Supramolecular Chemistry of Nanomaterials

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Lecture 5 – Molecular Switches

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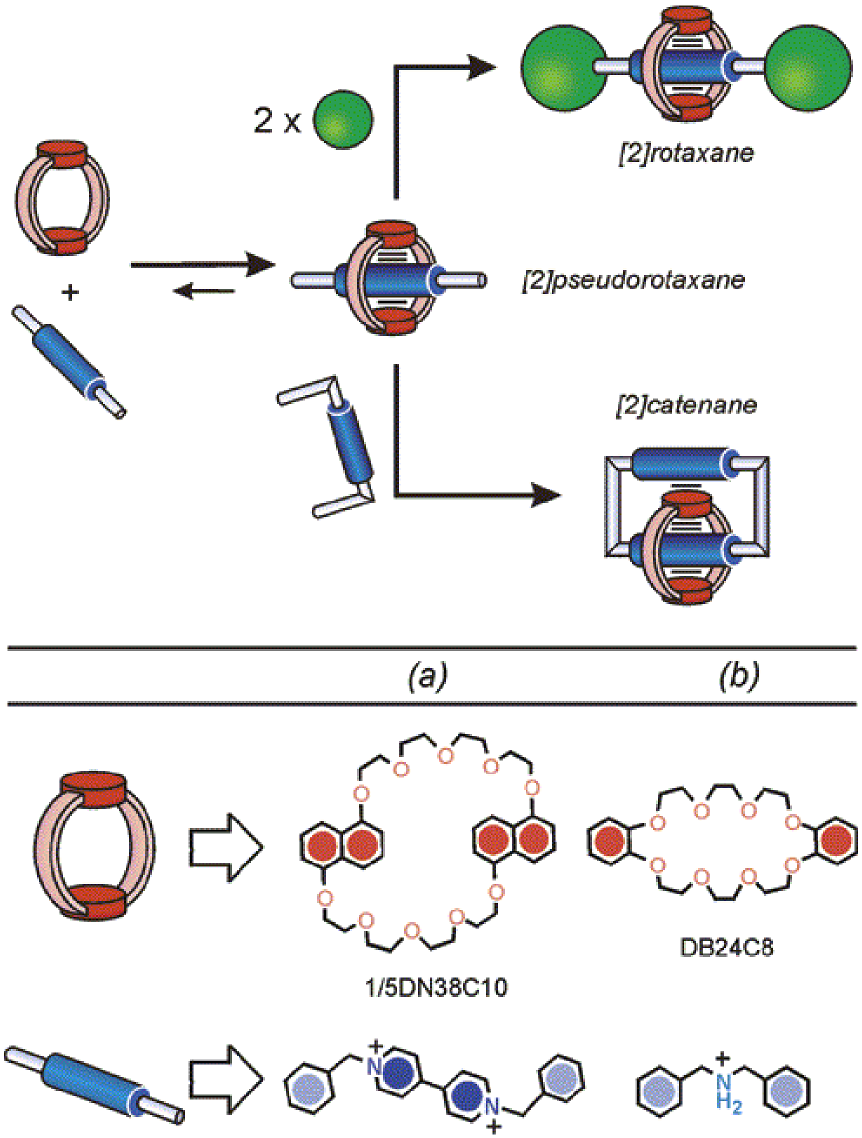
Synthesis of rotaxanes/catenanes

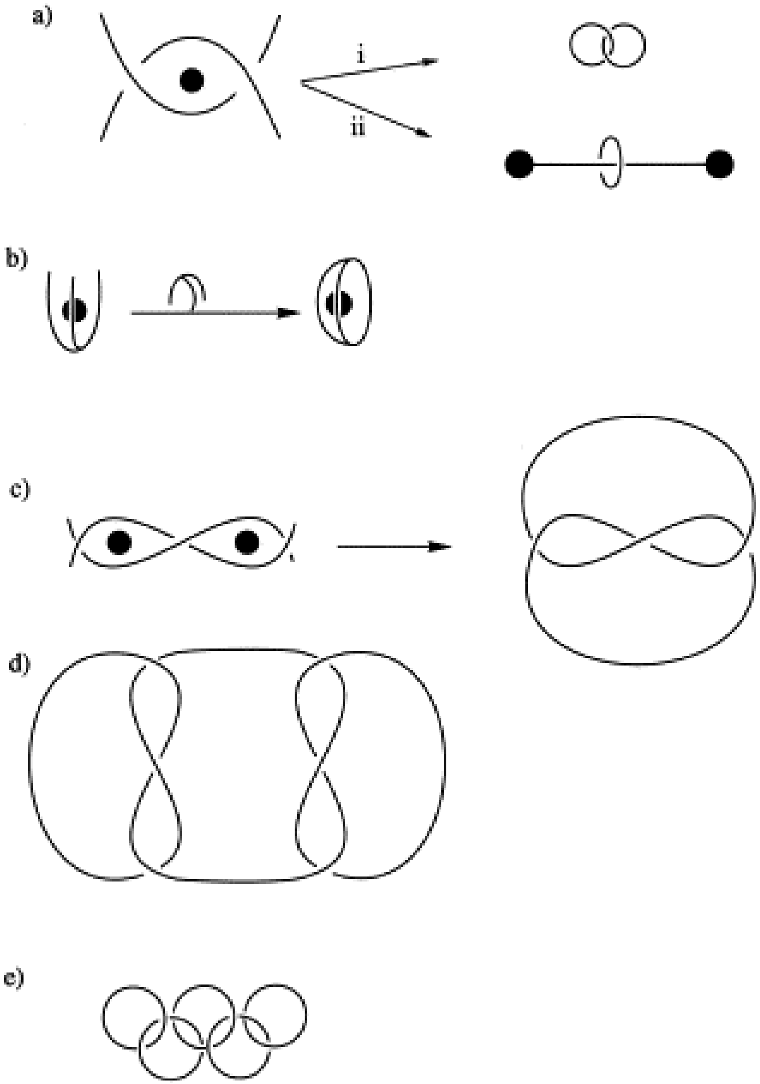
Pictorial representation of the self-assembly of pseudorotaxanes based on

- (a) CT and C-H···O hydrogen-bonding interactions and
- (b) N^+-H···O hydrogen-bonding interactions. A possible route toward the synthesis of rotaxanes and catenanes is also indicated.



Acc. Chem. Res., **34** (6), 445 -455, 2001

"Crossovers" - Interlocking

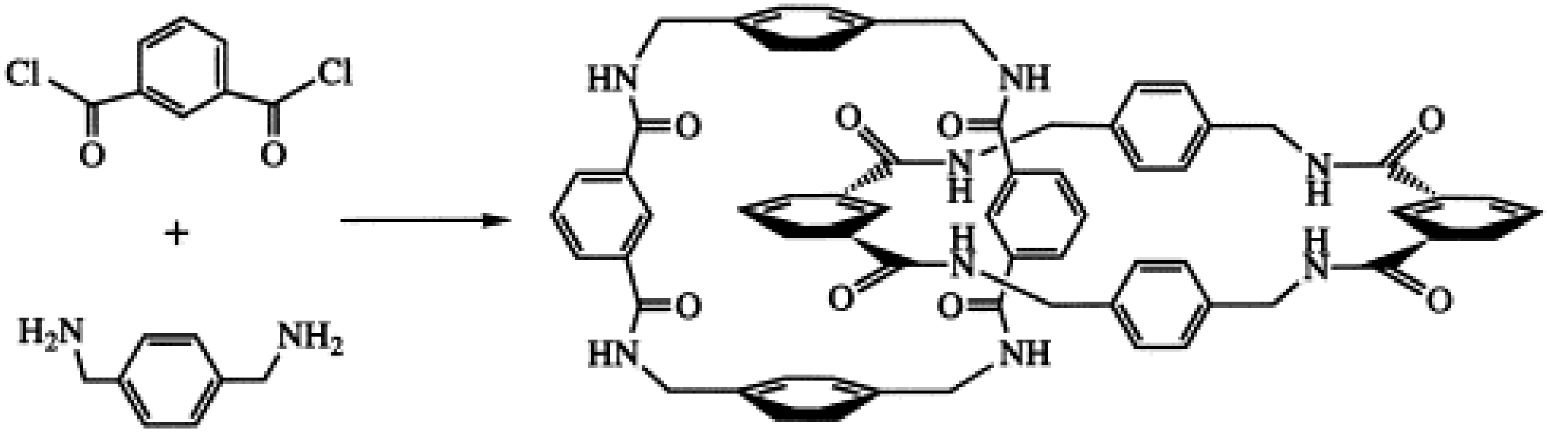


- (a) A simple cross-over gives (i) a catenane upon two ring closures or (ii) a rotaxane upon one ring closure and blocking
- (b) a fused turn can be used for macrobicycle syntheses
- (c) use of two anchors and ditopic turns to form a trefoil knot
- (d) a composite knot from two two-anchor templates
- (e) an oligocatenane resulting from multiple cross-overs on the same anchor.

Coord. Chem. Rev. 2000, 200–202, 5–52

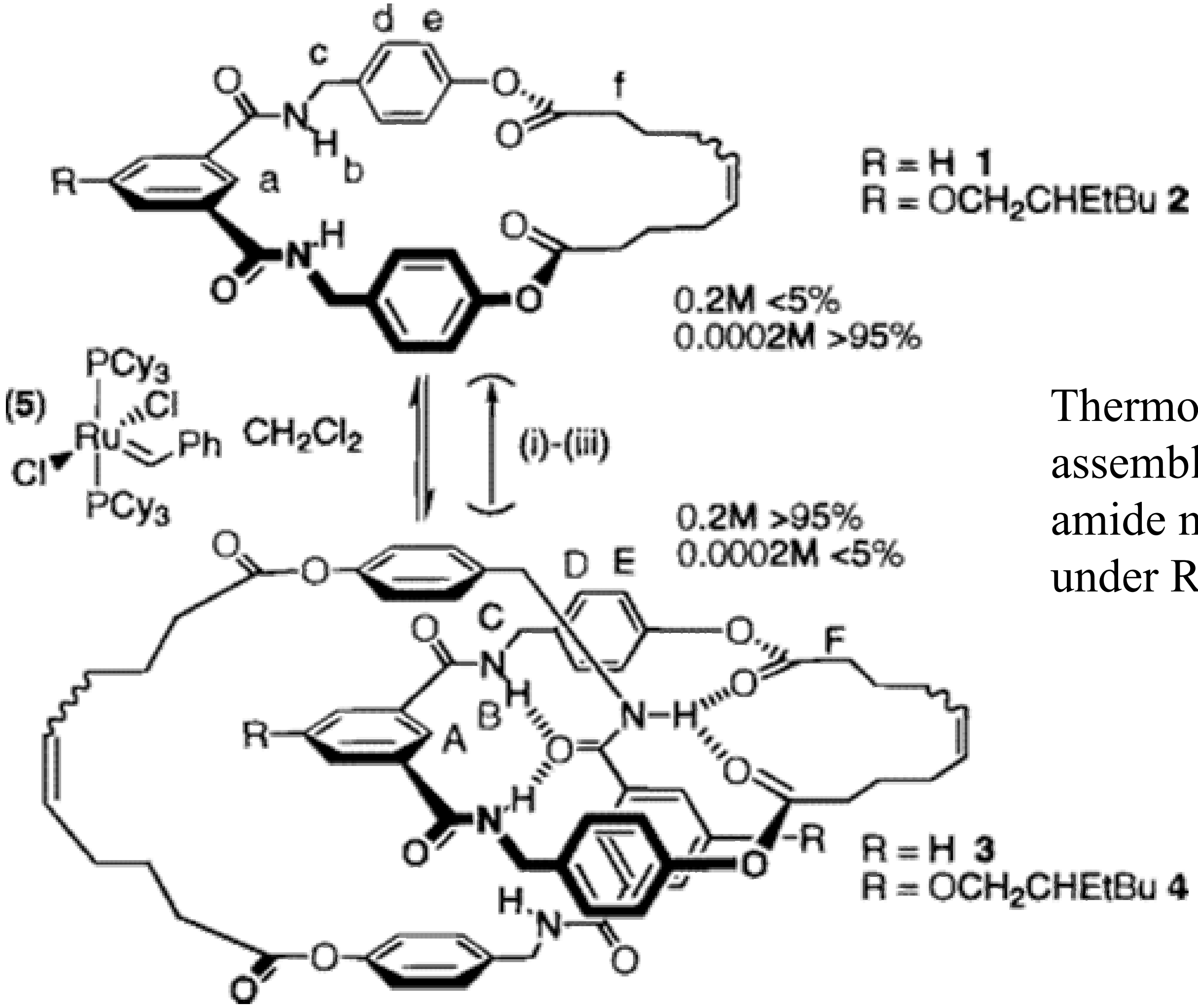
Hydrogen Bonding in Catenane Formation

- Leigh's simple and flexible synthesis of amide [2]-catenanes.



Coord. Chem. Rev. 2000, 200–202, 5–52

Magic Rings

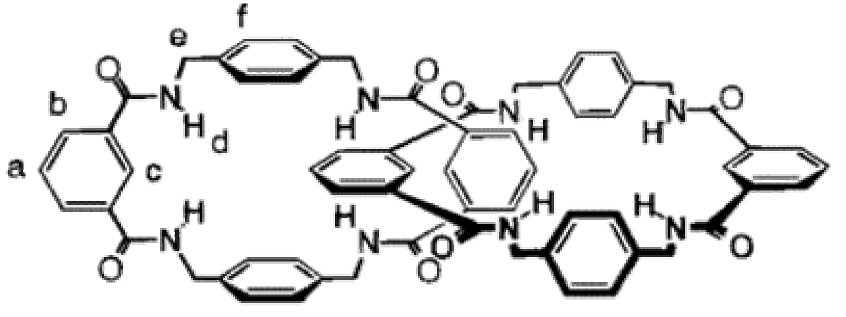


Thermodynamically controlled self-assembly / disassembly of benzylic amide macrocycles and [2]catenanes under RORCM *(*>95% yield).

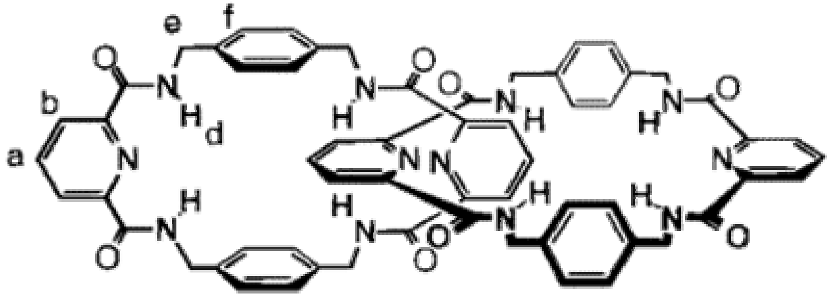
J. Am. Chem. Soc., **121** (7), 1599 -1600, 1999

Circumrotation

Solvent effects and structural modifications can induce large variations in the rate of circumrotation of benzylic amide catenanes (which can range from the submicro-second time scale (e.g., thiophene catenane **3** at elevated temperatures in polar solvents) to many hours to achieve a single circum-rotation (e.g., pyridine catenane **2** at low temperatures in nonpolar solvents)) allowing tremendous control over the kinetics of a mechanically interlocked molecular system.



1



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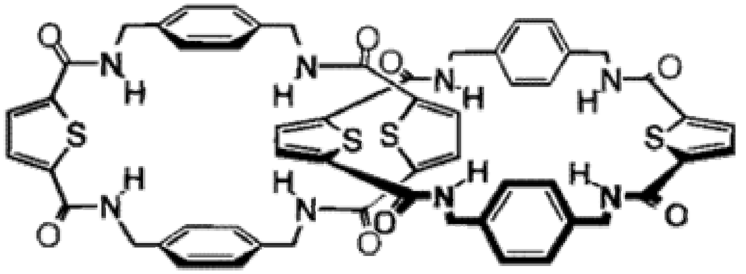

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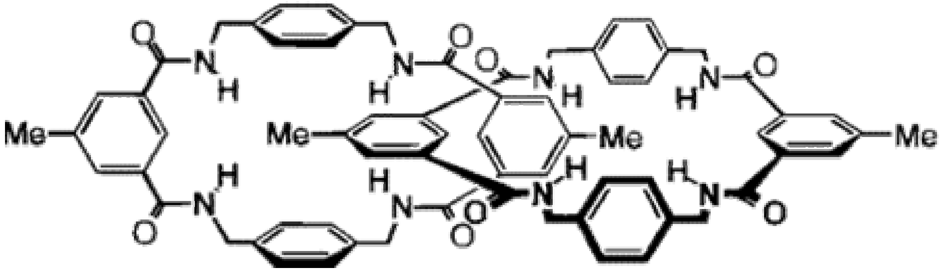

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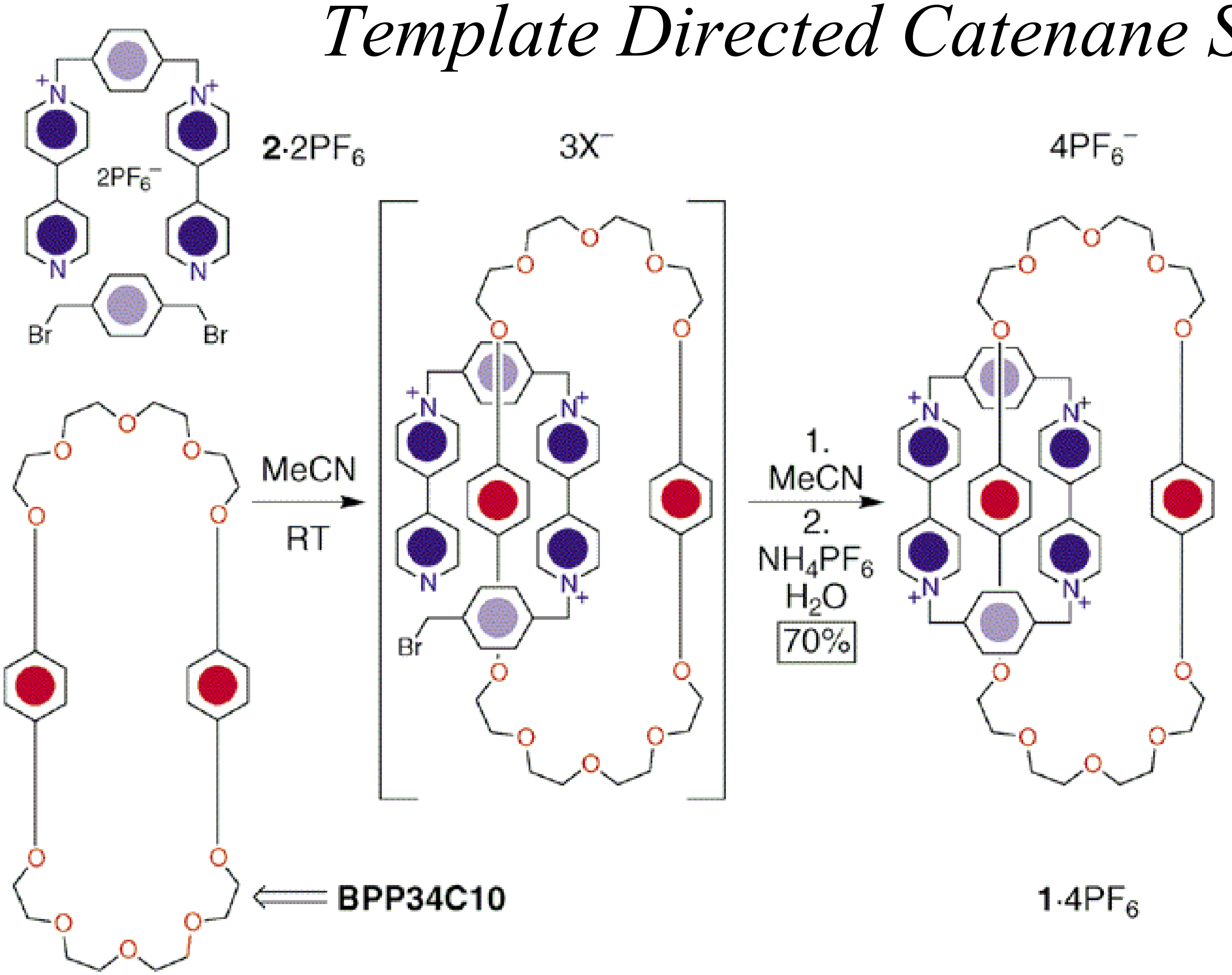
Template Directed Catenane Synthesis



- Template-directed synthesis of the [2]catenane **1**·4PF$_6$. The key step is the spontaneous threading through BPP34C10 of the tricationic intermediate, formed when **2**·2PF$_6$ reacts with *p*-xylylene dibromide. This supramolecular assistance is followed by covalent modification and counterion exchange to give **1**·4PF$_6$.

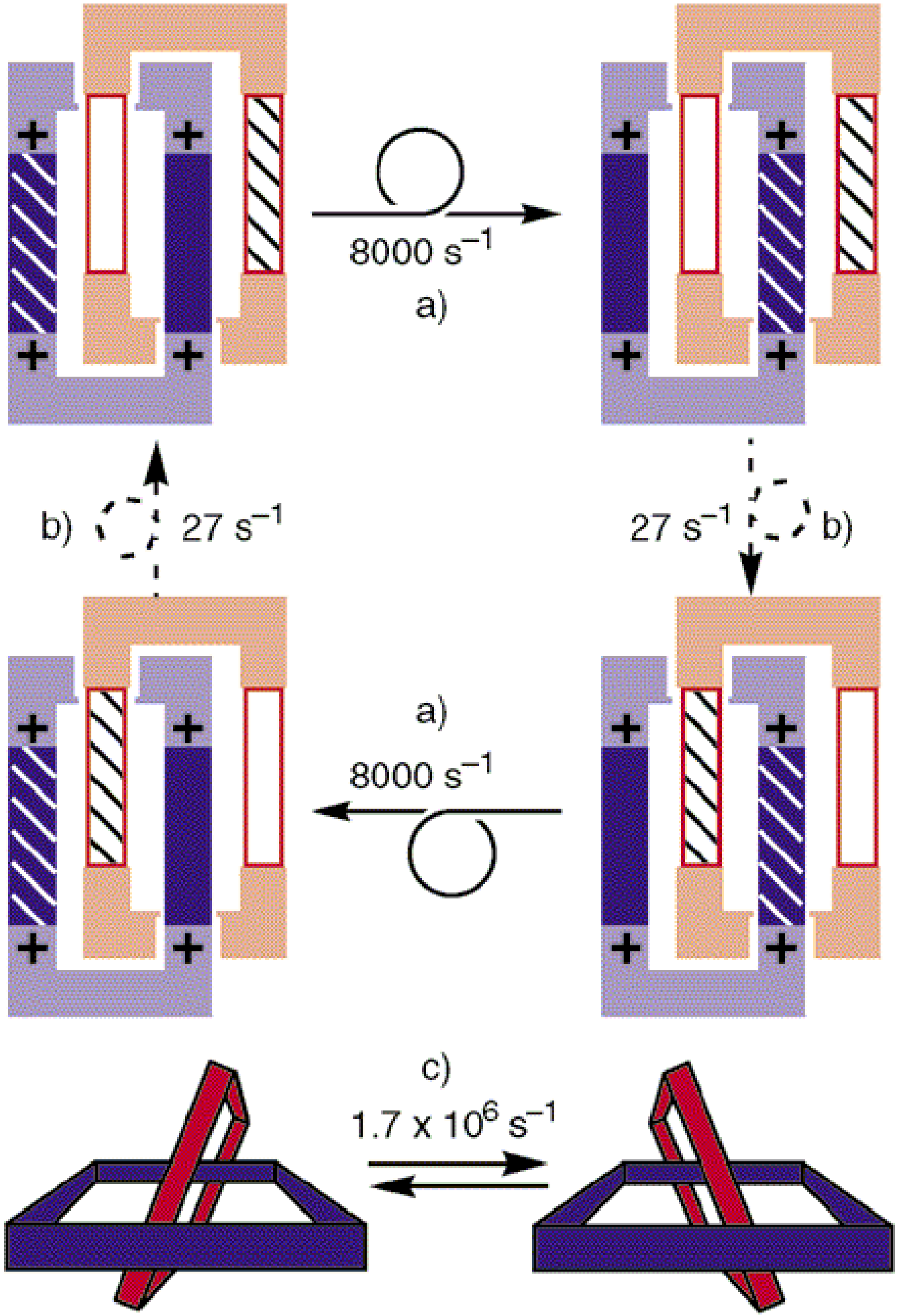
Catenane Kinetics

Three different degenerate co-conformational processes observed in temperature-dependent ^{1}H NMR spectra of the [2]catenane $\mathbf{1}^{4+}$:

(a) circumrotation of CBPQT^{4+} through BPP34C10;

(b) circumrotation of BPP34C10 through CBPQT^{4+}; and

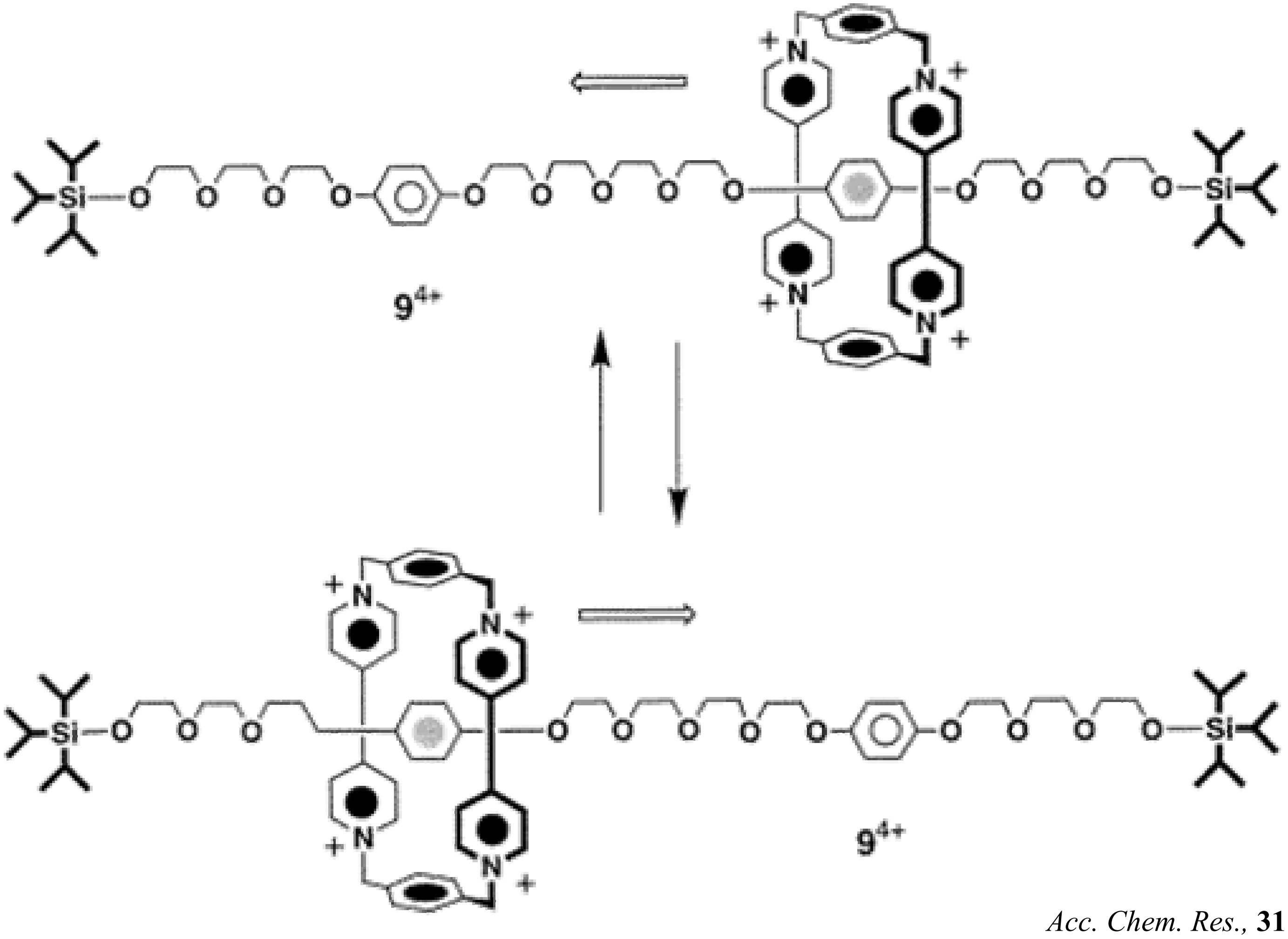
(c) rocking of BPP34C10 within CBPQT^{4+}. The rates of these processes at room temperature are shown.



Acc. Chem. Res., **34** (6), 433 -444, 2001

First Molecular Shuttle

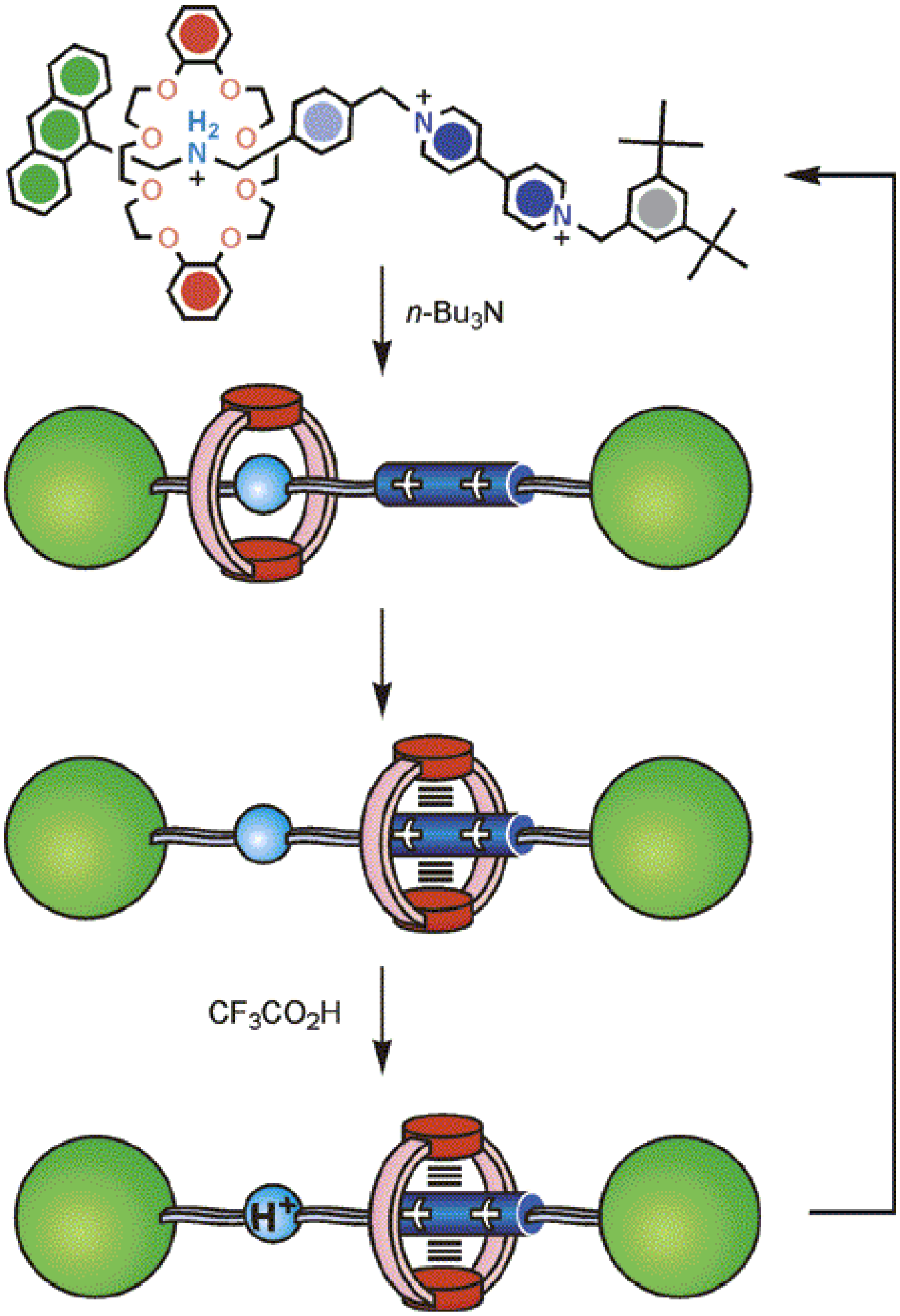
- The first molecular shuttle



Acc. Chem. Res., **31** (7), 405 -414, 1998

Molecular Switches
- Rotaxanes

A chemically controllable molecular shuttle: the ring can be switched between the two "stations" of the dumbbell component by base/acid “inputs”.



Acc. Chem. Res., **34** (6), 445 -455, 2001

Logic Operations – Rotaxanes and Catenanes

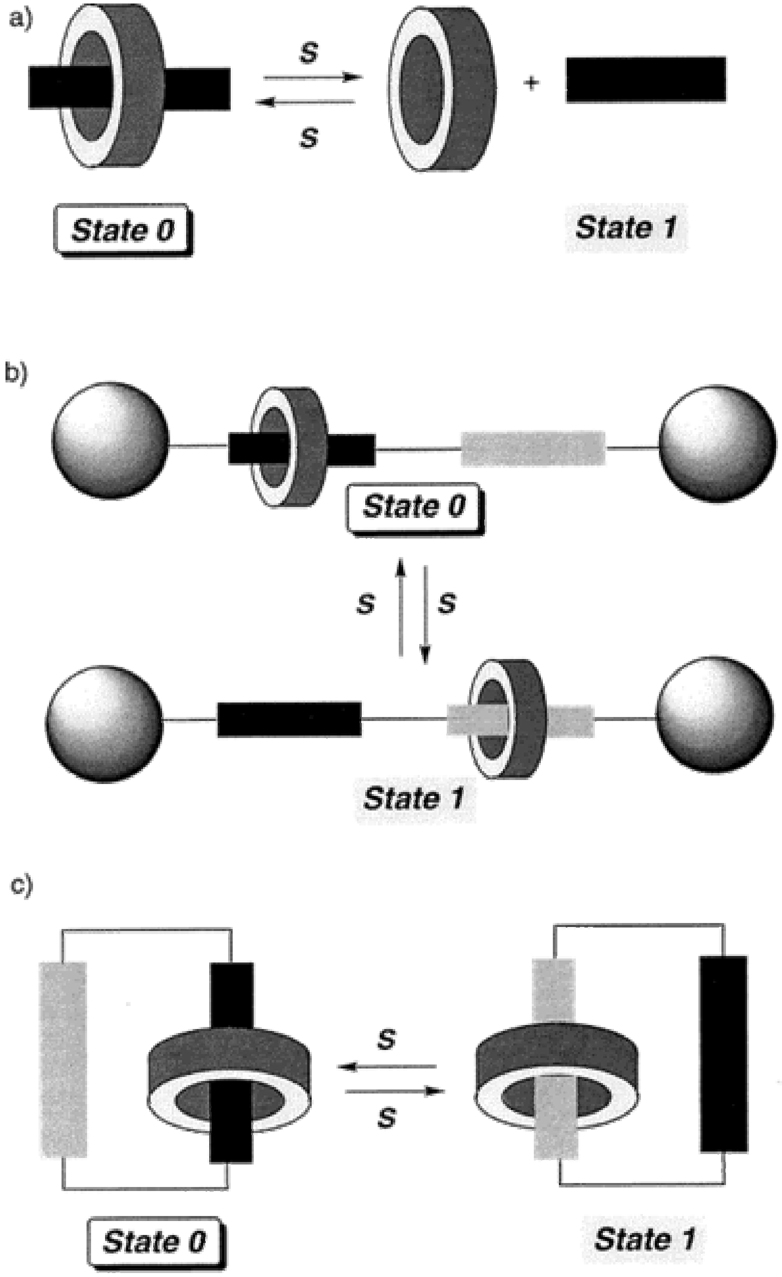
Schematic representations of the mechanical movements relating two states (0 and 1) in

(a) pseudorotaxanes

(b) rotaxanes

(c) Catenanes

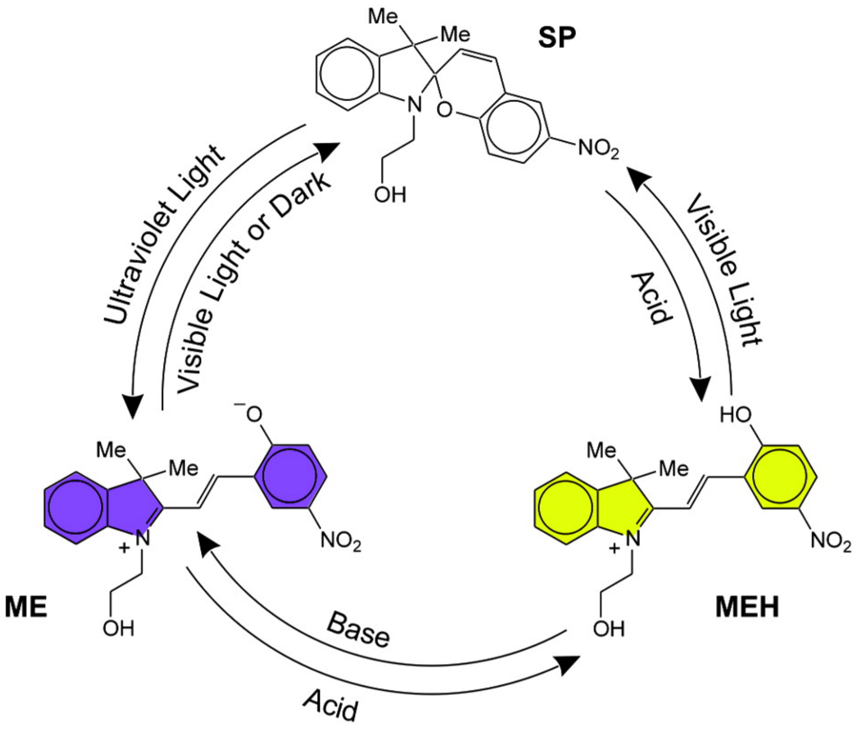
the stimulus (*S*) can be chemical or electrochemical energy, or it can be light.

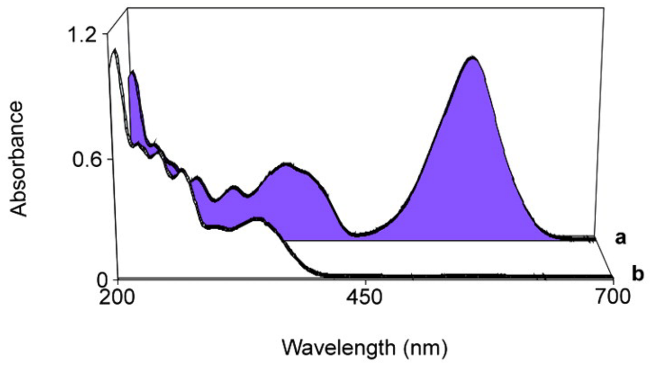


Acc. Chem. Res., **31** (7), 405 -414, 1998

Molecular Switch - All Optical Processing 1

UV light, visible light, and H^+ induce the interconversion between the three states **SP**, **ME**, and **MEH**. Absorption spectra of **SP** recorded after (a in *Lower*) and before (b in *Lower*) irradiation at 254 nm for 5 min.

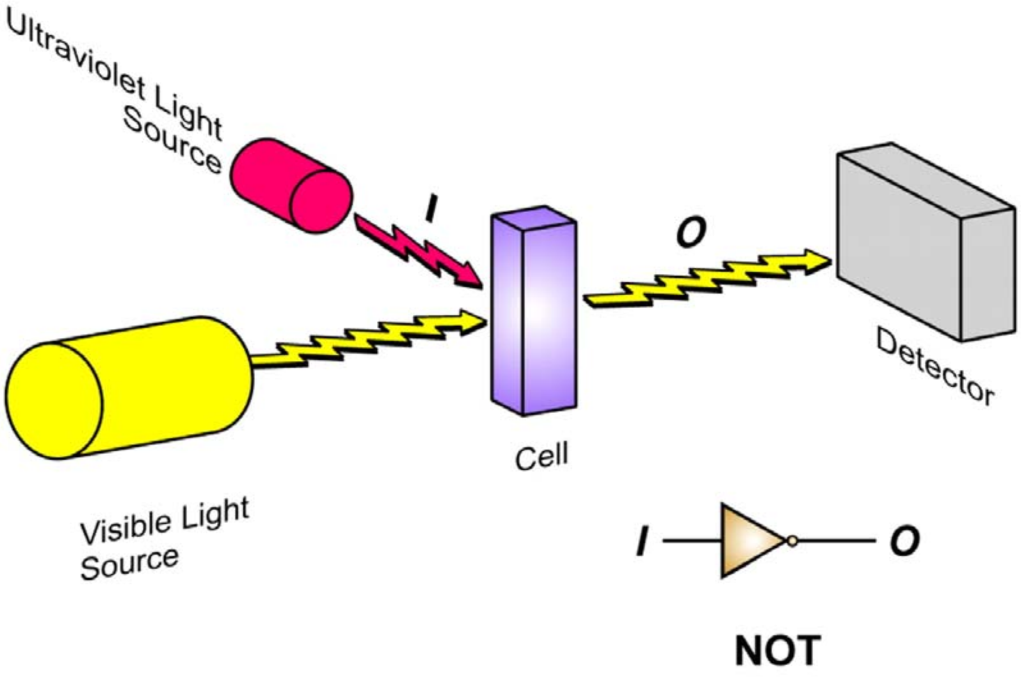




PNAS **2002,** 99, **4941–4944**

Molecular Switch - All Optical Processing 2

An optical signal (yellow arrows) travels from a light source to a detector after passing through a quartz cell containing a solution of **SP**. The intensity of the optical output (***O***) switches between low and high values as the optical input (***I***) is turned on and off. This signal transduction behavior is equivalent to a NOT operation.



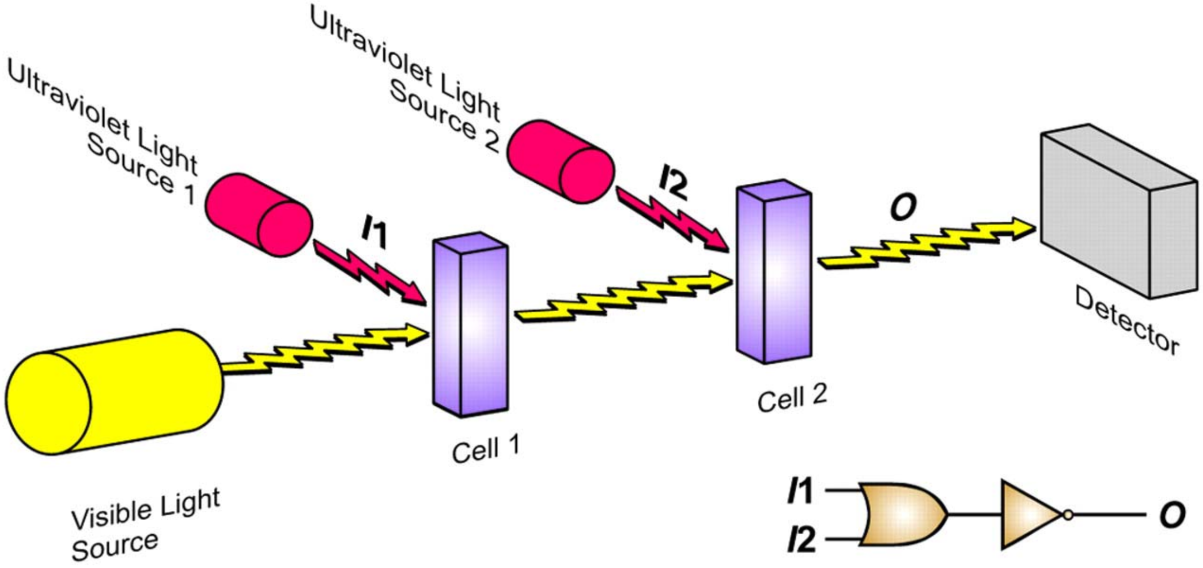
I	*O* (%)
Off	100
On	3

I	*O*
0	*1*
1	*0*

PNAS **2002,** 99, **4941–4944**

Molecular Switch - All Optical Processing 3

An optical signal (yellow arrows) travels from a light source to a detector after passing through two quartz cells containing a solution of **SP**. The intensity of the optical output (***O***) switches between low and high values as the two optical inputs (***I*1** and ***I*2**) are turned on and off. This signal transduction behavior is equivalent to a two-input NOR operation.



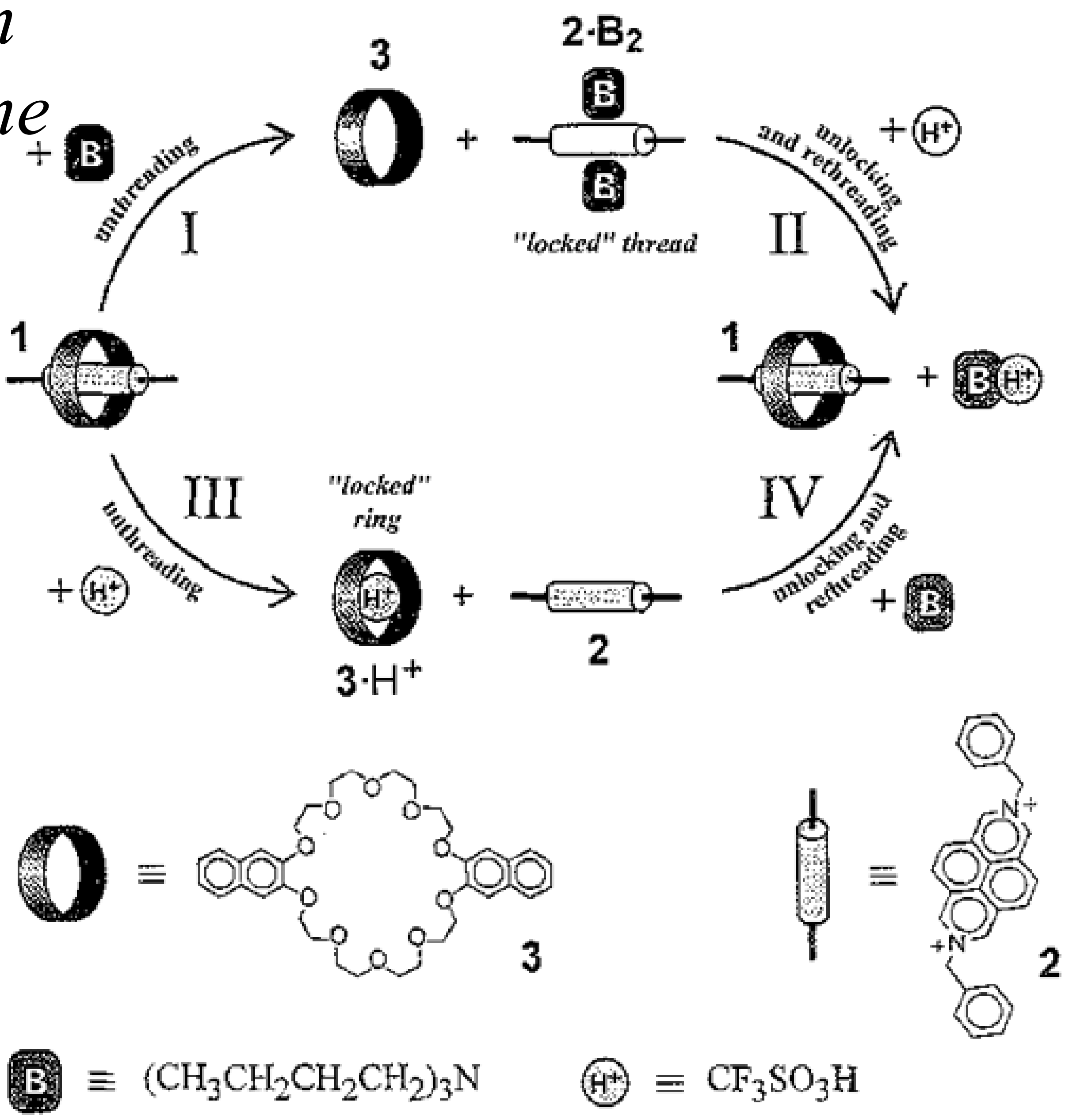
*I*1	*I*2	*O* (%)
Off	Off	100
Off	On	3
On	Off	4
On	On	0

Two-Input NOR

*I*1	*I*2	*O*
0	*0*	*1*
0	*1*	*0*
1	*0*	*0*
1	*1*	*0*

PNAS **2002,** 99, **4941–4944**

Logic Function
- Pseudrotaxane

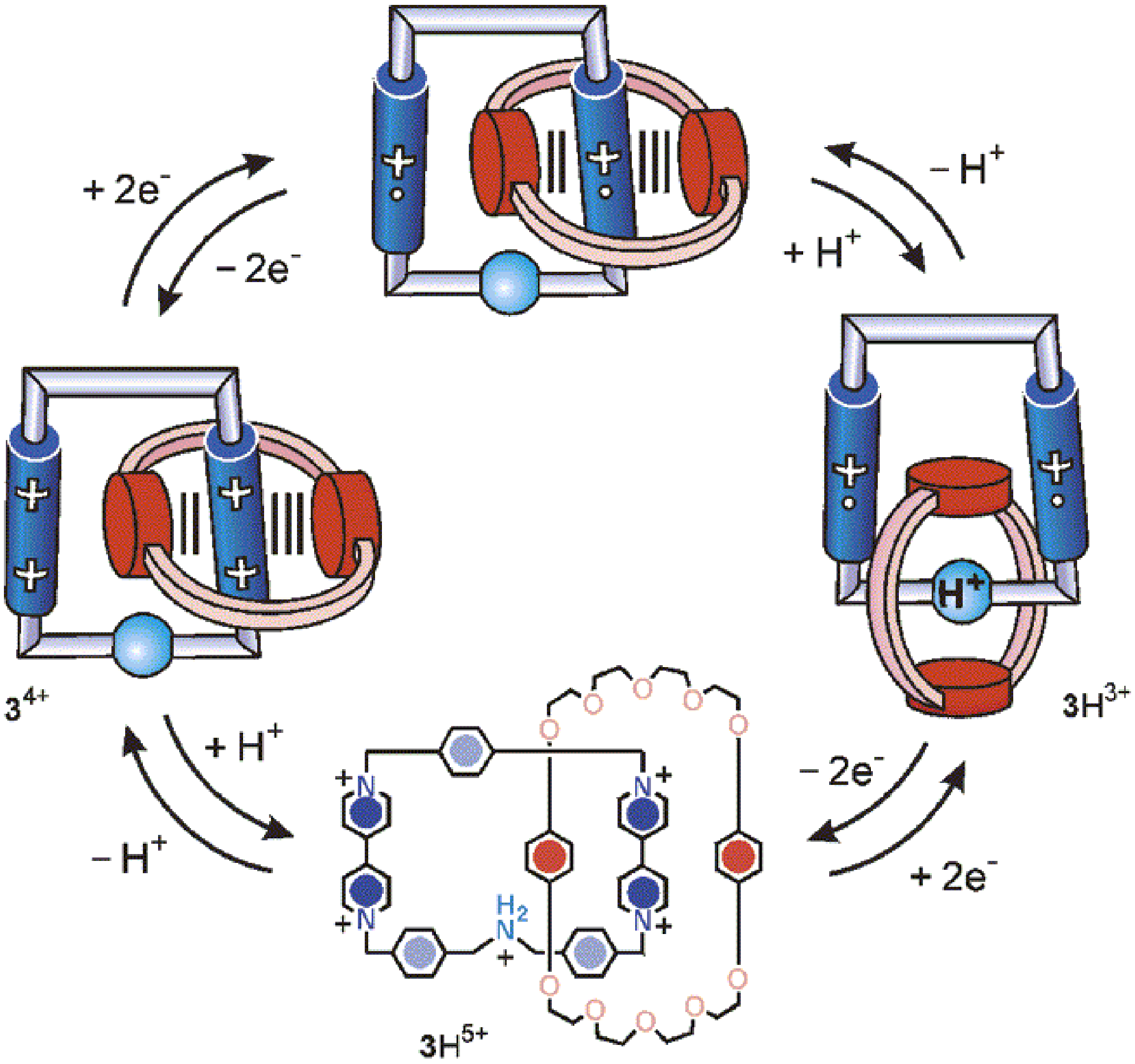


Schematic representation of the unthreading/ rethreading pattern of pseudorotaxane **1**, which corresponds to an XOR logic function.

J. Am. Chem. Soc., **119** (11), 2679 -2681, 1997

Molecular Switch – AND Logic Gate

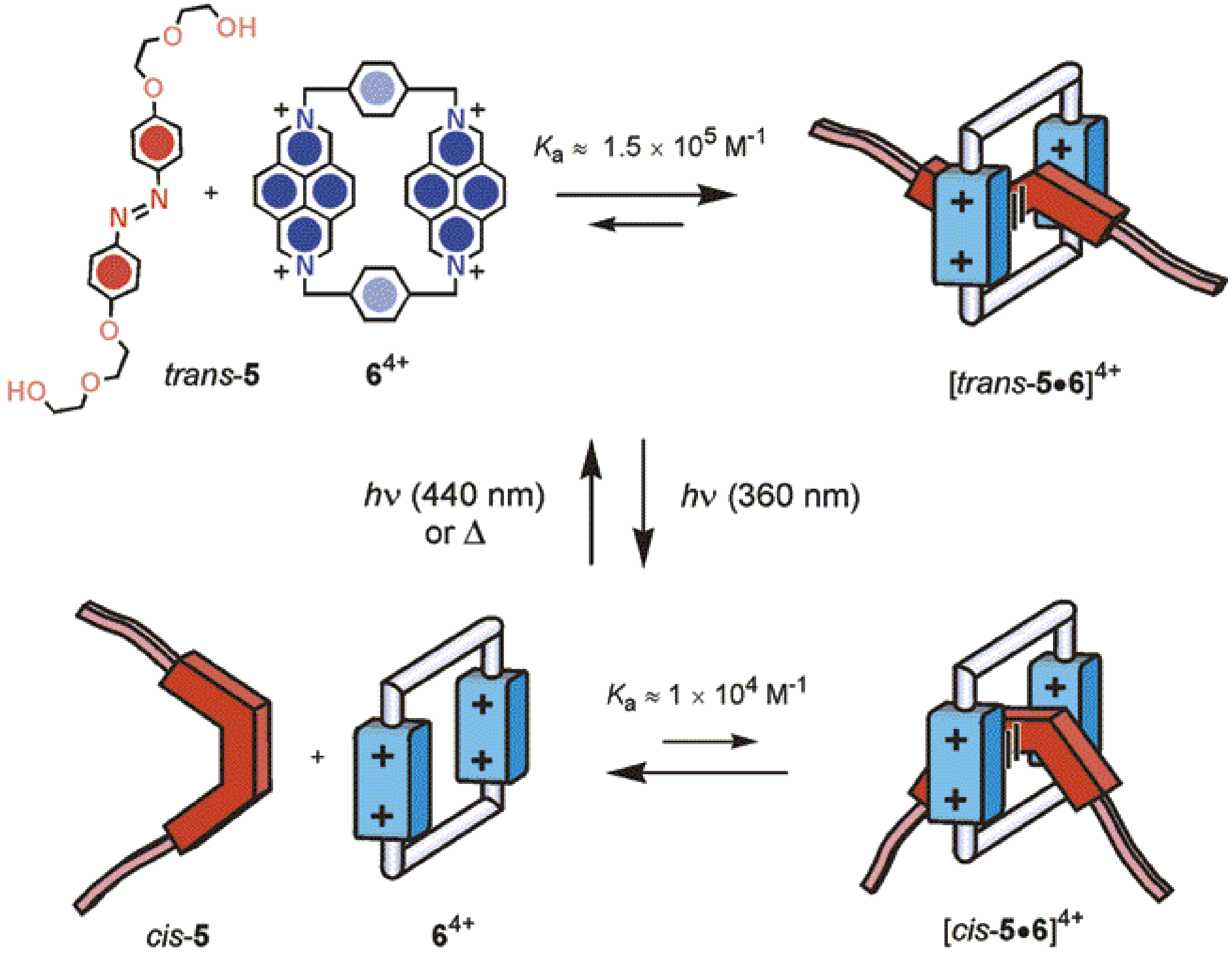
Switching processes of catenane **3**H^{5+}. Starting from catenane **3**$^{4+}$, the position of the macrocyclic polyether switches under acid/base and redox inputs (AND logic).



Acc. Chem. Res., **34** (6), 445 -455, 2001

Light Driven Dethreading

Controllable dethreading/rethreading of a pseudorotaxane based on a trans-cis photoisomerization reaction (80% complexed species).



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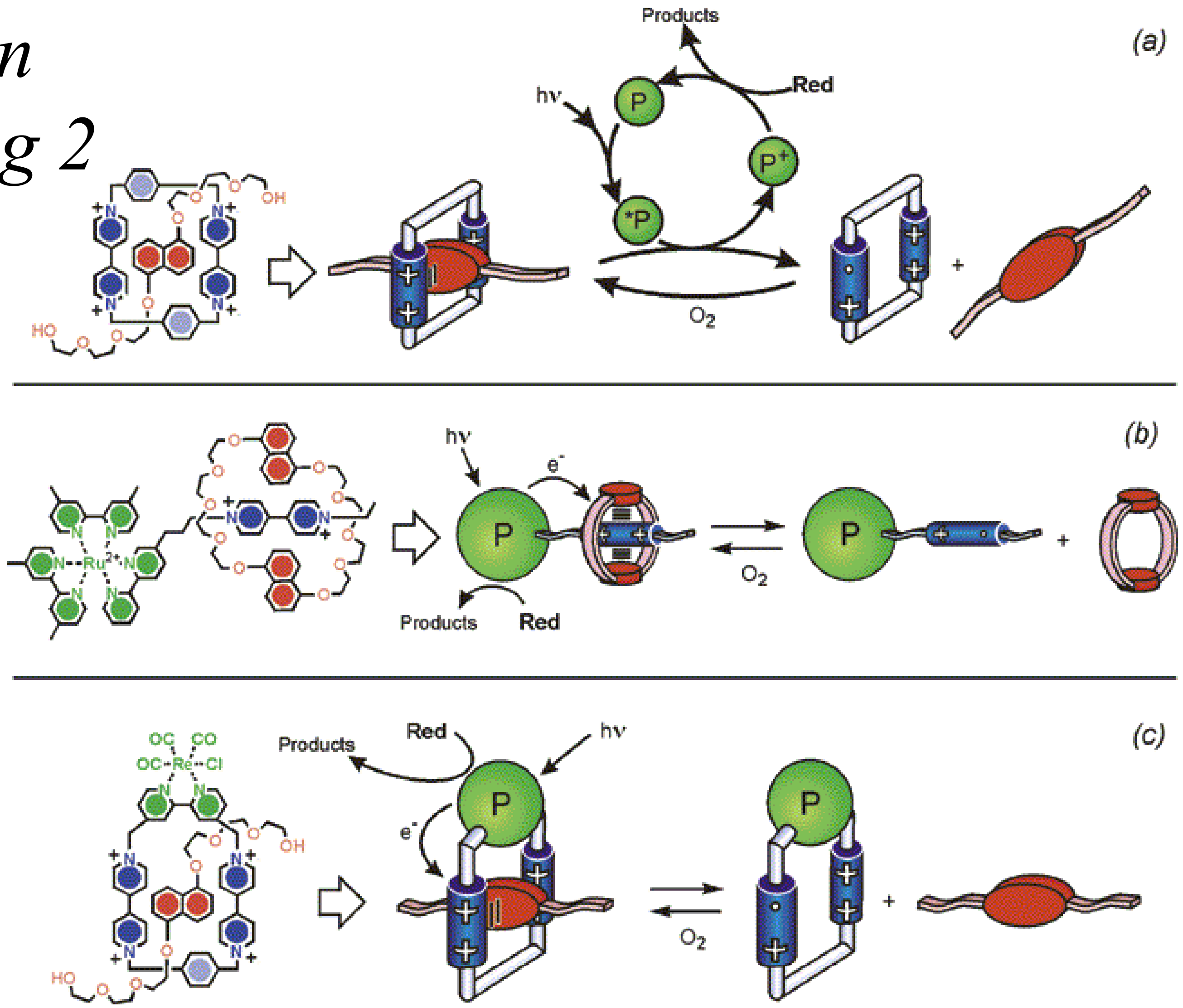
Light-driven Dethreading 2



Light-driven dethreading of pseudorotaxanes by excitation of a photosensitizer **P** as (a) an external reactant, (b) a stopper in the wire-type component, and (c) a component of the macrocyclic ring.

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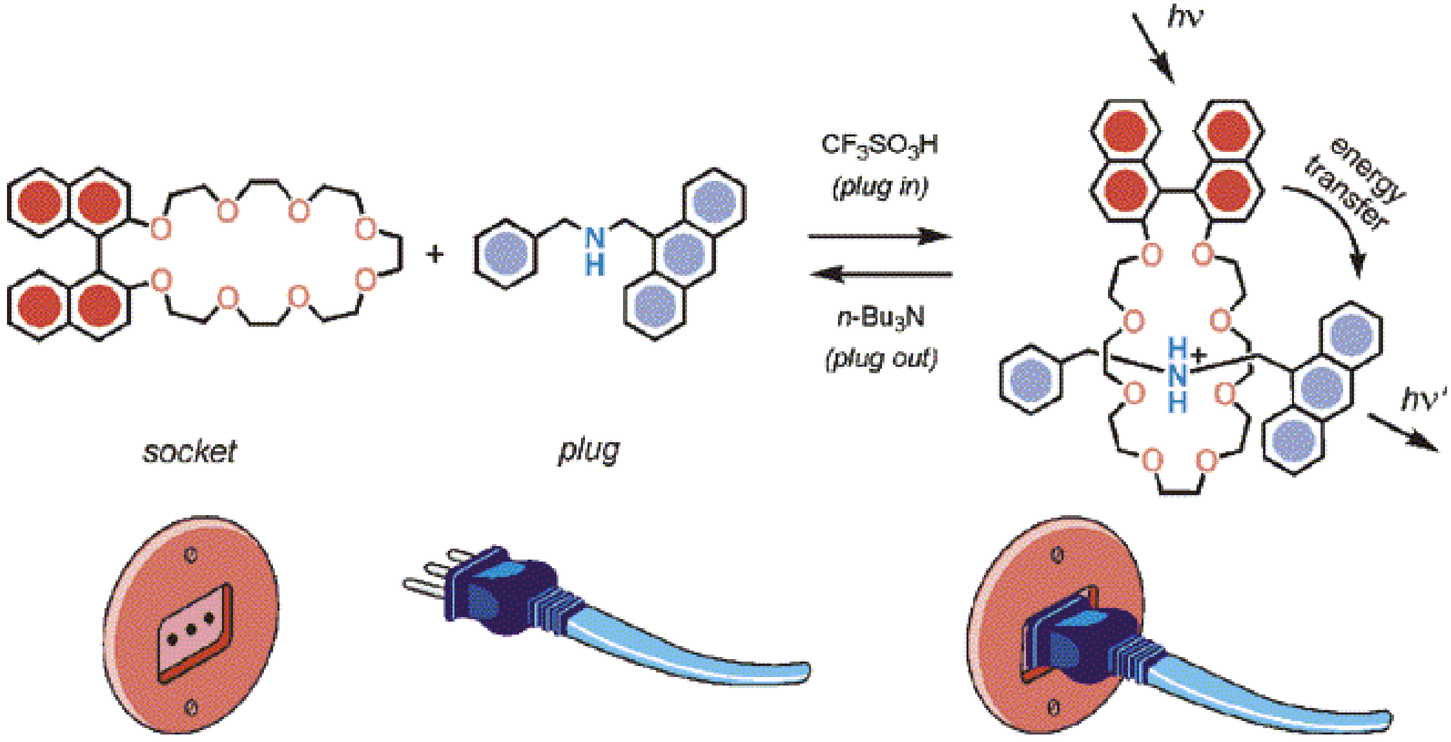
Molecular Level Plug

A molecular-level plug/socket device: "plug in/plug out" is acid/base controlled, and photoinduced energy transfer takes place in the "plug in" state (CH_2Cl_2, room temperature).



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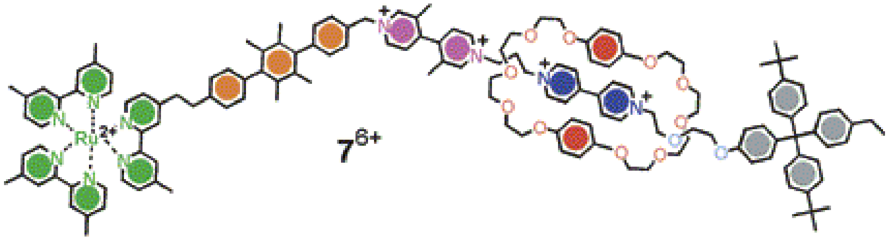
Photocontrollable Abacus

Rotaxane 7^{6+}: photoinduced abacus-like movement of macrocycle **R** between the two stations $\mathbf{A_1}$ and $\mathbf{A_2}$.



Macrocycle **R**
Dumbbell component (**P**, $\mathbf{A_1}$, $\mathbf{A_2}$, **S**, **T**):
(i)a photoactive Ru(II) polypyridine complex (**P**) as a stopper
(ii)a 4,4'-bipyridinium unit ($\mathbf{A_1}$) and a 3,3'-dimethyl-4,4'-bipyridinium unit ($\mathbf{A_2}$) as electron-accepting stations
(iii)a *p*-terphenyl-type ring system as a rigid spacer (**S**)
(iv)a tetraarylmethane group as the second stopper (**T**).
The stable translational isomer: **R** encircles the better electron-acceptor $\mathbf{A_1}$.

The intramolecular mechanism, which implies the conversion of light energy into mechanical energy without generating waste products, is based on the four operations

(a) Destabilization of the stable translational isomer: light excitation of **P** (step 1) is followed by the transfer of an electron to the $\mathbf{A_1}$ station (step 2), which is encircled by ring **R**; such a photoinduced electron-transfer process, which competes with the intrinsic excited-state decay (step 3), "deactivates" the $\mathbf{A_1}$ station.
(b) Ring displacement: the ring movement from $\mathbf{A_1}^-$ to $\mathbf{A_2}$ (step 4) has to compete with the back-electron-transfer process from $\mathbf{A_1}^-$ (still encircled by **R**) to the oxidized photoactive unit $\mathbf{P}^+$ (step 5).
(c) Electronic reset: the back-electron-transfer process from the "free" reduced station $\mathbf{A_1}^-$ to $\mathbf{P}^+$ (step 6) restores the electron-acceptor power to the $\mathbf{A_1}$ station.
(d) Nuclear reset: as a consequence of the electronic reset, back movement of the ring from $\mathbf{A_2}$ to $\mathbf{A_1}$ occurs (step 7).

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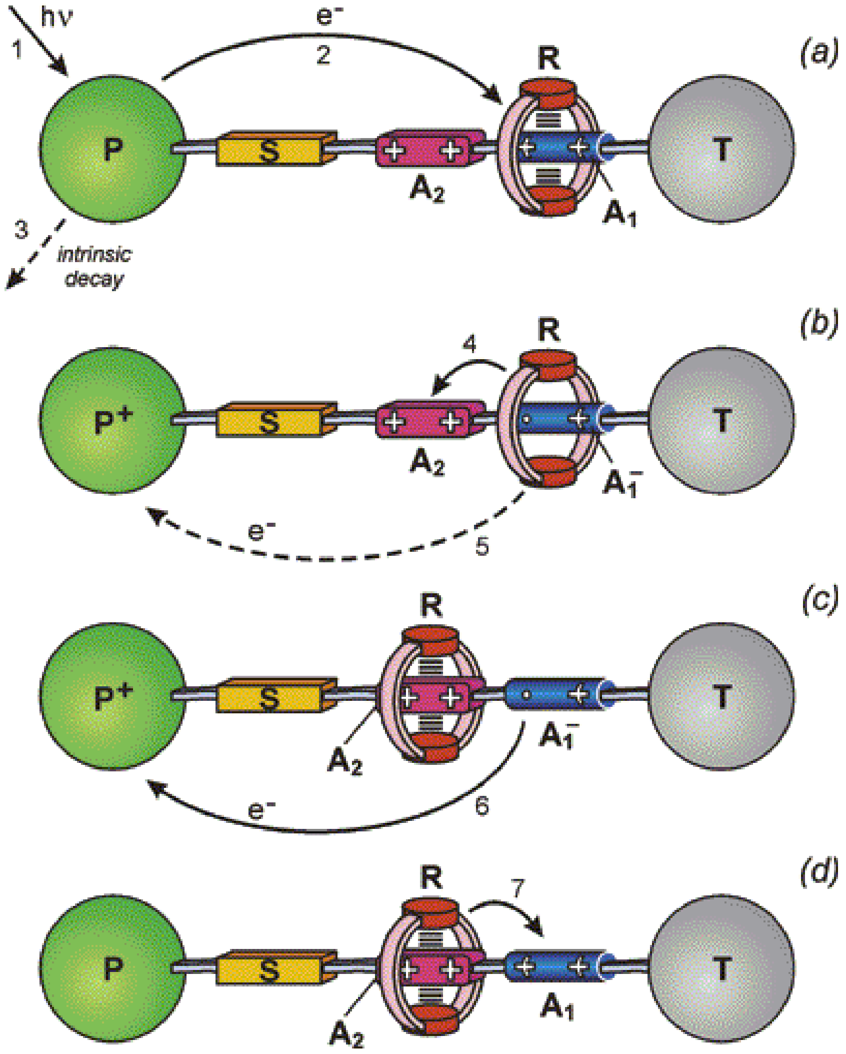
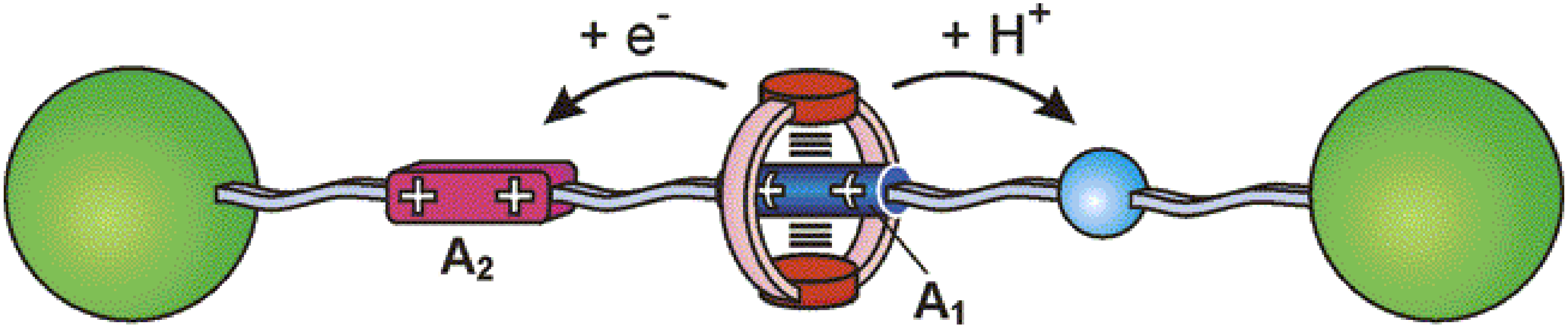


Directionality

A three-station rotaxane in which the direction of ring displacement is determined by the selected input.



The **A_1** and **A_2** stations can be a 4,4'-bipyridinium and a 3,3'-dimethyl-4,4'-bipyridinium unit, respectively. Depending on the sequence in which the three stations are assembled, a suitable macrocyclicpolyether component can be moved along the thread according to predetermined patterns.

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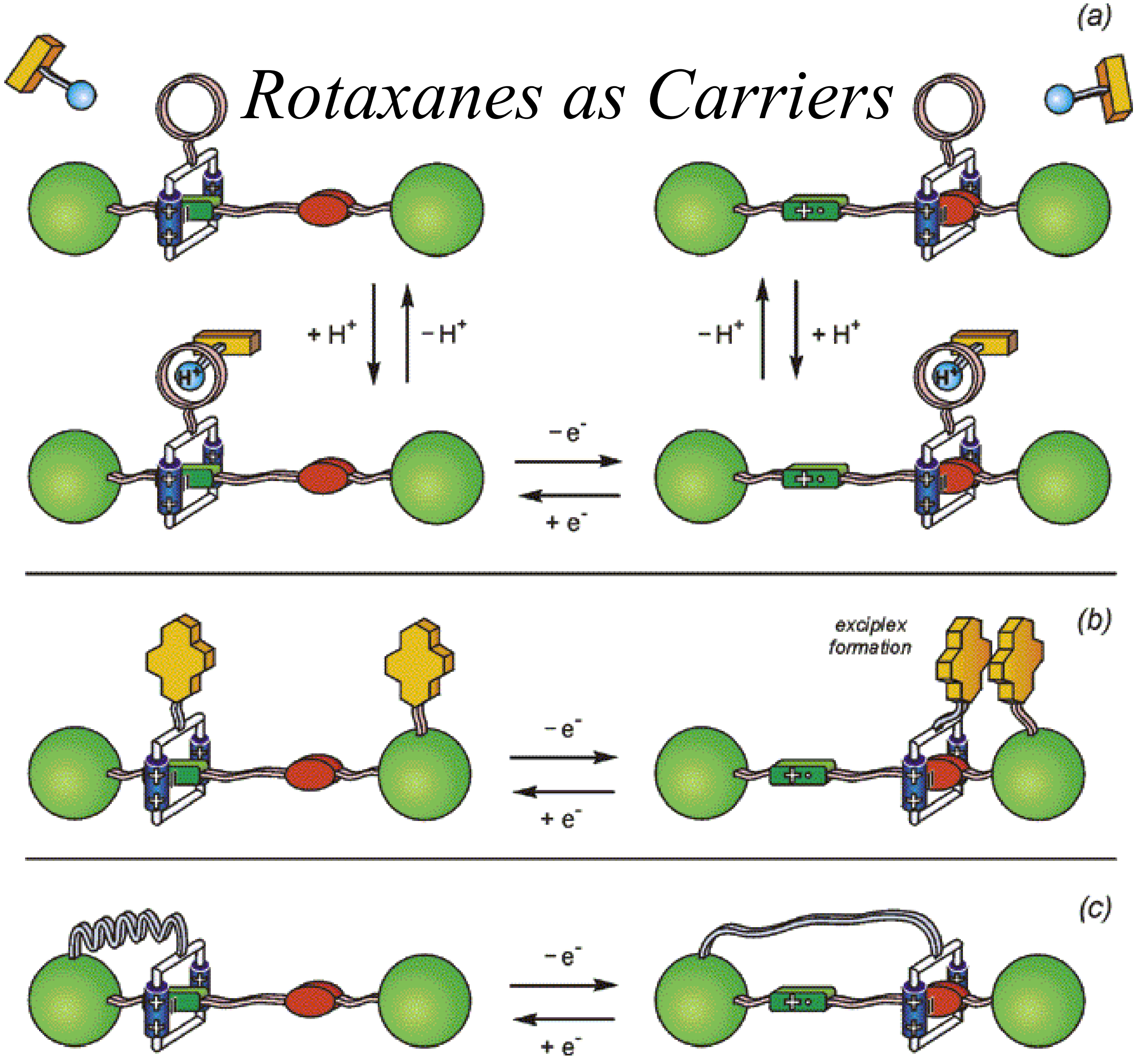
Rotaxanes as Carriers



A rotaxane carrier powered by electrochemical inputs designed to perform (a) transport of an amine, (b) formation of an exciplex, and (c) stretching of a molecular spring.

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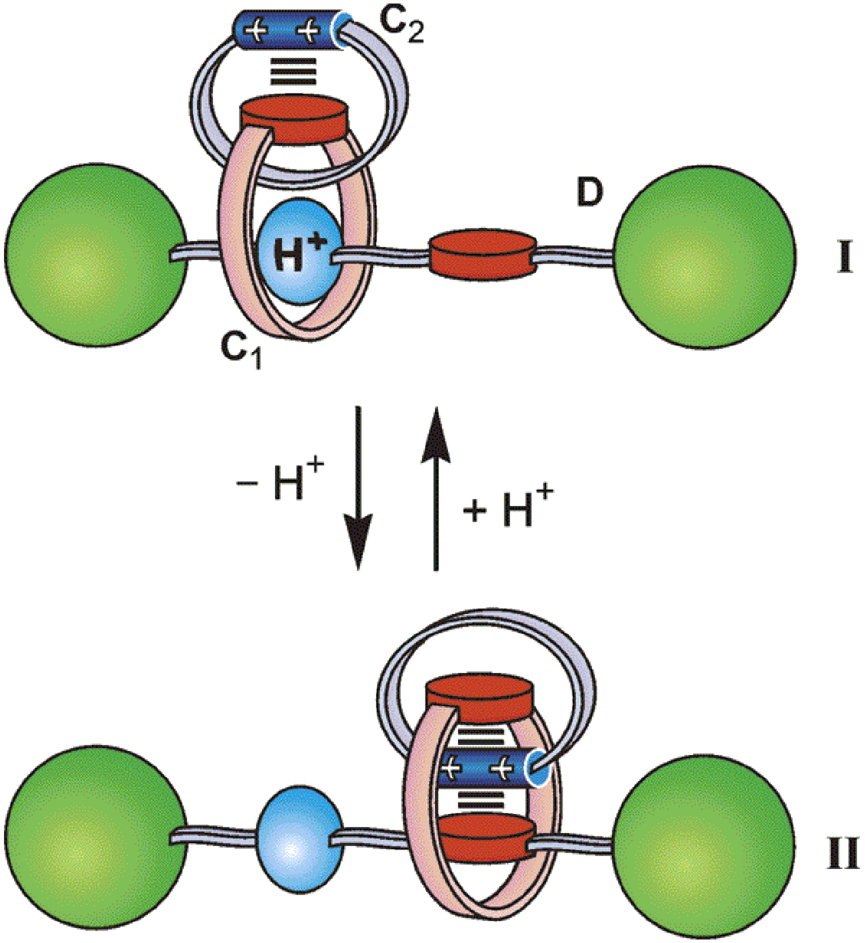
Rotaxane as Molecular Gears



A rotacatenane designed to couple linear and rotary motions under acid/base stimuli.

Acc. Chem. Res., **34** (6), 445 -455, 2001

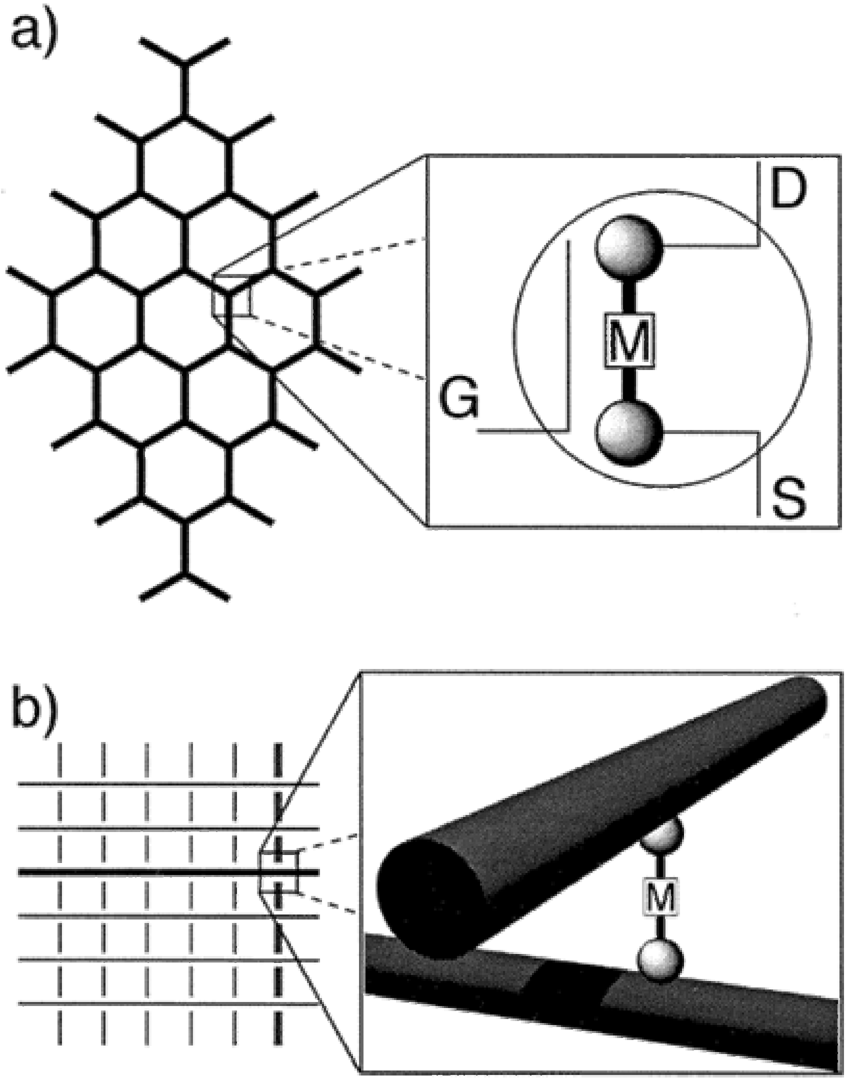
Device Architectures

Two possible device architectures that tile in two dimensions and so may potentially be fabricated through chemical techniques.

(a) Three-terminal devices (transistors) arranged in a hexagonal lattice

(b) two-terminal devices arranged in a square lattice or crossbar structure.

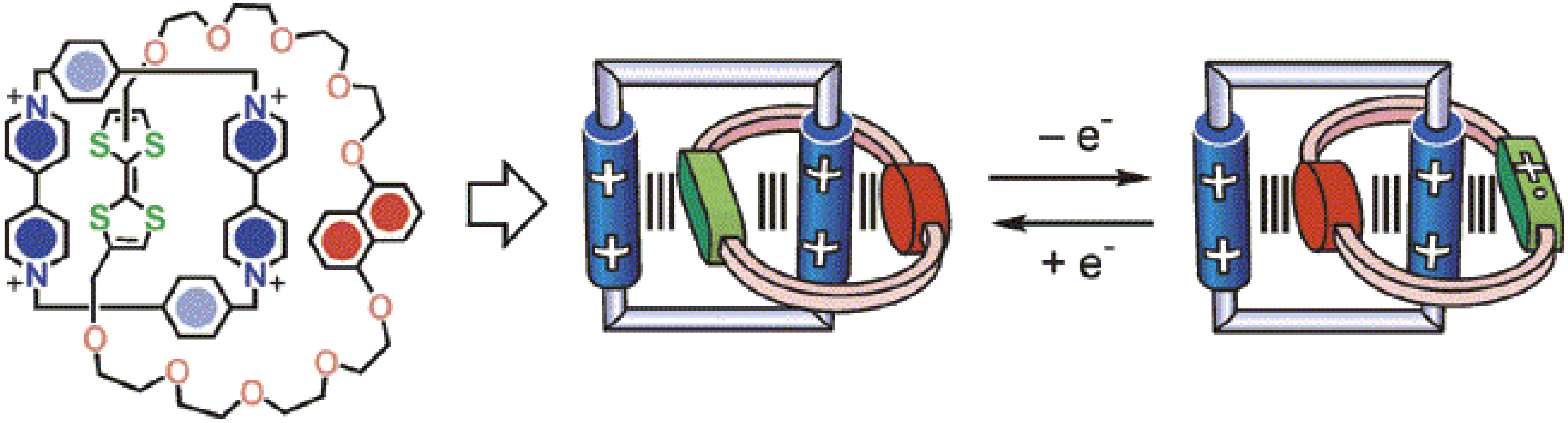
G, S, and D represent the gate, source, and drain terminals of a field effect transistor; M stands for a molecule.



Acc. Chem. Res., **34** (6), 433-444, 2001

Molecular Switches - Catenanes

Electrochemically controlled movements upon one-electron oxidation/reduction of a TTF unit in a catenane containing a nonsymmetric ring.



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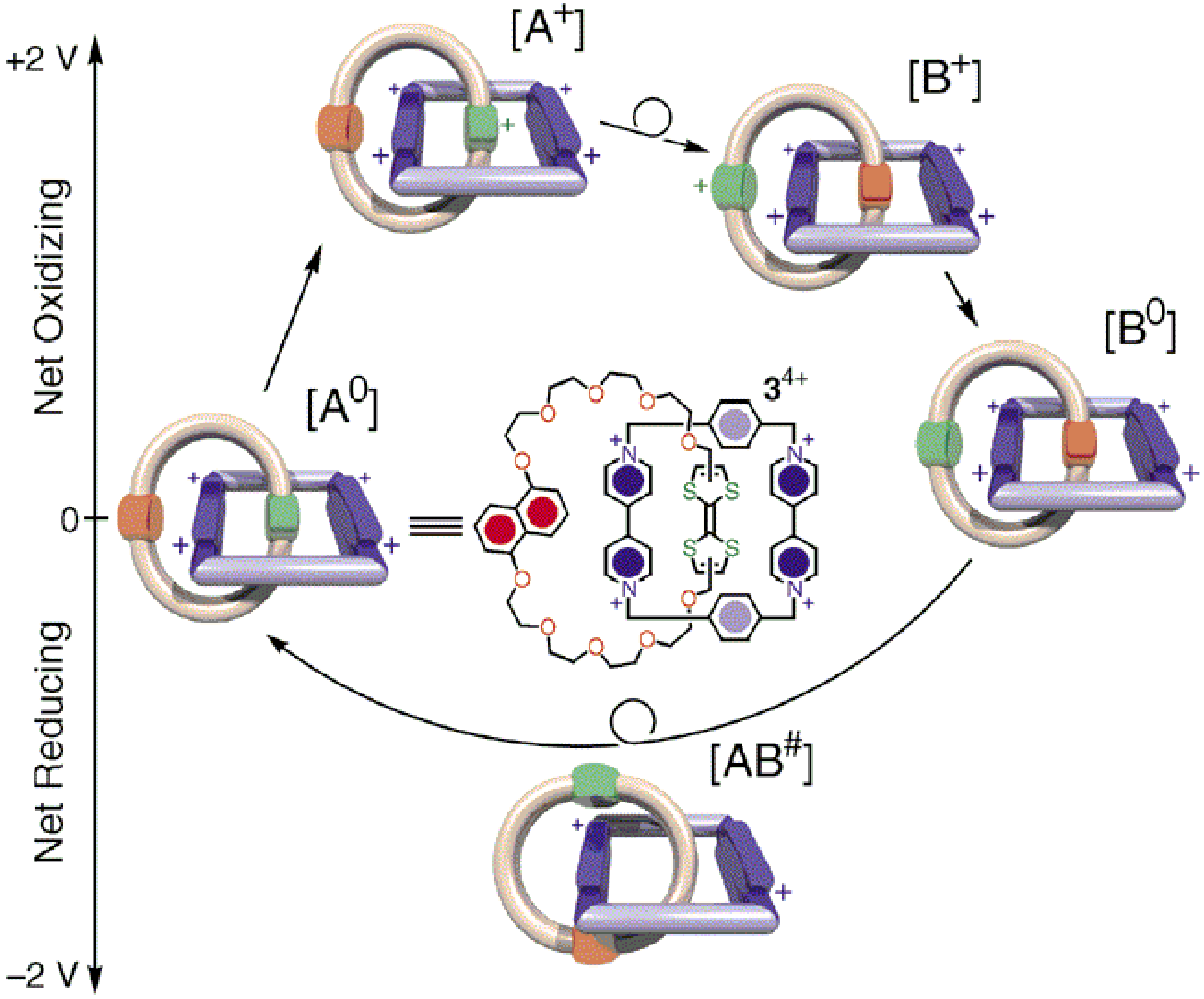
Mechanomechanical Mechanism



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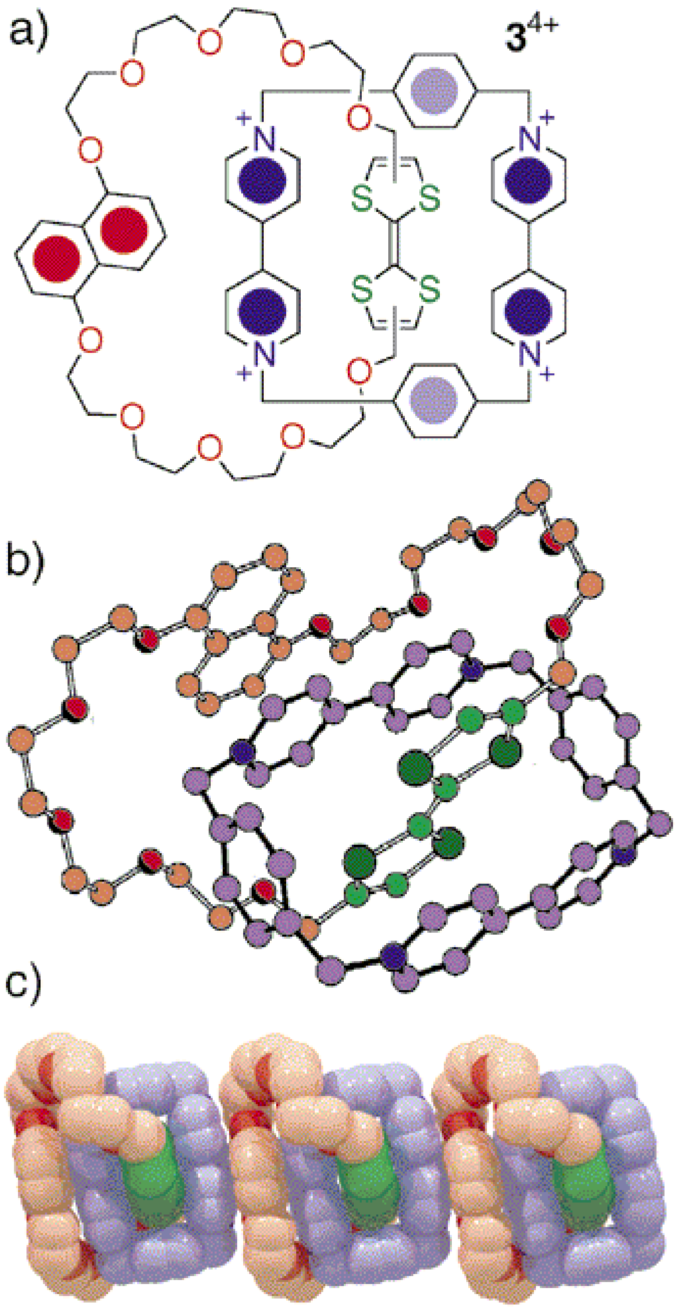
Electroswitchable Catenane

(a) Structural formula of the [2]catenane $\mathbf{3}^{4+}$.

(b) Ball-and-stick representation of the catenane's solid-state structure showing the TTF unit of the crown ether residing inside the CBPQT^{4+} component.

(c) Space-filling representation of its solid-state superstructure.



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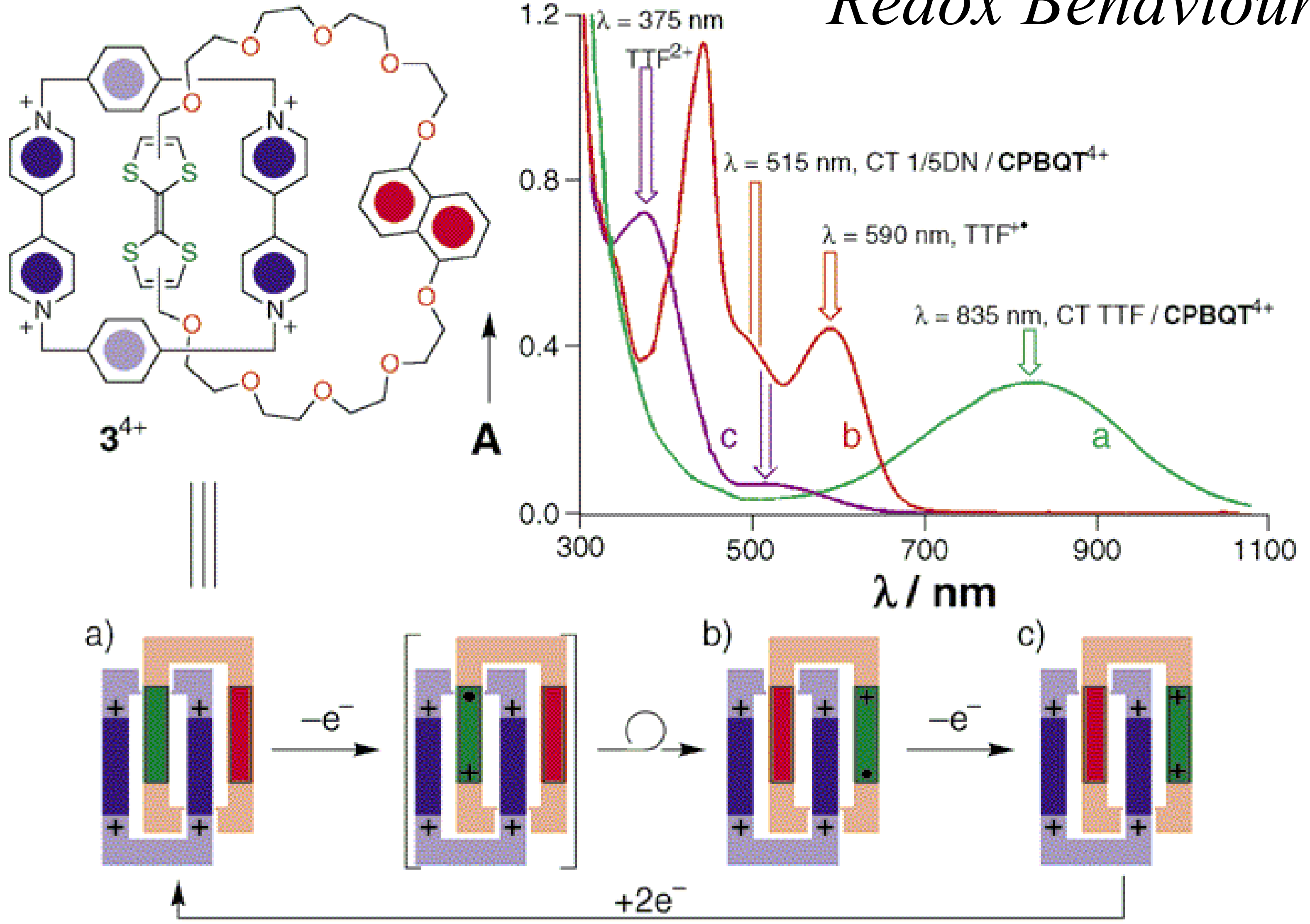
Redox Behaviour



UV-vis spectroscopic evidence for the redox switching of the [2]catenane **3**$^{4+}$. (a) Spectrum of the catenane prior to addition of (b) 1 equiv of $Fe(ClO_4)_3$ followed by (c) a second equivalent of $Fe(ClO_4)_3$. Oxidation is reversed on addition of 2 equiv of ascorbic acid.

Acc. Chem. Res., **34** (6), 433-444, 2001

Redox Switch Device Construction

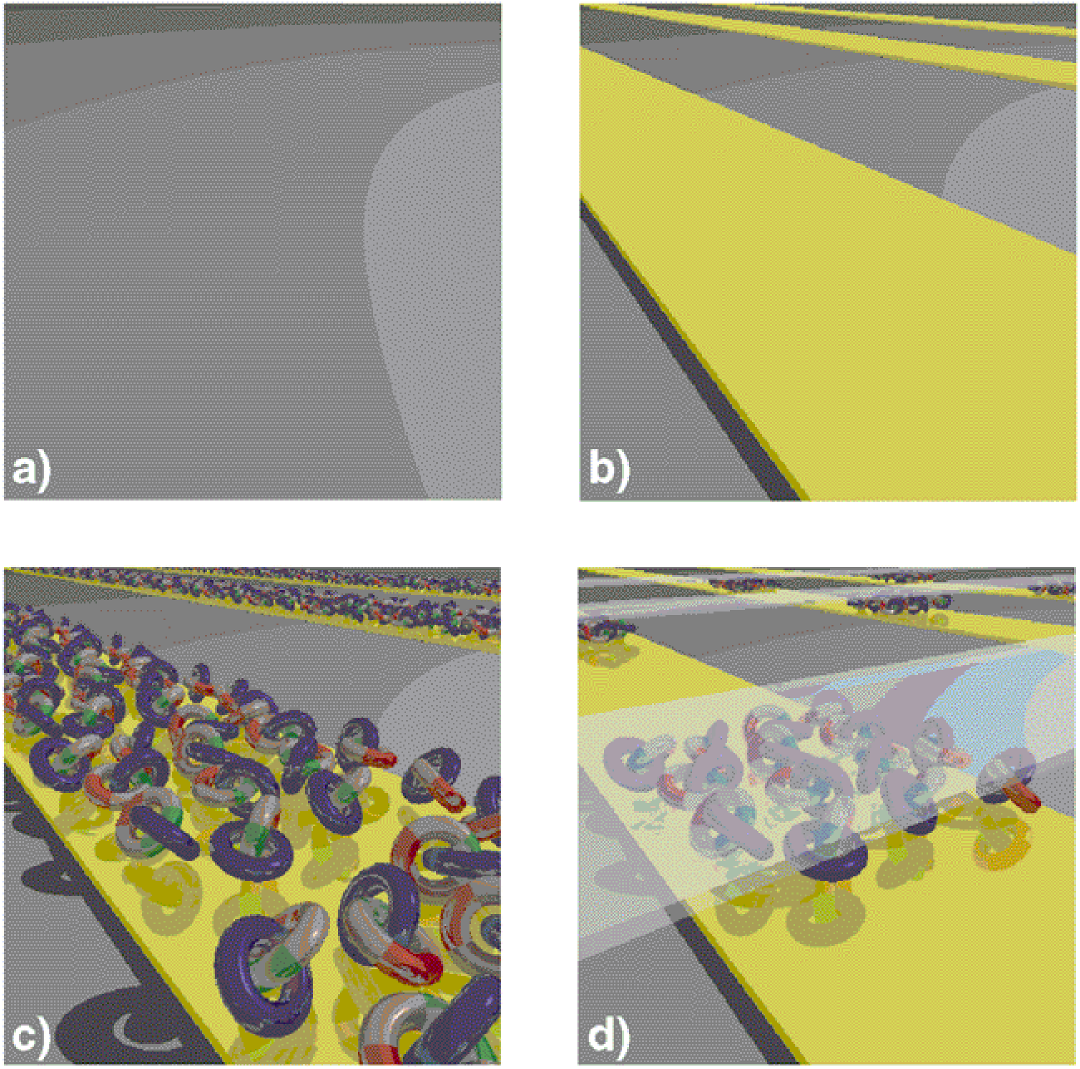
Construction of a molecular-based device.

(a) A smooth silicon substrate.

(b) A series of parallel polysilicon wires etched onto the substrate photolithographically.

(c) Following deposition of the catenane monolayer onto the wafer by a LB procedure.

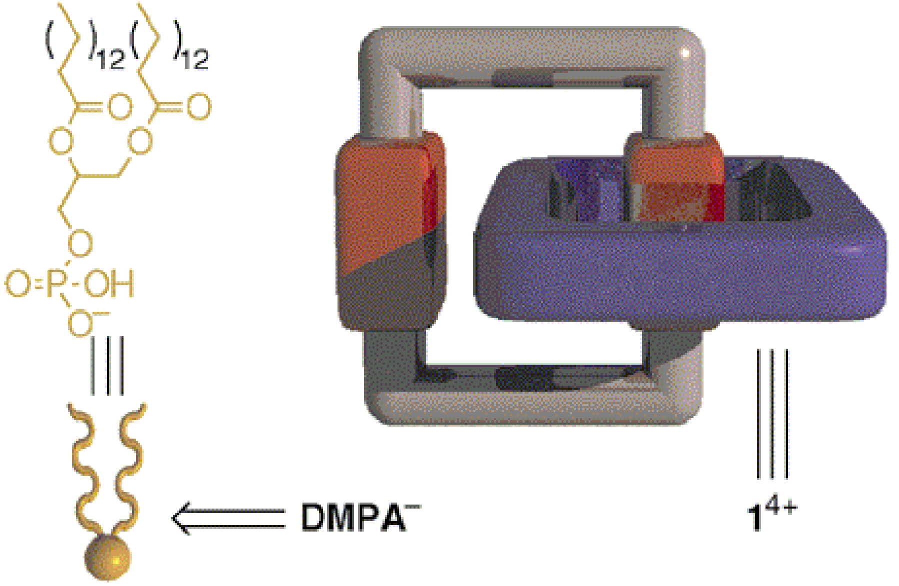
(d) The result when titanium vapor is condensed through a shadow mask, depositing a second layer of wires aligned perpendicularly with respect to the first.

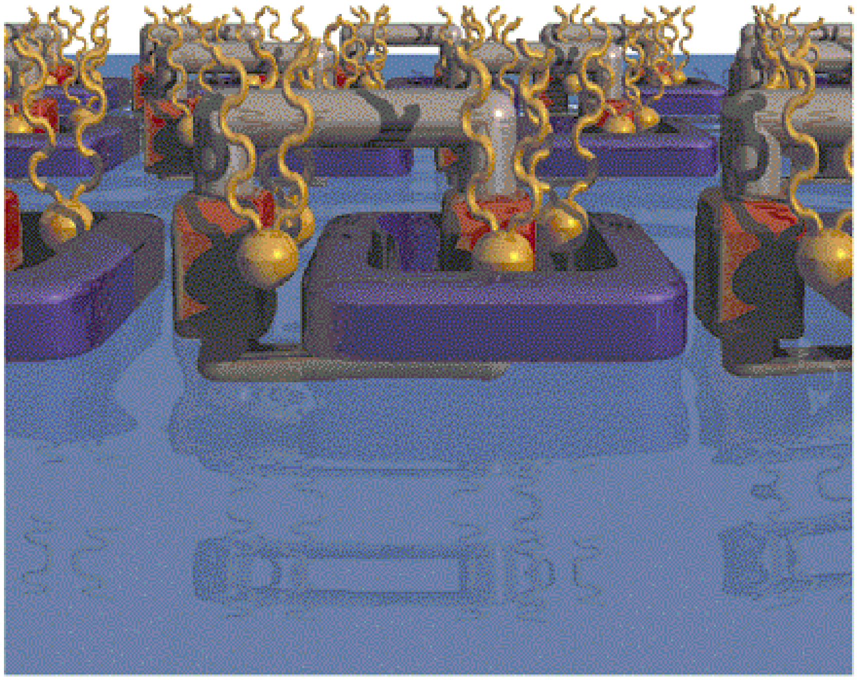


Acc. Chem. Res., **34** (6), 433-444, 2001

Redox Switch SAM

Schematic representation of the monolayer of **1**$^{4+}$·4DMPA at the air-water interface. Note the intermolecular π-π stacking interactions between the catenane tetracations.





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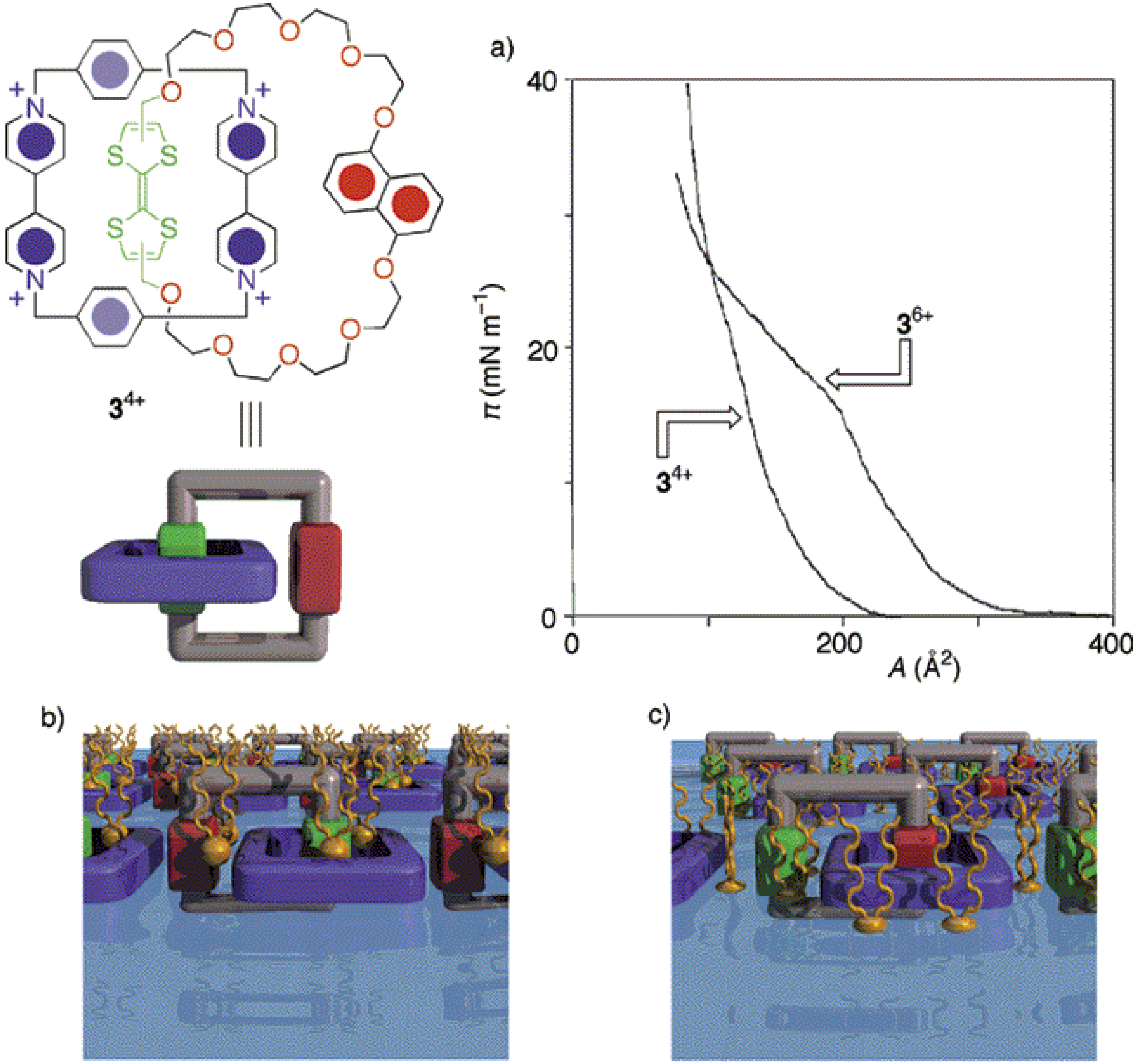
Redox Switch LB Behaviour



(a) π-A isotherms of monolayers of the [3]catenane **3**$^{4+}$ and its oxidized derivative **3**$^{6+}$ anchored with 4 and 6 equiv of DMPA$^-$ anions, respectively.

(b) Schematic representation of the monolayer of **3**·4DMPA stabilized by extensive π-π interactions.

(c) Schematic depiction of the first stable monolayer formed by **3**·6DMPA. The dicationic TTF units show no affinity for the neighboring catenane hexacations, and so the six DMPA$^-$ anions fill the voids in the monolayer.

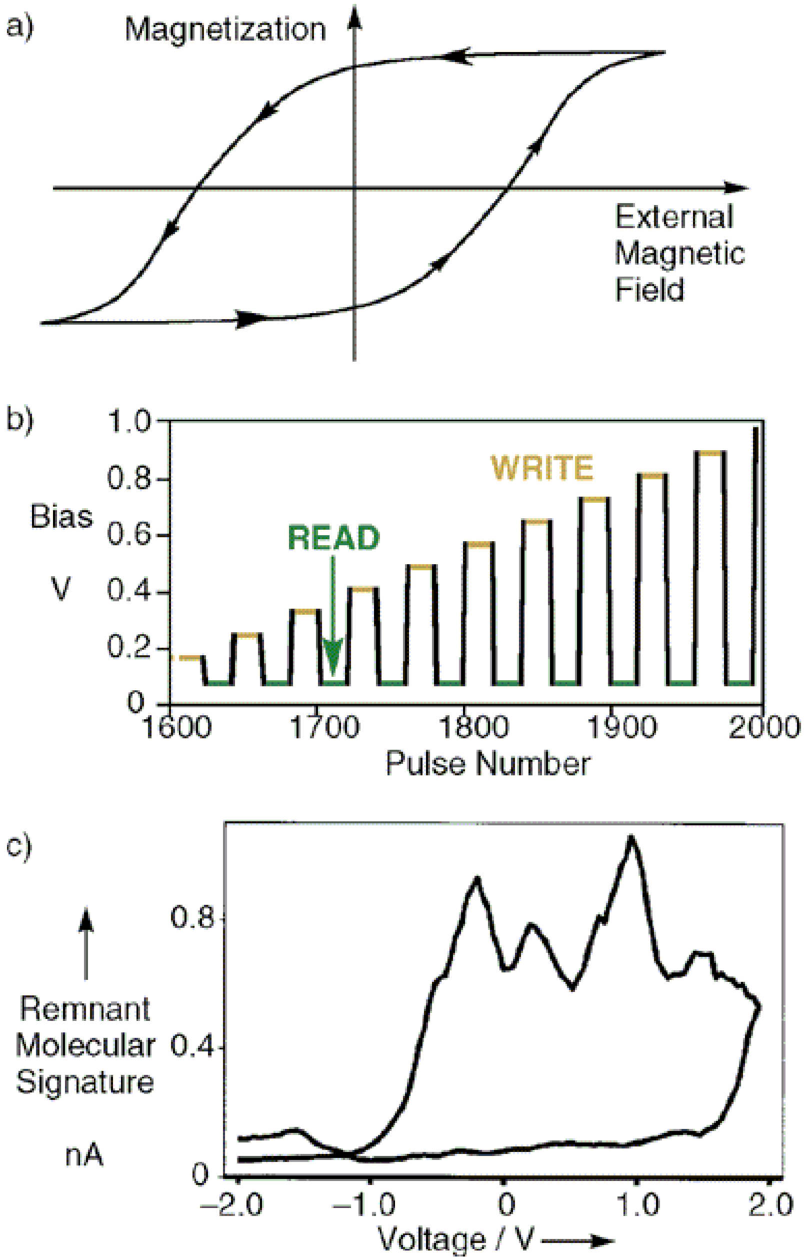
Acc. Chem. Res., **34** (6), 433-444, 2001

Redox Switch SAM - Hysteresis

(a) Hysteresis curve associated with a conventional magnetic memory bit.

(b) Voltage profile used in the acquisition of

(c) the remnant molecular signature of a device incorporating the switchable [2]catenane **3**$^{4+}$.

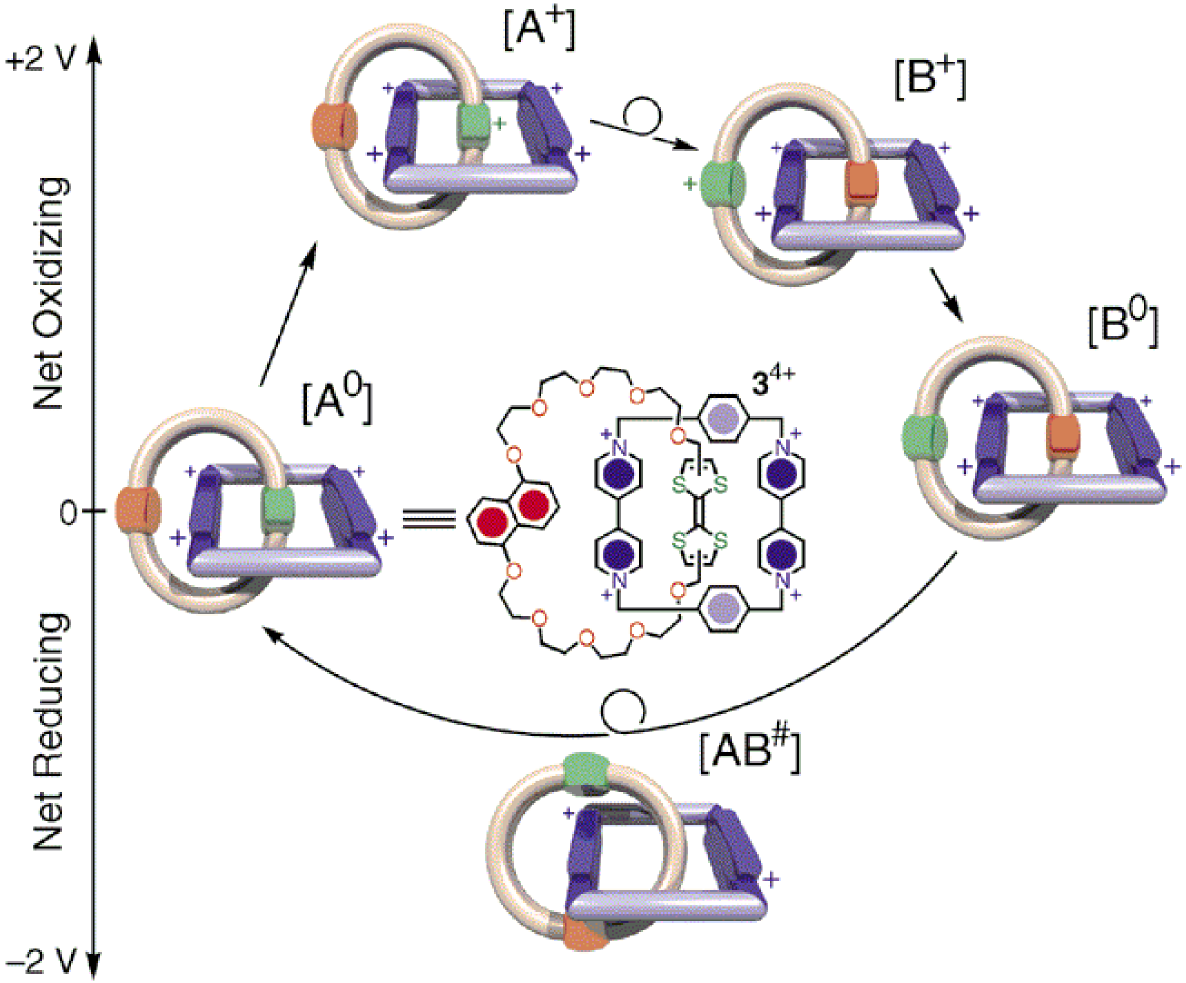


The device response was monitored at 0.1 V (b). Robust and significant hysteresis (c) was observed in the bistable [2]catenane, but not in the control devices, indicating that the bistable [2]catenane device is, in fact, a solid-state molecular switch. It exhibited a "read" current difference between the open and closed states of approximately a factor of 3, a "close" voltage of about 1.8 V, and an "open" voltage of about -1.0 V. The bistable [2]catenane device was fairly stable. It was intermittently cycled many times over a two-month period before it showed signs of failure.

Acc. Chem. Res., **34** (6), 433-444, 2001

Mechanoechanical Mechanism

Proposed mechanochemical mechanism for the operation of the device fabricated from the bistable [2]catenane $\mathbf{3}^{4+}$. Co-conformation [A^0] is the "switch open" state and co-conformation [B^0] the "switch closed" state of the device. When $\mathbf{3}^{4+}$ is oxidized, the TTF unit is ionized in state [A^+] and experiences a Coulomb repulsion inside the $CBPQT^{4+}$ component, resulting in circumrotation of the crown ether and formation of co-conformation [B^+]. When the voltage is reduced to near-zero bias, the TTF^+ unit is reduced to give co-conformation [B^0], which does not return to co-conformation [A^0] by further circumrotation of the crown ether ring via state [$AB^\#$] until the cyclophane component is reduced.



Acc. Chem. Res., **34** (6), 433-444, 2001