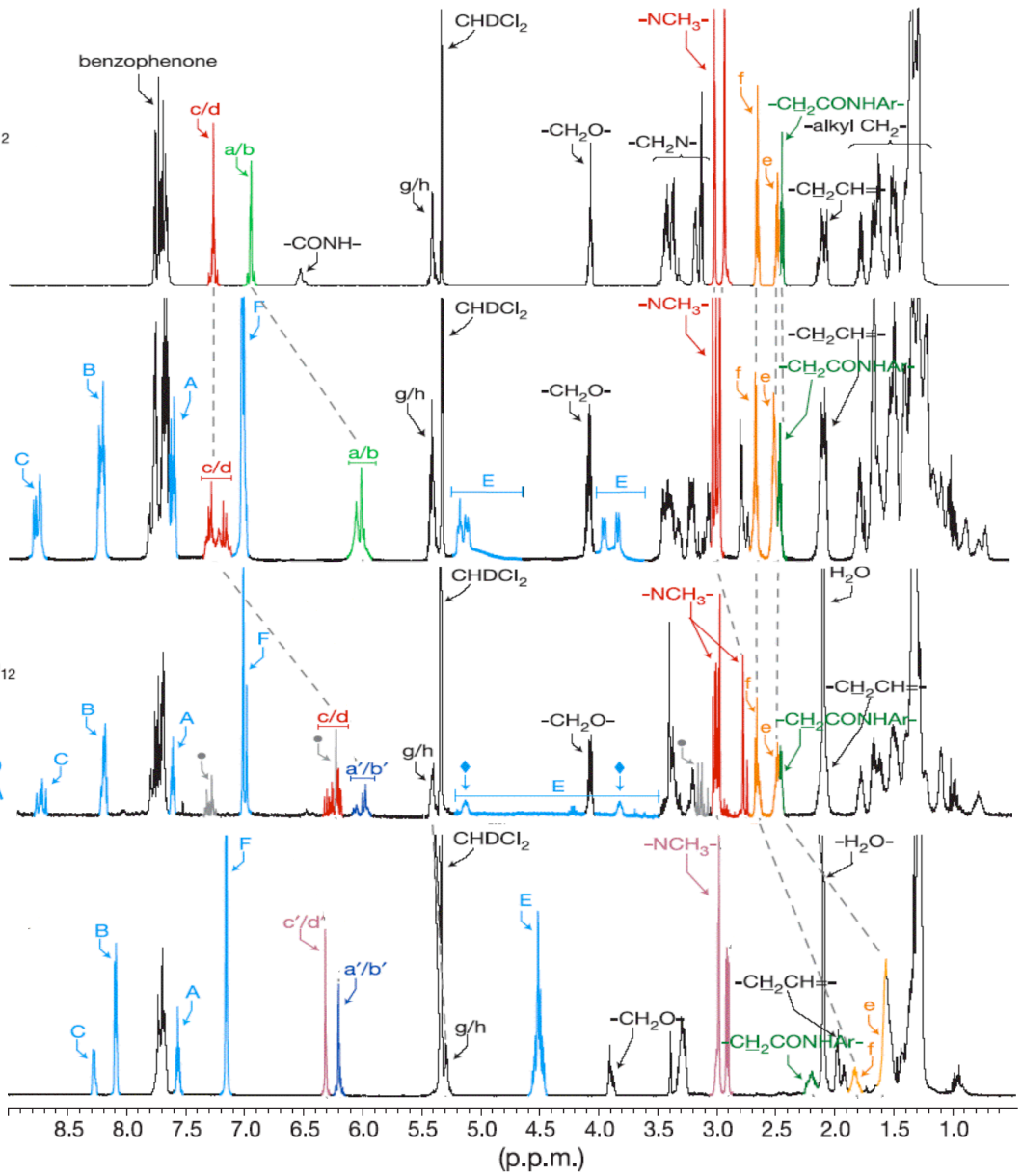
A
B
C
D

A
B
C
D

A→A′
B
C
D

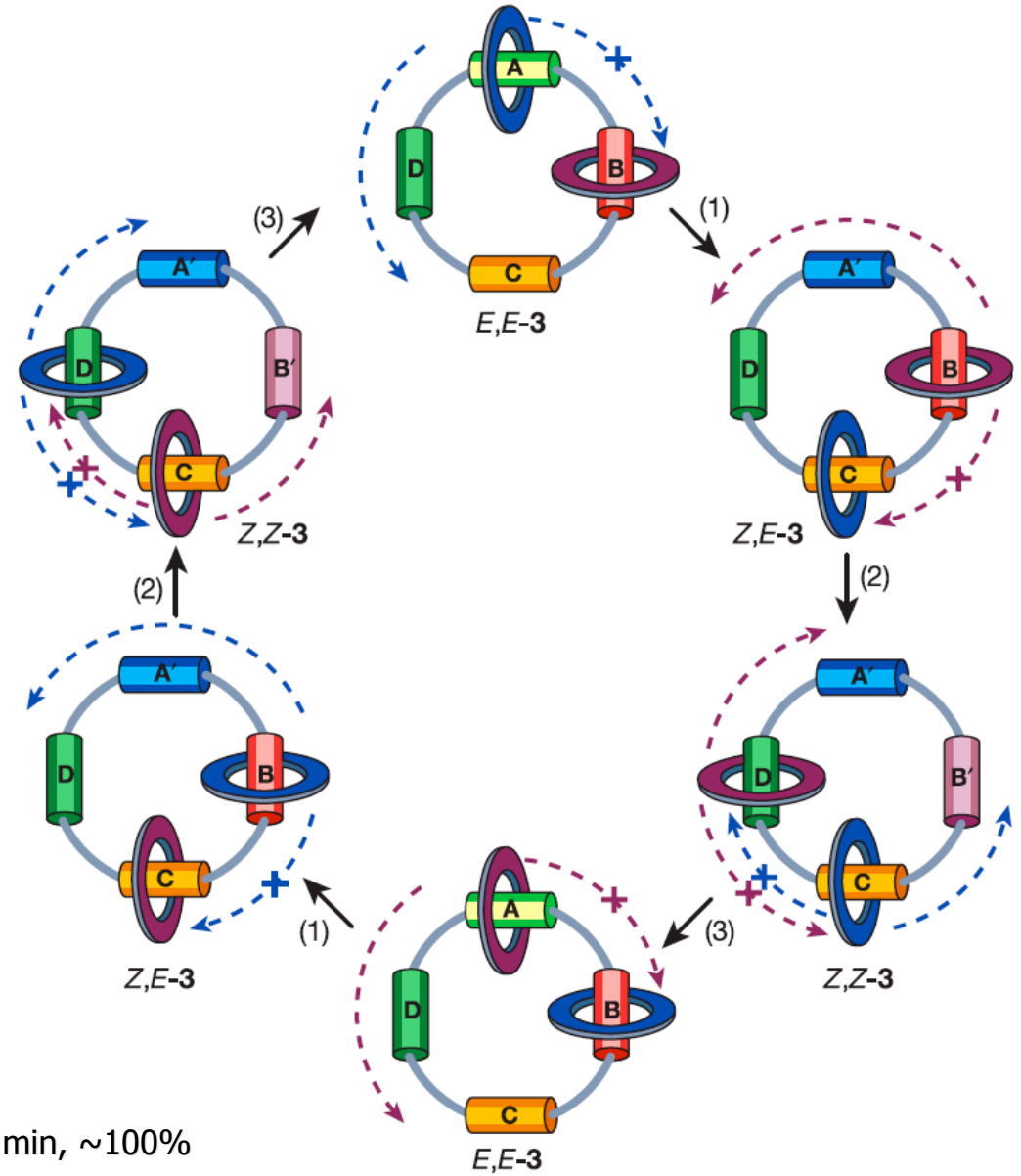
A→A′
B→B′
C
D





Photochemically Driven Switching Systems

[3]Catenane Inducing Unidirectional Rotation



(1) 350 nm, CH_2Cl_2, 5min, 67%
(2) 254 nm, CH_2Cl_2, 20min, 50%
(3) heat, 100 °C, $C_2H_2Cl_4$, 24h, ~100%;
or cat. Br_2, 400-670 nm, CH_2Cl_2, -78 °C, 10 min, ~100%

Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174-179.

Photochemically Driven Switching Systems

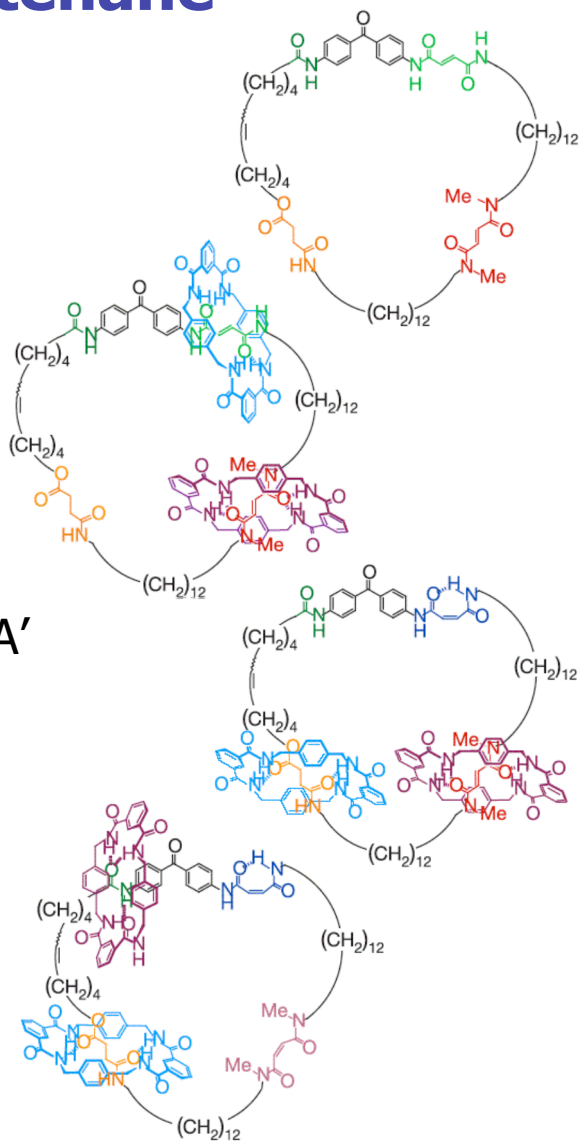
[3]Catenane

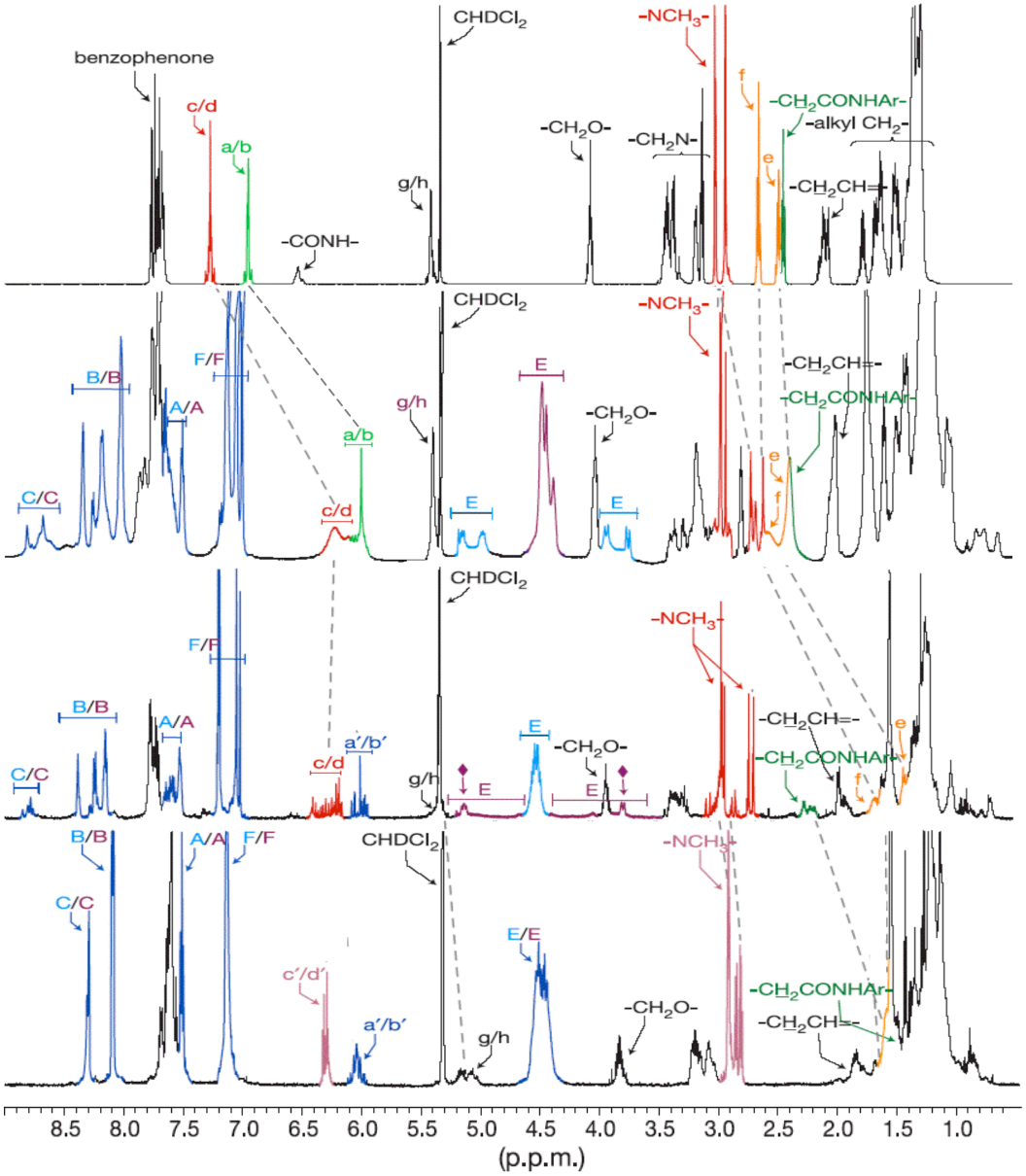
A
B
C
D

A
B
C
D

A→A′
B
C
D

A→A′
B→B′
C
D



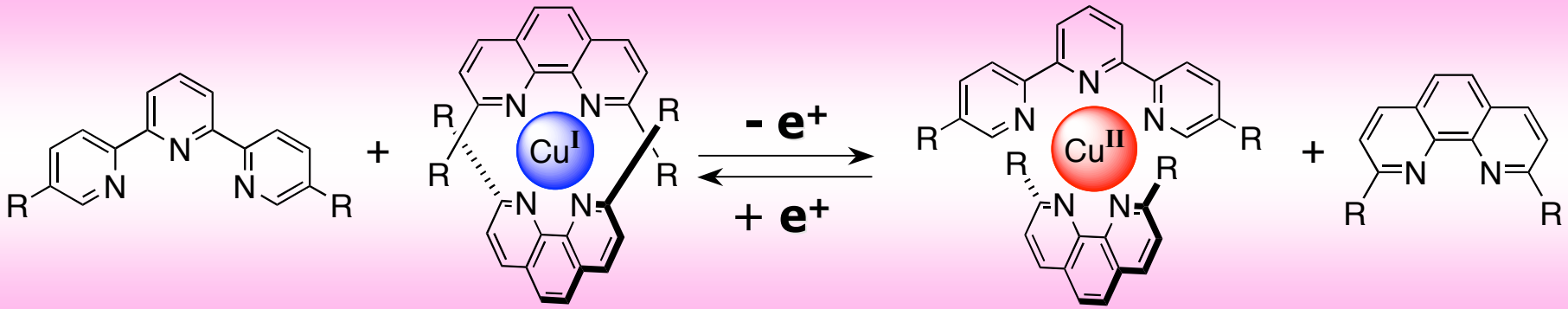


External Stimuli for Switching Systems

- **Chemically Driven Switching Systems**
  - Acid-Base Reaction
- **Photochemically Driven Switching Systems**
  - Olefin Isomerization
- **Electrochemically Driven Switching Systems**
  - Reduction-Oxidation Reaction

Electrochemically Driven Switching Systems

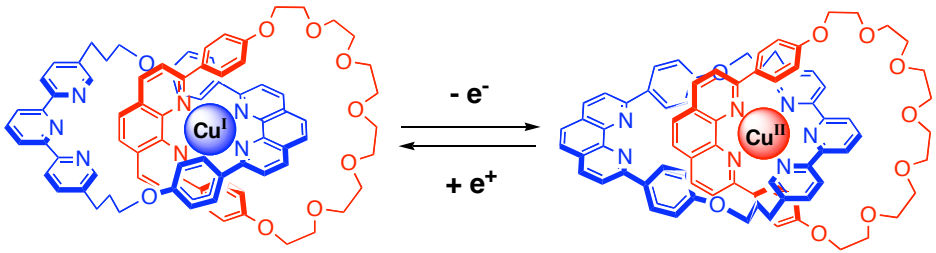
Reduction-Oxidation Reaction



Jean-Pierre Sauvage
Universite Louise Pasteur
France

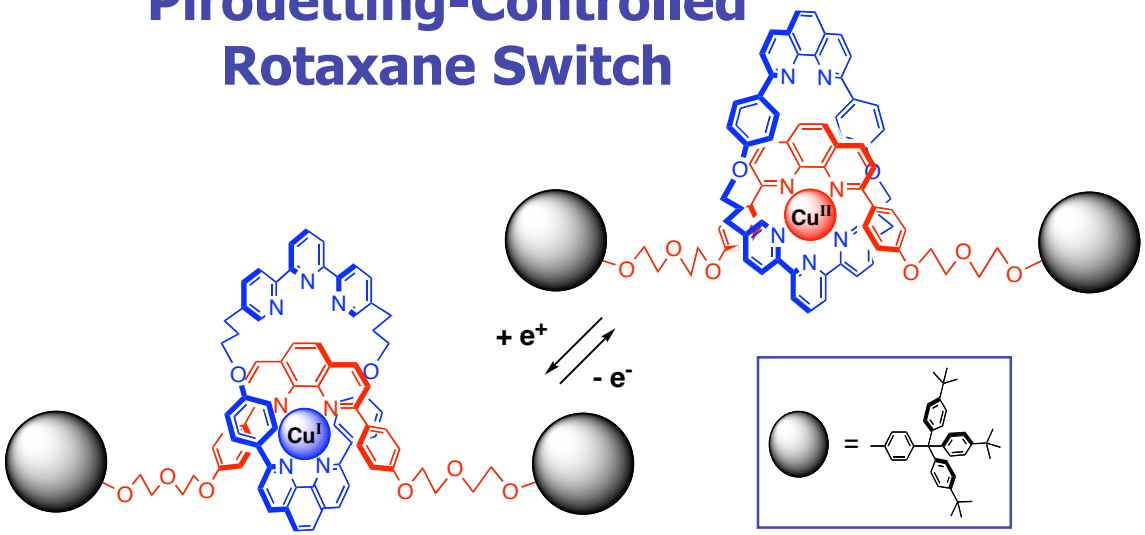
Electrochemically Driven Switching Systems

Catenane Switch



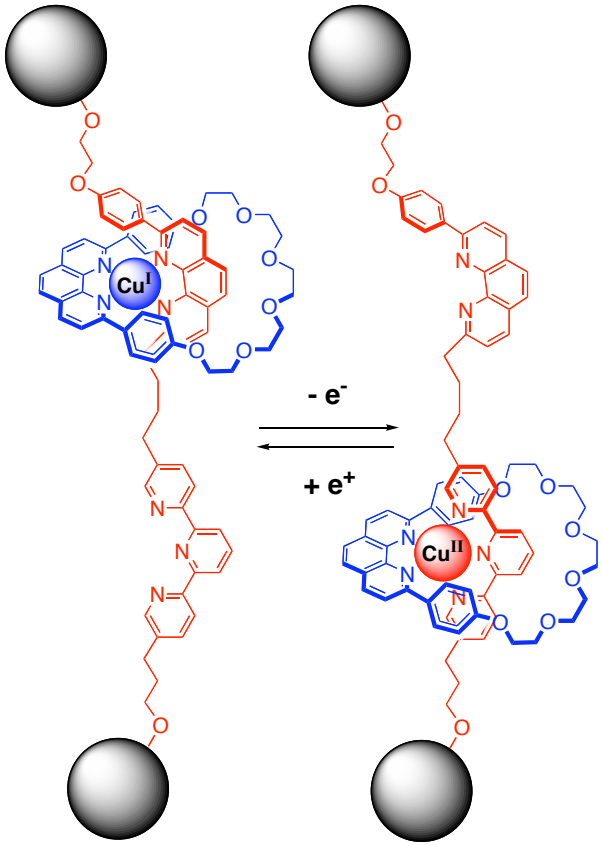
Livoreil, A.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 9399-9400.

Pirouetting-Controlled Rotaxane Switch



Kern, J.-M.; Raehm, L.; Sauvage, J.-P.; Divisia-Blohorn, B.; Vidal, P.-L. *Inorg. Chem.* **2000**, *39*, 1555-1560.

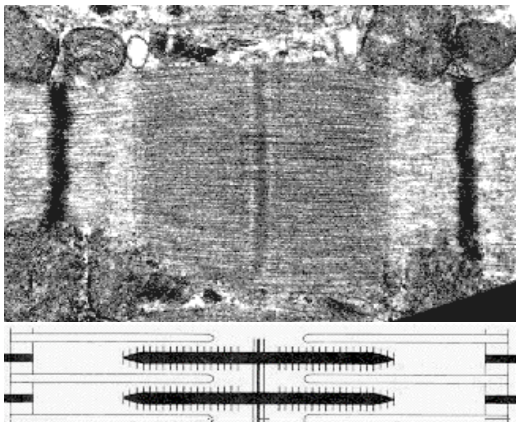
Shuttling-Controlled Rotaxane Switch

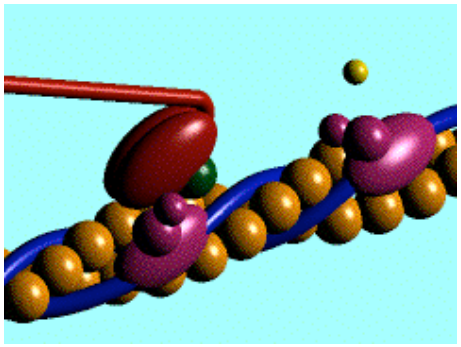


Armaroli, N.; Balzani, V.; Collin, J.-P.; Gavin, P.; Sauvage, J.-P.; Ventura, B. *J. Am. Chem. Soc.* **1999**, *121*, 4397-4408.

Biomotor *vs.* Artificial Motor

Myosin - Linear Motor





Role: muscle movement
moving along the actin
in linear fashion

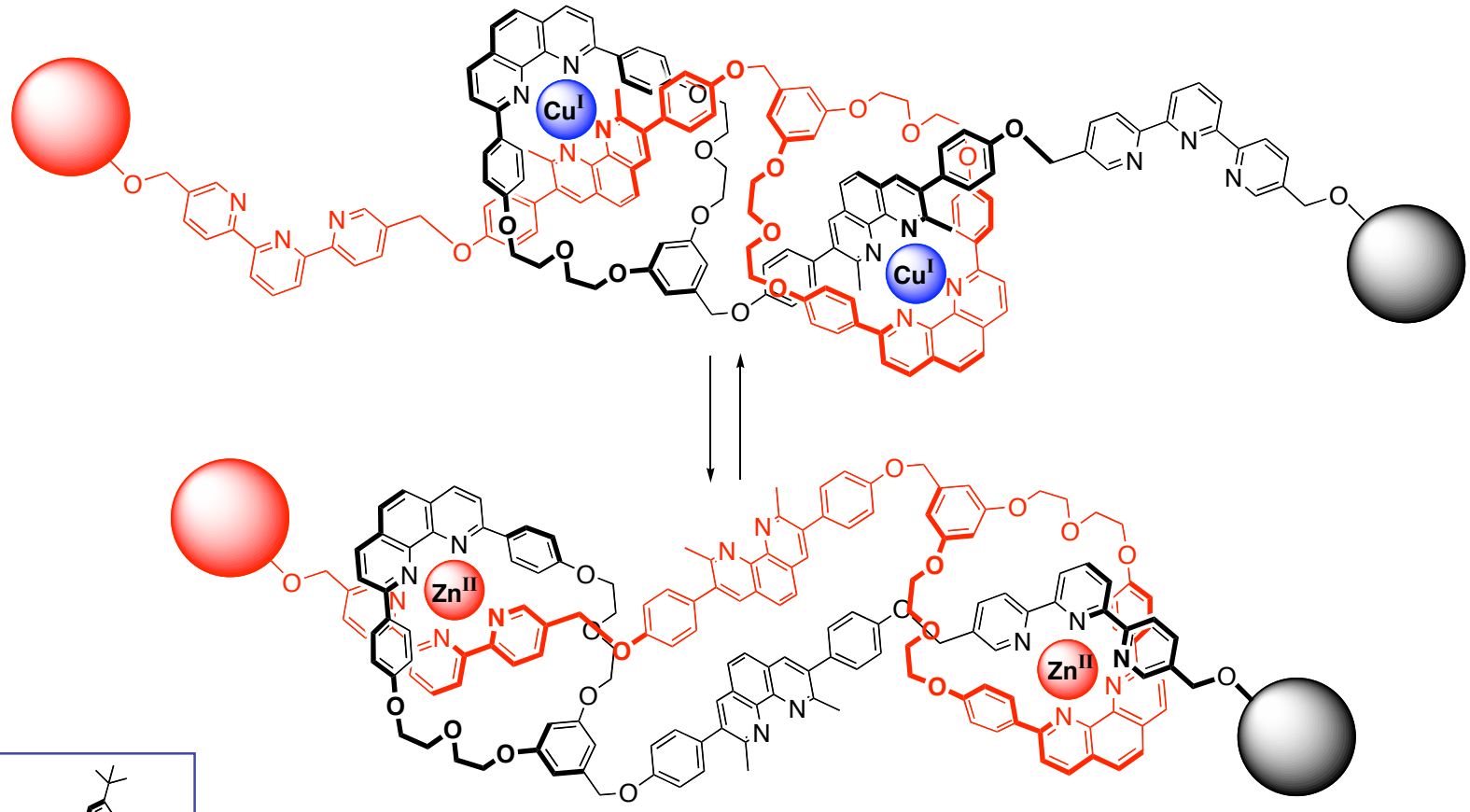
Driving force: ATP hydrolysis

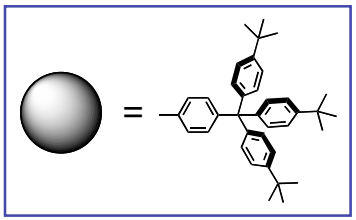
http://www.sci.sdsu.edu/movies/actin_myosin.html

Artificial Molecular Muscle ... ?

Molecular Muscle

Chemically Driven Switching System

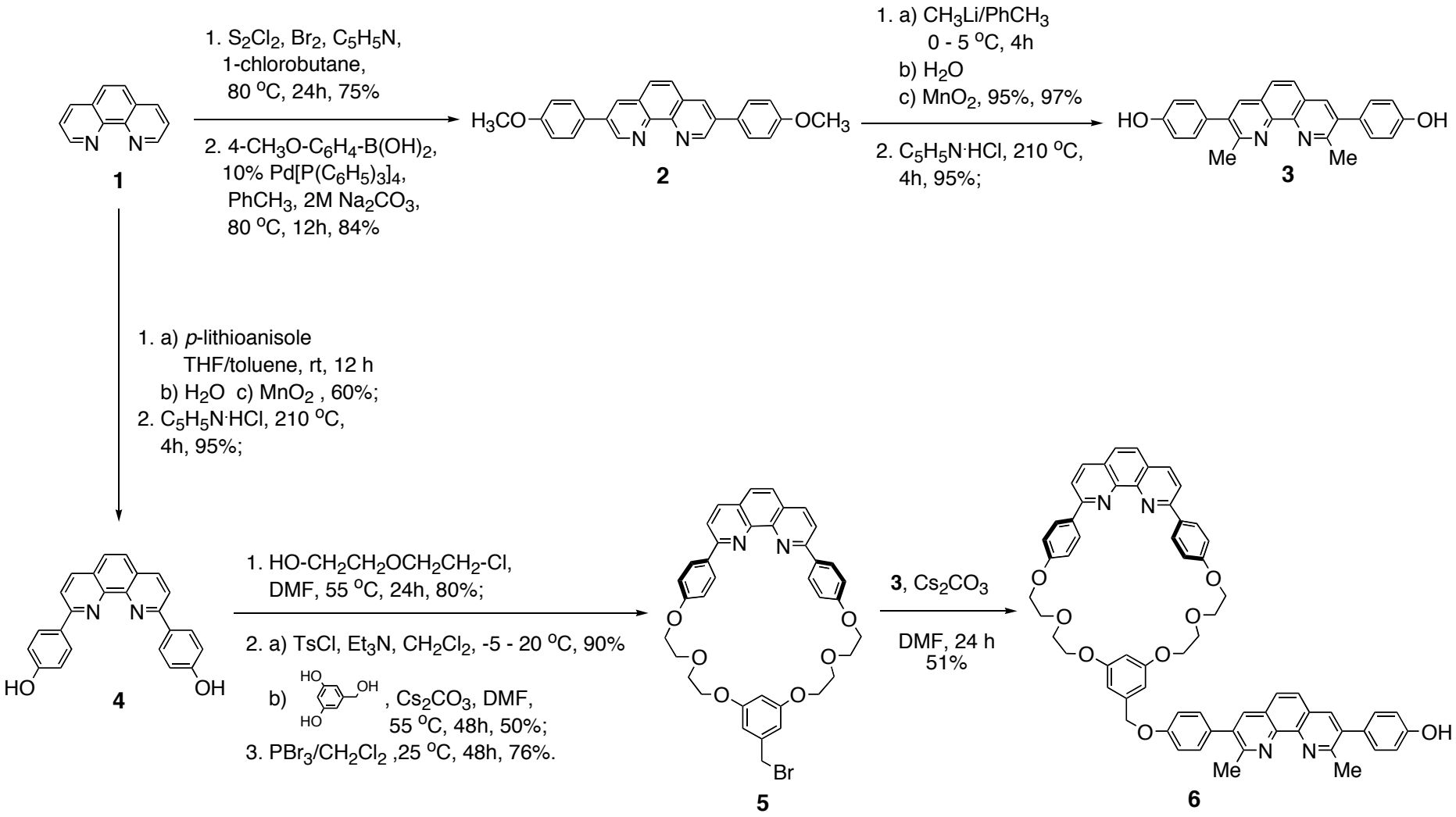




Jimenez, M. C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Angew. Chem. Int. Ed.* **2000**, *39*, 3284-3287.
Jimenez-Molero, M. C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Commun.* **2003**, 1613-1616.

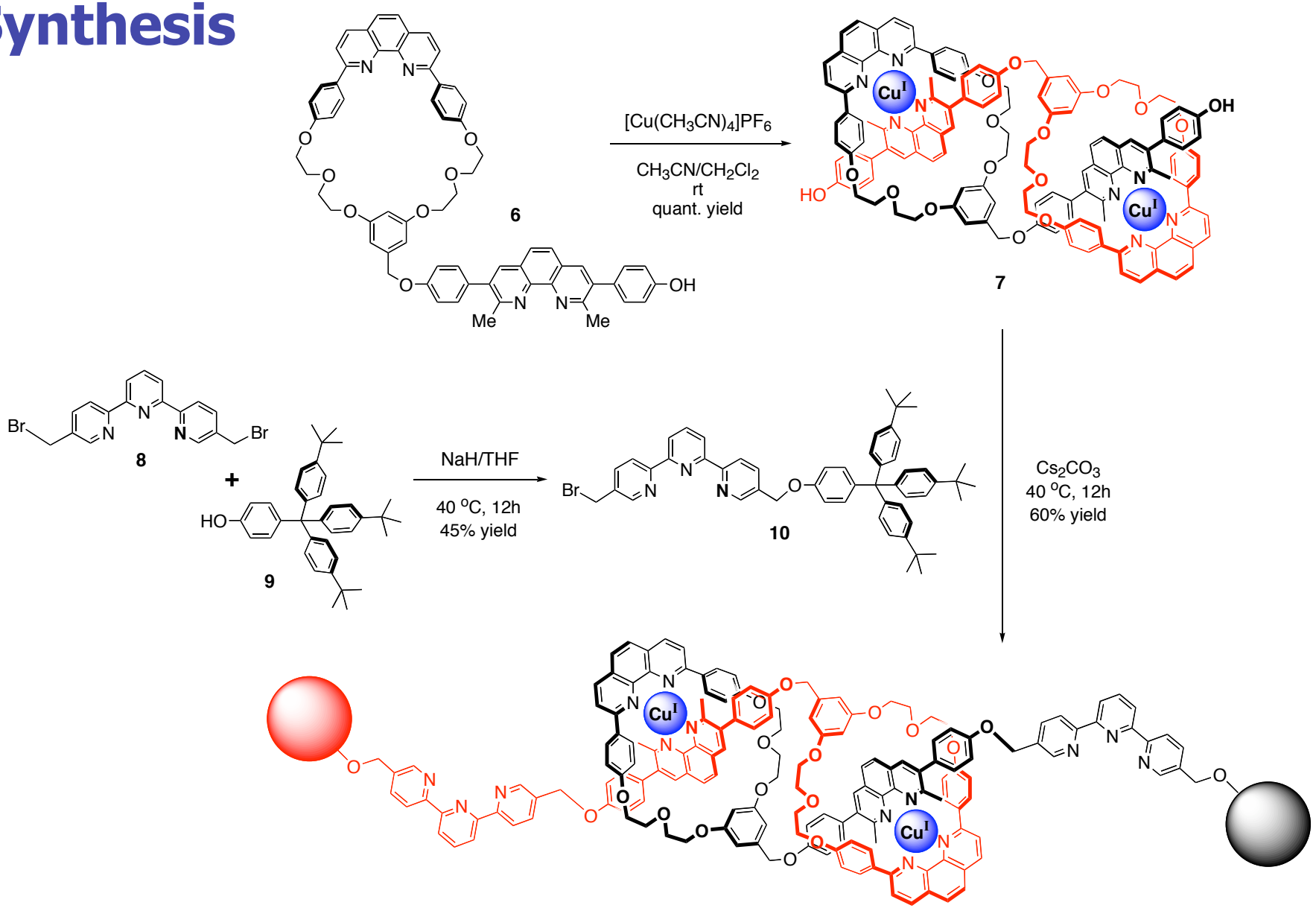
Molecular Muscle

Synthesis



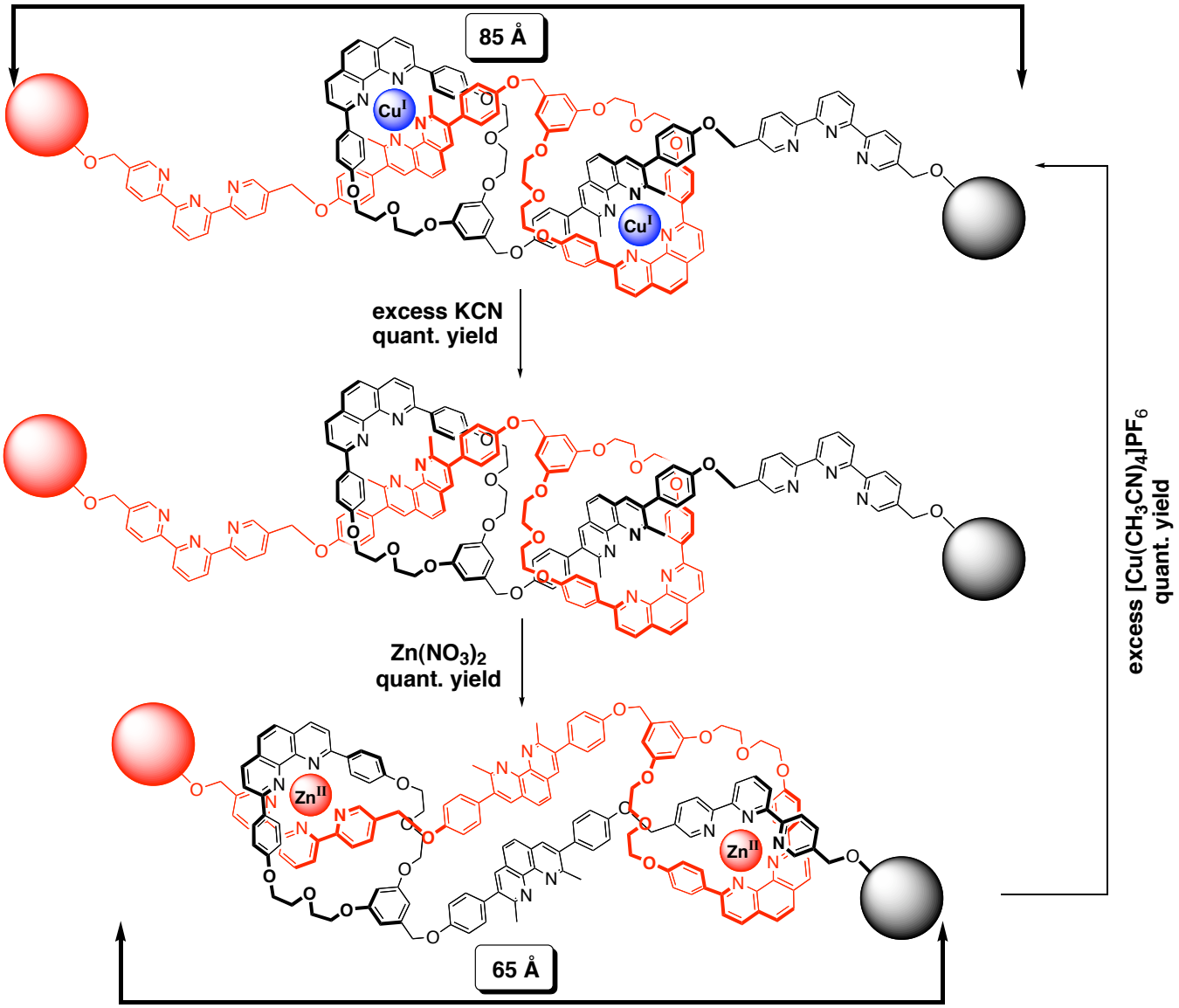
Molecular Muscle

Synthesis



Molecular Muscle

Switching Mechanism



Conclusions

- Many **artificial molecular machines** have been investigated not only to develop new methods for fabricating electronic devices, but also to understand and mimic nature.
- **Rotaxanes & catenanes** have attracted attention due to their high potential for **molecular switches** or **molecular motors**.
- Chemists have developed methods to make rotaxanes & catenanes efficiently using various **template effects** and have applied rotaxanes & catenanes to **molecular switches**.
- Under some conditions, **rotaxanes & catenanes** can act as **switching systems** by **external stimuli** and can be developed to the **artificial molecular motors**.

Acknowledgment

- **Professors**

  Dr. Robert E. Maleczka, Jr.
  Dr. Babak Borhan

- **Group Members**

  Edith
  Ron
  Jill
  Feng
  Kyoungsoo
  Bani
  Sanjit

- **Friends**

  Chris
  Jinwoo
  Rob A.

Many thanks for your great attention!!!