Supramolecular Chemistry of Nanomaterials

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Lecture 2 – Self-assembly

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Topics to be covered in the course:

1 - Introduction (definition of terms, etc.)
2 – Self-assembly
3 – Nano-capsules for delivery and reactions
4 – Supramolecular Switches
5 – Molecular Machines
6 – Self assembly on surfaces
7 – Supramolecular chemistry of polymeric materials

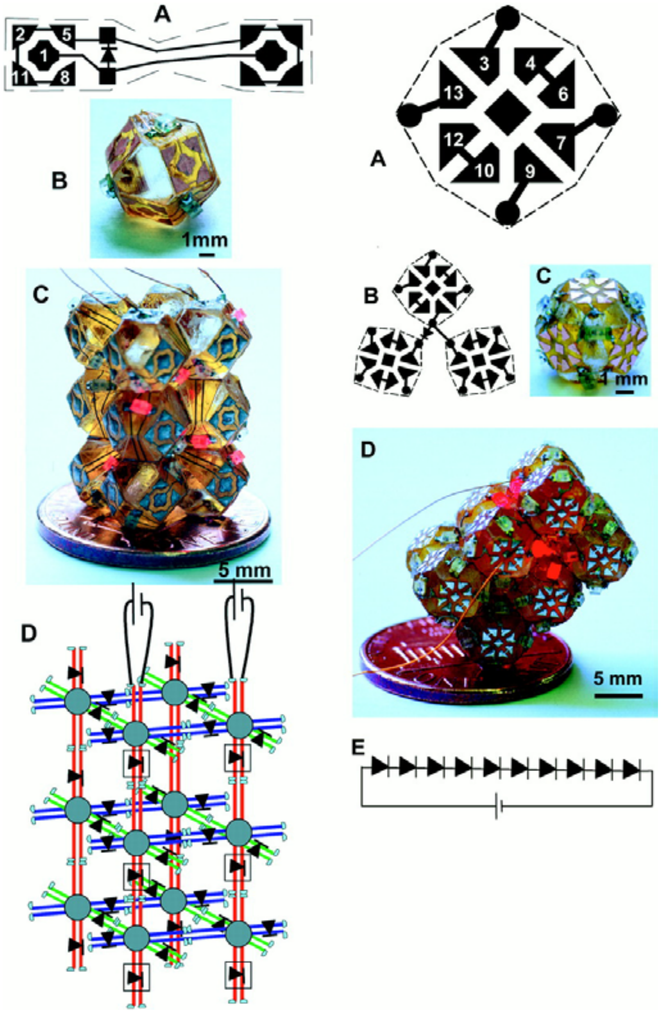
Self-assembly

- Non-metal involving strategies
  - Solution
    - Rotaxanes
    - Catenanes
    - Other interlocked molecules
    - 1-dimensional structures
  - Solid state
    - Monolayers
    - 3-dimensional structures

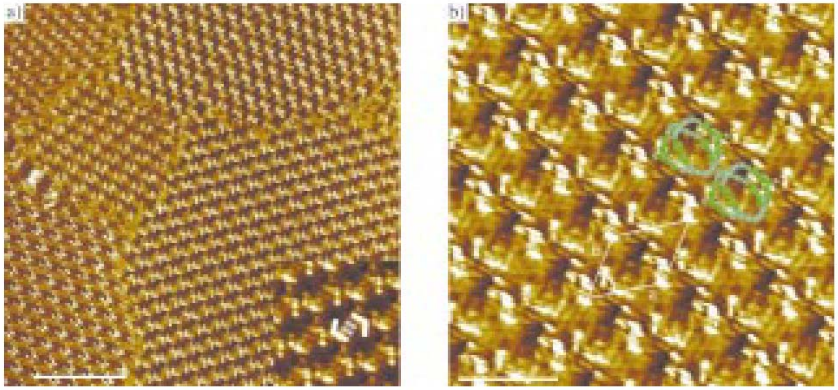
Literature

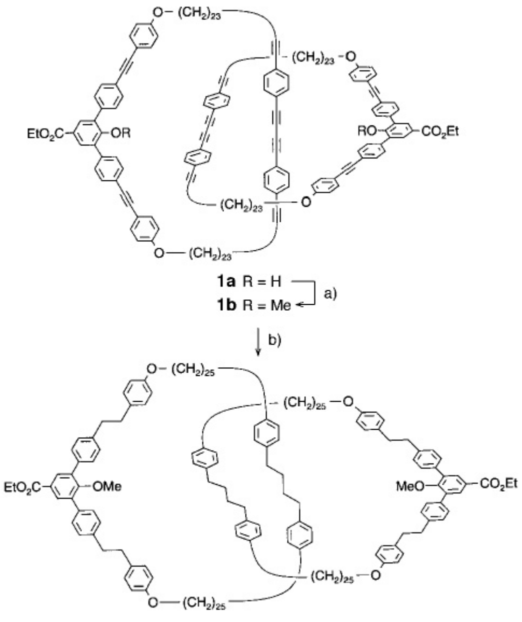
- Acc. Chem. Res. 2001, 34 (6).
- Proc. Natl. Acad. Sci. U.S.A. 2002, 99 (8).

Self-assembly



Science Aug 18 2000: 1170-1172.





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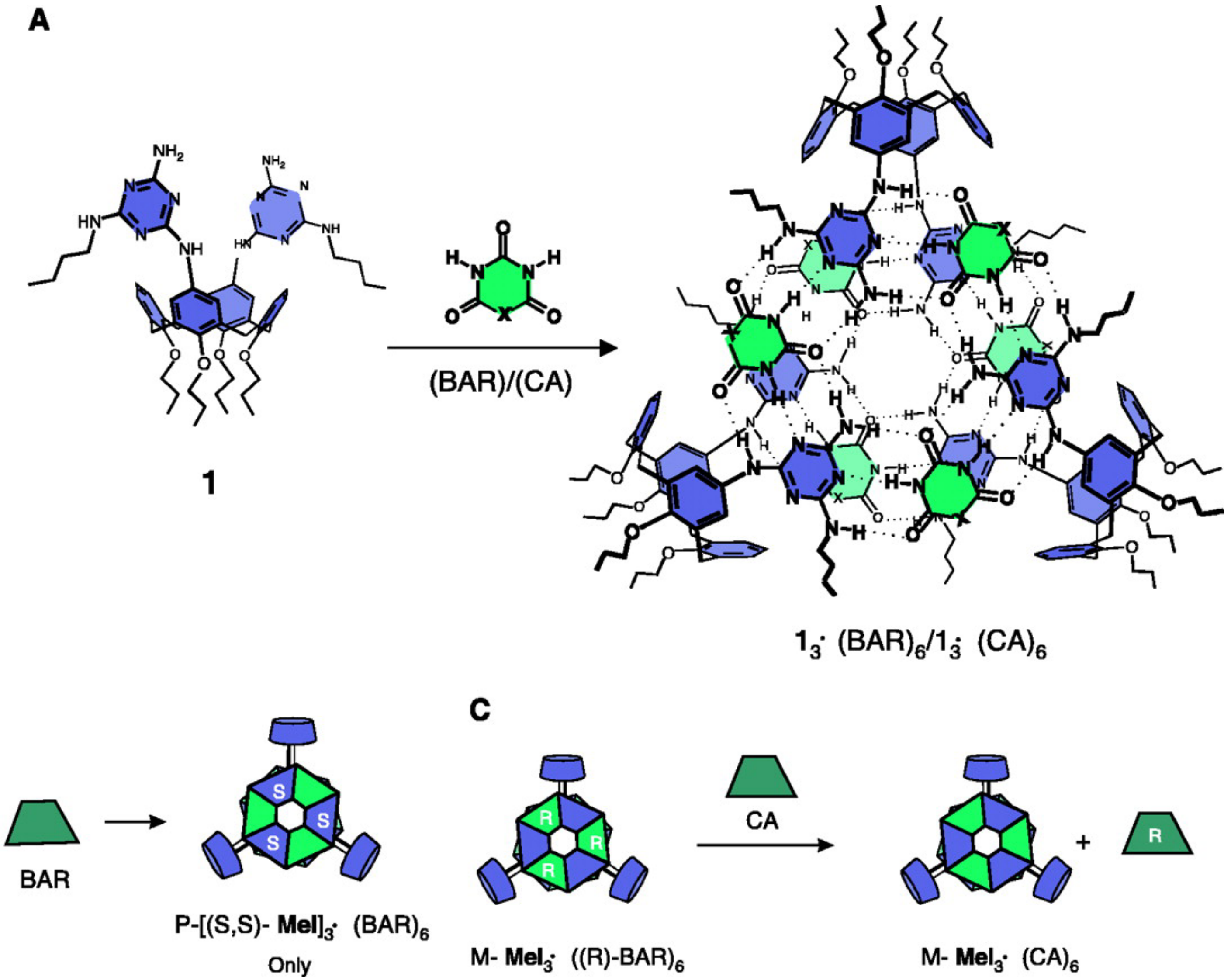
CHEMPHYSCHEM 2001, 2, 462

Chiral Hydrogen Bond Assemblies (Reinhoudt)



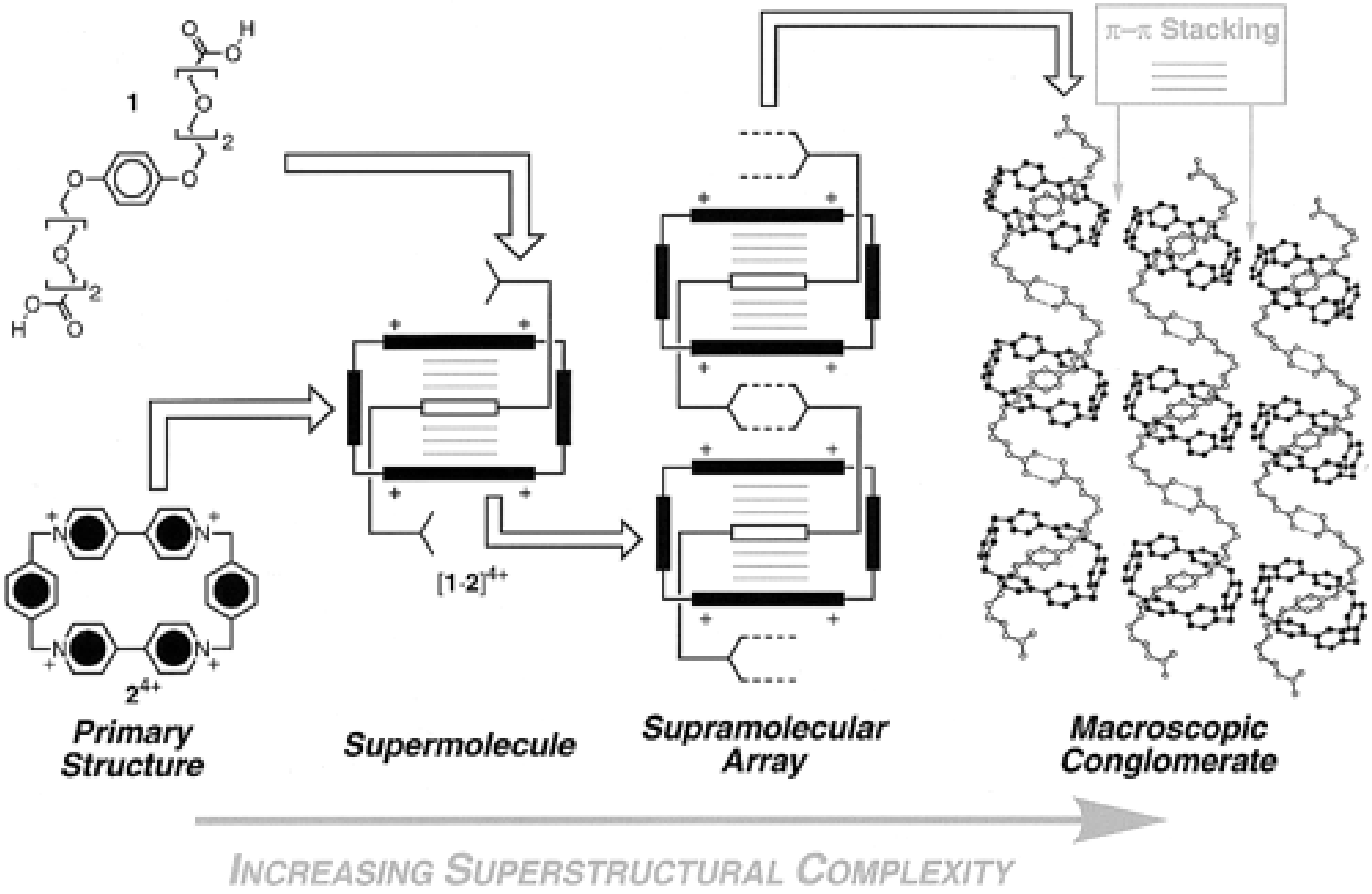
(**A**) Formation of noncovalent chiral assemblies with general composition $\mathbf{1}_3 \cdot (\mathrm{DEB})_6$ and $\mathbf{1}_3 \cdot (\mathrm{CA})_6$.

(**B**) Schematic representation of diastereoselective noncovalent synthesis.

(**C**) Noncovalent synthesis of an enantiomerically pure hydrogen-bonded assembly.

Supramolecular Hierarchy

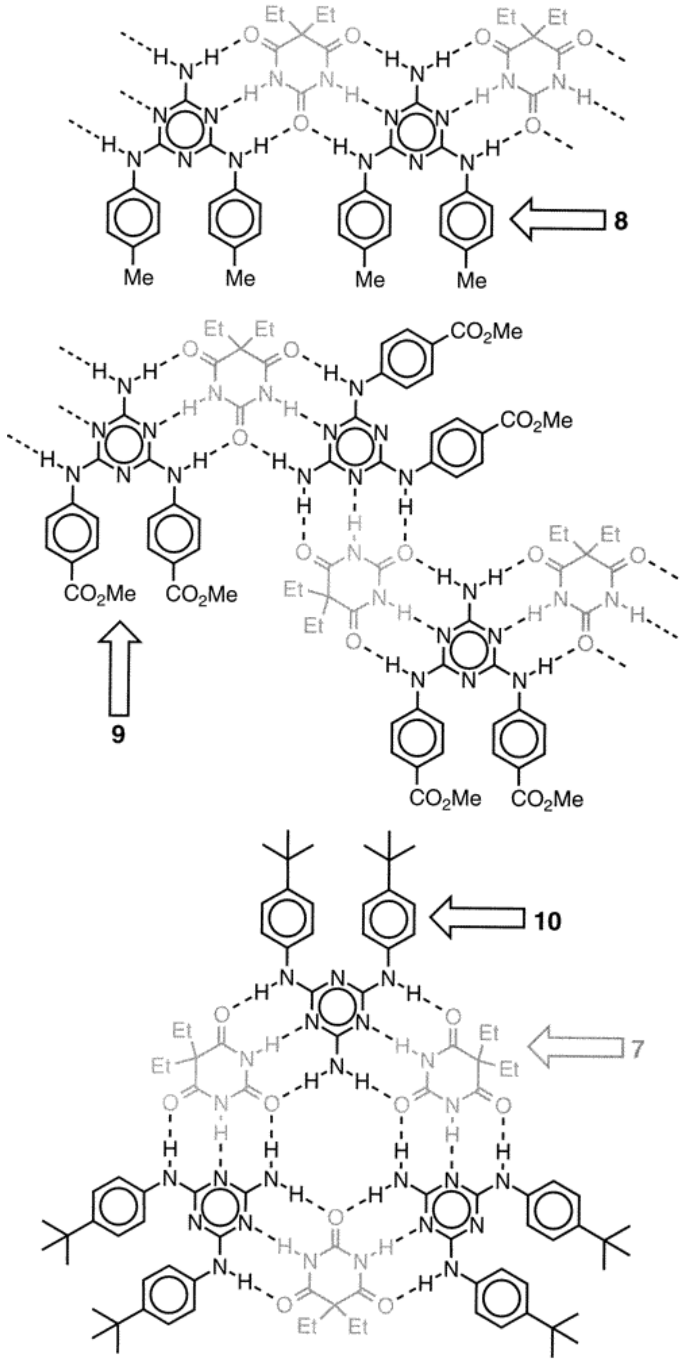
- Supramolecular hierarchy illustrated using rotaxane$[1{\cdot}2]^{4+}$



Acc. Chem. Res., **30** (10), 393 -401, 1997

Self-assembly of Molecular Sheets

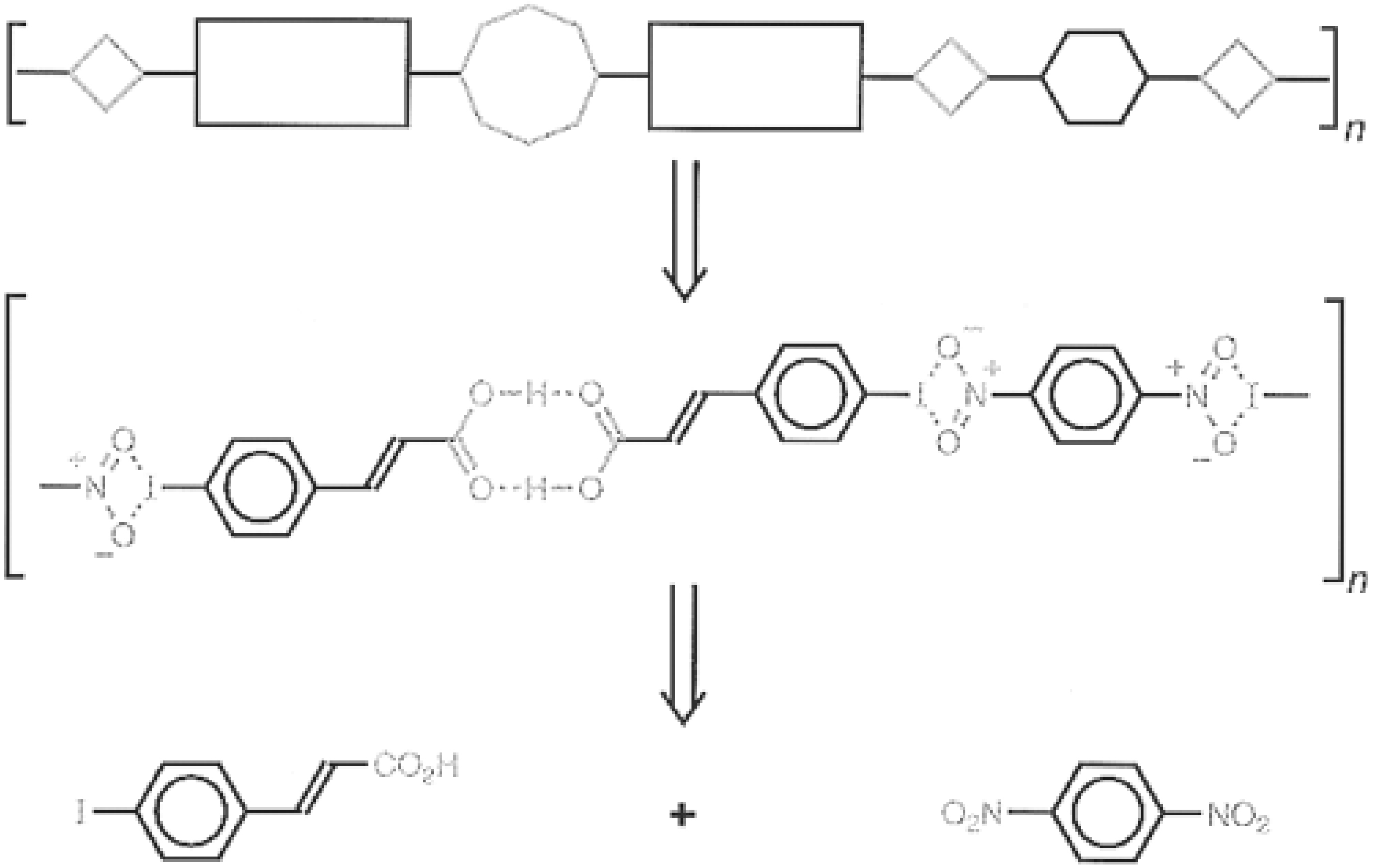
- Wide range of supramolecular architectures that can be created using the barbituric acid (gray)-melamine (black) couple.



Acc. Chem. Res., **30** (10), 393 -401, 1997

Linear Tape

- "Retrosynthetic Analysis"of the Linear Tape [11·12].



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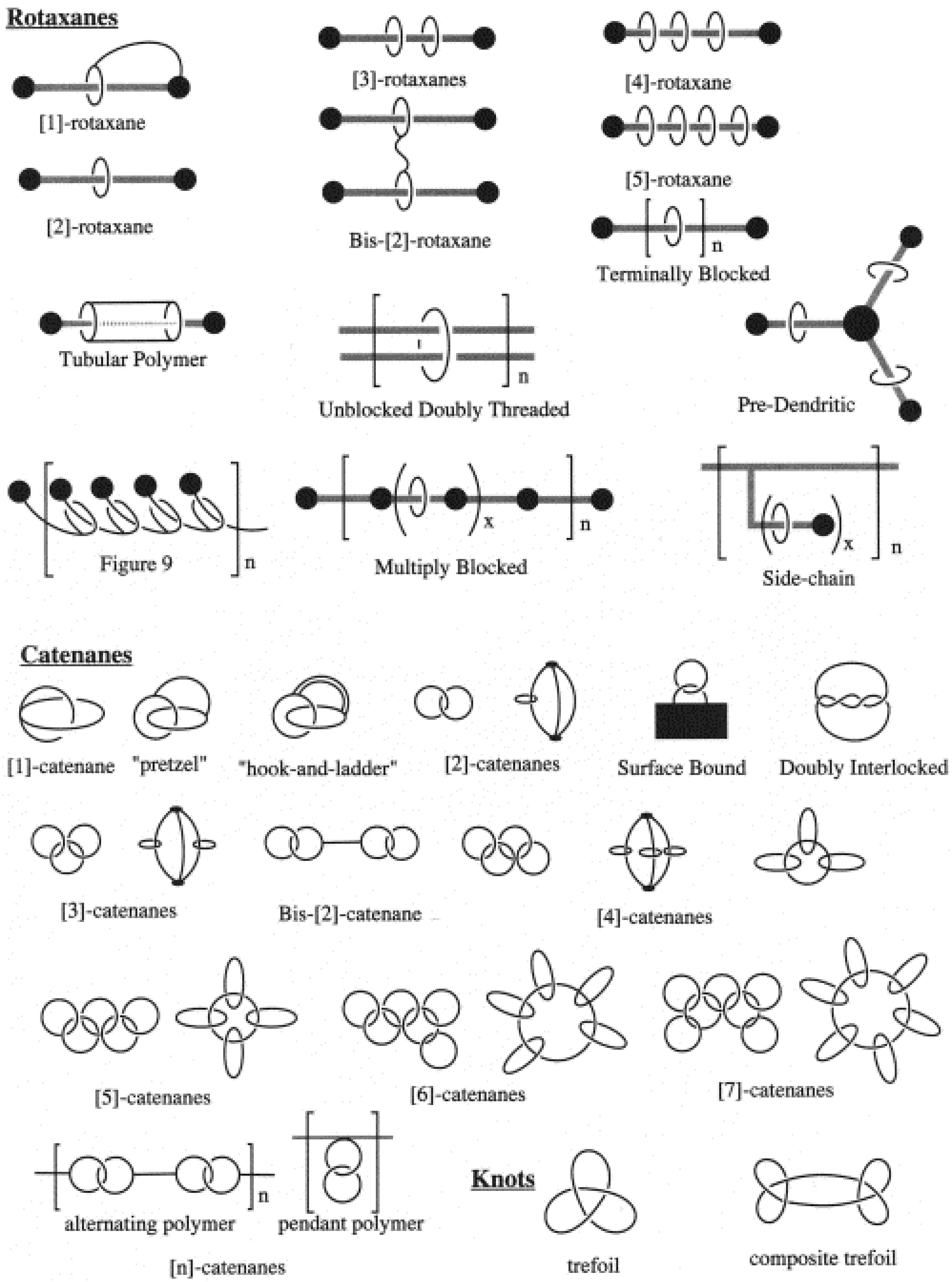
Acc. Chem. Res., **30** (10), 393 -401, 1997

Rotaxanes Catenanes and Knots

- The various interlocked structures which have resulted from template syntheses: rotaxanes, catenanes, and knots.

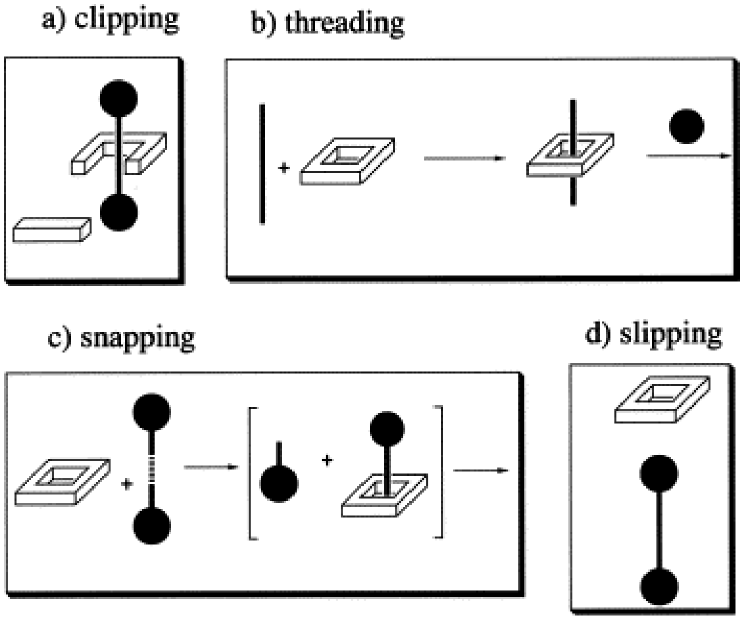


Coord. Chem. Rev. 2000, 200–202, 5–52

Synthetic Strategies for Rotaxanes

Various approaches to rotaxane formation

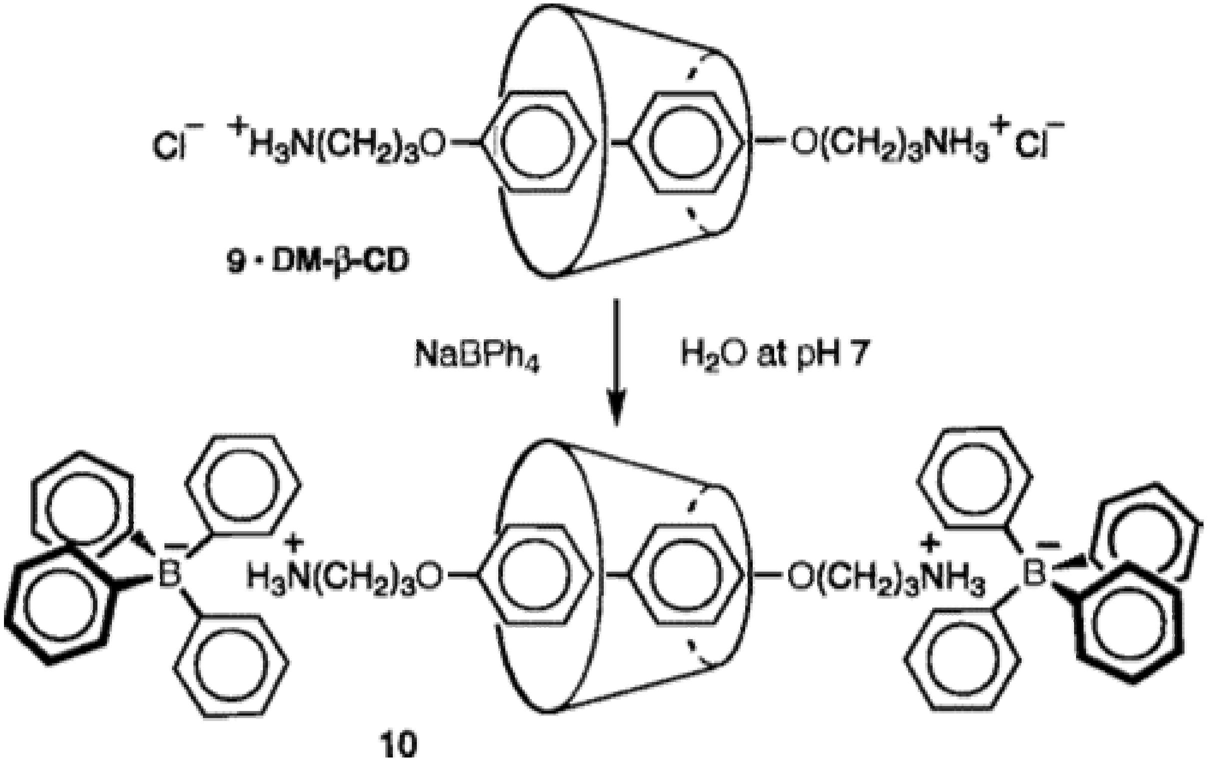
(a) clipping
(b) threading
(c) snapping
(d) slipping



Coord. Chem. Rev. 2000, 200–202, 5–52

Template Directed – Ionic Stoppering

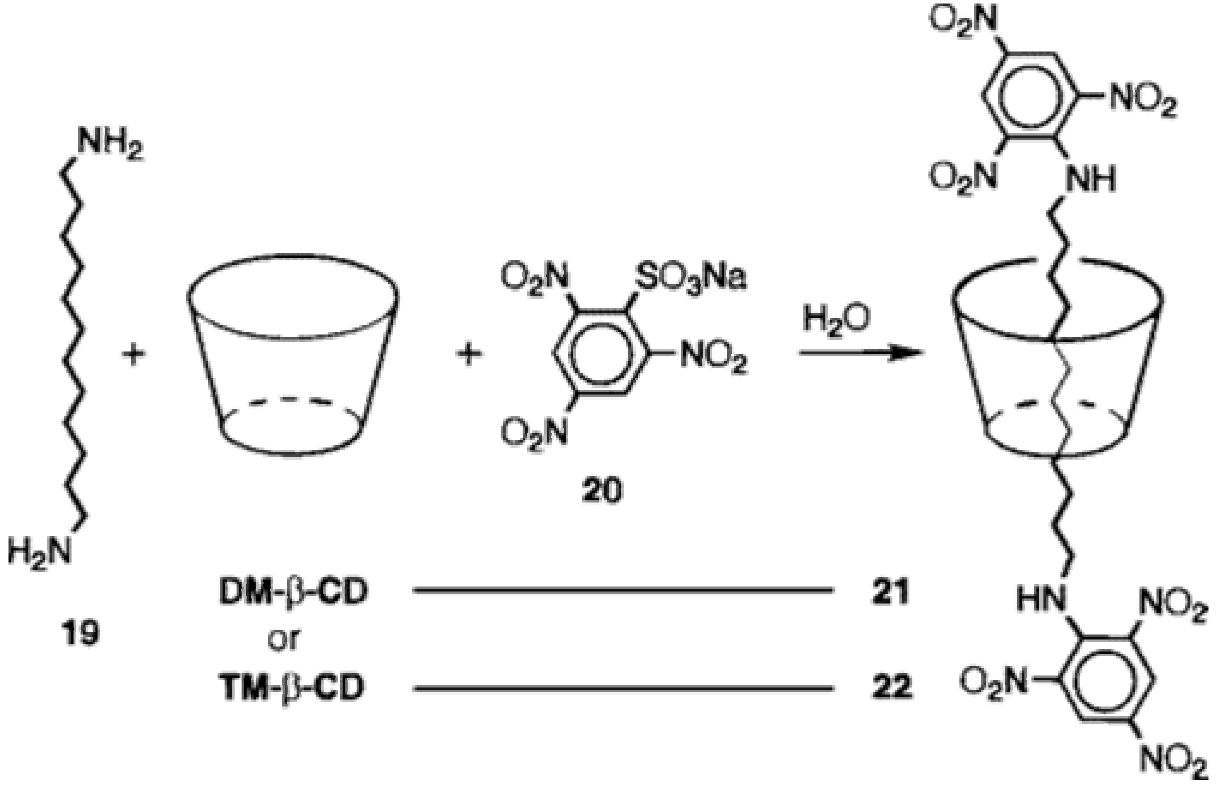
- Template-directed self-assembly of a [2]rotaxane in aqueous media.



Chem. Rev., **98** (5), 1959 -1976, 1998

Template Directed – Covalent Stoppering

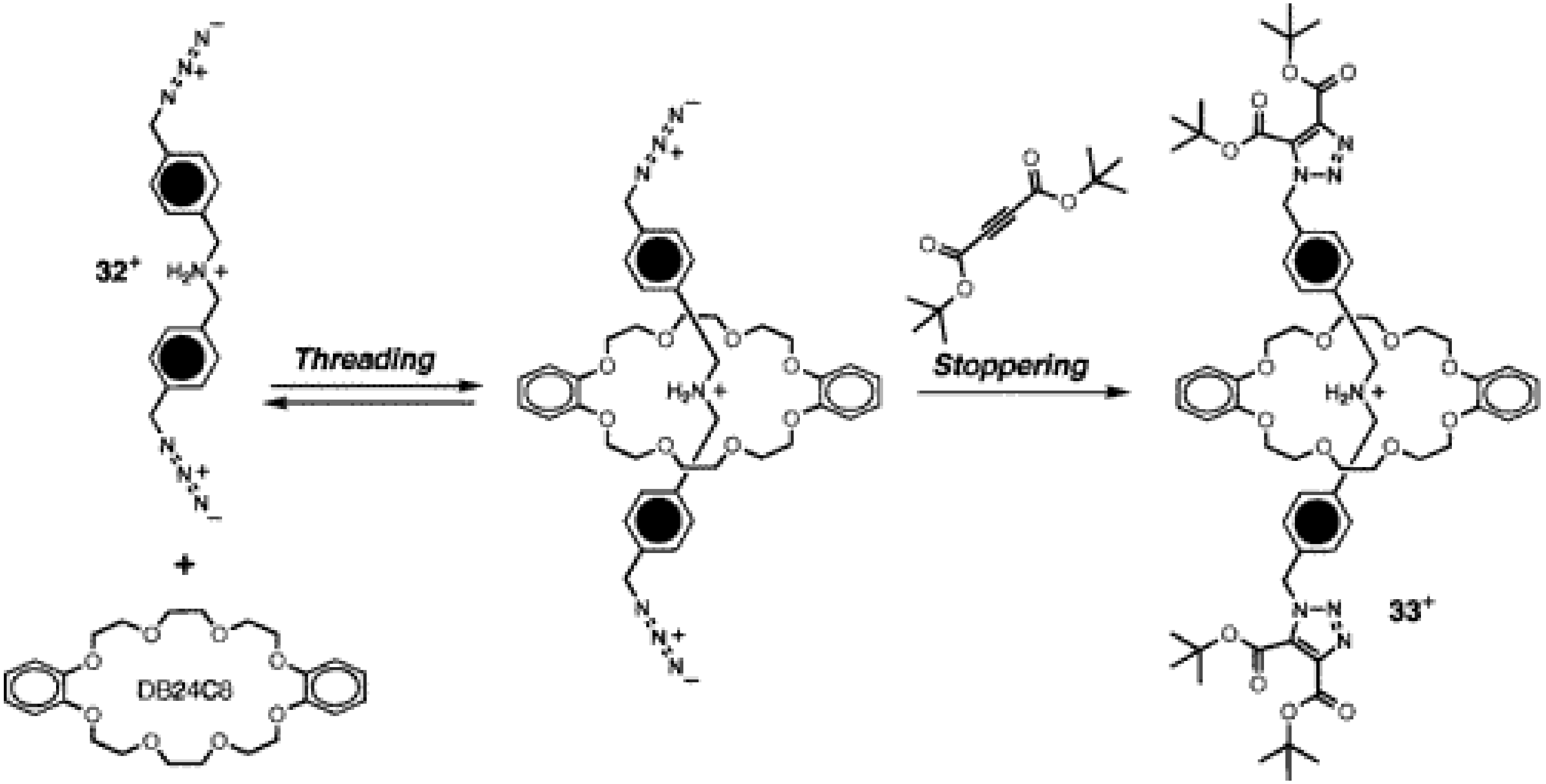
- Self-assembly of two [2]rotaxanes incorporating **DM-β-CD** and **TM-β-CD** in aqueous solution (1997!).



Chem. Rev., **98** (5), 1959 -1976, 1998

Templated Threading – Covalent Stoppering

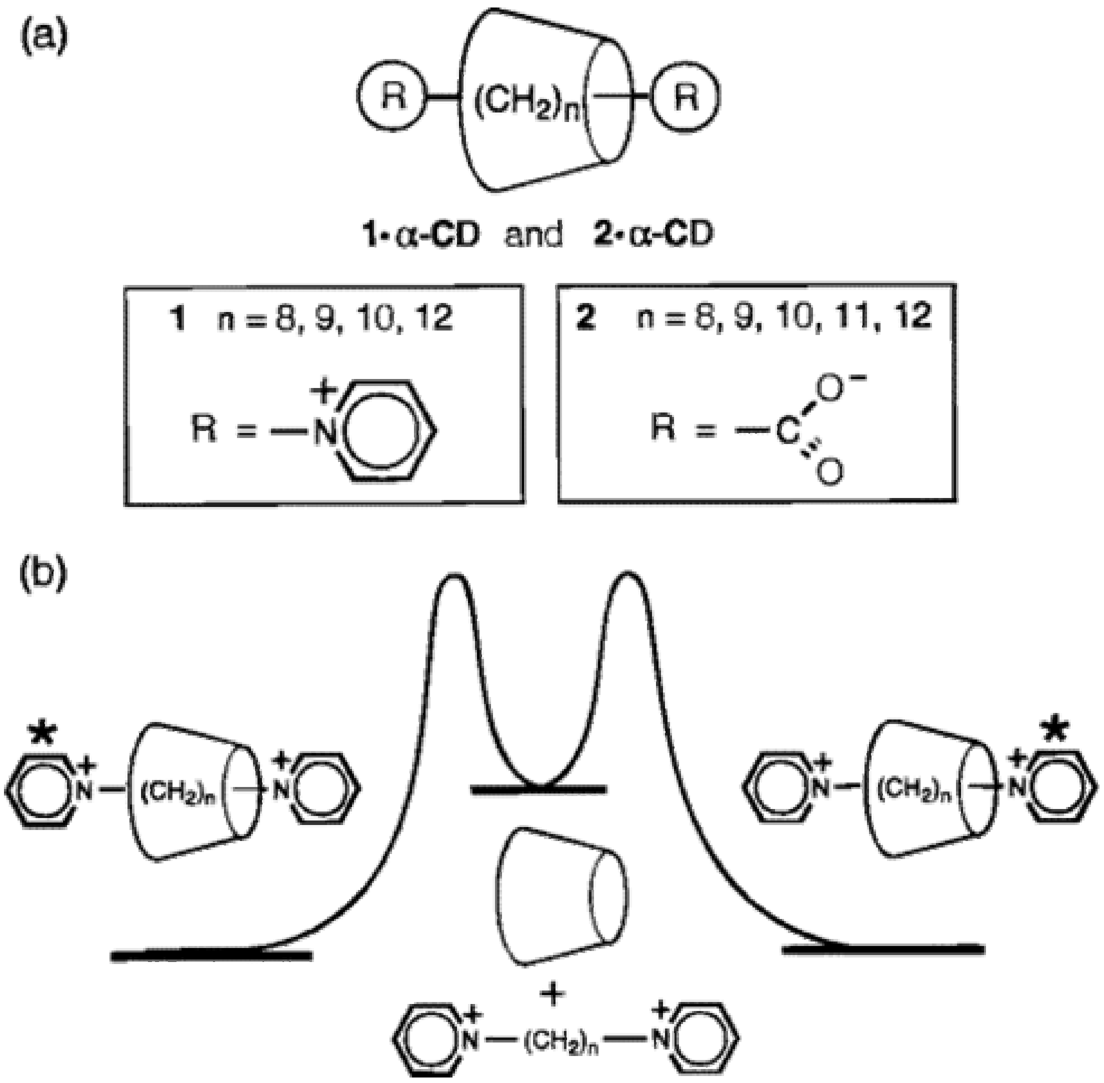
- Synthesis of the [2]rotaxane 33^+ via a "Threading-Followed-by-Stoppering" approach



Acc. Chem. Res., **30** (10), 393 -401, 1997

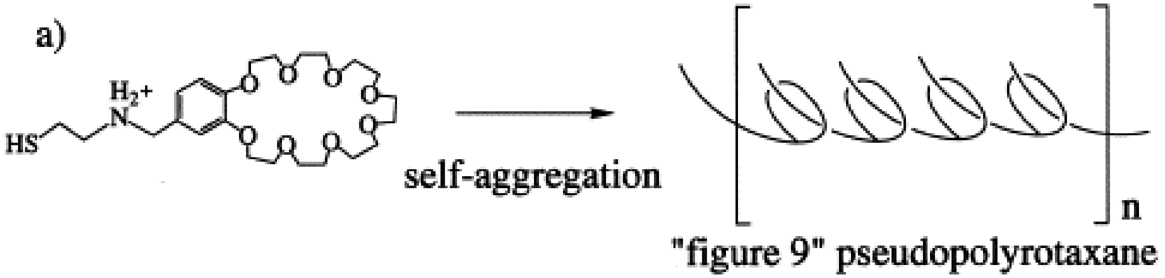
Influence of Spacer Length

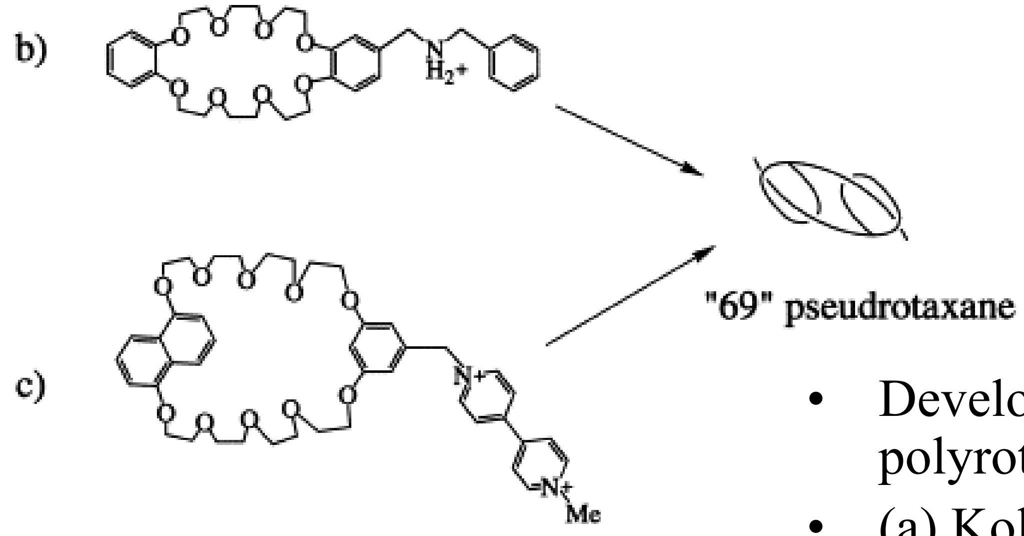
- (a) Pseudorotaxanes built up from **CD** and linear guests in the form of oligomethylene chains as binding sites.
- (b) Schematic representation of the energy profile for the complexation/decomplexation process for **CD** as it relates to the NMR site exchange process observed for the "symmetrical" guest bound within the cavity of the "unsymmetrical" **CD** ring.
- Free energy of activation for the site exchange process increases with the number (*n*) of CH_2 groups (*n* = 8-12) and reaches an asymptotic value at ca. 17.2 kcal mol^{-1}.

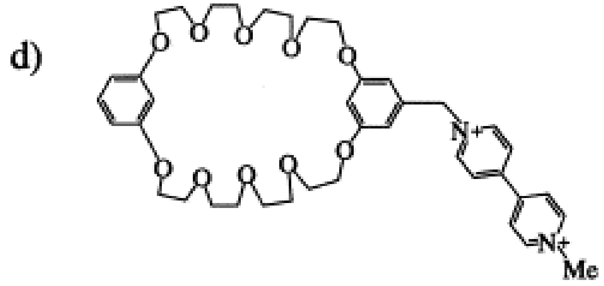


Chem. Rev., **98** (5), 1959 -1976, 1998

Daisy Chains





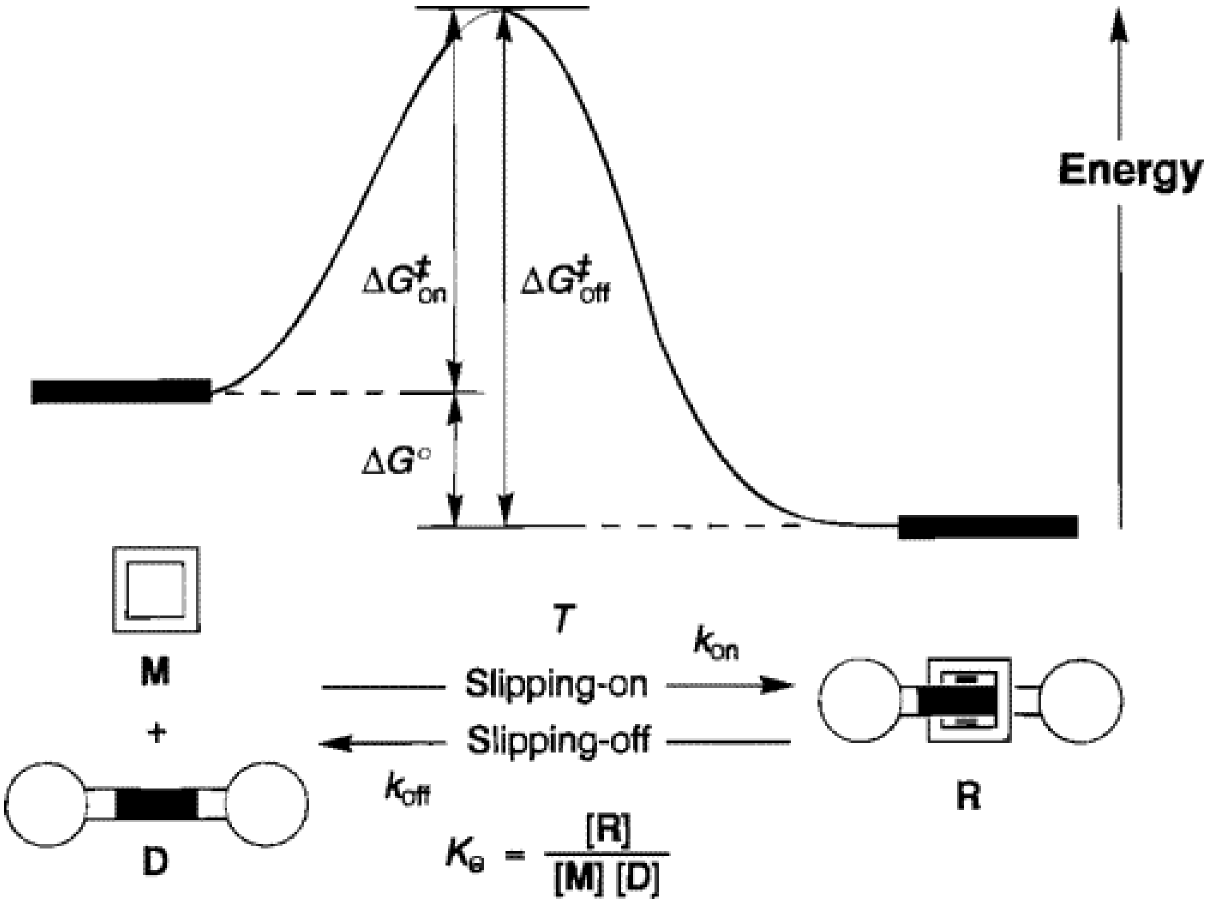


- Development of the figure 9 polyrotaxane concept
- (a) Kolchinski and Busch's original figure 9 pseudopolyrotaxane
- (b) and (c) Stoddart's attempts at figure 9 polyrotaxanes have yielded a new motif, the 69 dimer,
- (d) Gibson's figure 9 precursor.

Coord. Chem. Rev. 2000, 200–202, 5–52

Slipping Approach - Thermodynamics

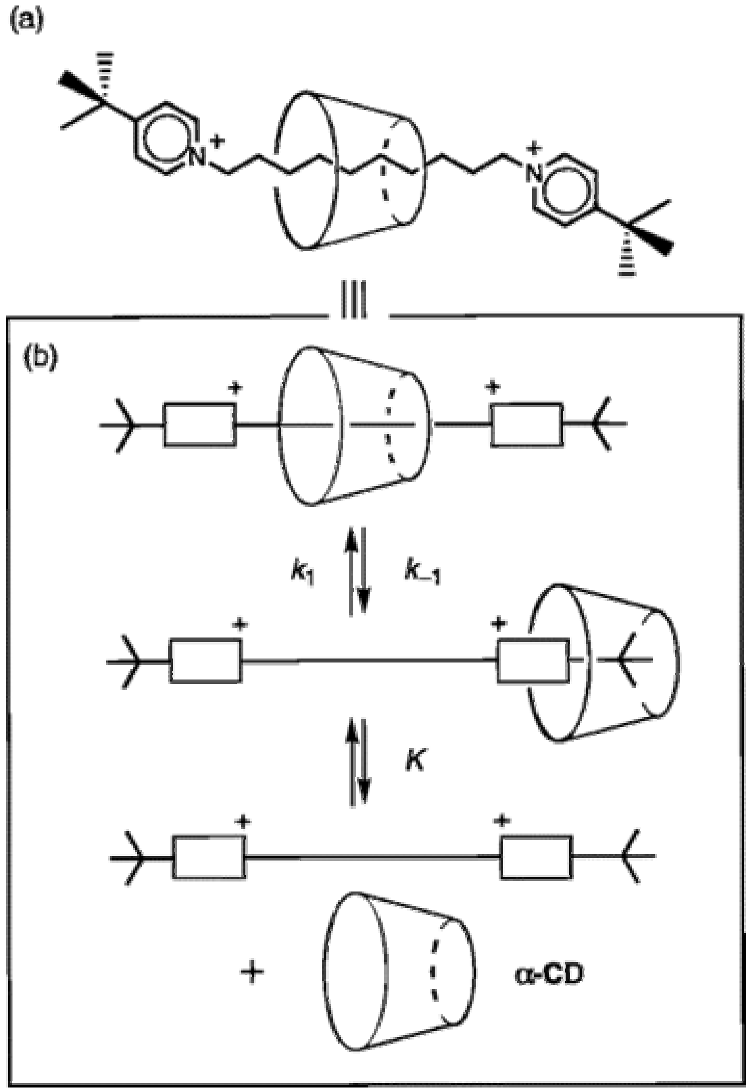
Schematic illustration of the slipping approach to rotaxanes.



J. Am. Chem. Soc., **119** (2), 302 -310, 1997

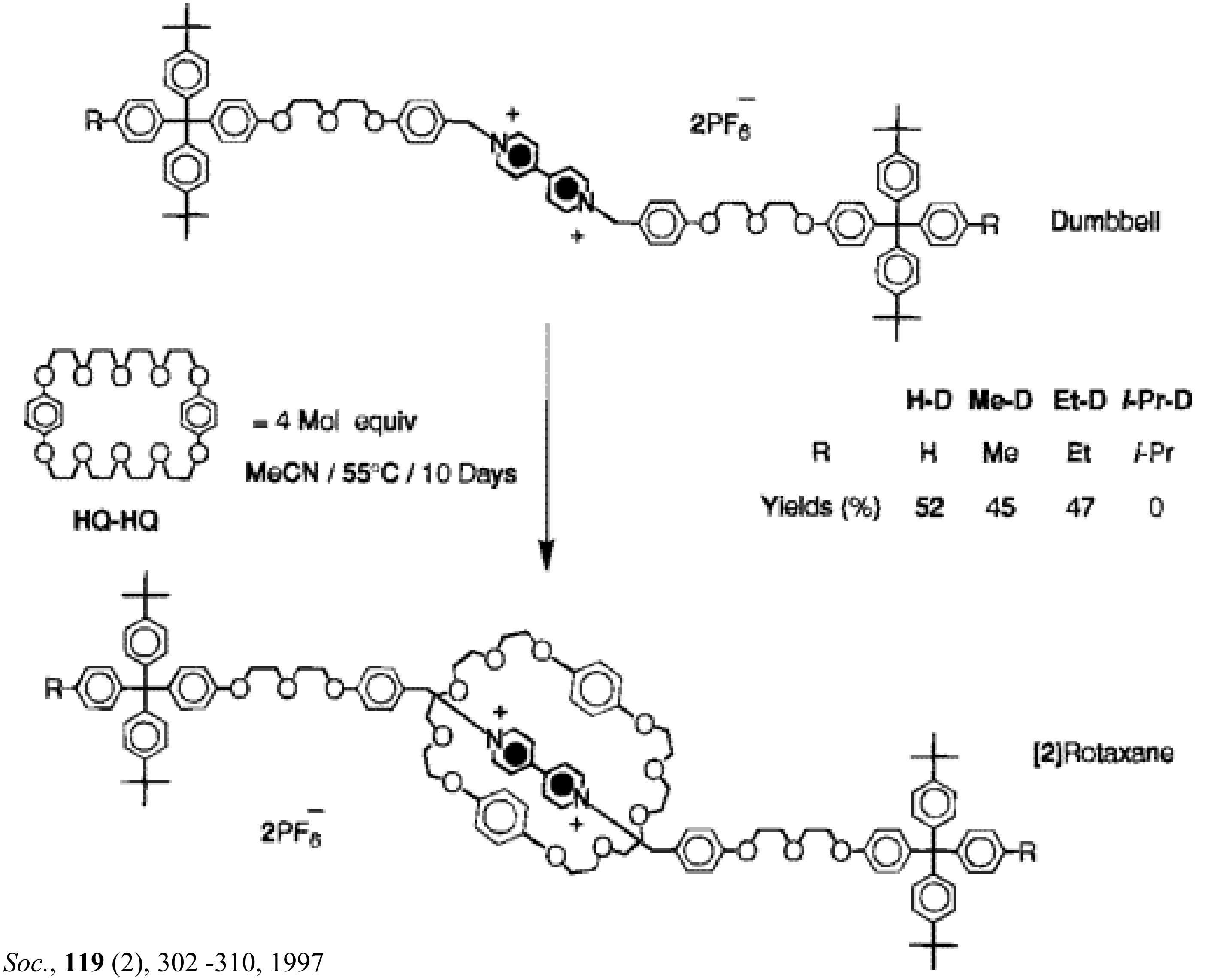
Slippage

- (a) **CD**-based rotoxane prepared using the "slippage" procedure
- (b) Scheme proposed for the "slippage" mechanism to account for the kinetics of the formation of the [2]pseudorotaxane, shown in (Note that the association constant $K_a = k_1 K / k_{-1}$.



Chem. Rev., **98** (5), 1959 -1976, 1998

Slipping Approach - Selectivity

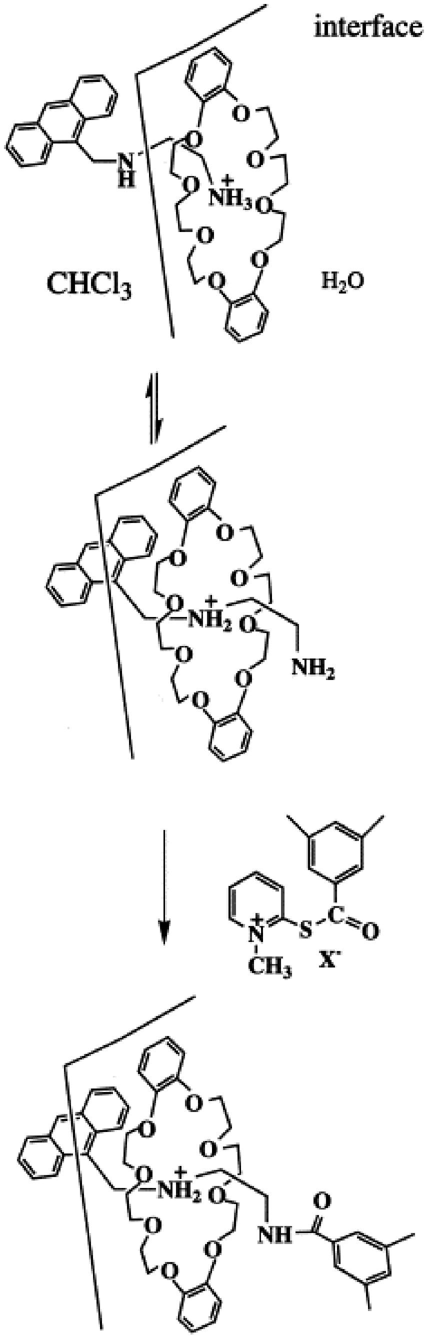


	H-D	**Me-D**	**Et-D**	***i*-Pr-D**
R	H	Me	Et	*i*-Pr
Yields (%)	52	45	47	0

J. Am. Chem. Soc., **119** (2), 302 -310, 1997

Relay Threading

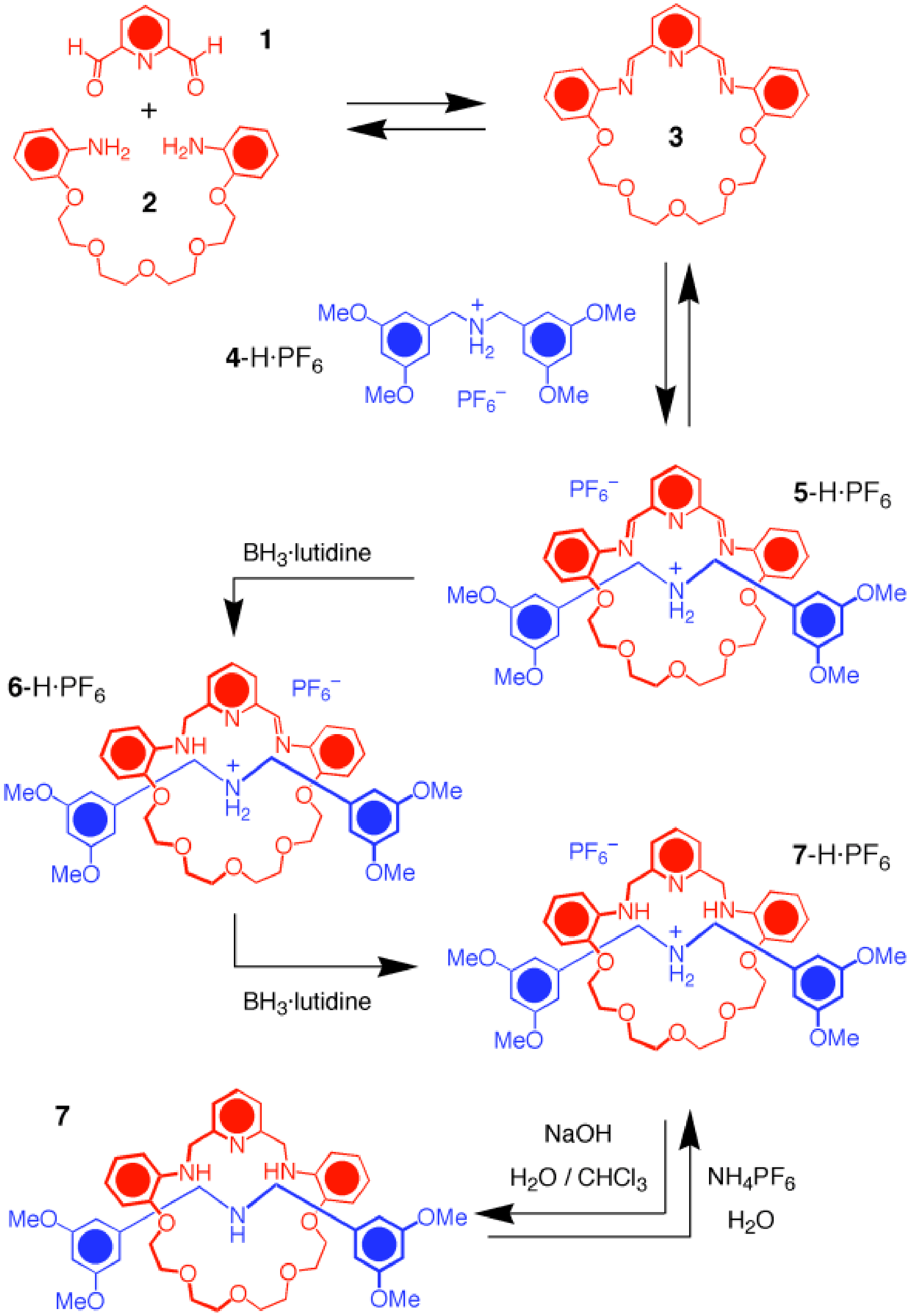
- Kolchinski and Busch's use of relay threading and a solvent interface to enhance rotaxane formation.



Coord. Chem. Rev. 2000, 200–202, 5–52

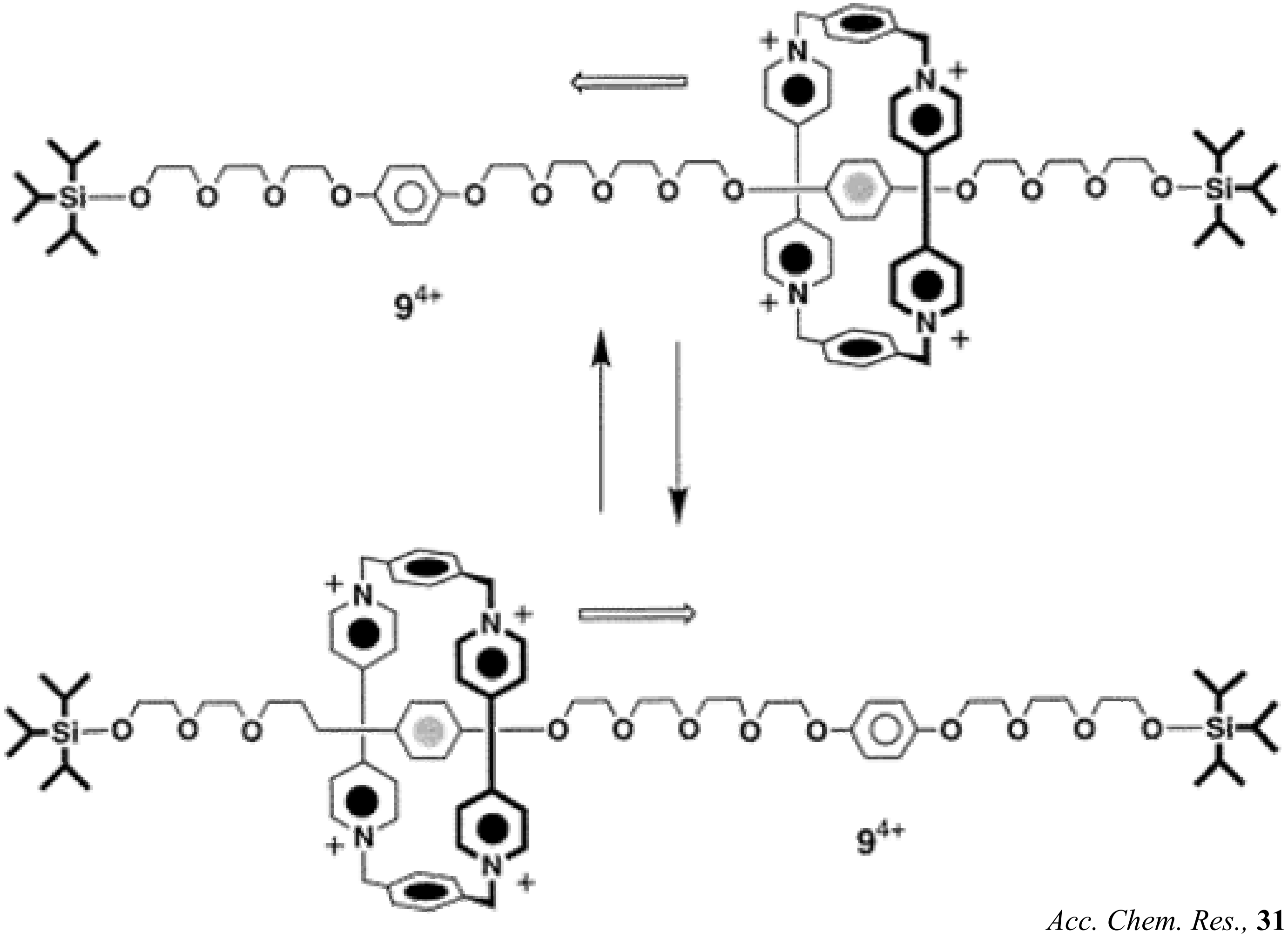
Clipping - Thermodynamically

Synthesis of the [2]rotaxane **7**-H PF_6 by the clipping of dialdehyde **1** and diamine **2** around the dialkylammonium ion **4**-H^+, followed by reduction of the imino bonds.



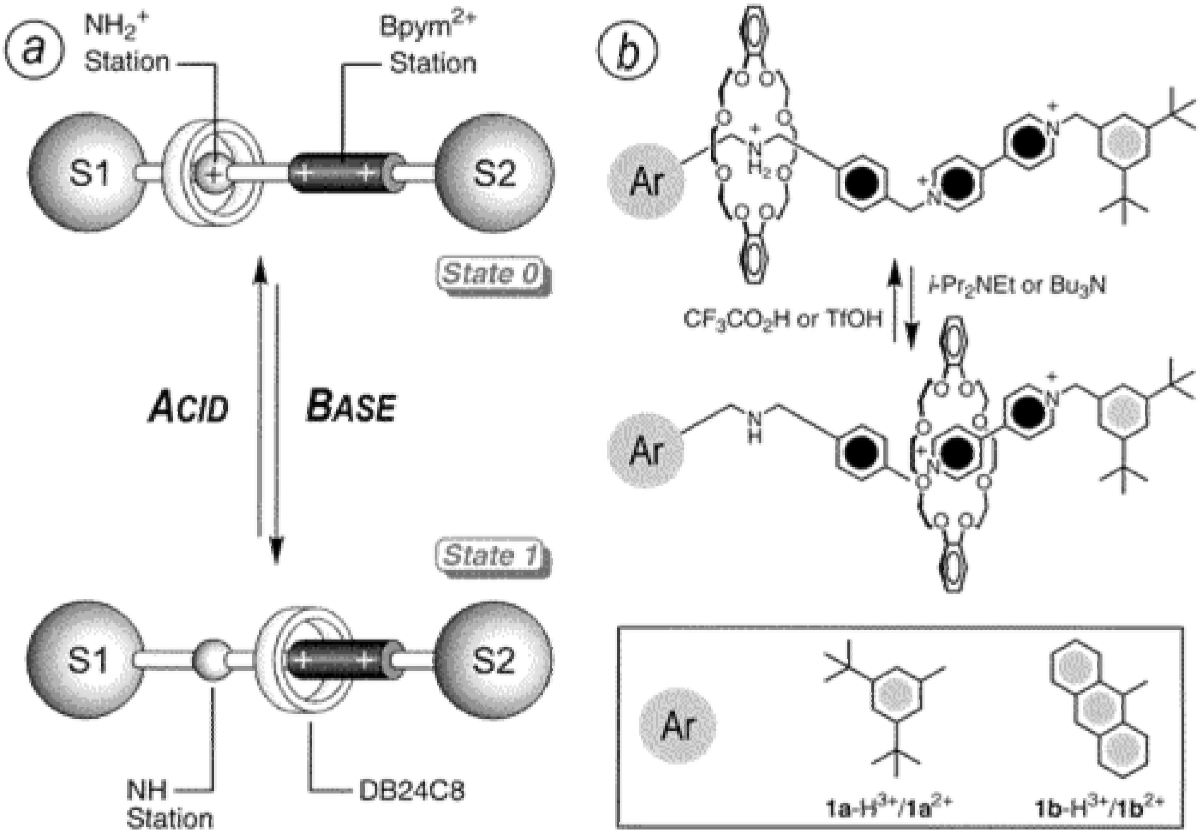
First Molecular Shuttle

- The first molecular shuttle



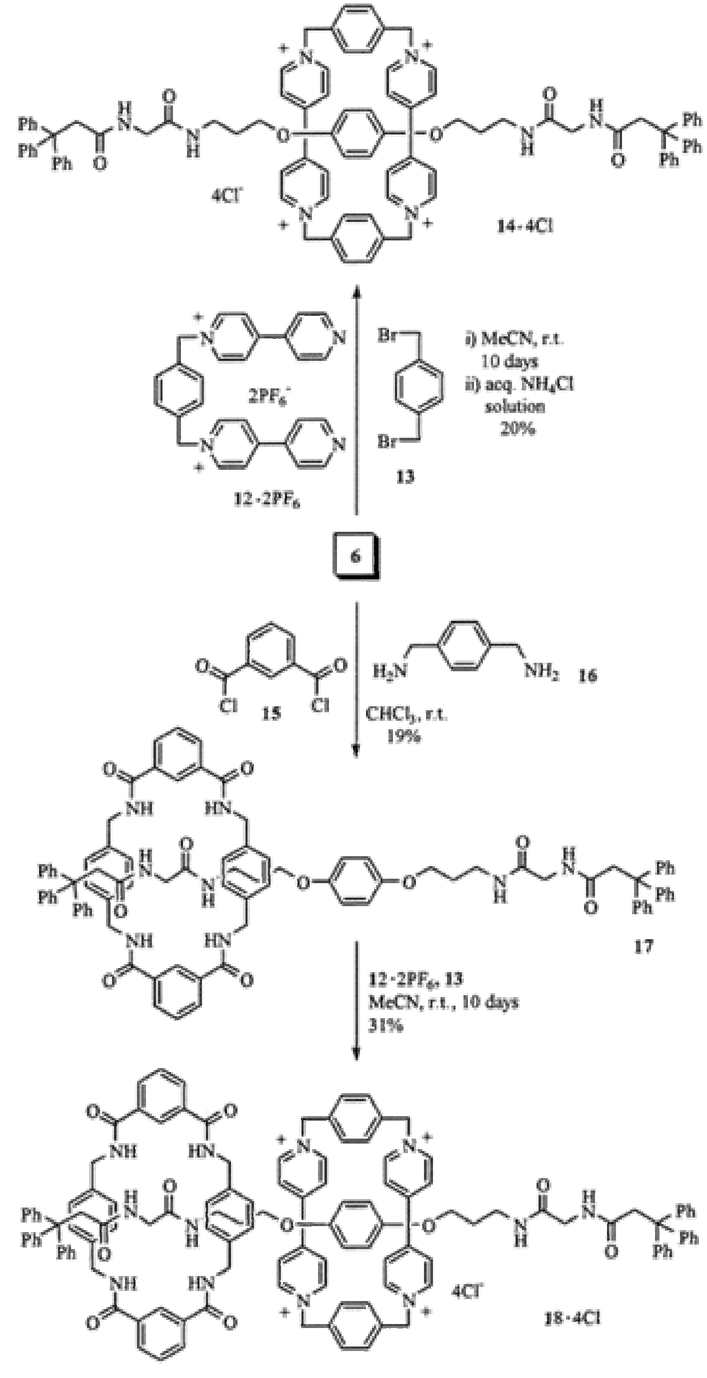
Acc. Chem. Res., **31** (7), 405 -414, 1998

Acid/Base Shuttle Concept



- (a) Cartoon showing an acid-base controllable molecular shuttle. Initially (State 0), the macrocyclic component resides solely on the NH_2^+ station. After treatment with a nonnucleophilic base, deprotonation coerces the macroring to move to the $Bpym^{2+}$ station (State 1). Addition of acid regenerates the NH_2^+ center, moving the macrocyclic component back to bind its original station and rendering the switching cycle reversible. (b) Structural formulas of the switchable [2]rotaxanes described here.

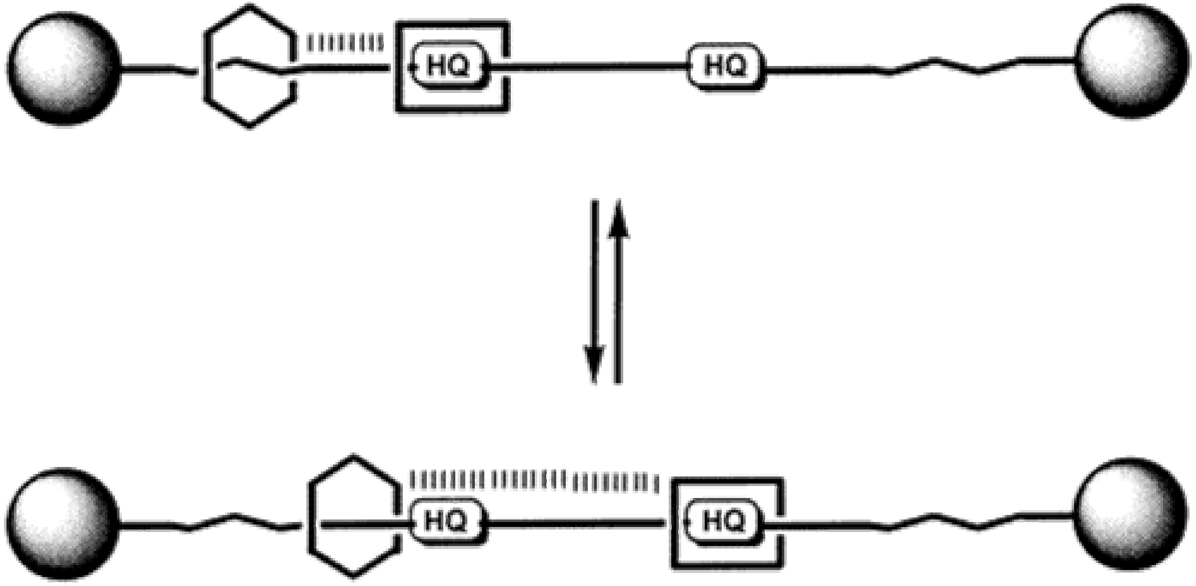
Synthesis of Heterotopic Rotaxanes



J. Org. Chem., **66** (21), 7035 -7043, 2001

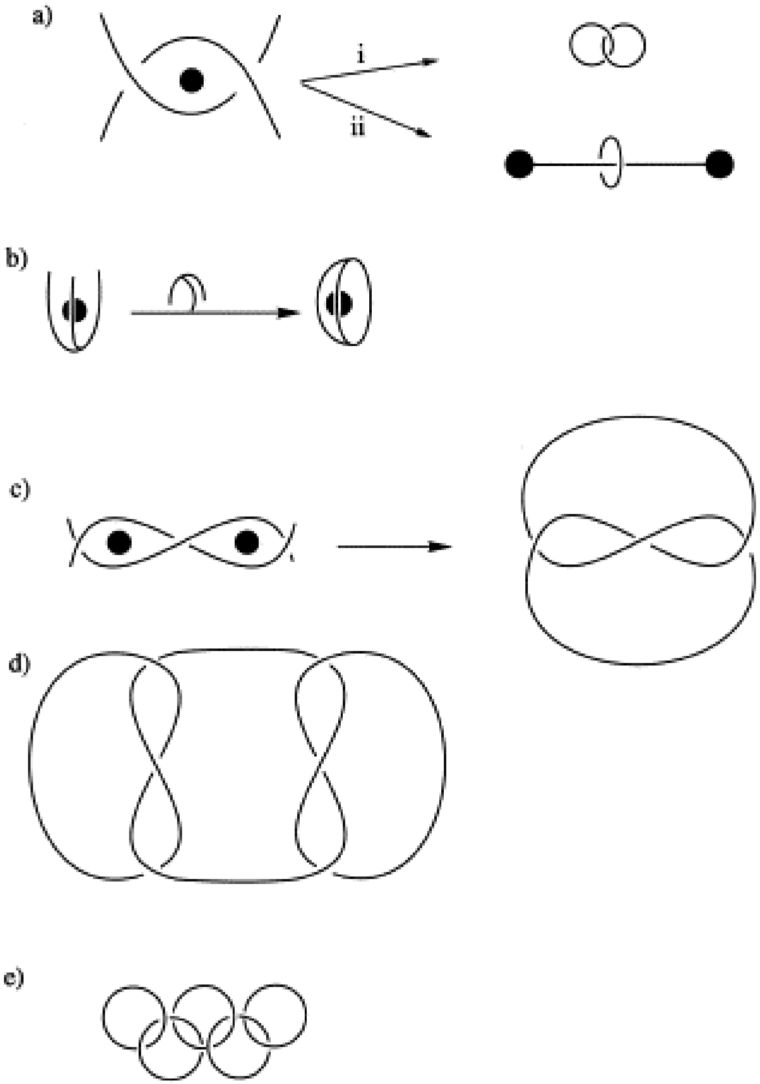
Mixed Rotaxanes - Shuttling

- The neutral cyclophane (represented by the hexagon) always imposes a repelling interaction on the tetracationic cyclophane (represented by the tetragon), regardless of the latter's orientation over either of the two hydroquinones of the linear component in hetero[3]rotaxanes **21a**·4Cl and **21b**·4Cl.



J. Org. Chem., **66** (21), 7035 -7043, 2001

“Crossovers” - Interlocking



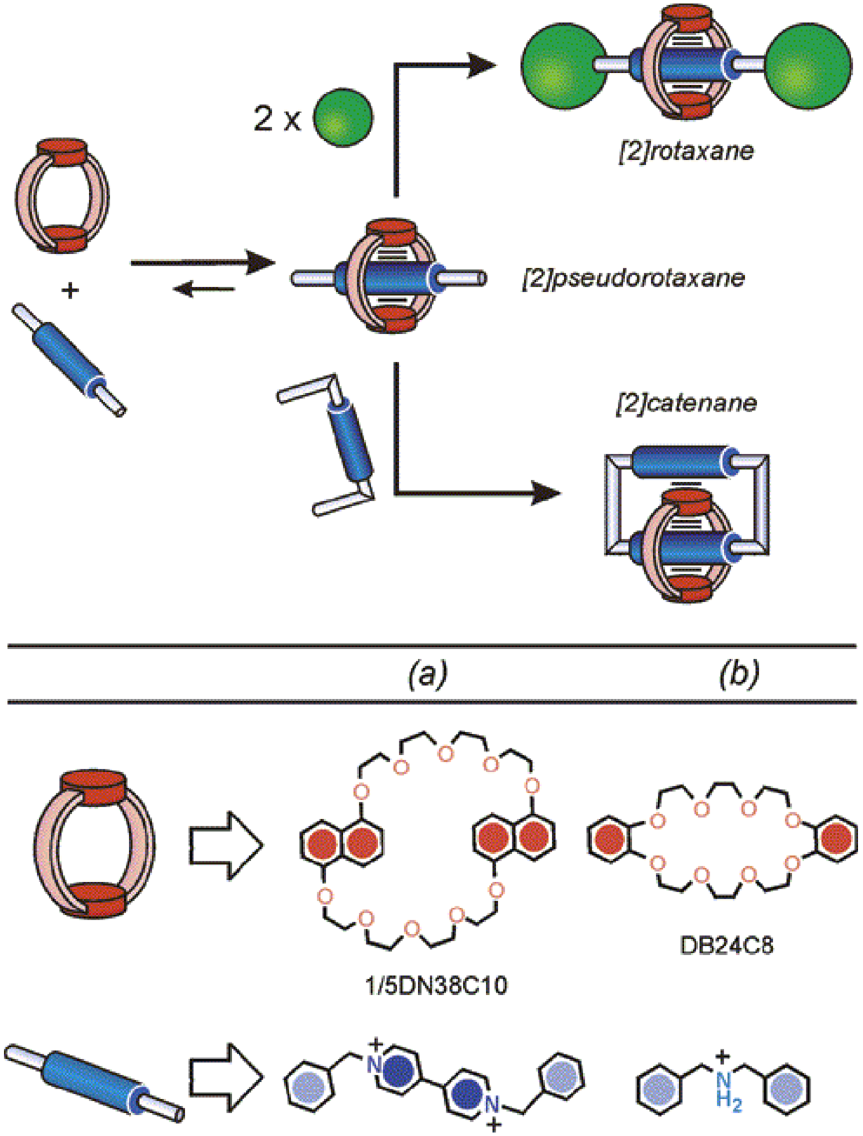
- (a) A simple cross-over gives (i) a catenane upon two ring closures or (ii) a rotaxane upon one ring closure and blocking
- (b) a fused turn can be used for macrobicycle syntheses
- (c) use of two anchors and ditopic turns to form a trefoil knot
- (d) a composite knot from two two-anchor templates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

Coord. Chem. Rev. 2000, 200–202, 5–52

Synthesis of rotaxanes/catenanes

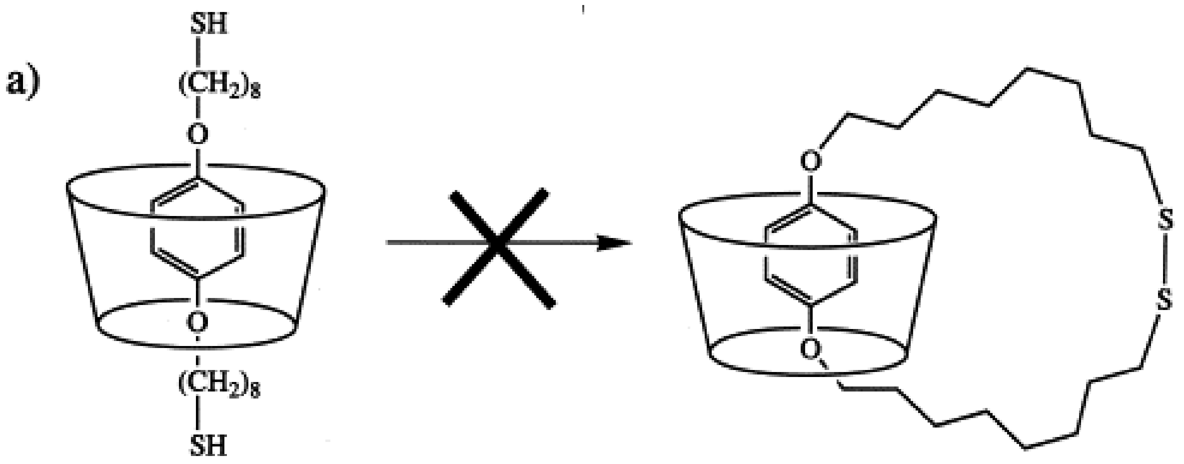
Pictorial representation of the self-assembly of pseudorotaxanes based on

- (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.



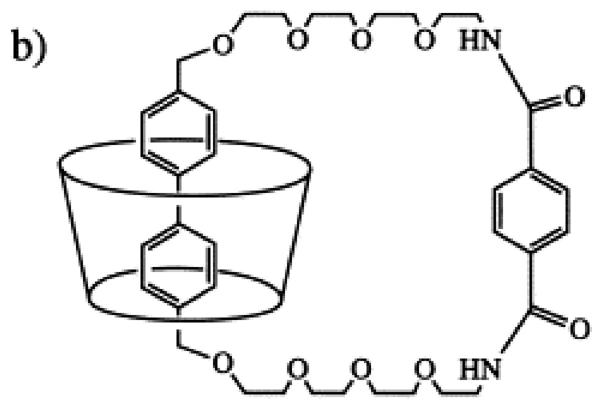
Acc. Chem. Res., **34** (6), 445 -455, 2001

[2]Catenane Synthesis



(a) Luttringhaus' failed cyclodextrin catenane reaction and

(b) Stoddart's first successful cyclodextrin [2]-catenane (35 years later).

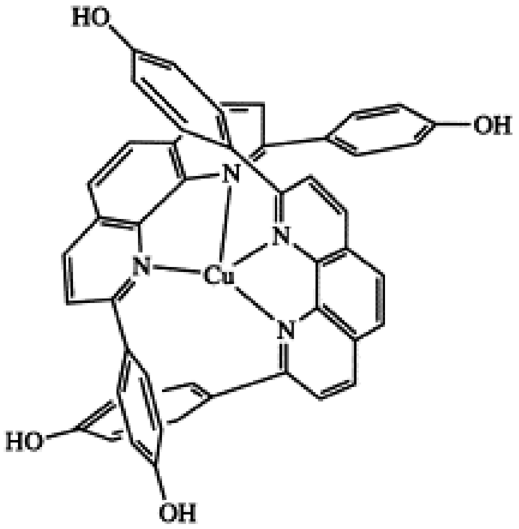


The nature of the molecules that typically thread cyclodextrins probably contributes to their lack of success as catenane components. They are poor turns – the threading molecules are often flexible and their terminals are not specifically oriented. An oriented turn is not so important to rotaxane formation, but to close a turn into a ring, it is vital.

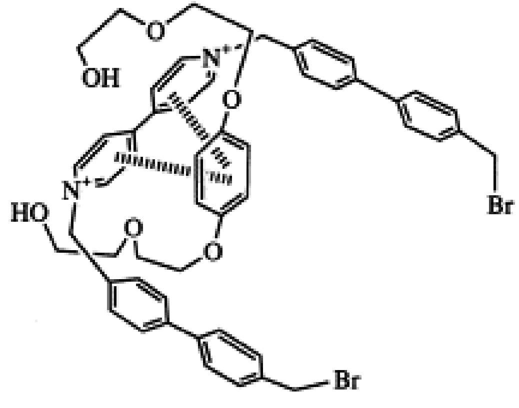
Coord. Chem. Rev. 2000, 200–202, 5–52

Catenanes

a)

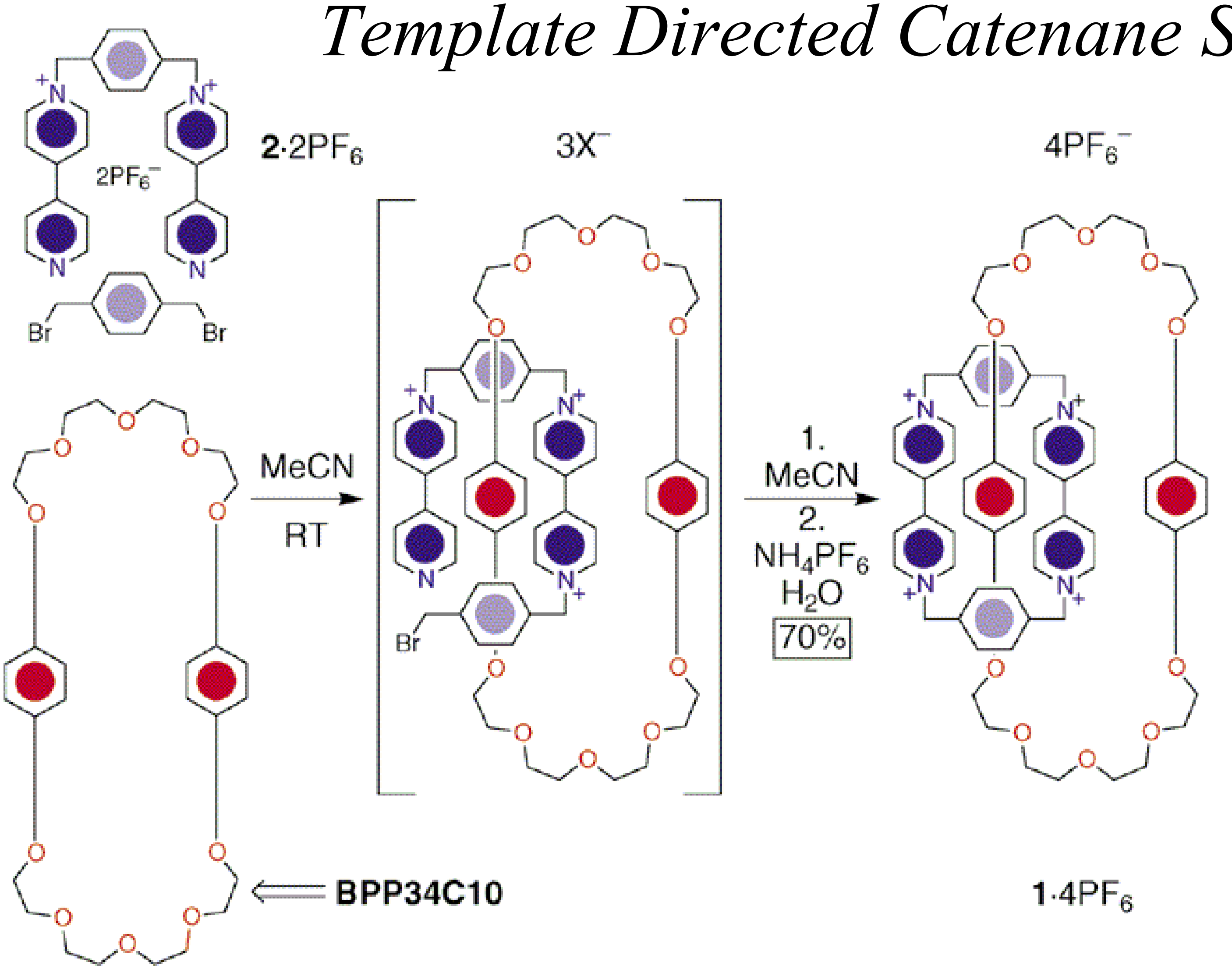


b)



Coord. Chem. Rev. 2000, 200–202, 5–52

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$_6$.

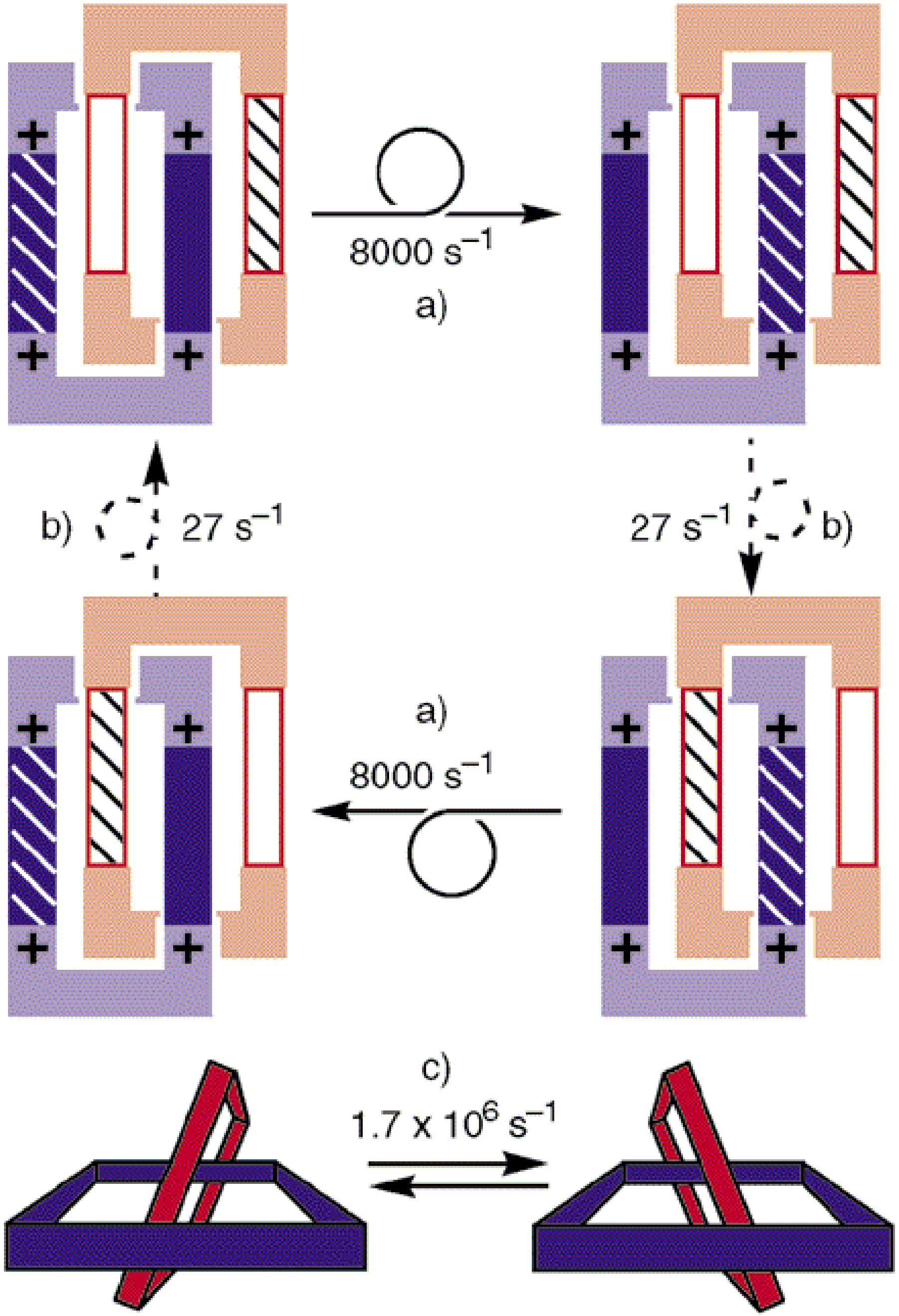
Catenane Kinetics

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

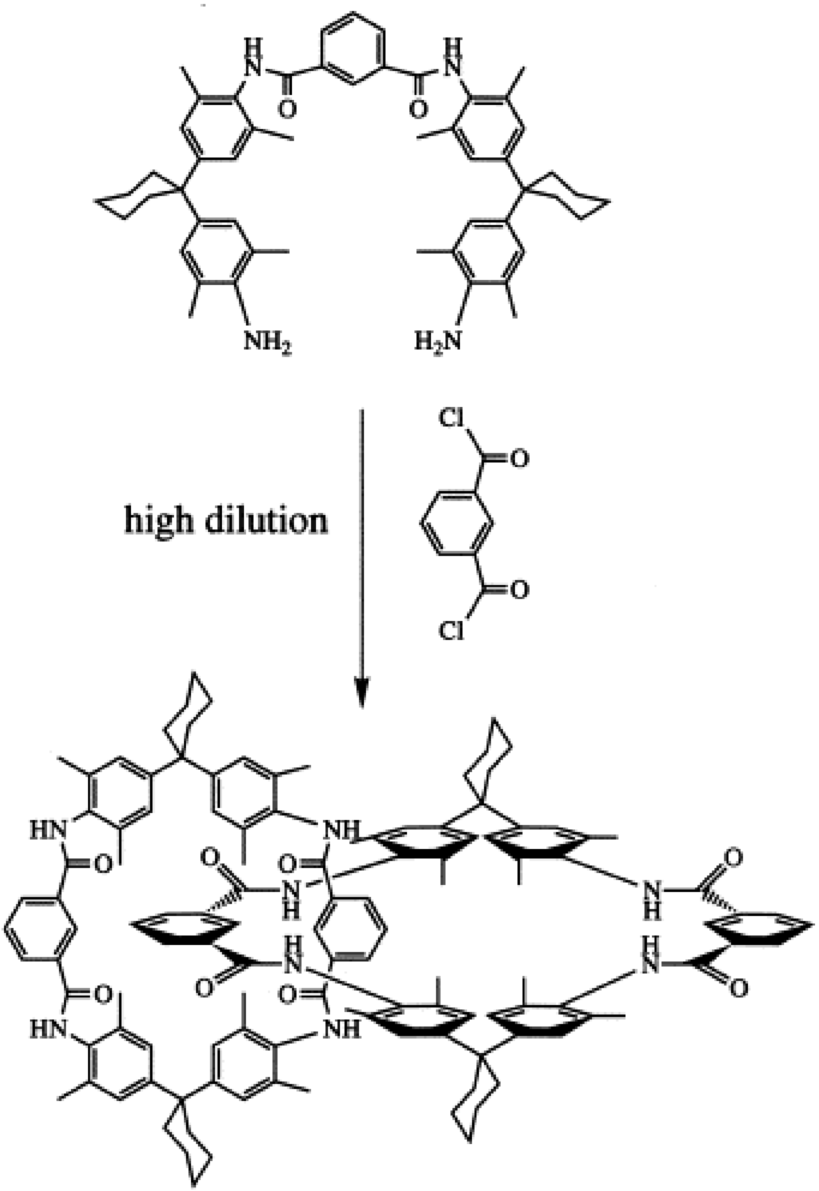
(c) rocking of BPP34C10 within CBPQT^{4+}. The rates of these processes at room temperature are shown.



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

Hydrogen Bonding in Catenane Formation

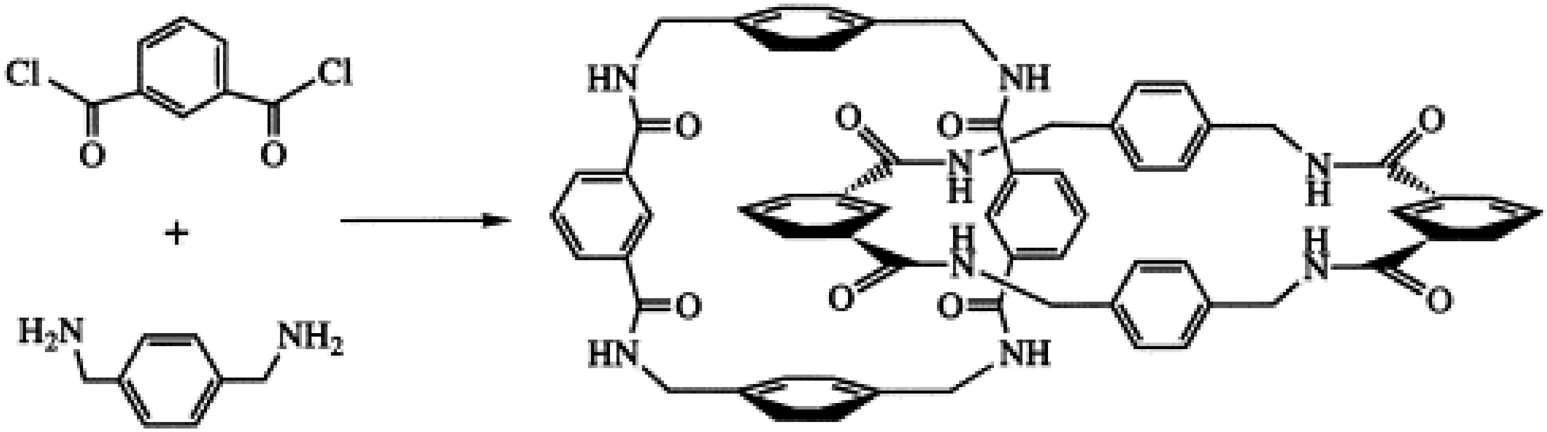
- The synthesis of Hunter's first amide [2]-catenane.



Coord. Chem. Rev. 2000, 200–202, 5–52

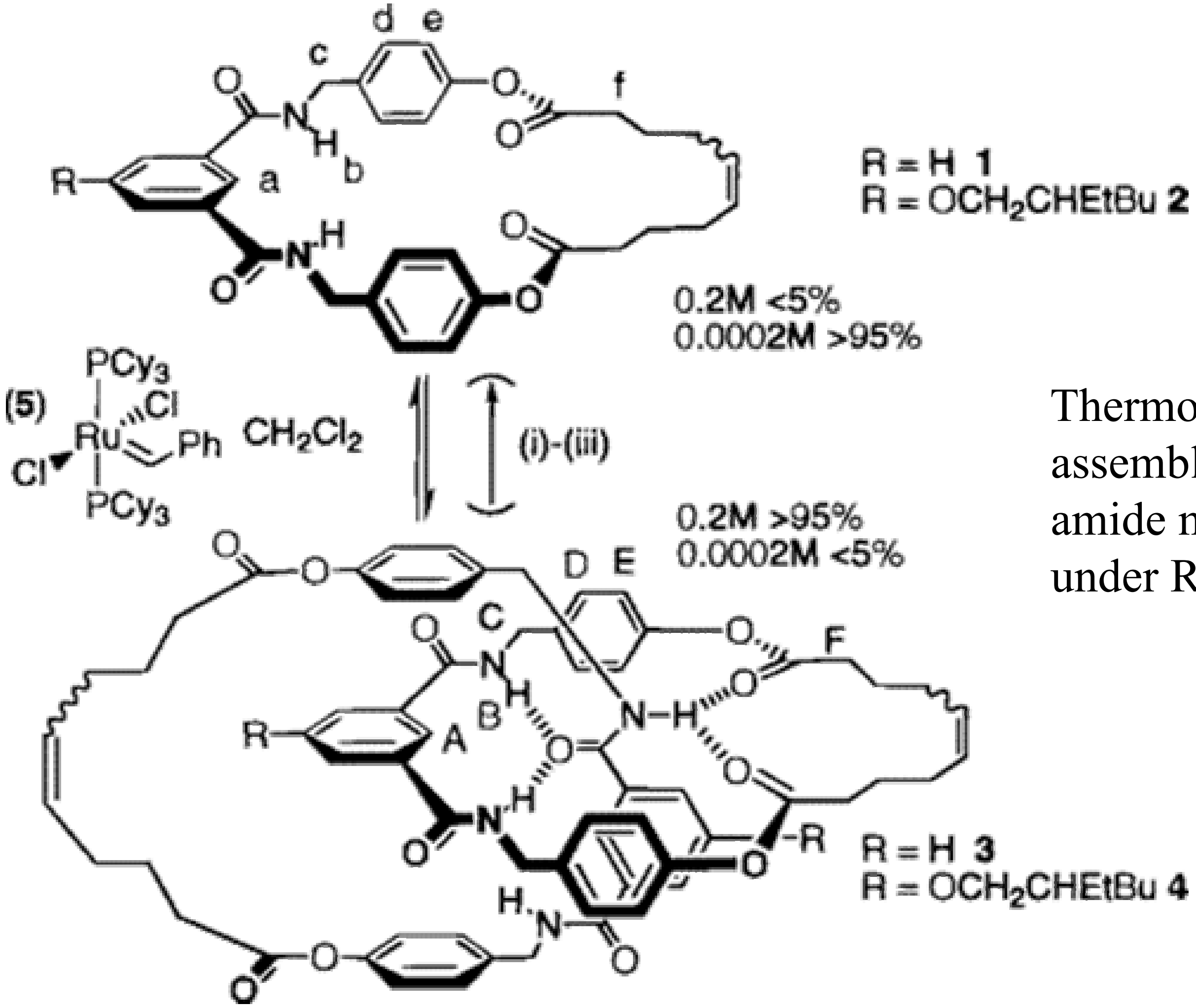
Hydrogen Bonding in Catenane Formation

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



Coord. Chem. Rev. 2000, 200–202, 5–52

Magic Rings

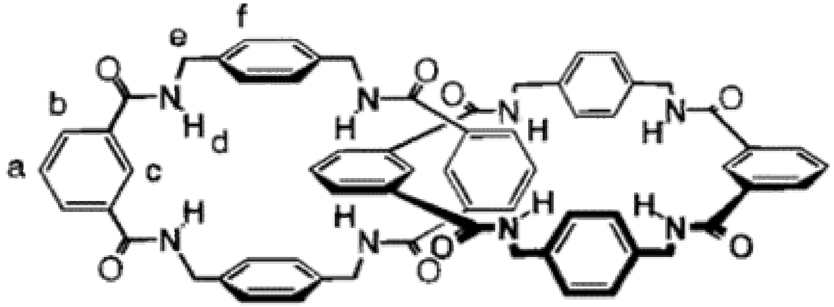


Thermodynamically controlled self-assembly / disassembly of benzylic amide macrocycles and [2]catenanes under RORCM *(*>95% yield).

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.



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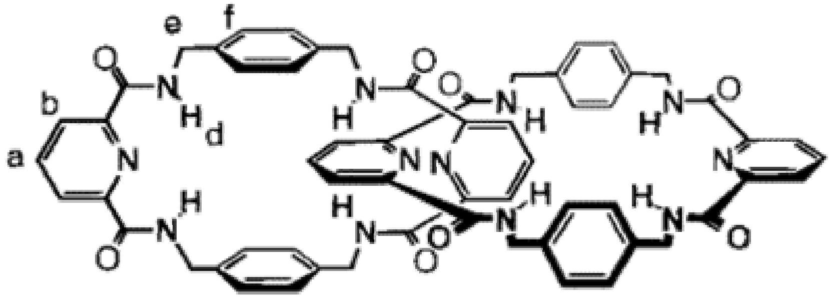

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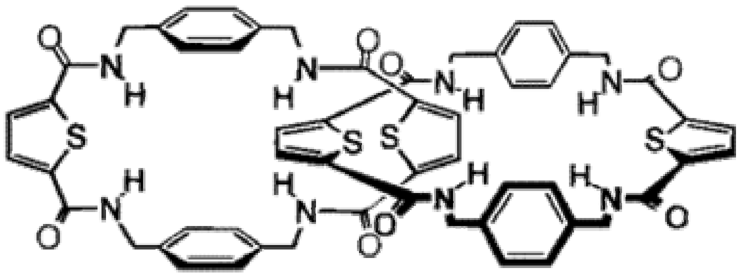

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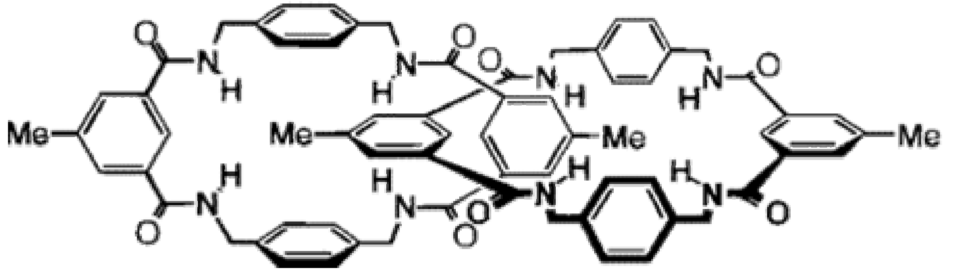

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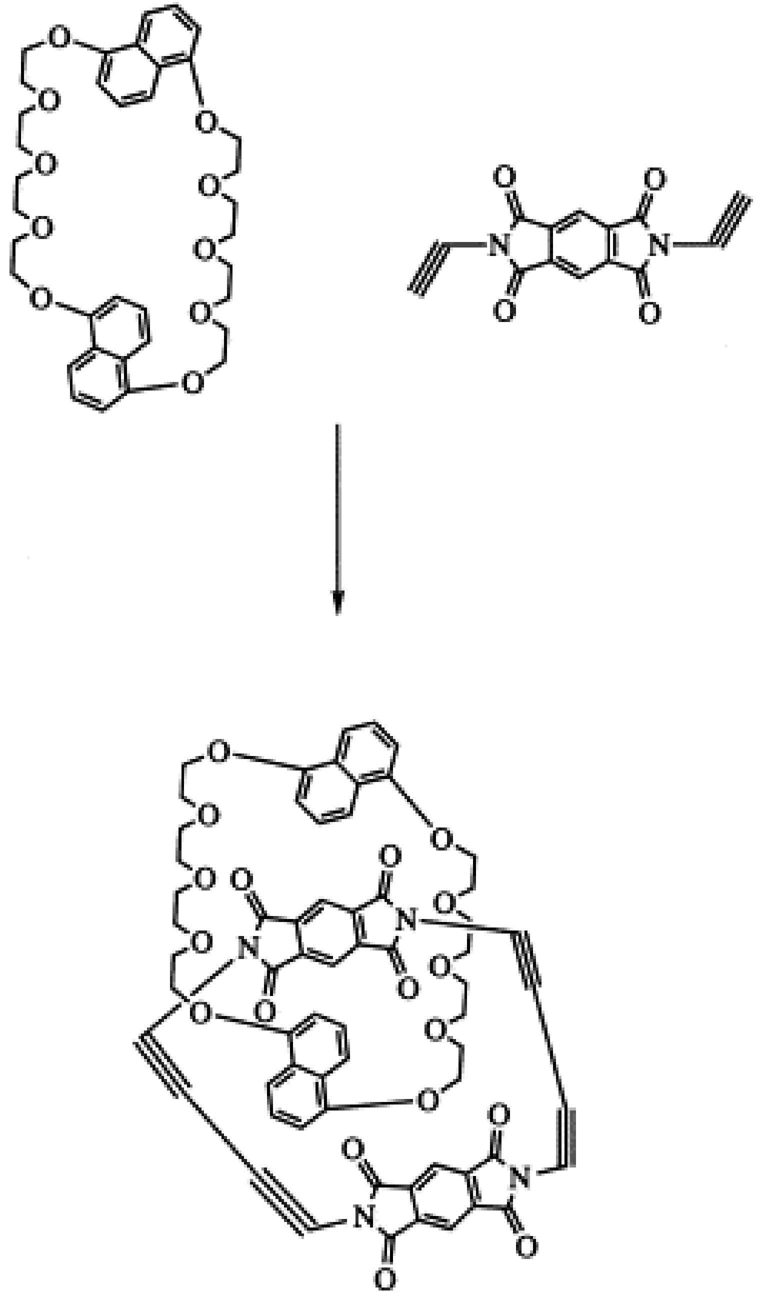
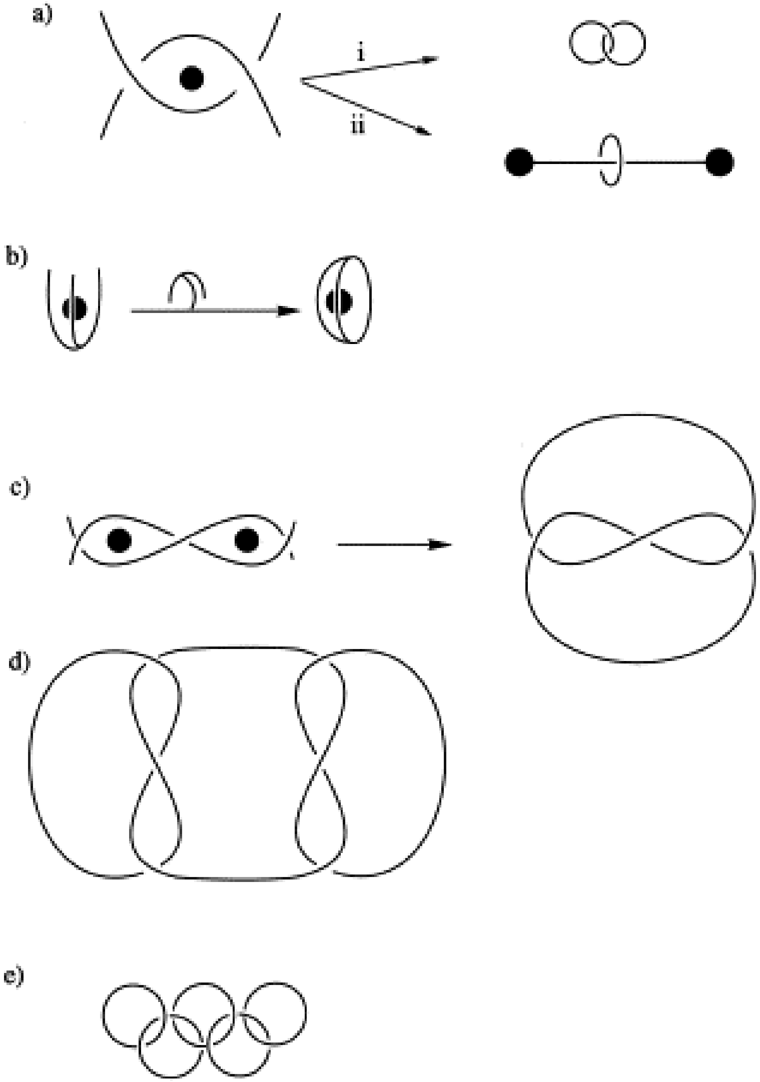
Neutral Catenanes

- Sander's use of neutral π–π template pairs to form a [2]-catenane.



Coord. Chem. Rev. 2000, 200–202, 5–52

"Crossovers" - Interlocking



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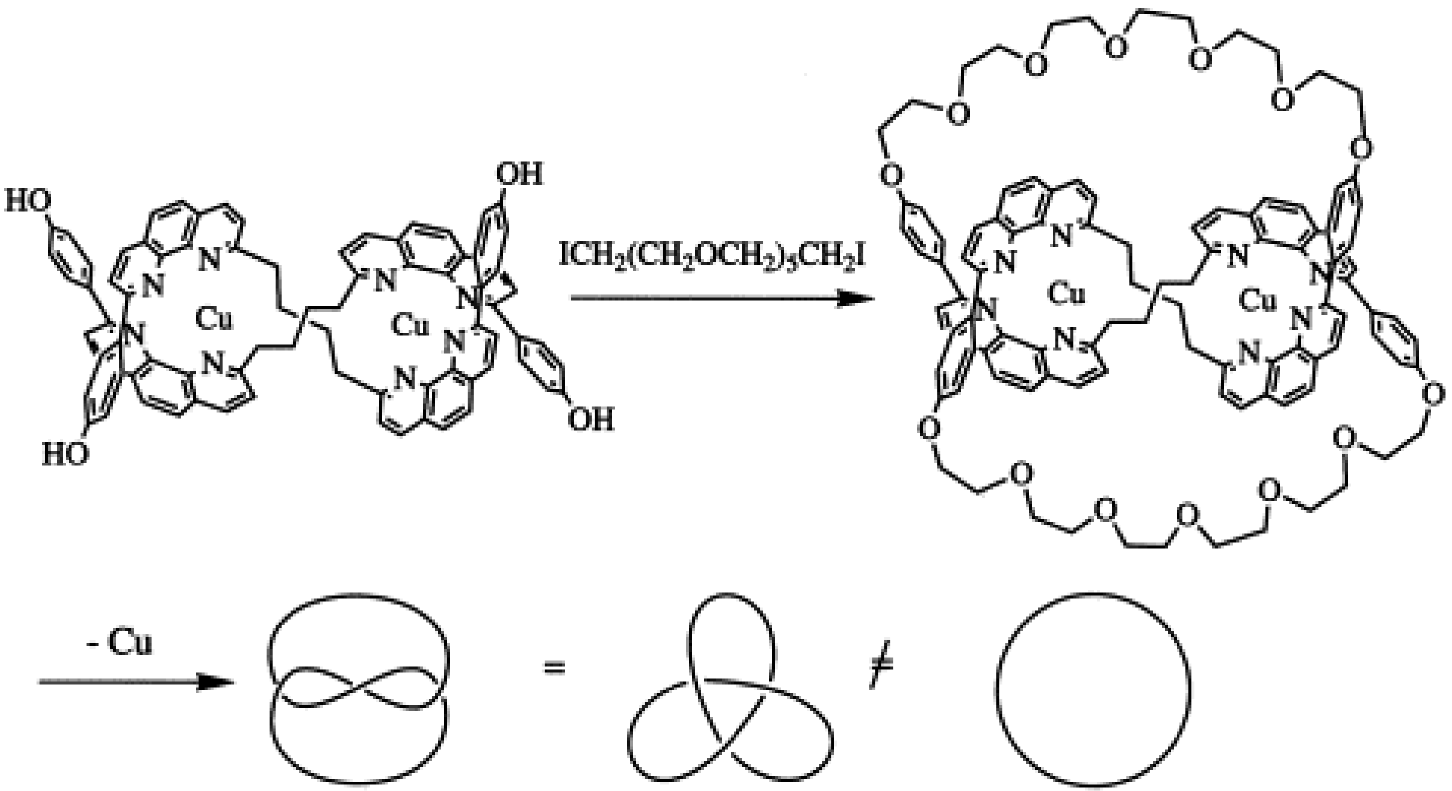
Coord. Chem. Rev. 2000, 200–202, 5–52

Trefoil Knot

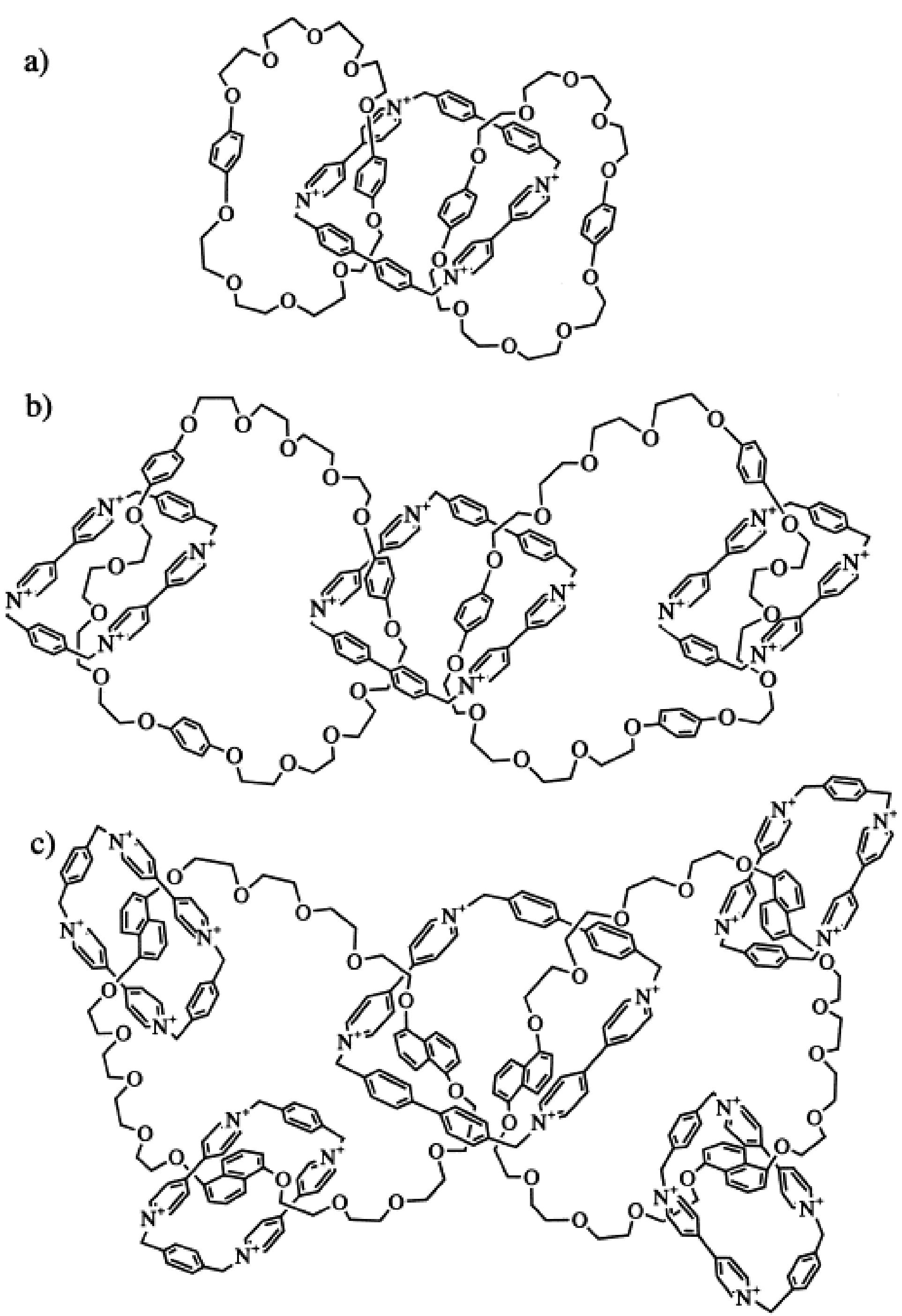
- Synthesis of the first trefoil knot using a two-anchor helical template.



Coord. Chem. Rev. 2000, 200–202, 5–52

Olympiadane

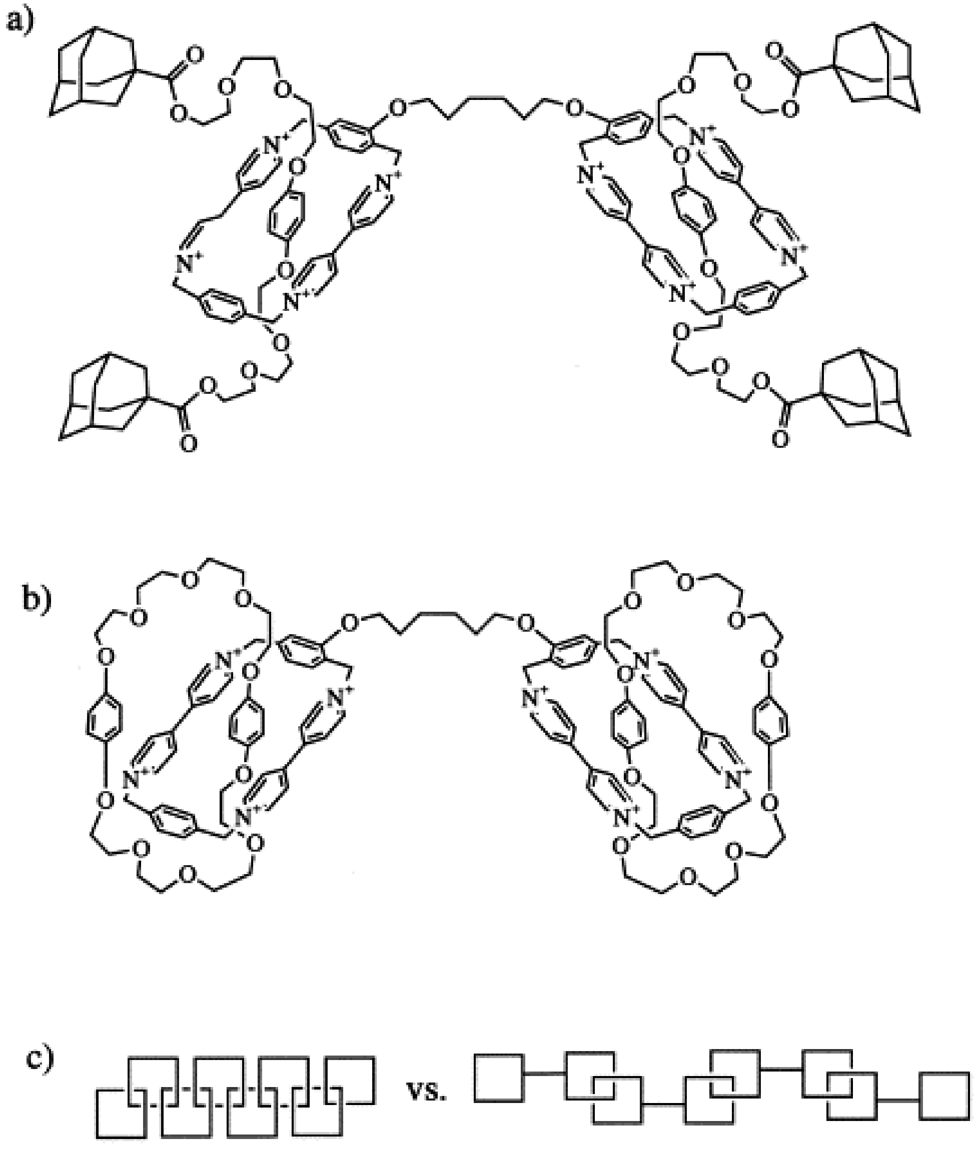
Advancement of the π–π template oligocatenanes from (a) the first [3]-catenane to (b) the [5]-catenane Olympiadane and finally to (c) a branched [7]-catenane.



Coord. Chem. Rev. 2000, 200–202, 5–52

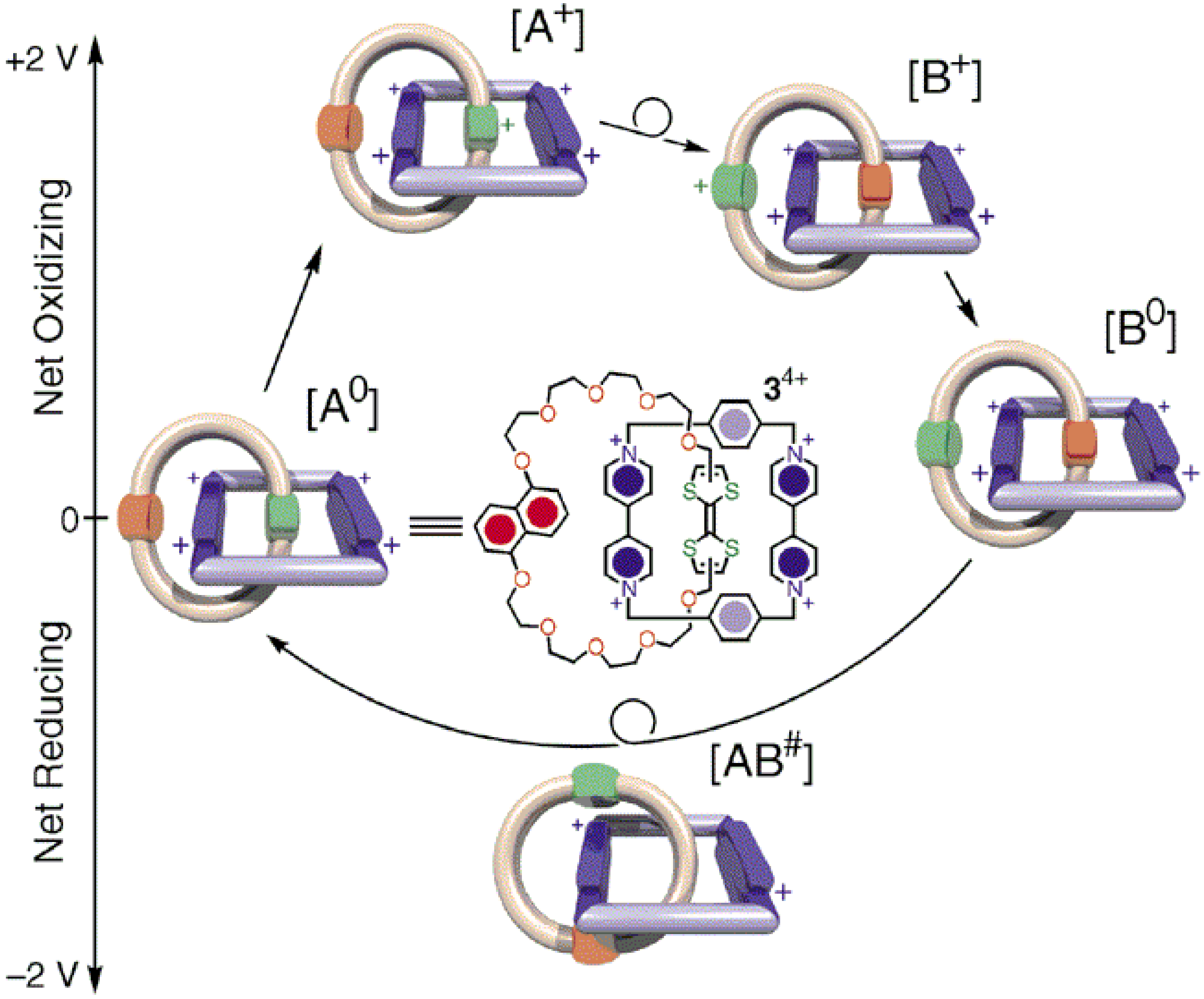
Bis Rotaxane Bis Catenane

- (a) Bis-[2]-rotaxanes and
- (b) bis-[2]-catenanes, which can be used in the formation of
- (c) polycatenanes with alternating covalent and mechanical bonds (compared with a polymeric catenane of only mechanical bonds).



Coord. Chem. Rev. 2000, 200–202, 5–52

Mechanomechanical Mechanism



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