

Molecular Devices and Machines

“**Molecular-level devices and machines** operate via electronic and/or nuclear rearrangements and, like macroscopic devices and machines need energy to operate and signals to communicate with the operator.”

“A **molecular-level machine** is a particular molecular-level device in which the relative position of the component parts can change as a result of some external stimulus.”

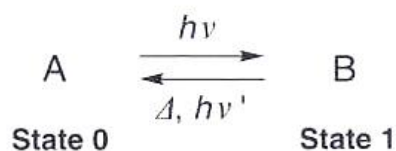
From: « Molecular Devices and Machines »
V. Balzani, M. Venturi, A. Credi

“A **molecular machine** is a system in which a stimulus triggers the controlled motion of one molecular or submolecular component relative to the other, potentially resulting in a net task being performed

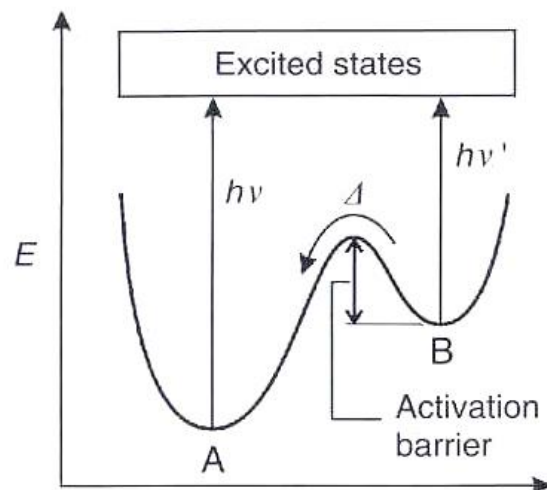
[B. L. Feringa, D. A. Leigh et al. Chem. Soc. Rev. 2017, 46, 2592.](#)

Photochromic Systems

a



b

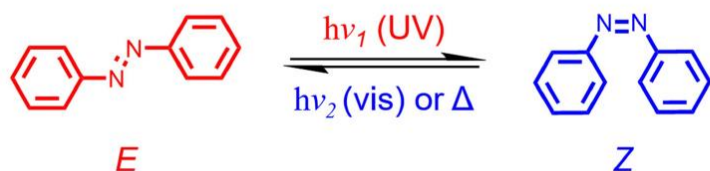


The term '**photochromic**' is applied to molecules that can be reversibly interconverted, with at least one of the reactions being induced by light excitation, between two forms with different absorption spectra.

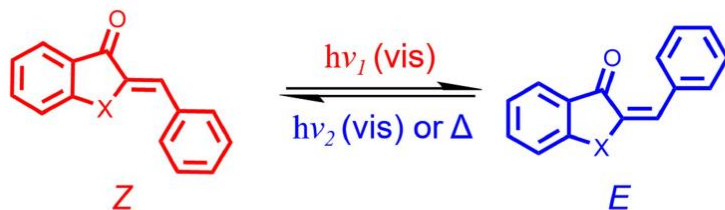
Photochromic Molecules

E/Z-isomerization

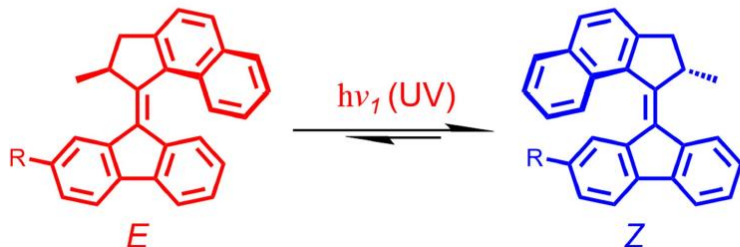
azobenzenes



indigoids (X = NH/S)

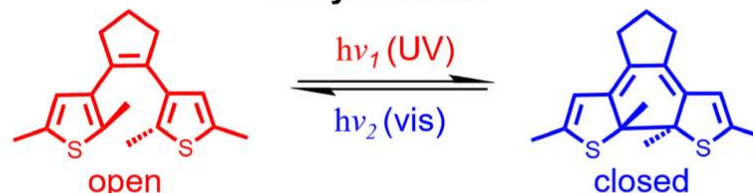


alkene-based motors

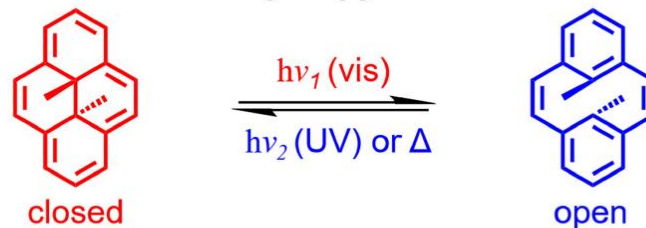


Electrocyclization

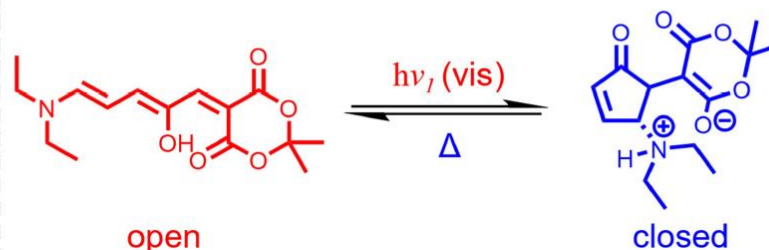
diarylethenes



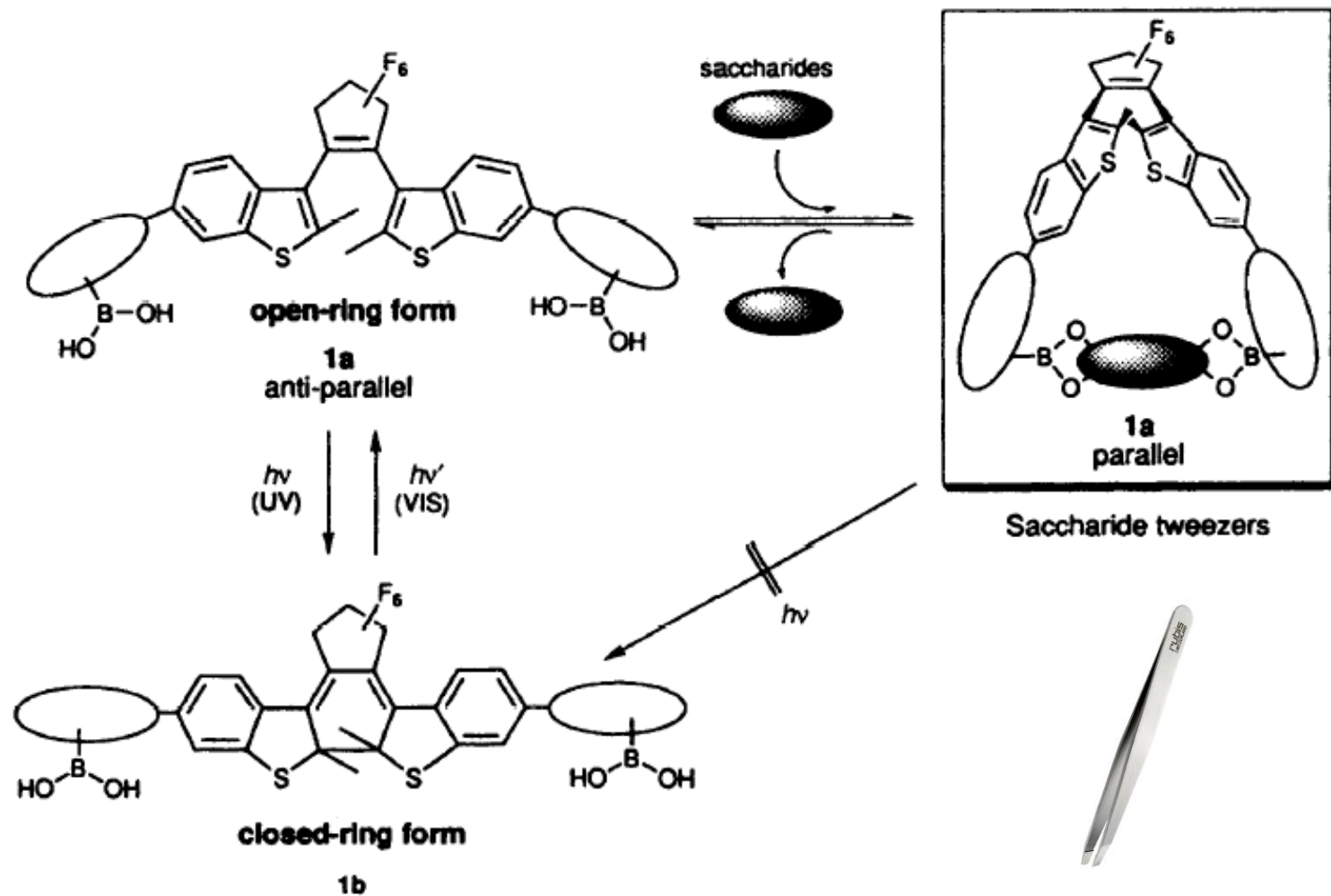
dihydropyrenes



donor-acceptor Stenhouse adducts

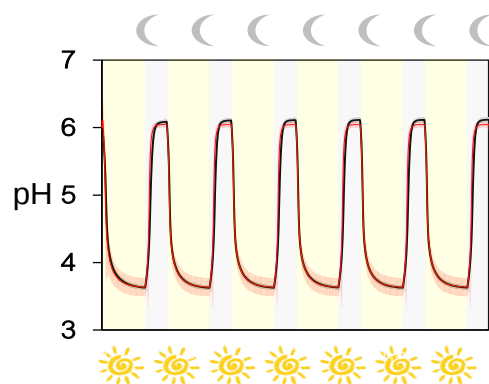
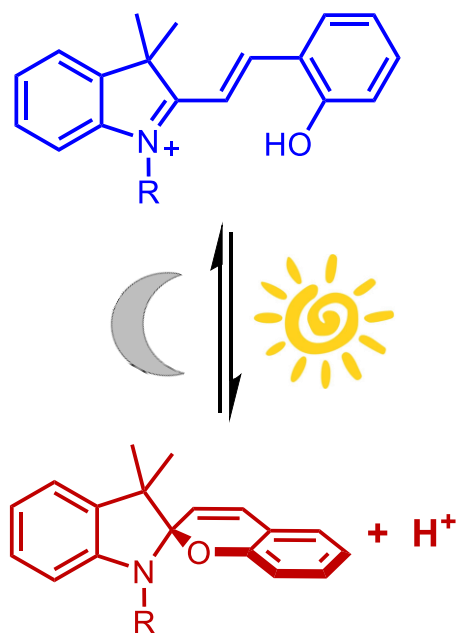


A Photoswitchable Molecular Tweezer



[M. Irie et al., Chem. Commun. 1996, 1807.](#)

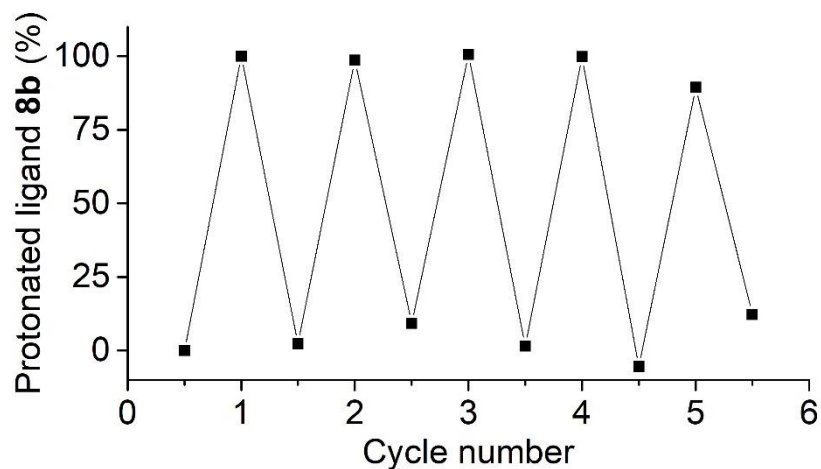
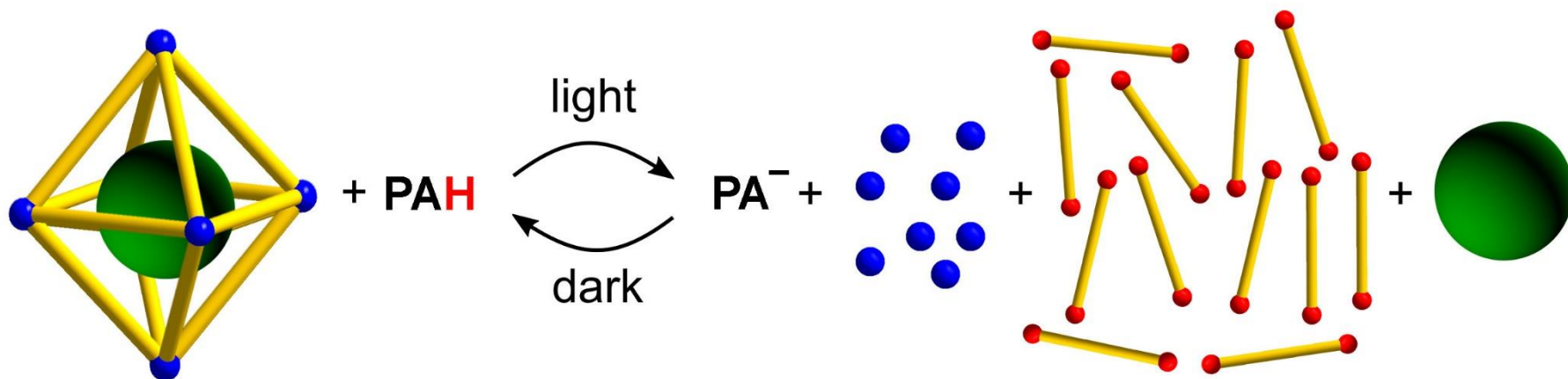
Mercocyanine Photoacids



[Y. Liao et al., J. Am. Chem. Soc. **2011**, 133, 14699.](#)

[C. Pezzato et al., Chem. Sci. **2020**, 11, 8457.](#)

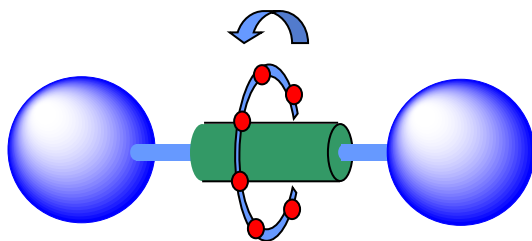
Light-Induced Disassembly of Coordination Cages



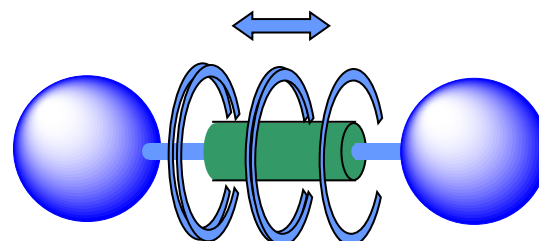
[K. Severin et al., Chem. Sci. 2018, 9, 4253.](#)

Controlling Motion in Mechanically Interlocked Architectures

Possible movements in a [2]rotaxane

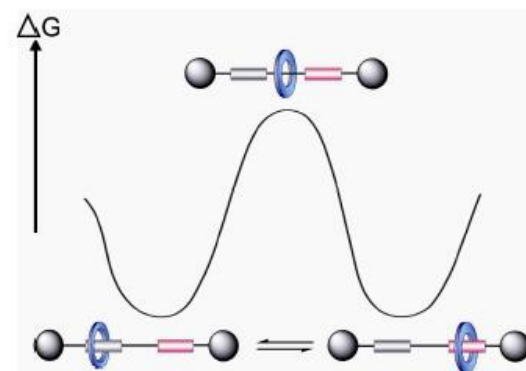
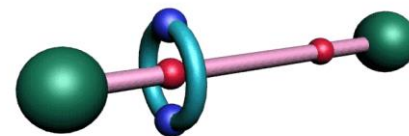
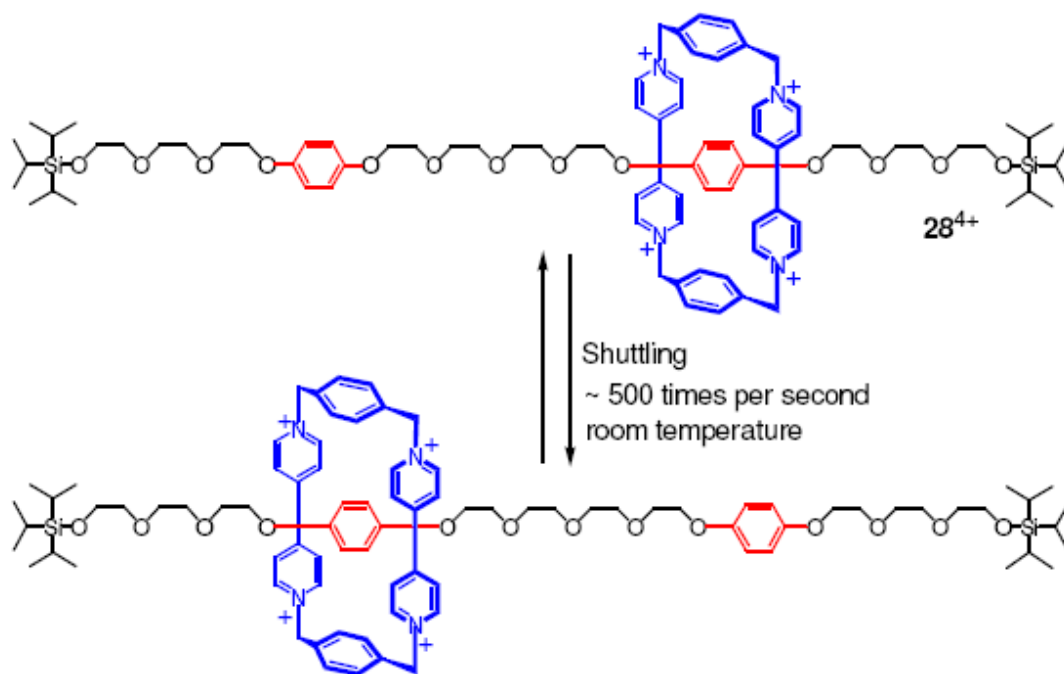


“Pirouetting”



“Shuttling”

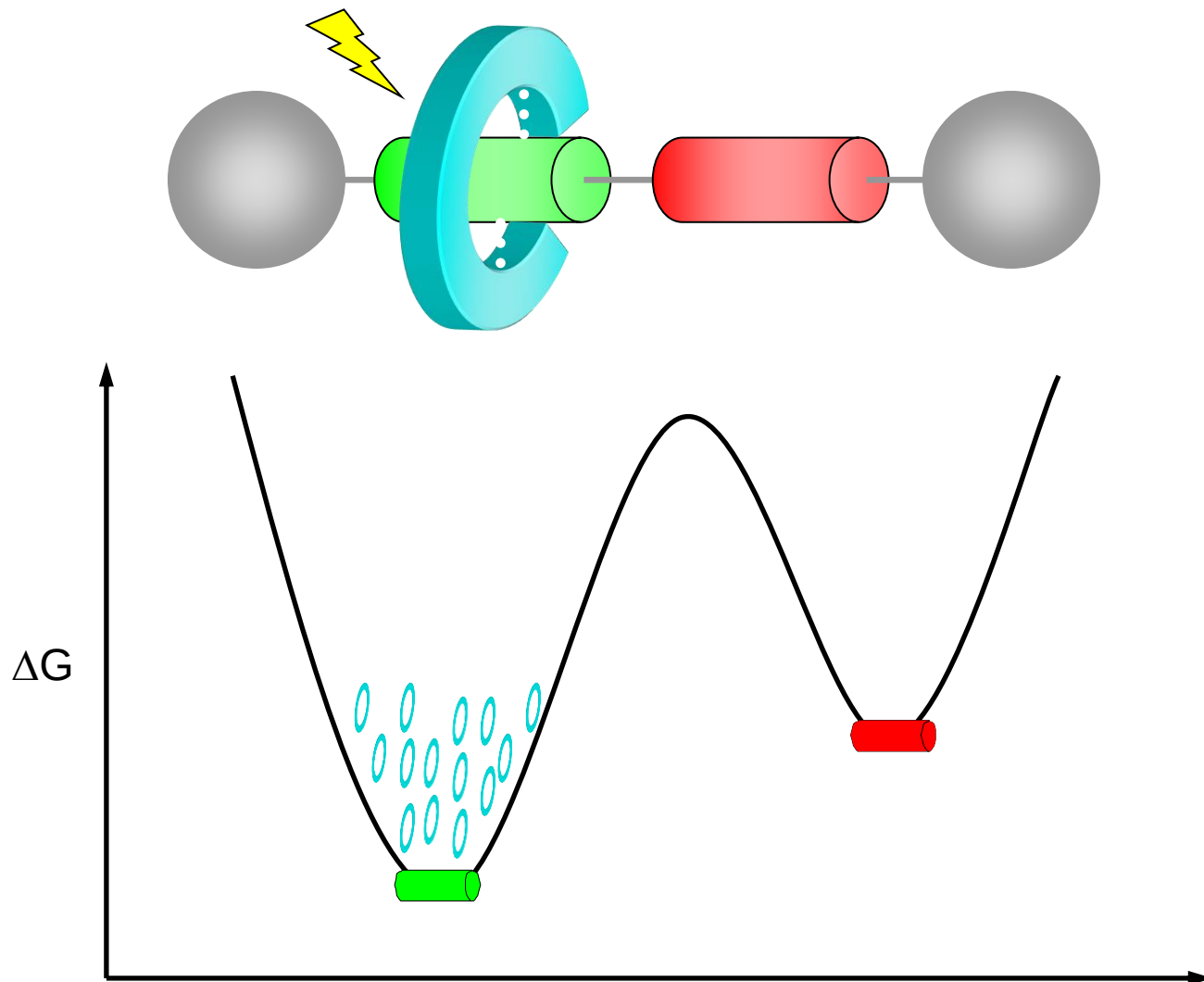
Rotaxane-Based Molecular Shuttles



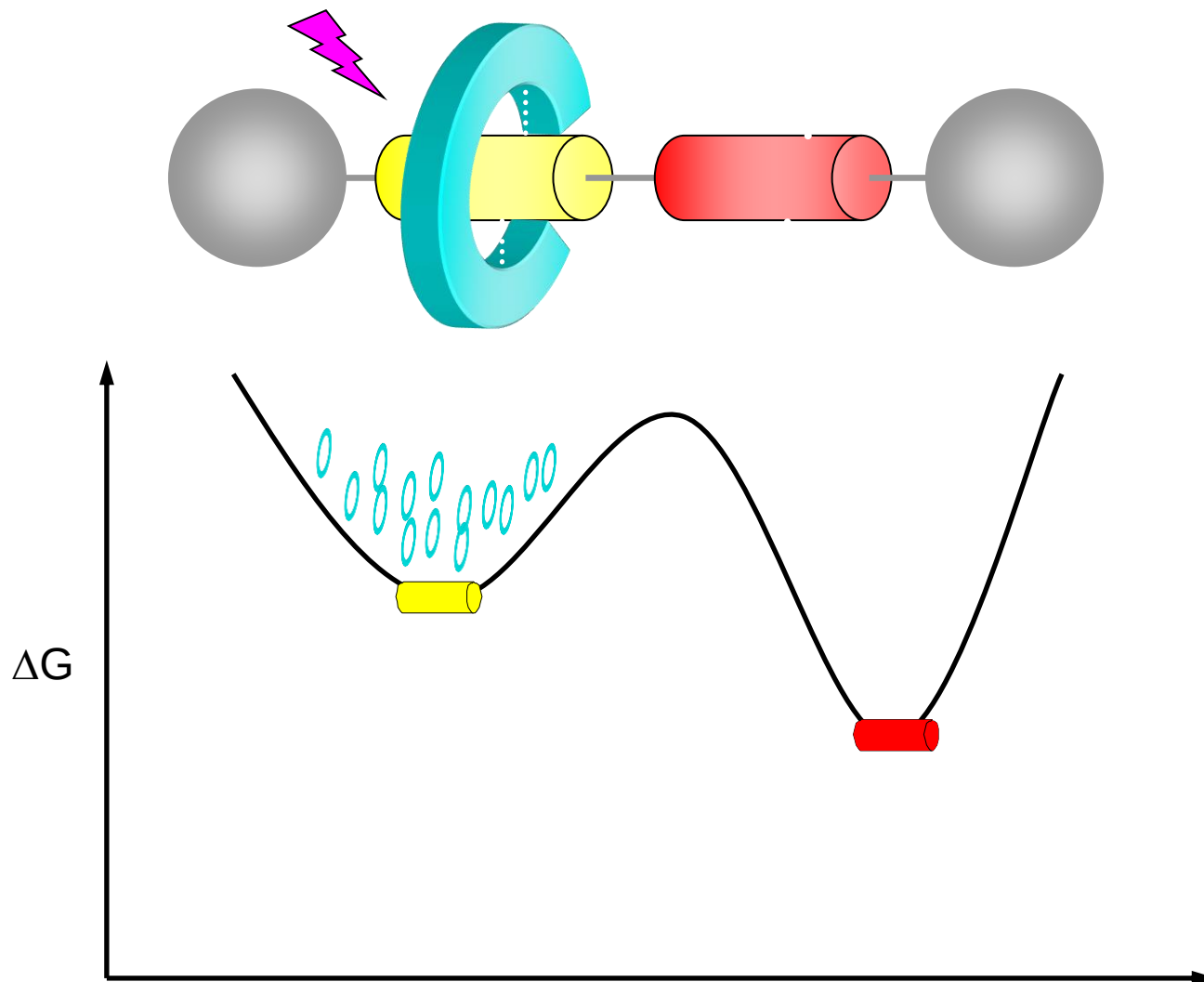
Kinetic association of the components – even when the attractive non-covalent interactions between them are broken – means the cyclophane macrocycle shuttles between two hydroquinone stations.

[J. F. Stoddart et al., J. Am. Chem. Soc. **1991**, 113, 5131.](#)

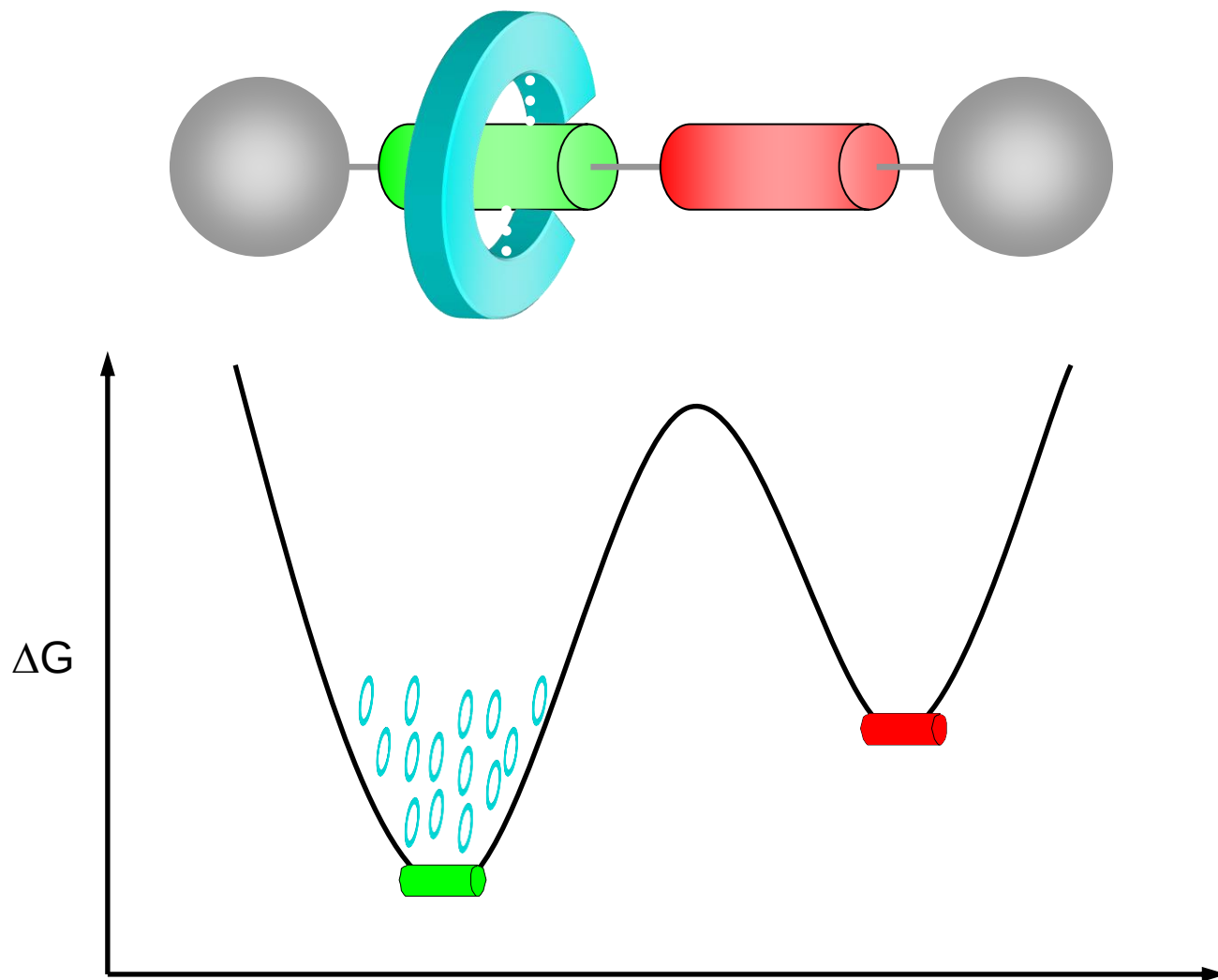
Stimuli Responsive Molecular Shuttles



Stimuli Responsive Molecular Shuttles

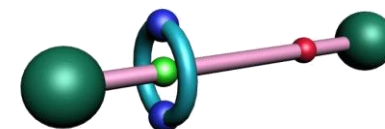
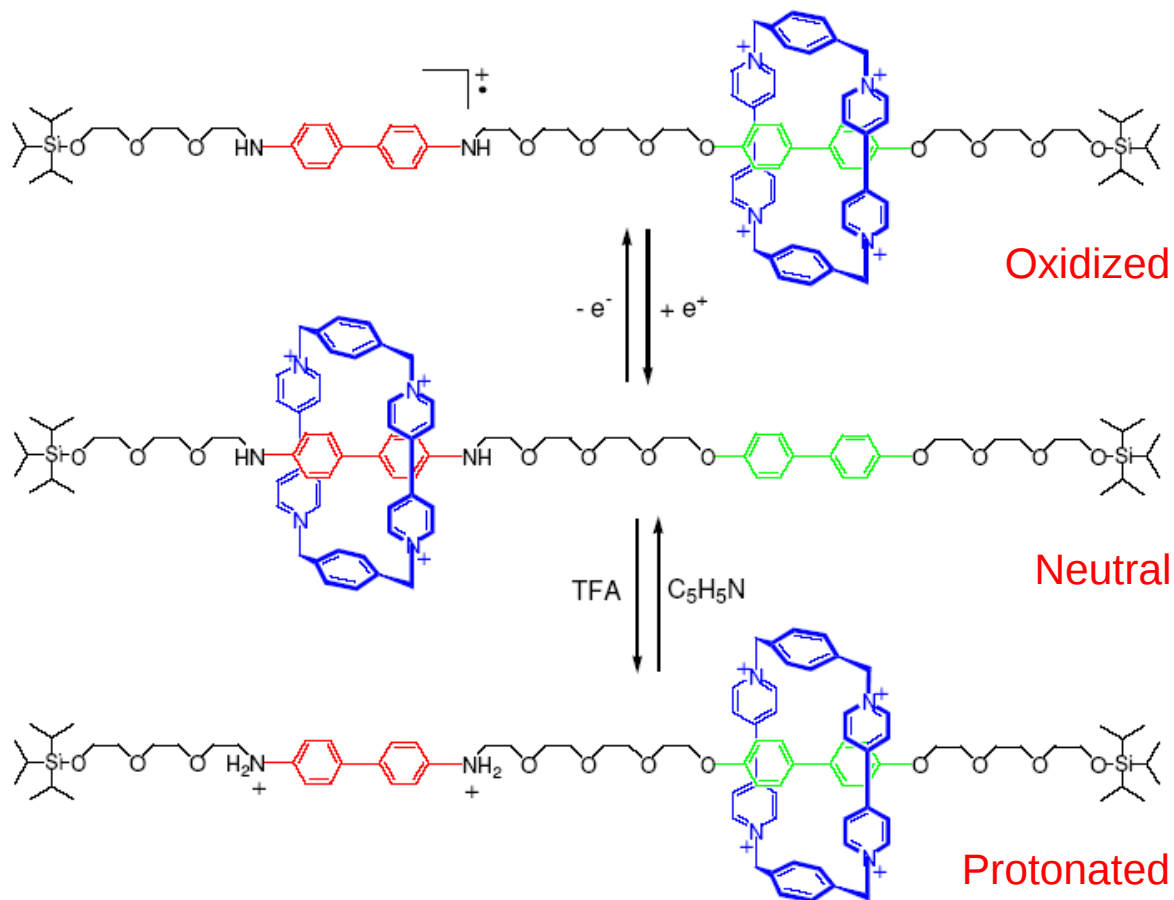


Stimuli Responsive Molecular Shuttles



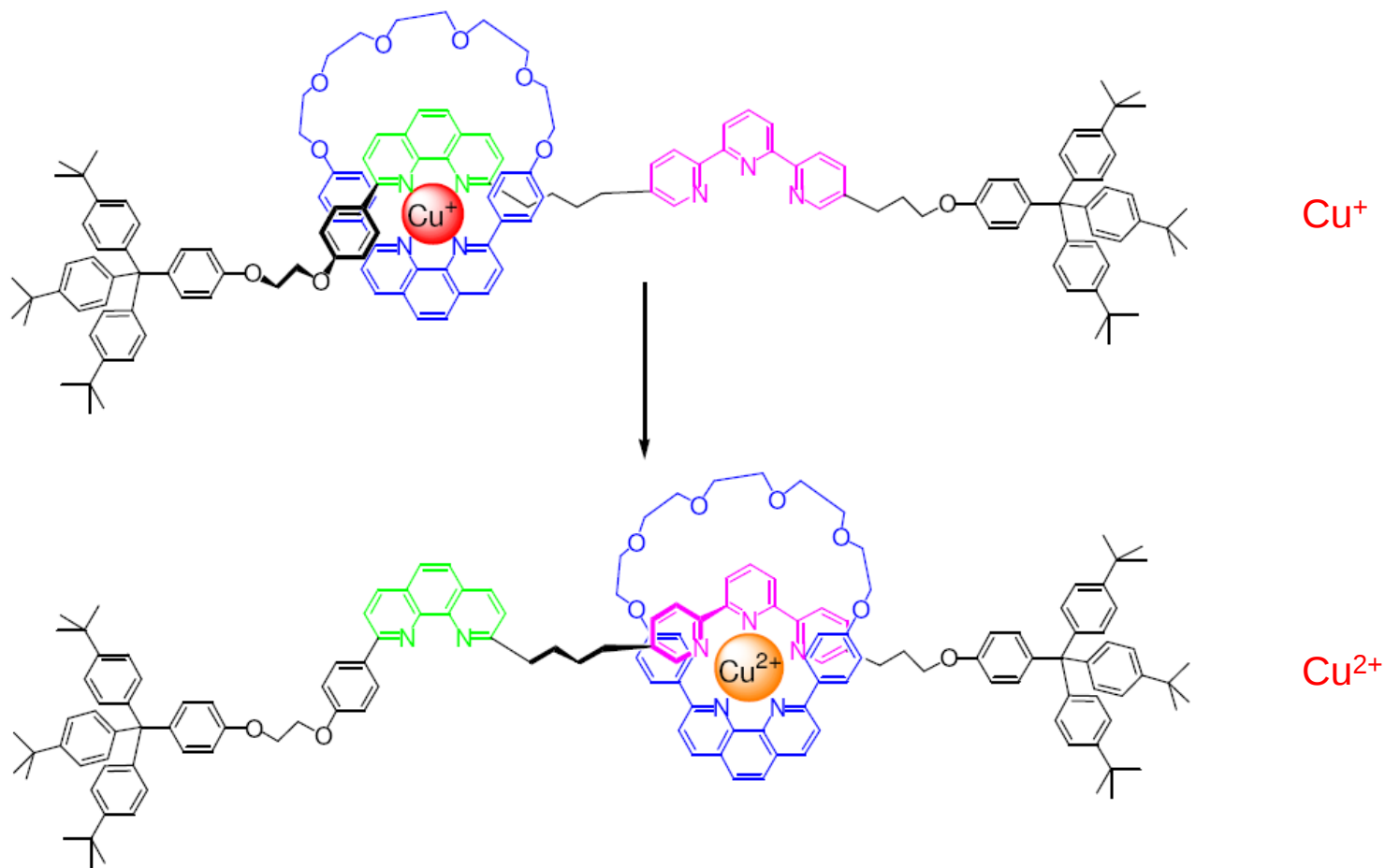
A reversible mechanical molecular switch

A Stimuli Responsive Molecular Shuttle



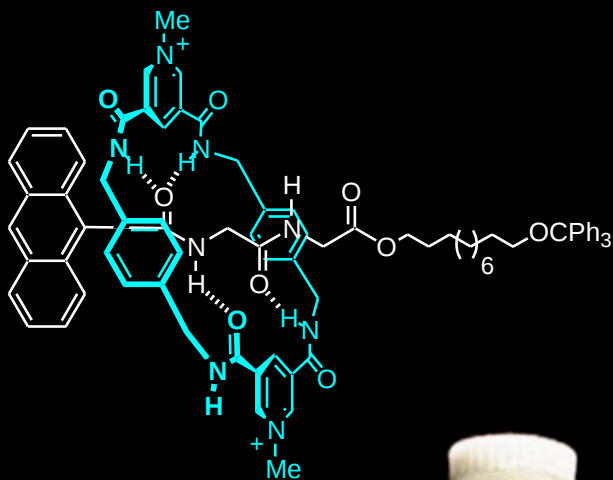
J. F. Stoddart et al., *Nature* **1994**, 369, 133.

A Metal-Coordinated Stimuli Responsive Molecular Shuttle



An electrochemically responsive shuttle based on the oxidation and reduction of Cu^+ and Cu^{2+} .

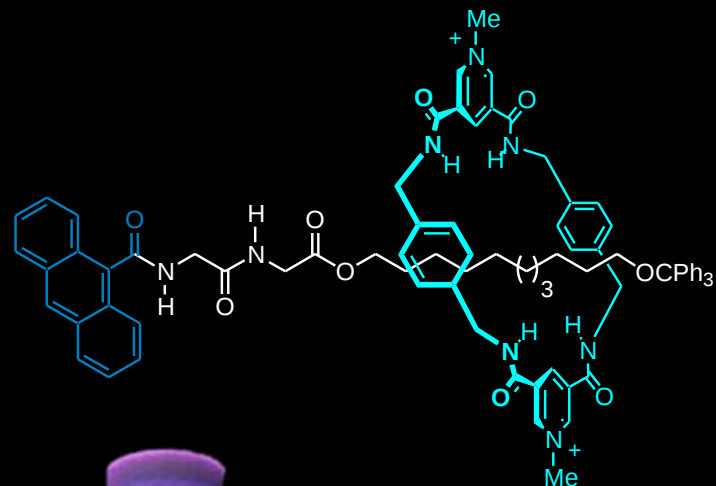
Optical Readout from a Molecular Shuttle



CH₂Cl₂



Off

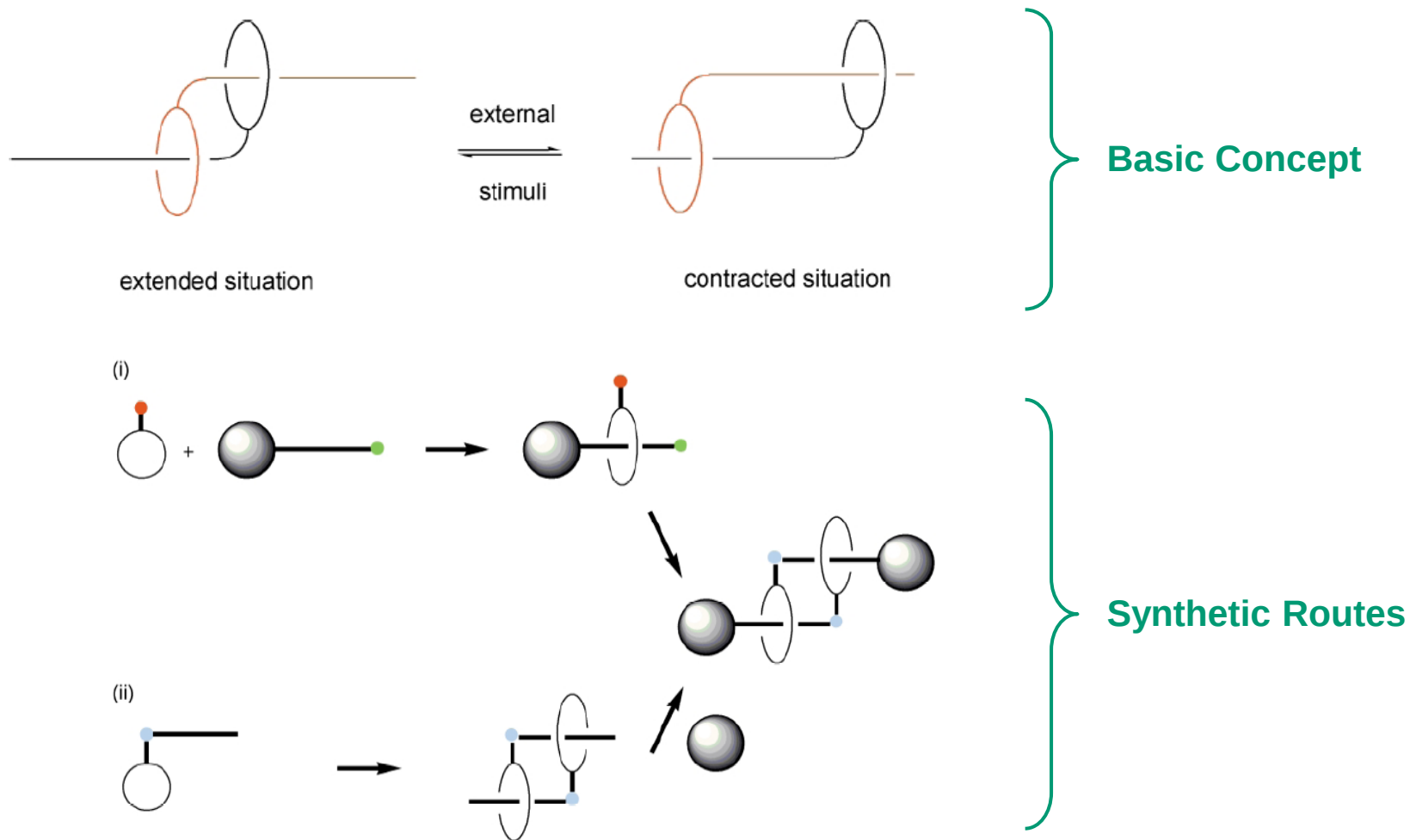


DMSO

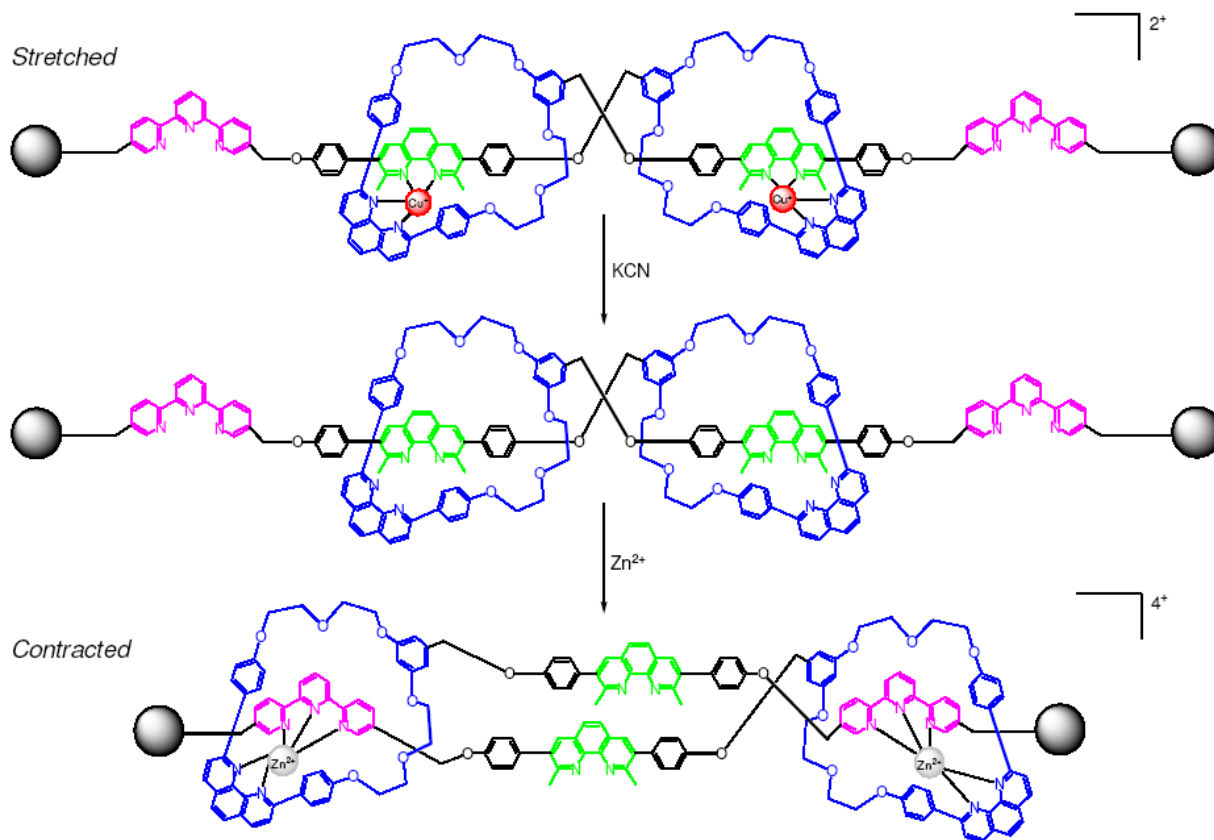


On

Towards Artificial Nanomuscles



A Molecular 'Muscle'



Jean-Pierre Sauvage

[nobel lecture](#)

The 'muscle' is stretched when coordinated to Cu^+ and contracted when coordinated to Zn^{2+} . Upon transition from its extended to contracted forms, the bis-rotaxane is estimated to change from 83 to 65 Å in length. The extent of this change is roughly comparable to those of natural muscles (~27%).

Artificial Molecular Motors



Chem Soc Rev

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Artificial molecular motors

Cite this: *Chem. Soc. Rev.*, 2017, 46, 2592

Salma Kassem,^{†a} Thomas van Leeuwen,^{†b} Anouk S. Lubbe,^{†b} Miriam R. Wilson,^{ID †a} Ben L. Feringa^{ID *b} and David A. Leigh^{ID *a}



Ben L. Feringa



David A. Leigh

[Chem. Soc. Rev. 2017, 46, 2592.](#)

Molecular Machines, Switches and Motors

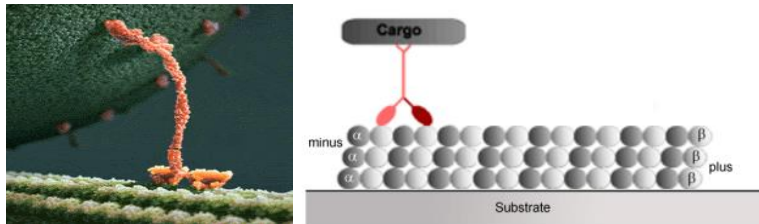
“A ‘**molecular machine**’ is a system in which a stimulus triggers the controlled motion of one molecular or submolecular component relative to another, potentially resulting in a net task being performed.”

“A ‘**molecular switch**’ is a type of molecular machine in which the change in relative positions of the components influences a system as a function of the state of the switch. (A consequence of this is that when a switch is returned to its original state, any mechanical work performed by the original switching action will be undone.)”

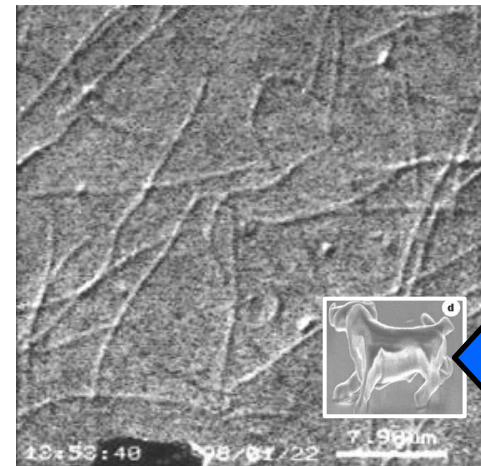
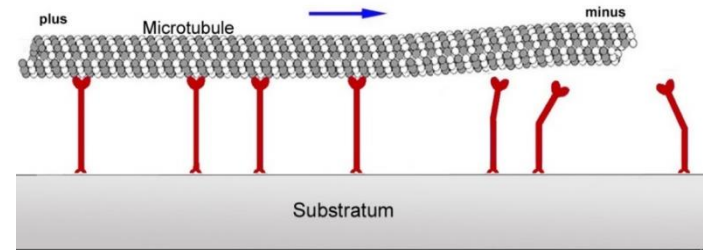
“A ‘**molecular motor**’ is a type of molecular machine in which the change in relative positions of the components influences a system as a function of the trajectory of the components. When a molecular motor returns to its original state at the end of the motor cycle, the work performed is not undone.”

from: [*Chem. Soc. Rev.* 2017, 46, 2592.](#)

ATP-Fueled Movements in Nature: Kinesins

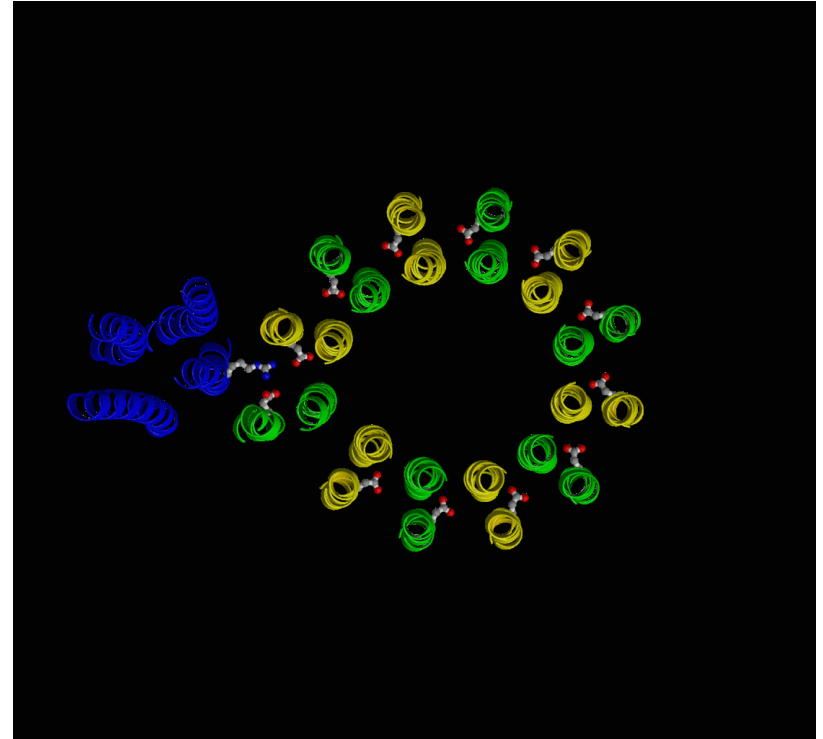
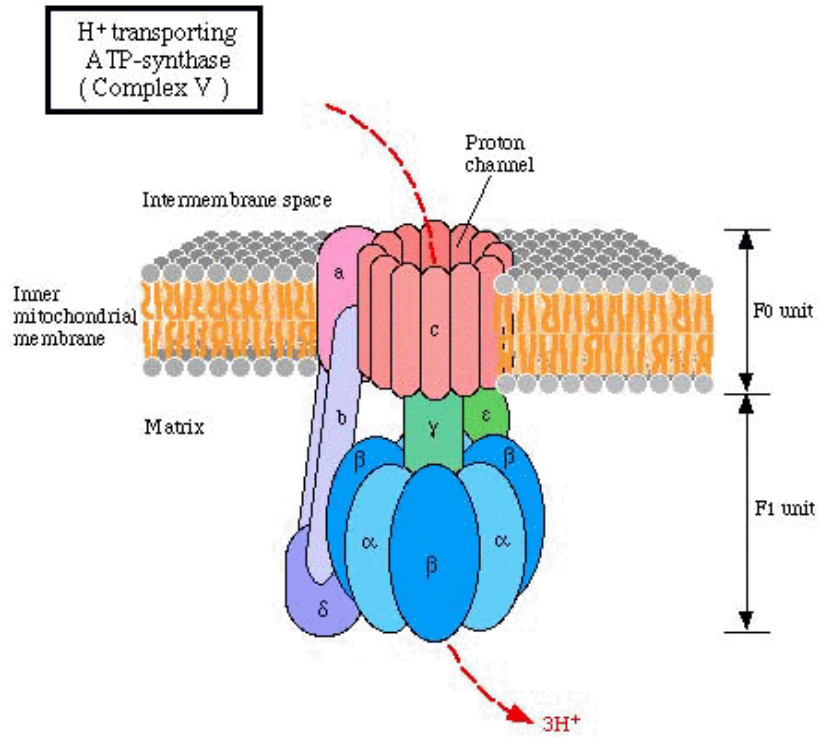


Kinesins are microtubule-associated motor proteins (also called mechanochemical proteins) which convert chemical energy released from nucleoside triphosphates (preferentially from ATP) into mechanical energy.



Intracellular movement and transport processes **can be mimicked *in vitro*** by gliding of microtubules across kinesin-coated glass surfaces

ATP Synthase – A Natural Rotary Motor



ATP synthase is the main source of cellular ATP. It uses a transmembrane proton gradient to drive the synthesis of ATP from ADP and phosphate.

General Considerations

“For large objects, inertial terms, which depend on the mass of the particle, dominate motion. As particle size decreases to or below the micrometre scale, viscous forces and Brownian motion become dominant while momentum and gravity become increasingly irrelevant.”

from: [*Chem. Rev.* 2015, 115, 10081.](#)

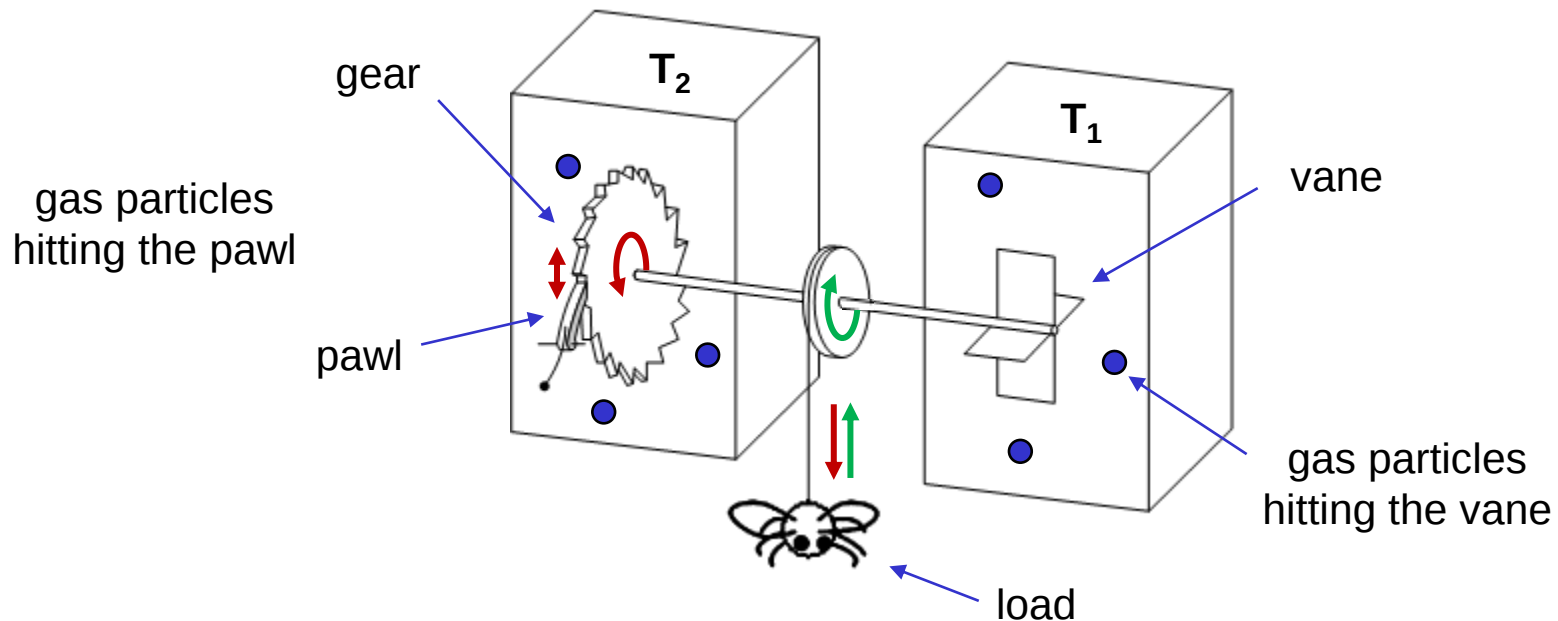
“The challenge of designing molecular motors lies not with producing motion at the molecular level, but in controlling the directionality of movement.”

“Molecular motors exploit random thermal fluctuations to produce directed motion by employing ratchet mechanisms.”

from: [*Chem. Soc. Rev.* 2017, 46, 2592.](#)

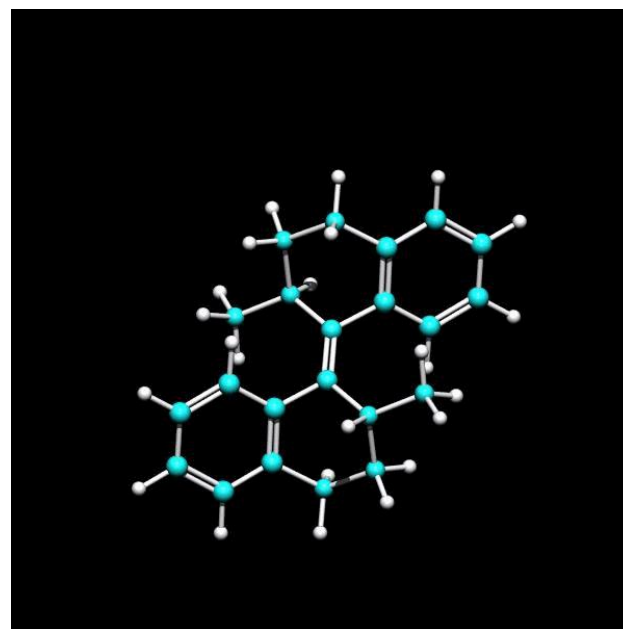
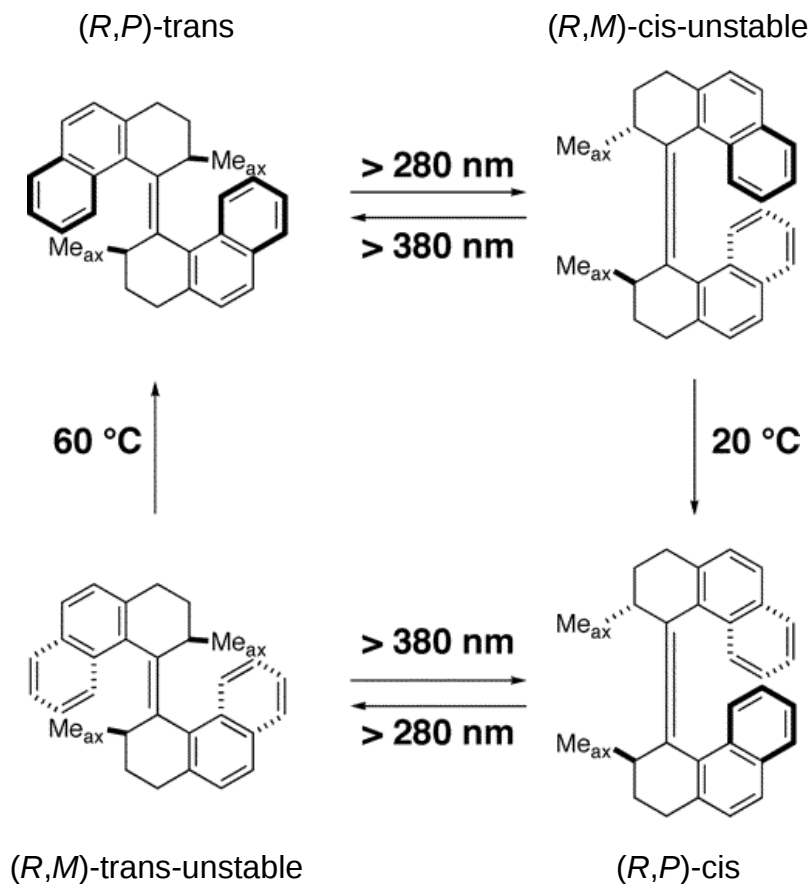
Feynman's Ratchet-and-Pawl

Brownian motion



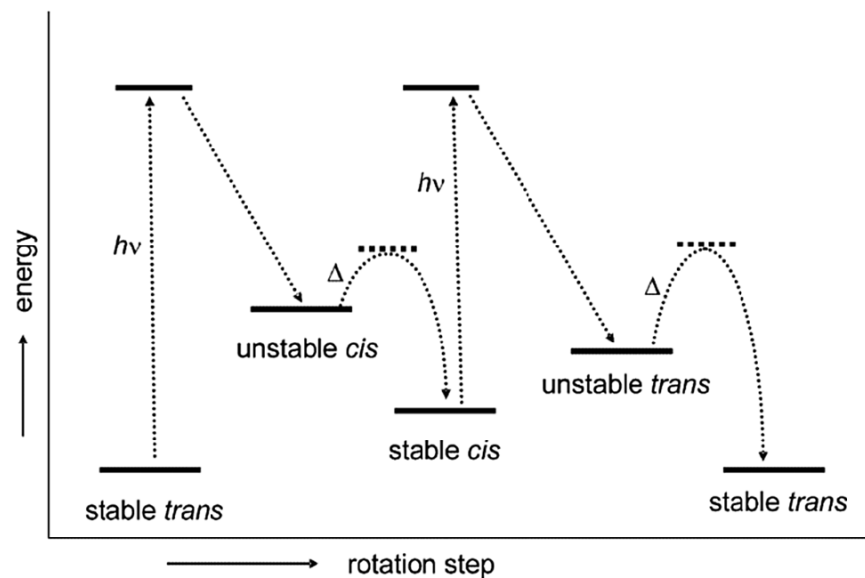
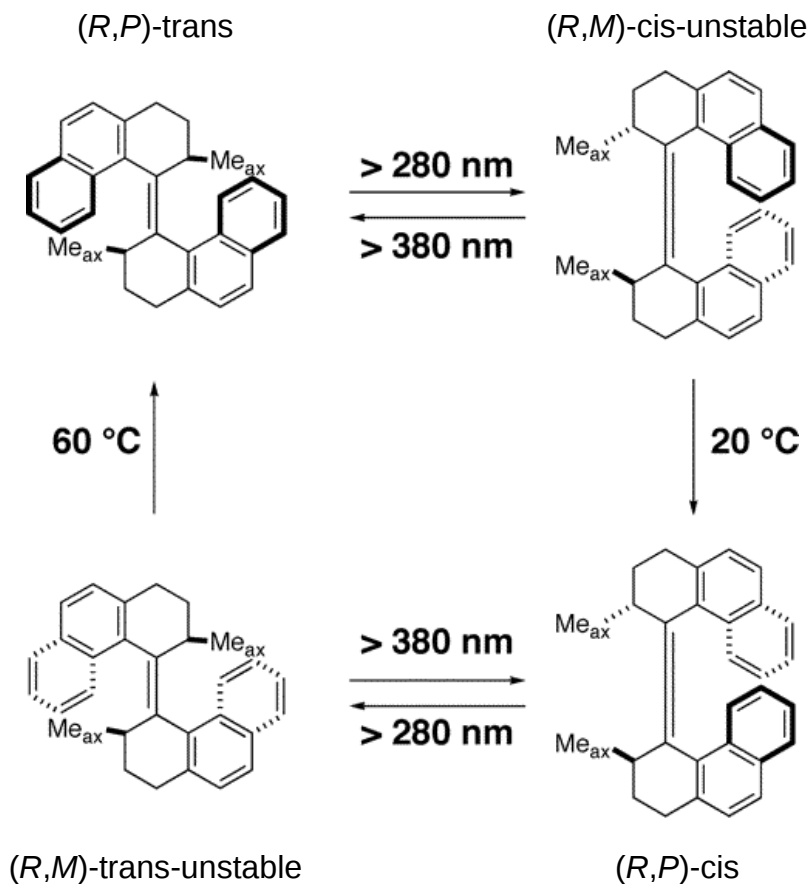
- Impossible in the case $T_1 = T_2$
- But possible when $T_1 > T_2$

A Photochemically Driven Motor with Unidirectional Rotation

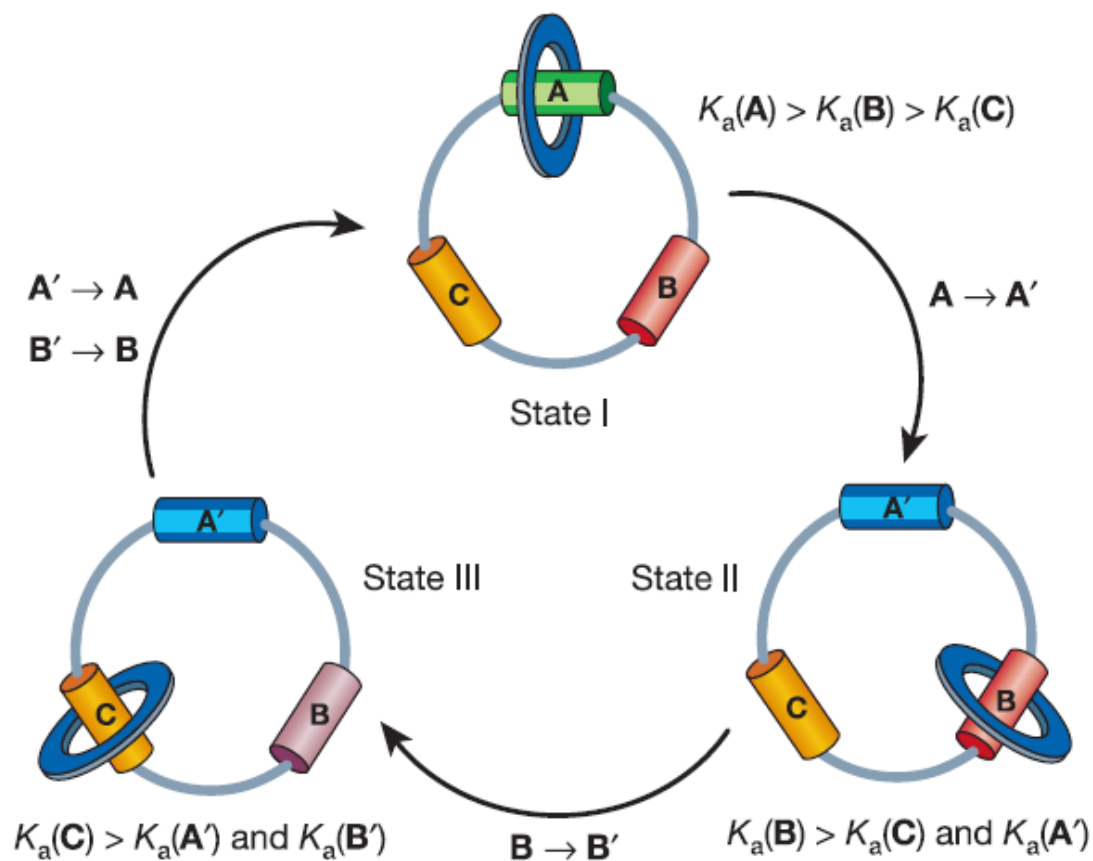


[B. L. Feringa et al., Nature 1999, 401, 152.](#)

A Photochemically Driven Motor with Unidirectional Rotation



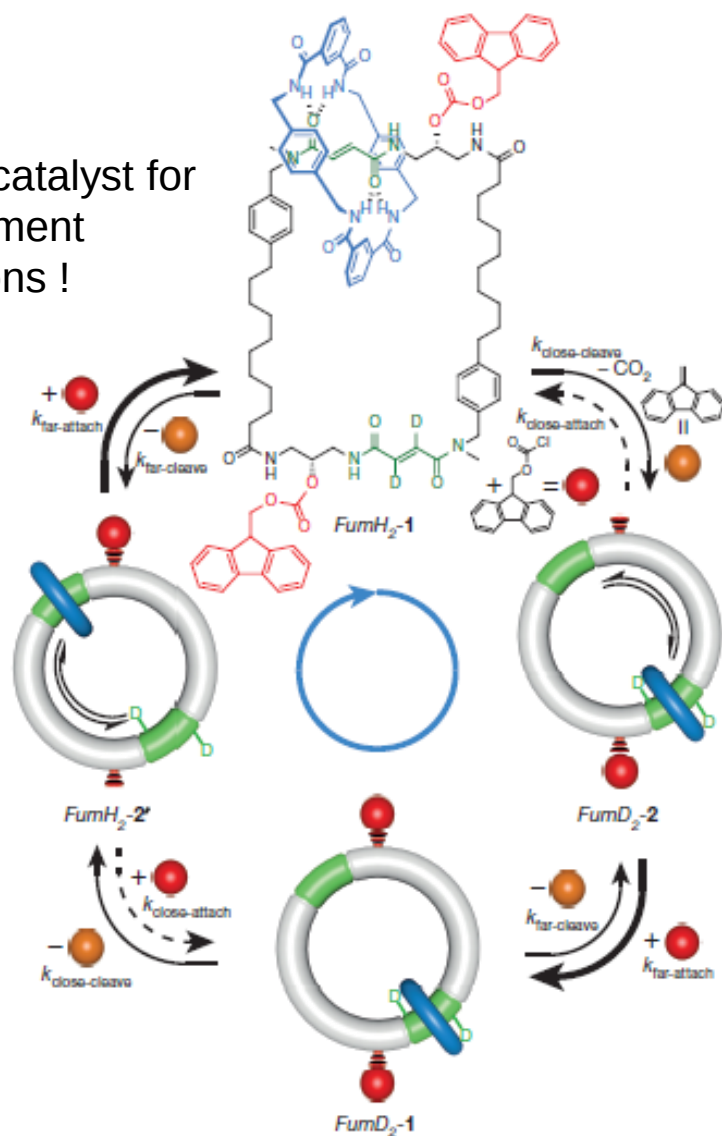
A Catenane-Based Molecular Motor



Stimuli-induced sequential movement of a macrocycle between three different binding sites in a [2]catenane.

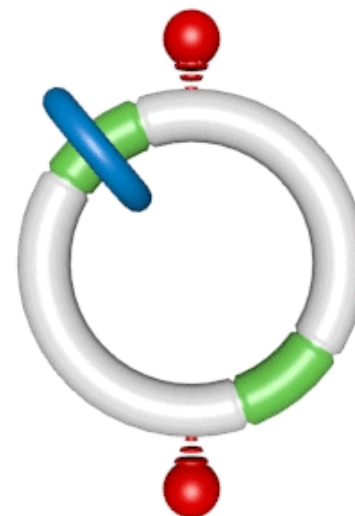
An Autonomous Chemically Driven Motor

Bulky catalyst for attachment reactions !



$$k_{\text{far-attach}} > k_{\text{close-attach}}$$

$$k_{\text{far-cleave}} = k_{\text{close-cleave}}$$



[D. A. Leigh et al., Nature 2016, 534, 235.](#)