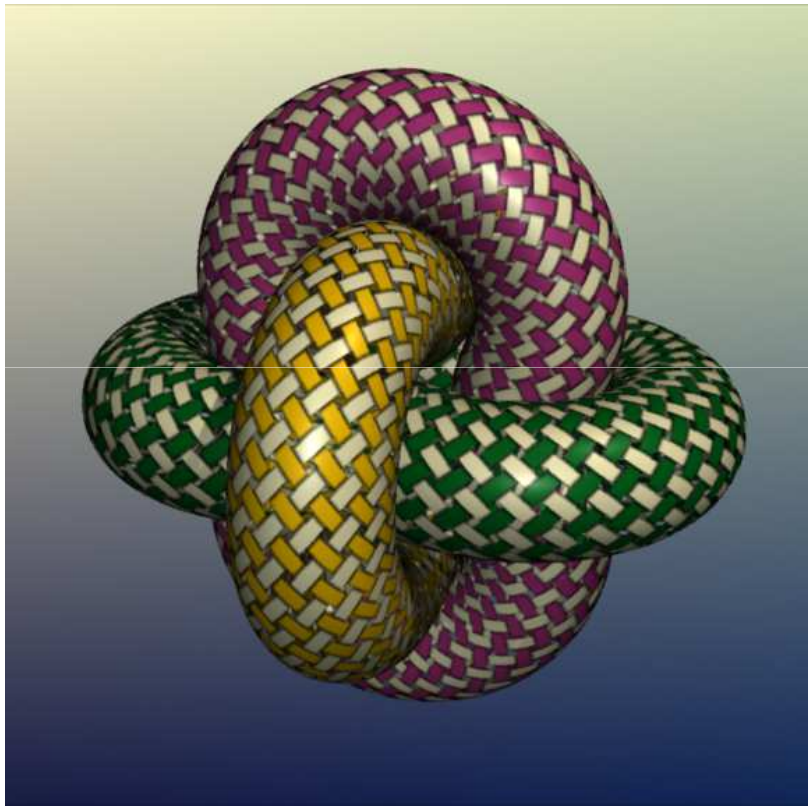
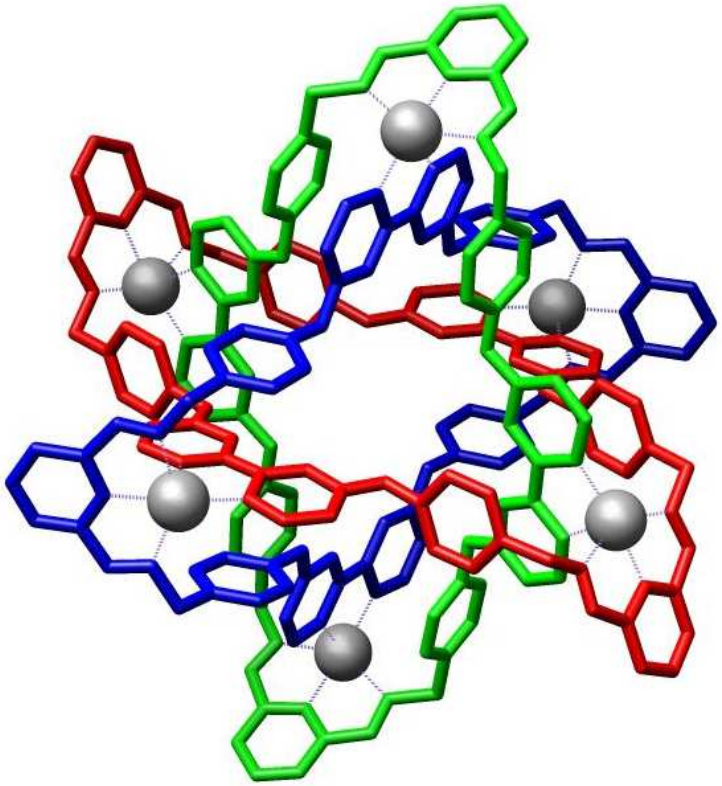
An introduction to topological chemistry





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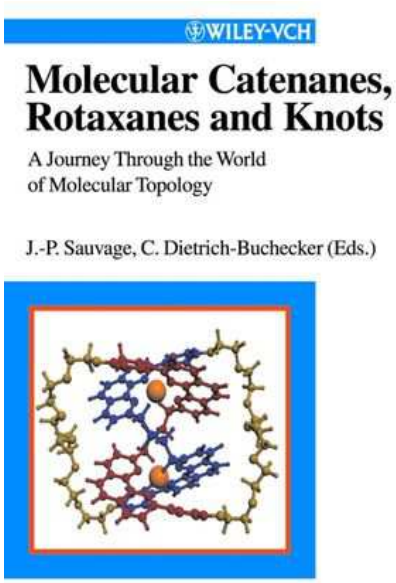

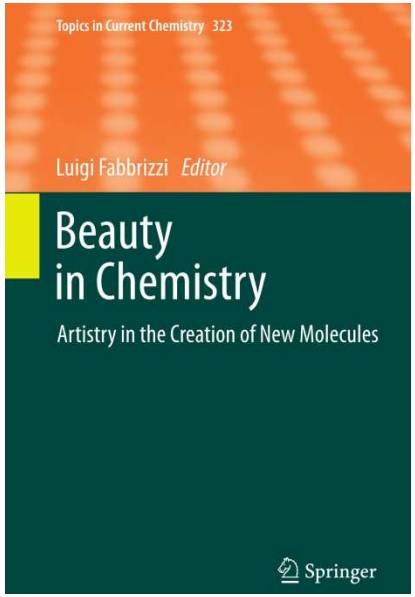

CHEMICAL REVIEWS **2011**, *111*, 5434-5464

REVIEW

pubs.acs.org/CR

Chemical Topology: Complex Molecular Knots, Links, and Entanglements

Ross S. Forgan, Jean-Pierre Sauvage,* and J. Fraser Stoddart*

Strategies and Tactics for the Metal-Directed Synthesis of Rotaxanes, Knots, Catenanes, and Higher Order Links

Jonathon E. Beves, Barry A. Blight, Christopher J. Campbell, David A. Leigh, and Roy T. McBurney* *Angew. Chem. Int. Ed.*, **2011**, *50*, 9260-9327

Bibliography

Chem Soc Rev **2013**, *42*, 1700

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Template synthesis of molecular knots†

Cite this: *Chem. Soc. Rev.*, 2013, **42**, 1700

Jean-François Ayme,[a,b] Jonathon E. Beves,[a] Christopher J. Campbell[a] and David A. Leigh*[a,b]

Angewandte Reviews

Angew. Chem. Int. Ed., **2015**, *54*, 6110

D. A. Leigh et al.

Catenanes

International Edition: DOI: 10.1002/anie.201411619
German Edition: DOI: 10.1002/ange.201411619

Catenanes: Fifty Years of Molecular Links

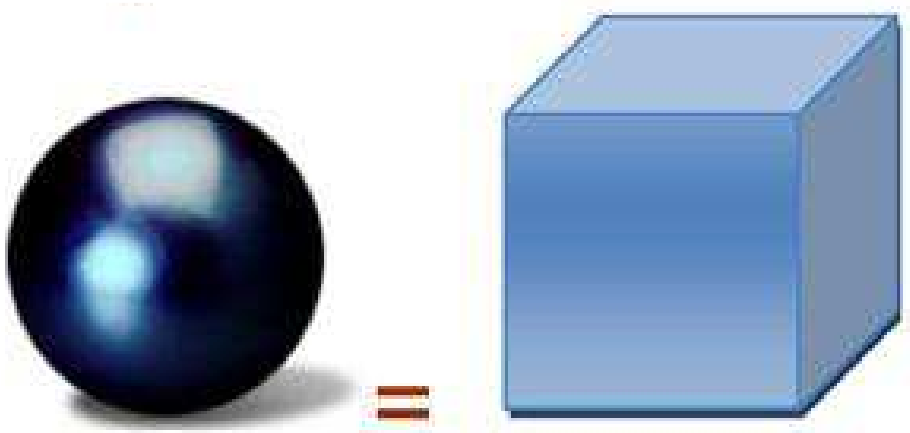
Guzmán Gil-Ramírez, David A. Leigh, and Alexander J. Stephens*

Many illustrations present in the slides are taken from these reviews

Contents

Topology

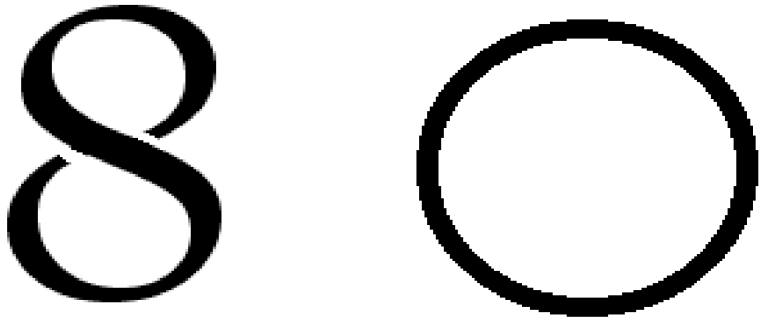
In topology, angles, distances or shapes have no meaning
But the object cannot be cut



Molecular graph

Representation of the bonds between atoms with no interest in their chemical nature

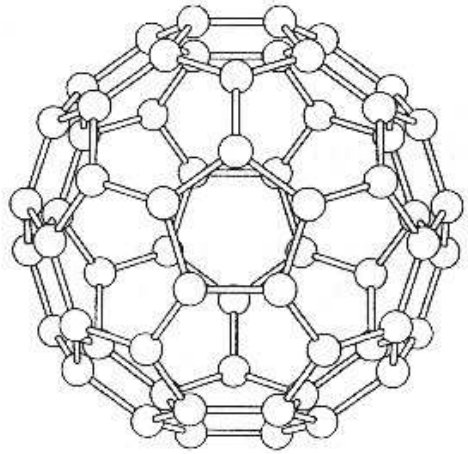
(a)



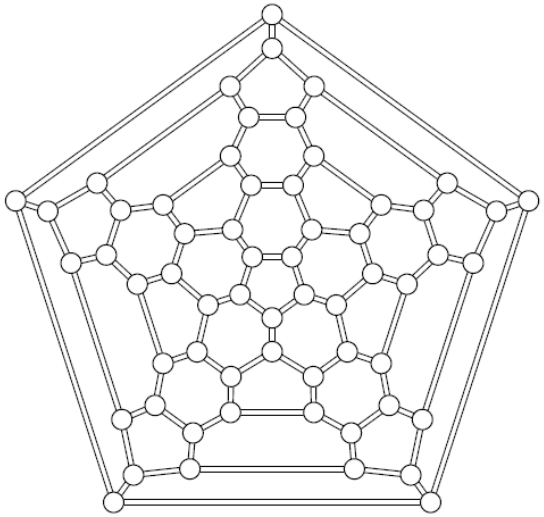
→ planar graph

One possible conformation with no crossing in 2D representation

C_{60} has a planar graph:



← topologically equivalent →

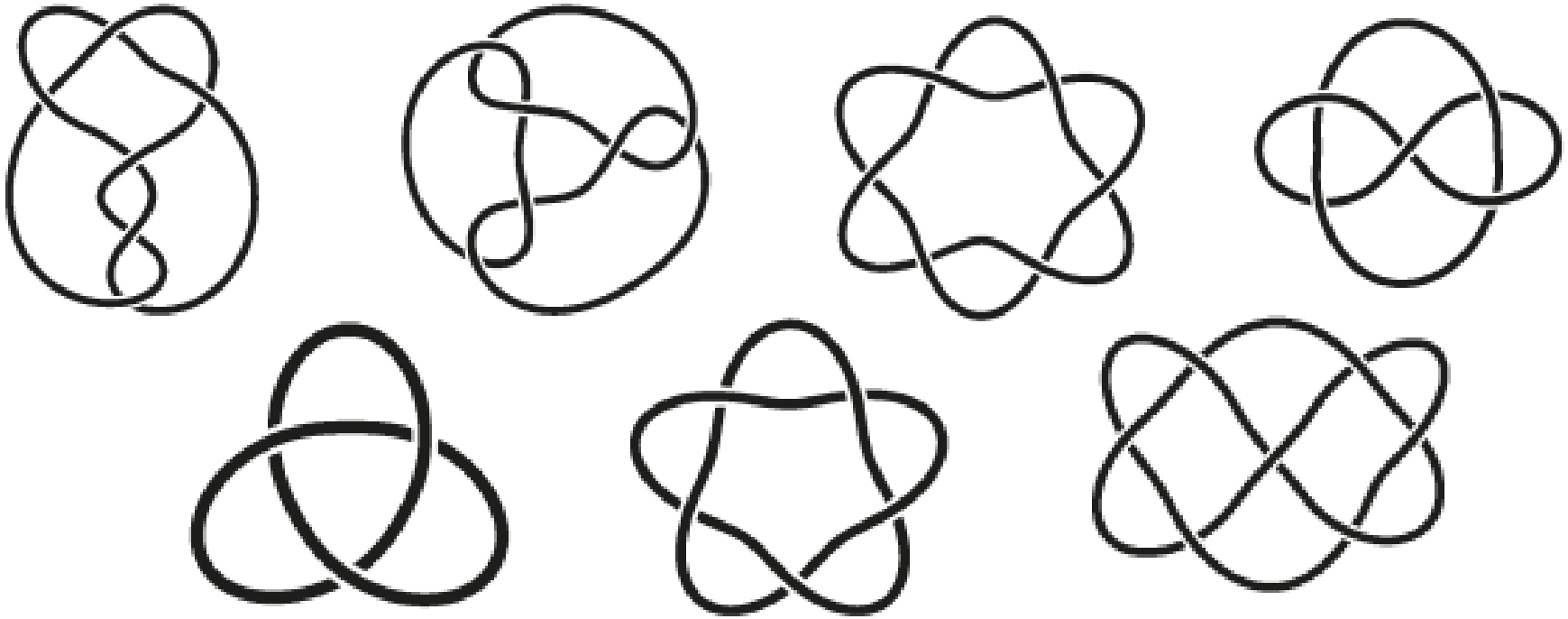


Molecular graph

non-planar graph

No possible conformation with no crossing in 2D representation

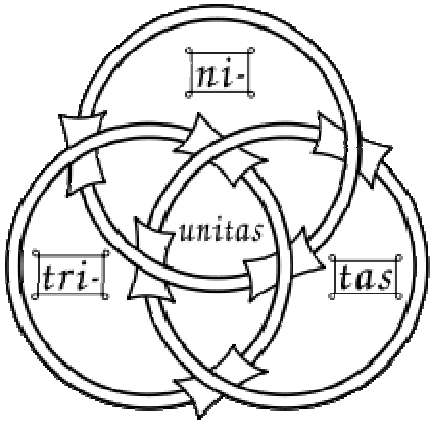
topological chemistry is the chemistry of molecules having a non planar graph



Topology in art

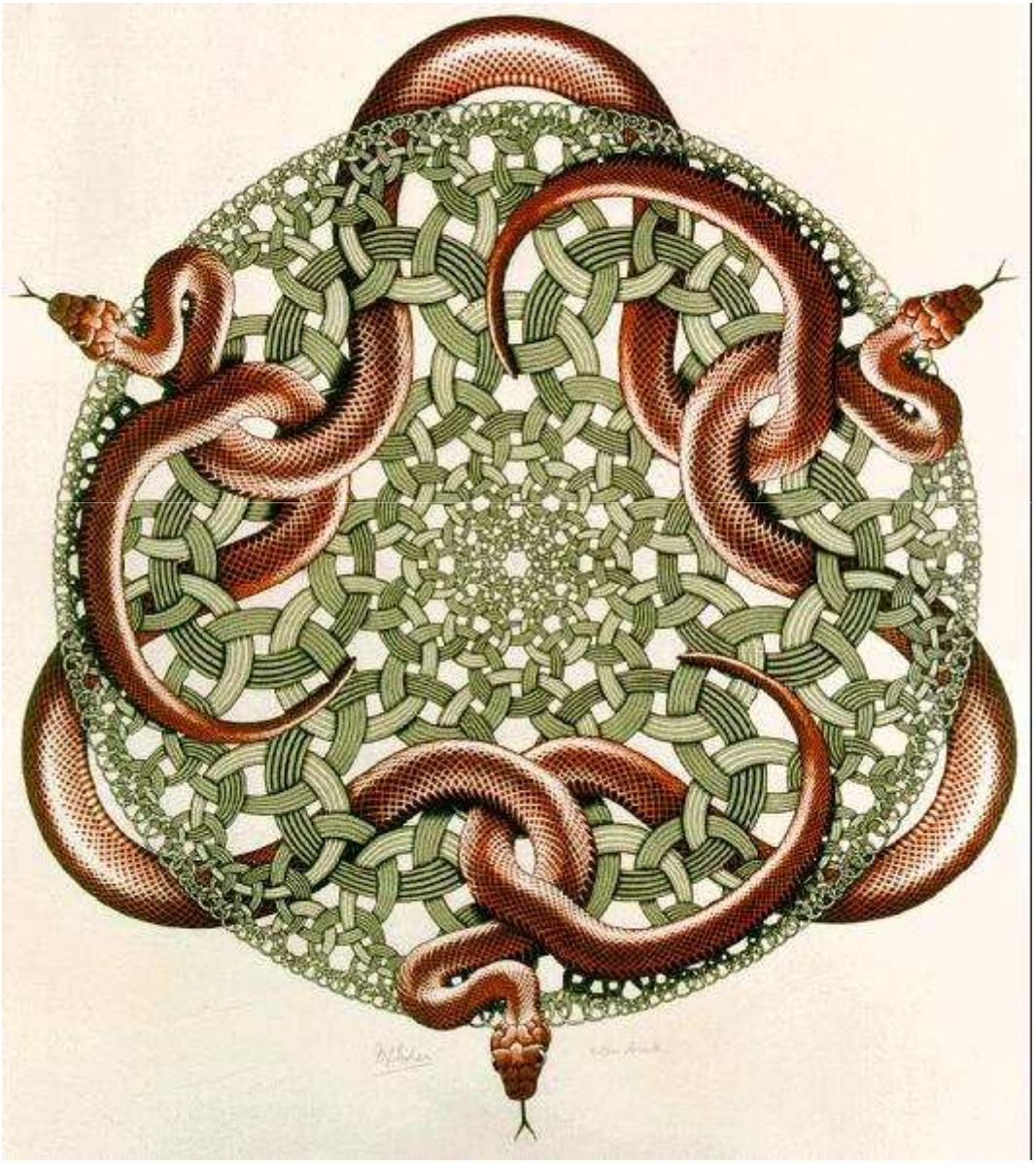
Aquilea, Italy

Book of Kells



Topology in art

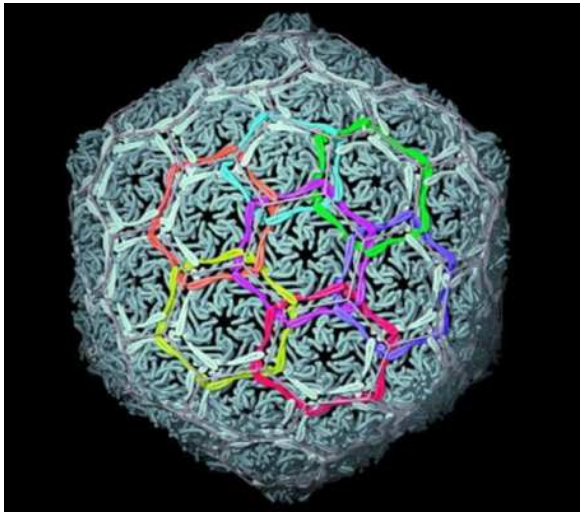
Snakes
M.C. Escher



Topology in art

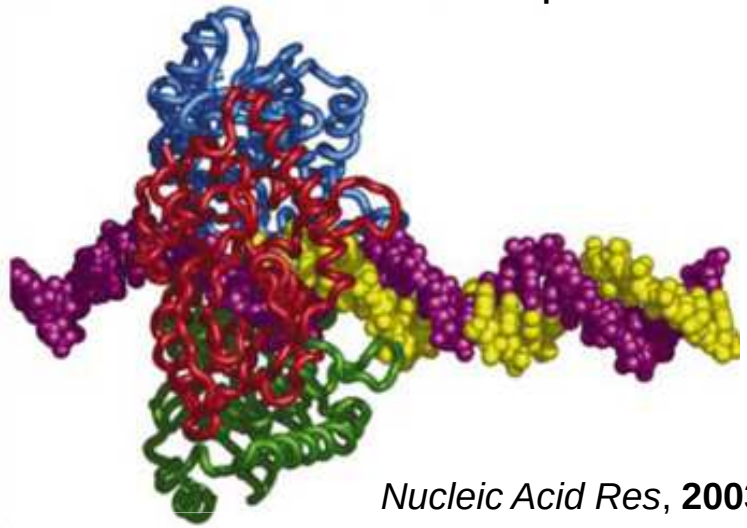
Topology in nature

Protein chainmail for a virus capside



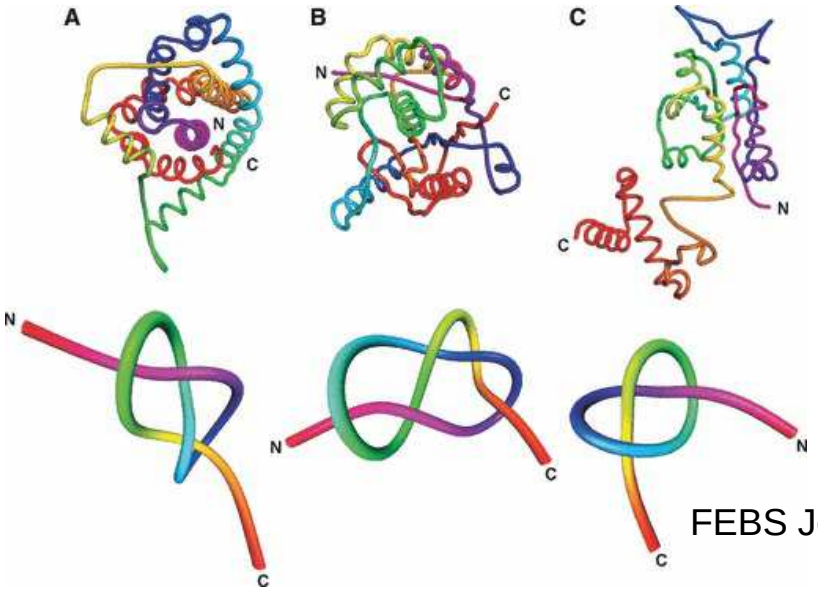
Science **2000**, *289*, 2129

Exonuclease-DNA complex



Nucleic Acid Res, **2003**, *31*, 1585

Knotted proteins



FEBS Journal, **2009**, 276, 365

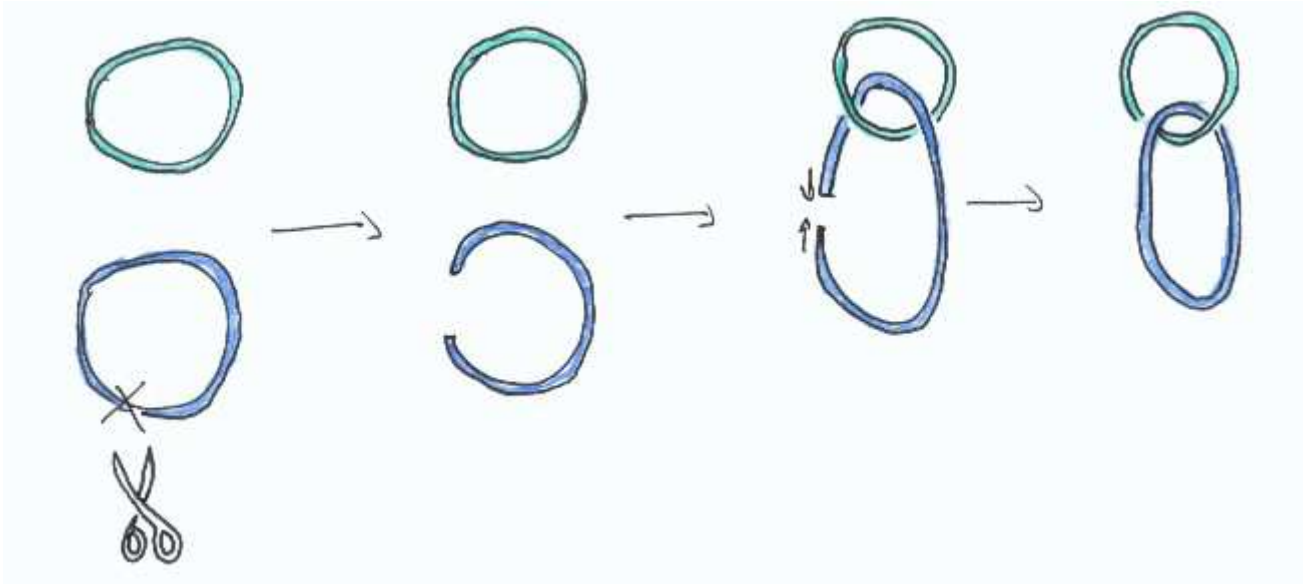
Topological chemistry

- If two molecules are different only for their graphs, they are **topological isomers**

a is an isomer of **b** and **c**.
b and **c** are topological enantiomers.

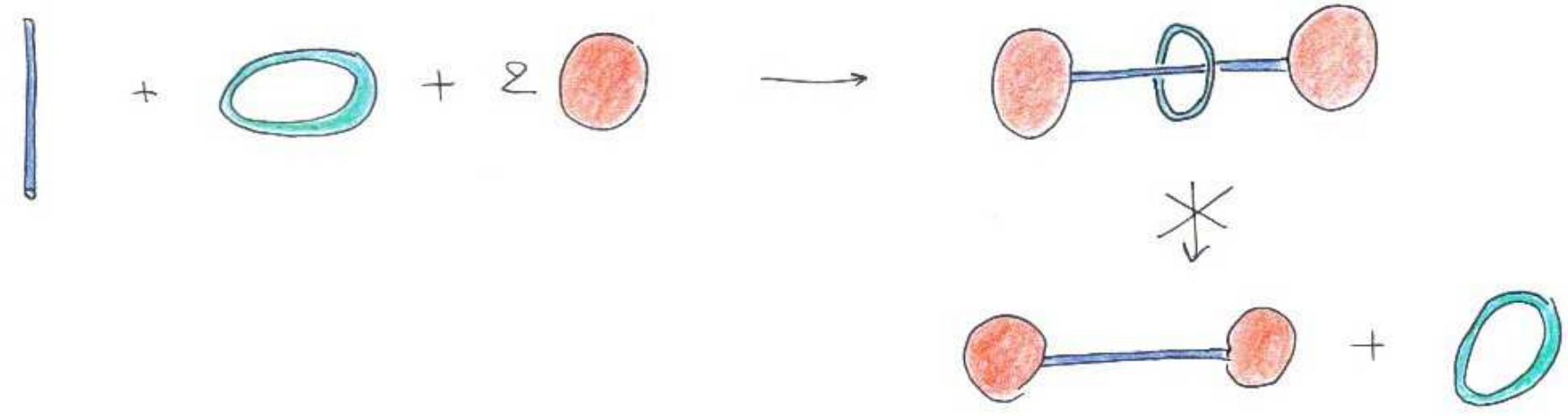
- Most popular classes of topological molecules are **catenanes** and **rotaxanes**

catenane:

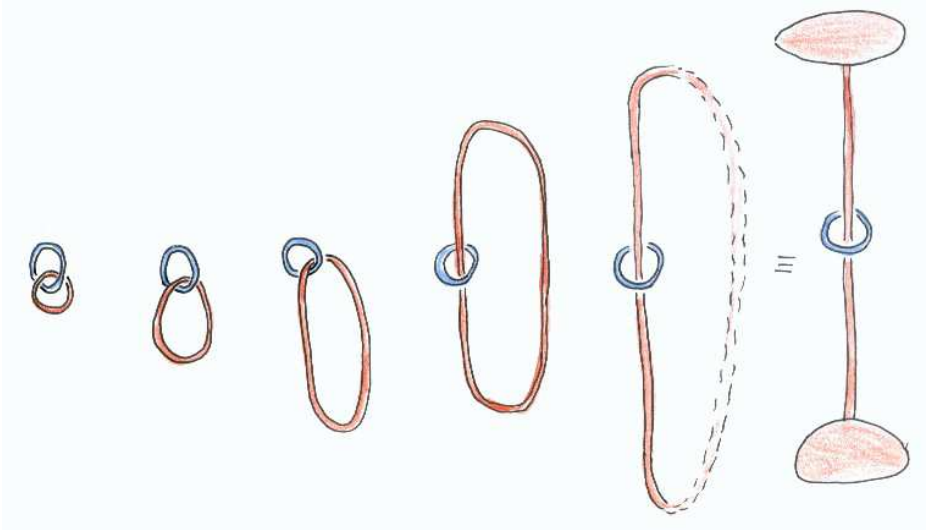


Topological chemistry

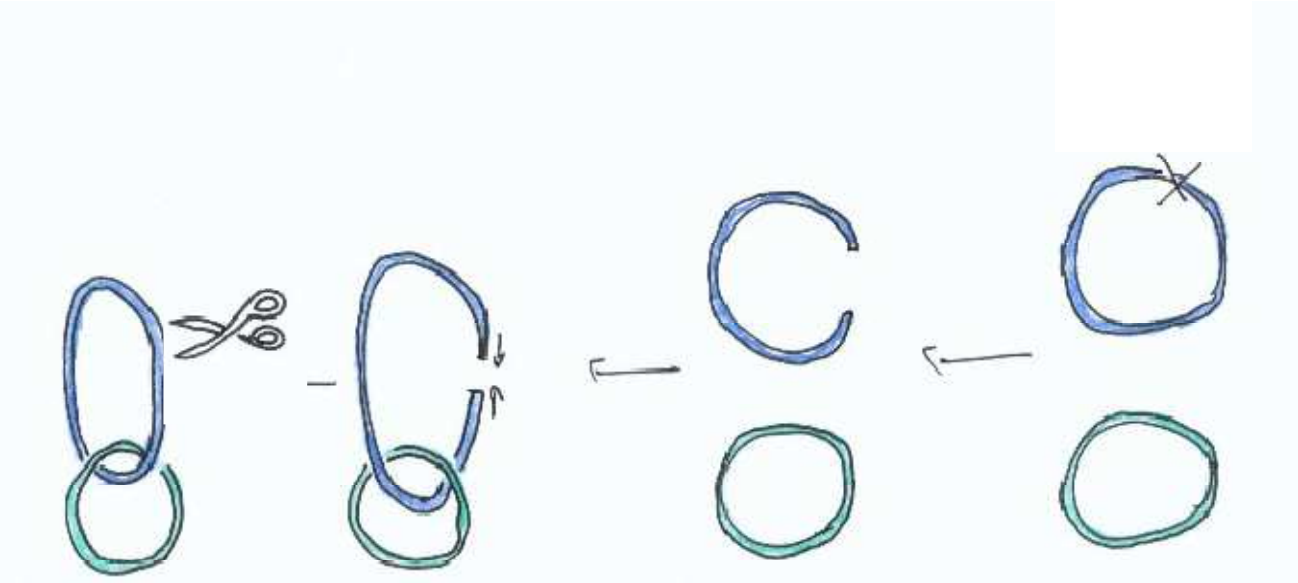
rotaxane:



rotaxane is not strictly speaking a topological object
but, in chemistry, there is a good reason to say so:



Topological chemistry



Loss of the structure by breaking a covalent bond
= interaction is strong: not supramolecular chemistry?

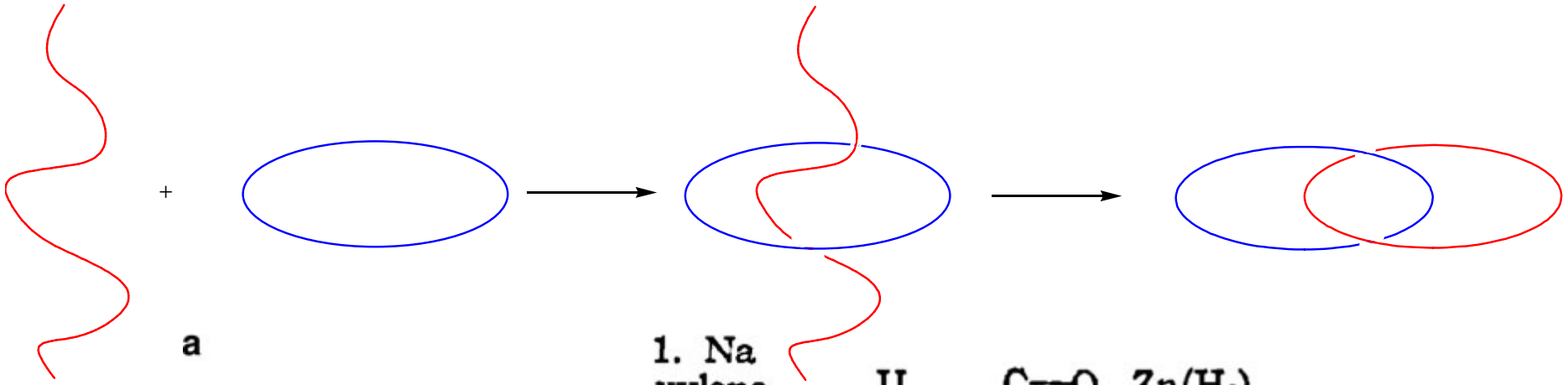
BUT: no covalent bond between the two rings!
= interaction is weak

mechanical bond

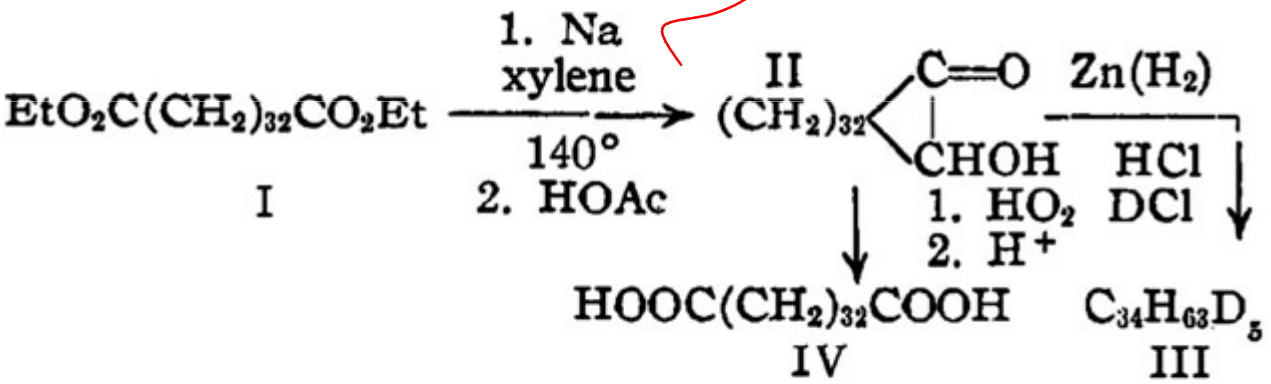
How can this kind of molecules be made?

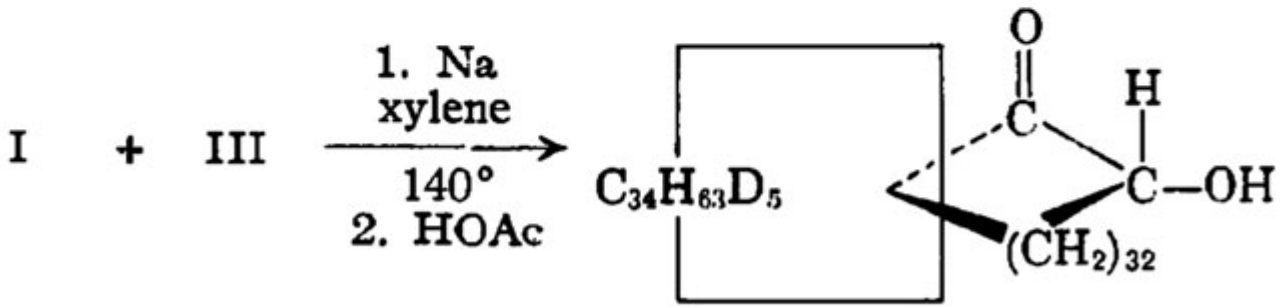
Catenane by statistical method

- 1960: statistical synthesis proposed by Wasserman. unsuccessful.



a



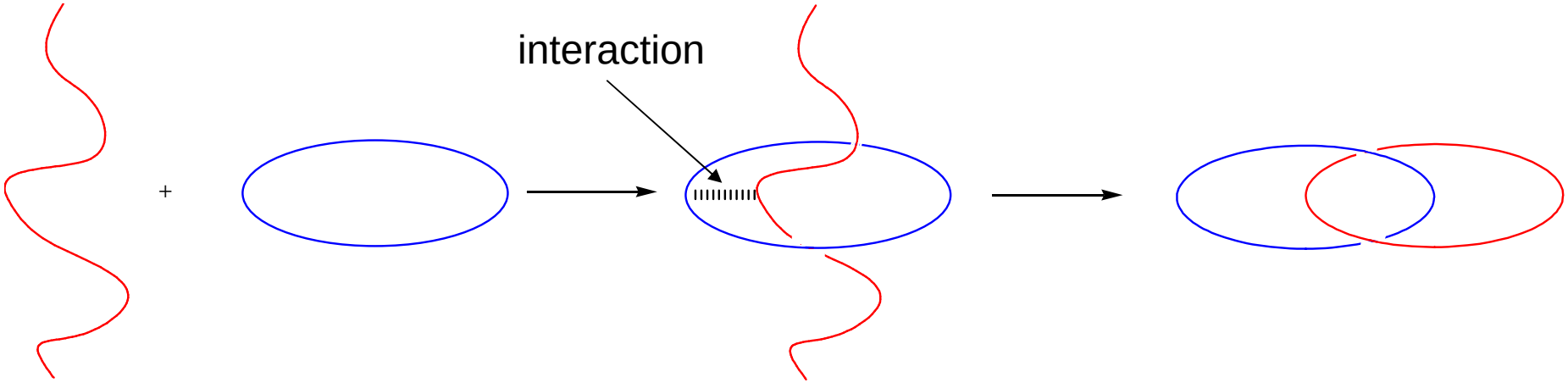


V

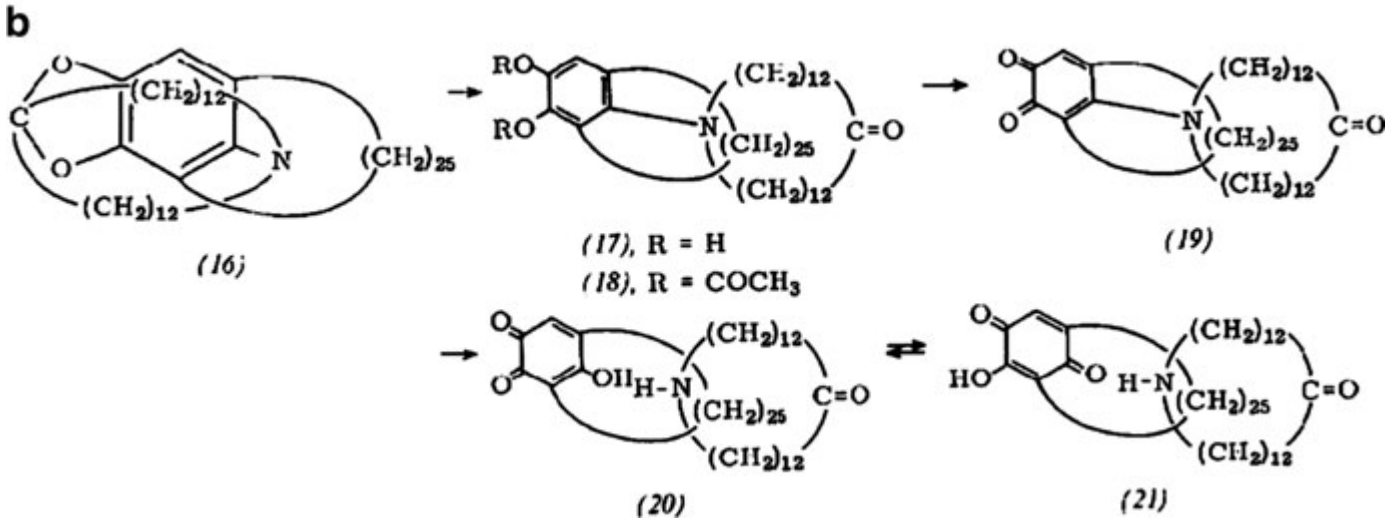
Wasserman, *J. Am. Chem. Soc.*,**1960**, *82*, 4433

Catenane by template synthesis

- Template synthesis:



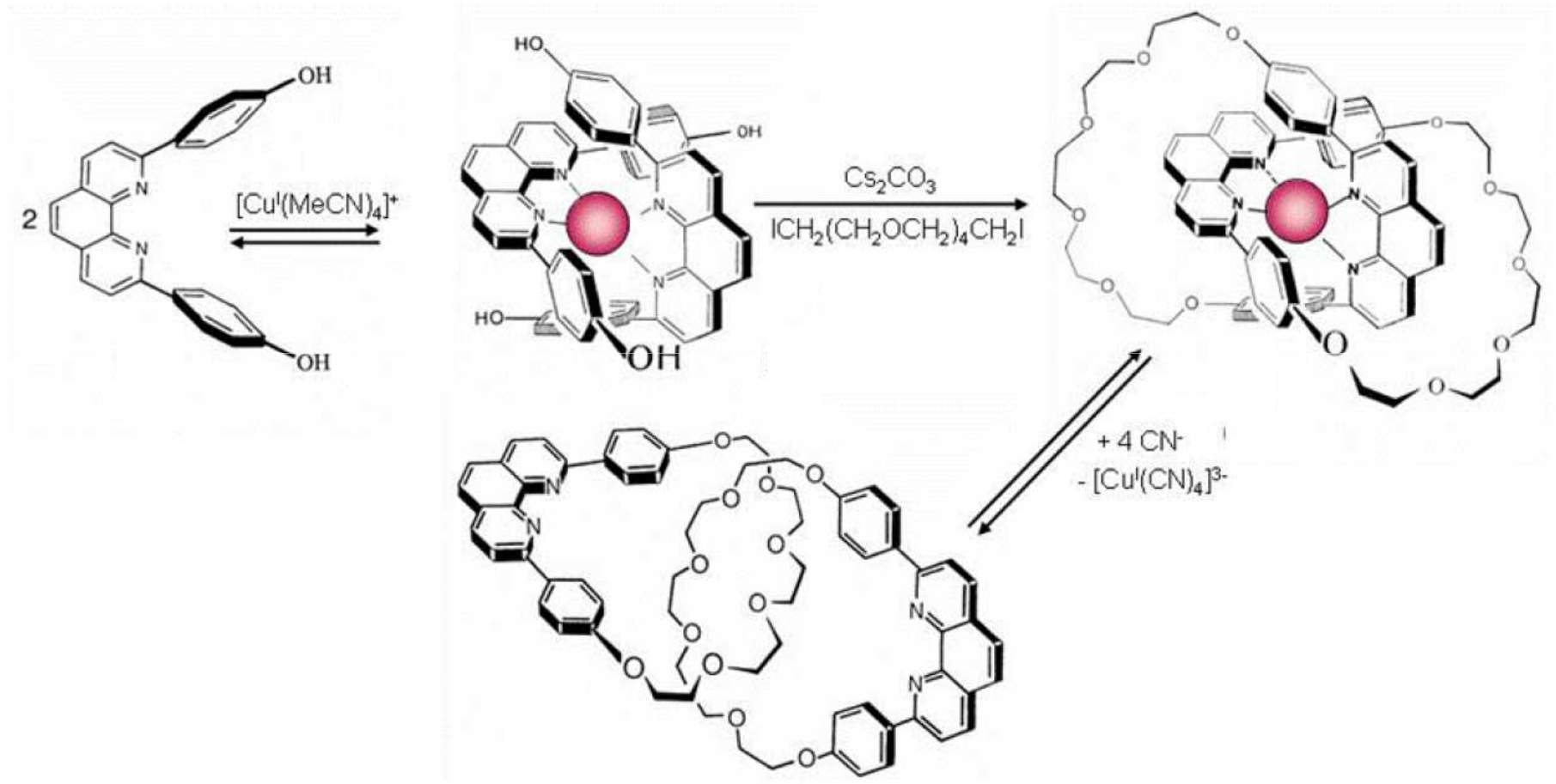
- First work by Schill and Lüttringhaus



Schill and Lüttringhaus, *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 546

Catenane: copper-template reaction

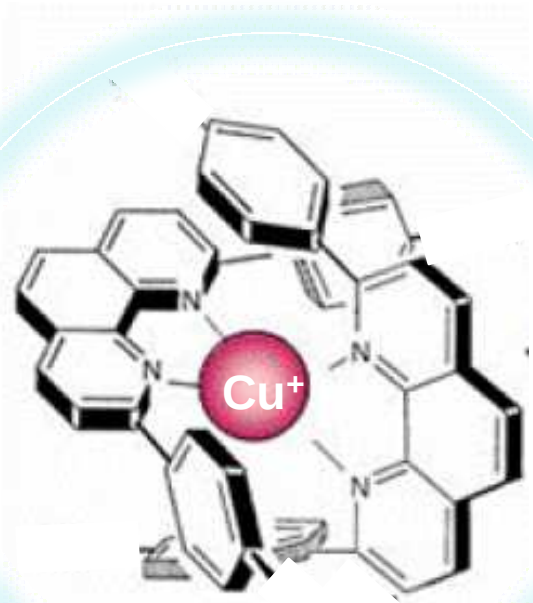
Sauvage's contribution: 1983



Dietrich-Buchecker, Sauvage et al. *Tet. Lett.,* **1983**, 24, 5095

Origin of the strategy

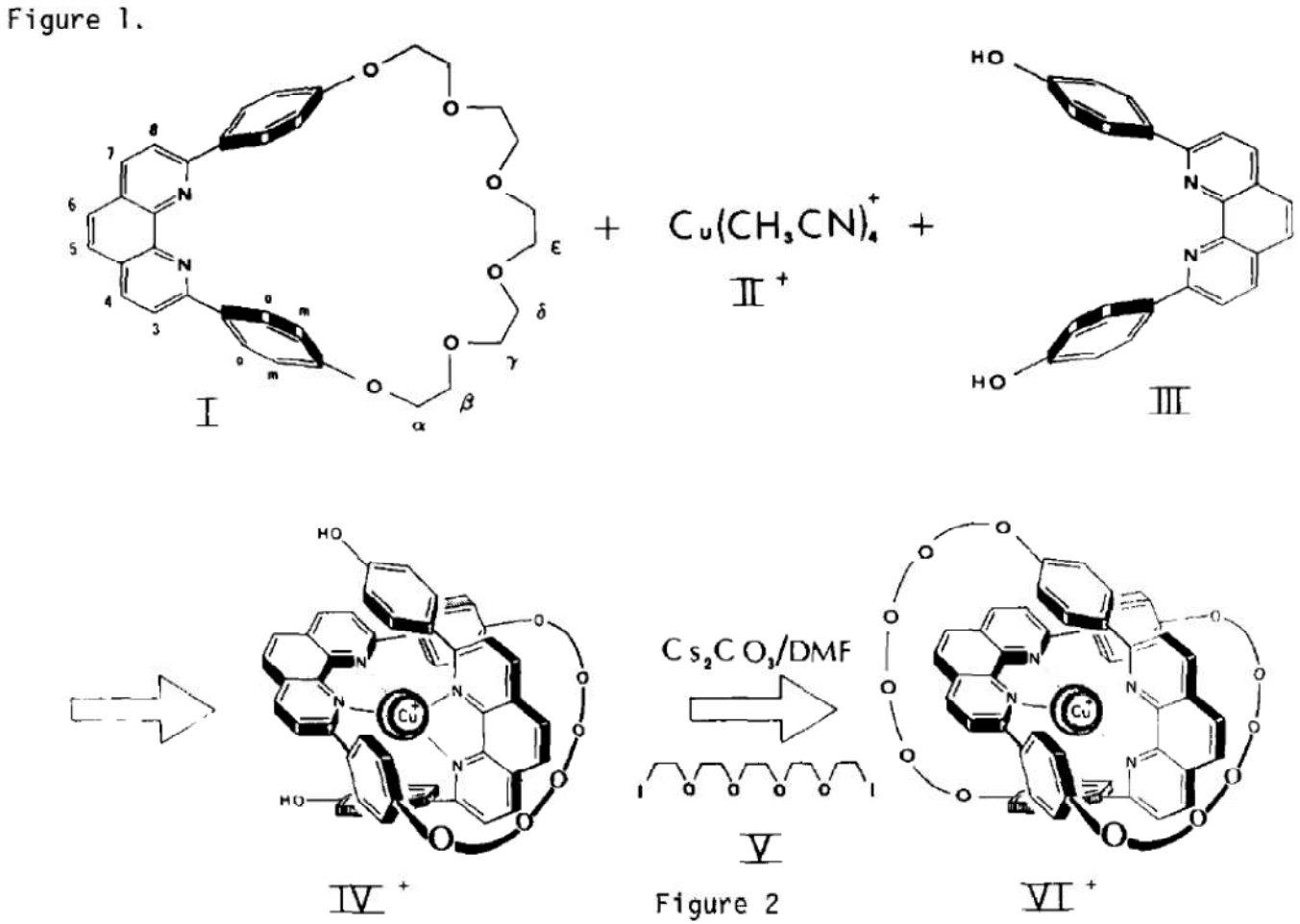
Water splitting project with McMillin
Copper photocatalyst instead of expensive Ruthenium



$$H_2O \longrightarrow H_2 + \tfrac{1}{2} O_2$$

Catenane: copper-template reaction

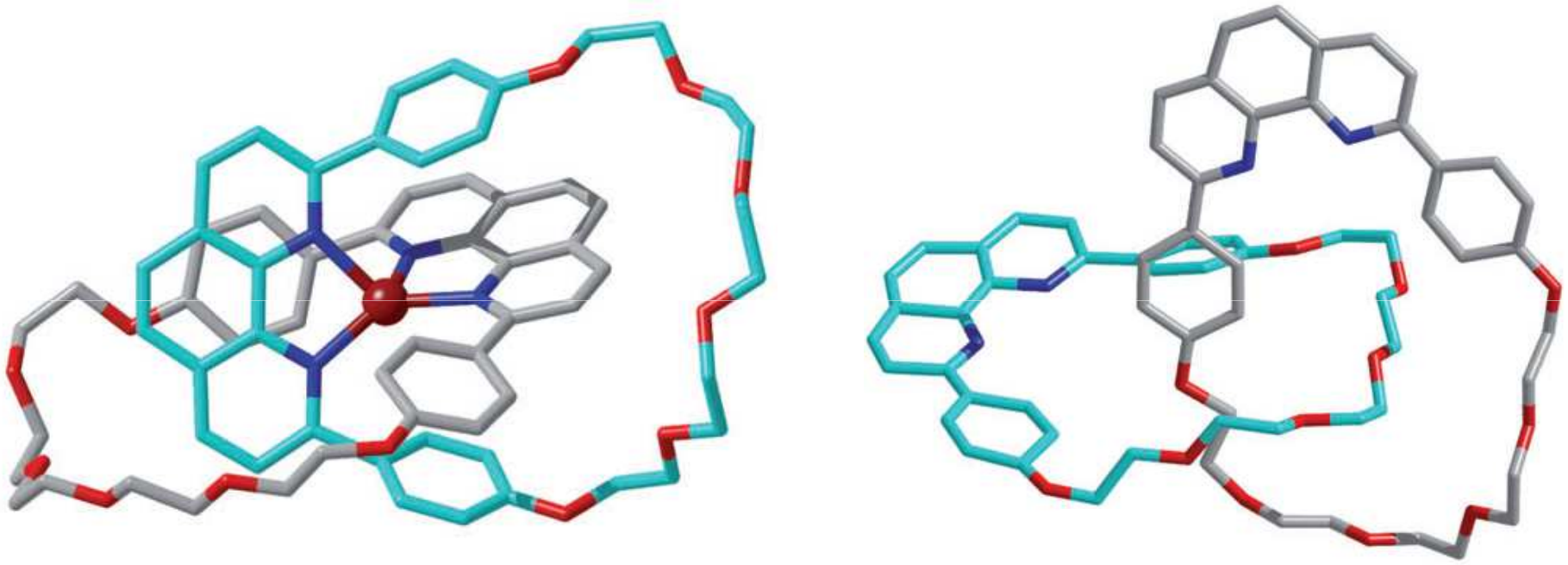
Sauvage's contribution: 1983, copper template synthesis.



(maximum site occupancy rule)

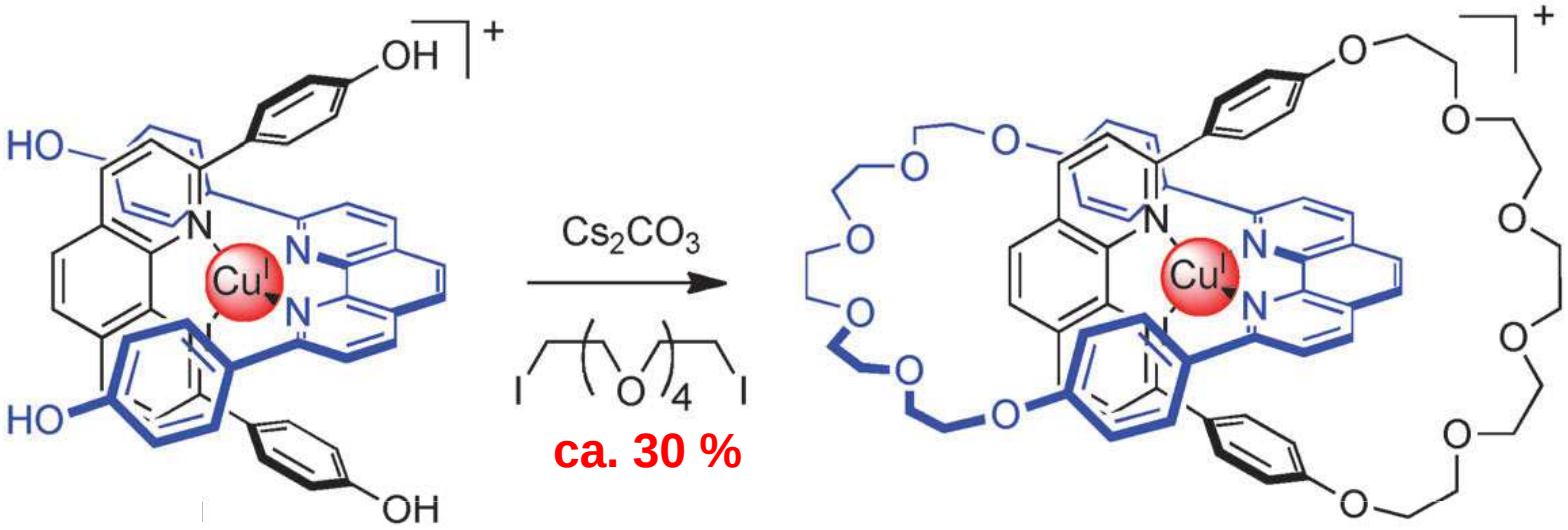
Sauvage et al. *Tet. Lett.,* **1983**, 24, 5095

Catenane: X-ray structure

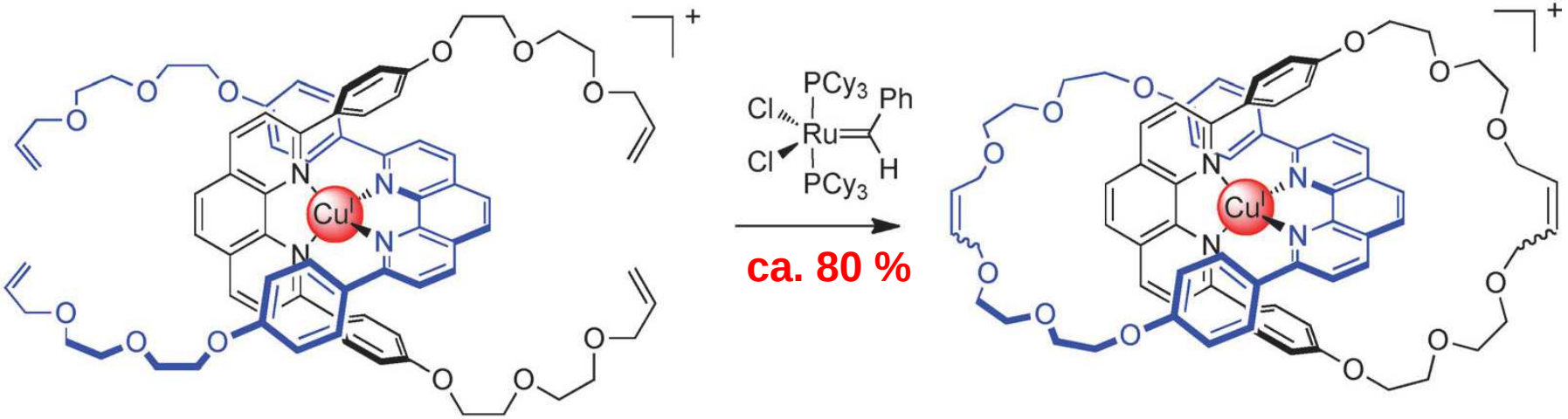


Template synthesis: importance of the closing reaction

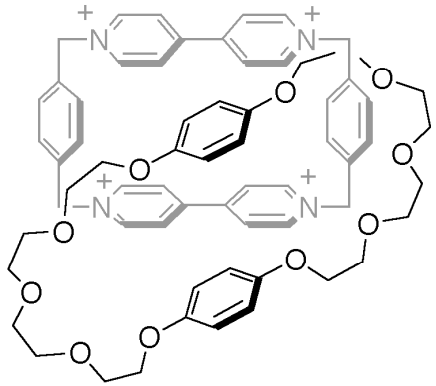
a) Williamson ether synthesis: R–OH + X–R' ⟶ R–O–R'



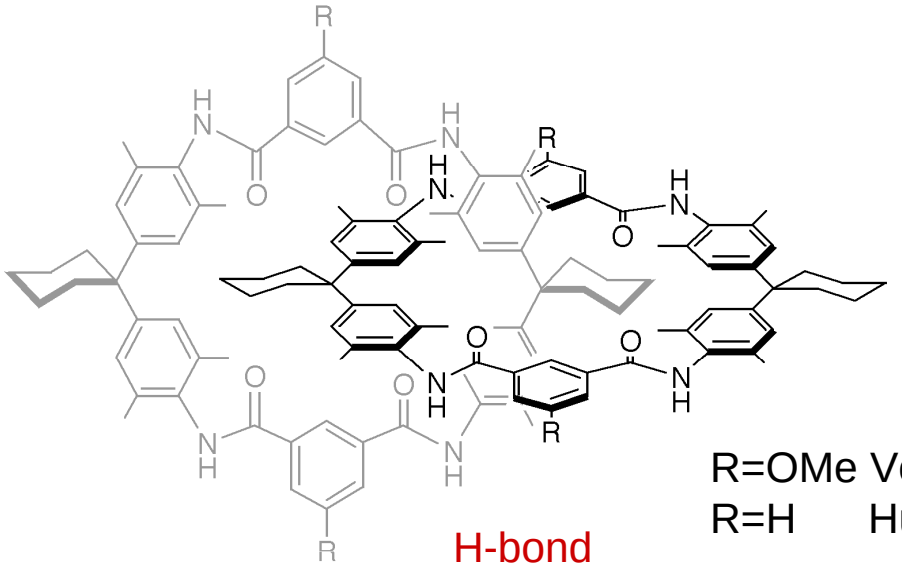
b) Ring closing metathesis (RCM): 2 x R ⟶ R R



Catenane: other template syntheses

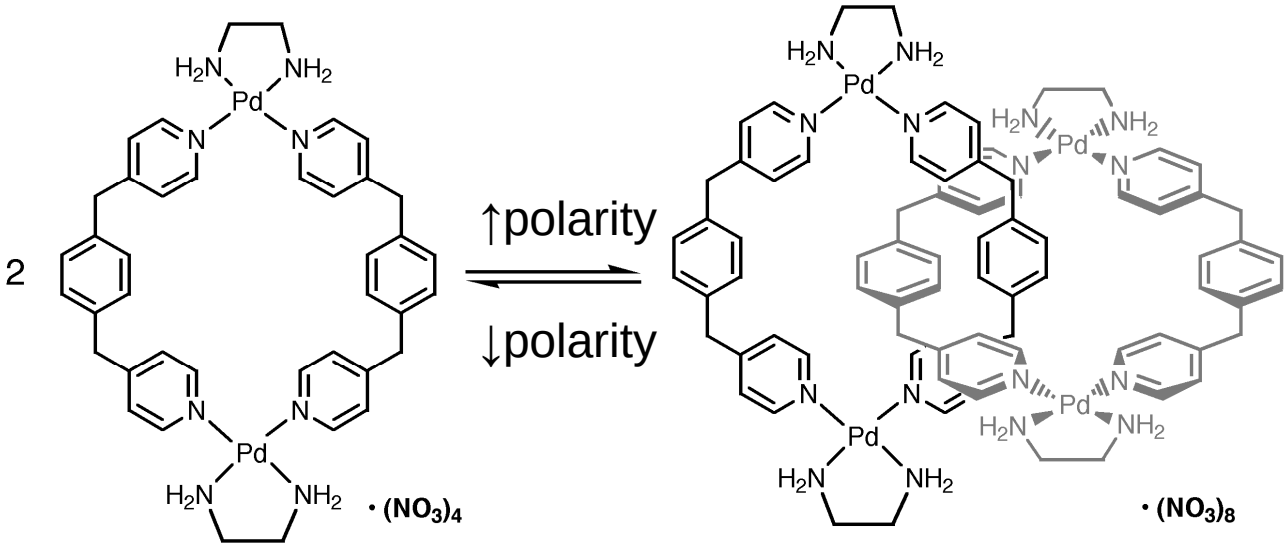


Π-stacking, Stoddart, 1989



H-bond

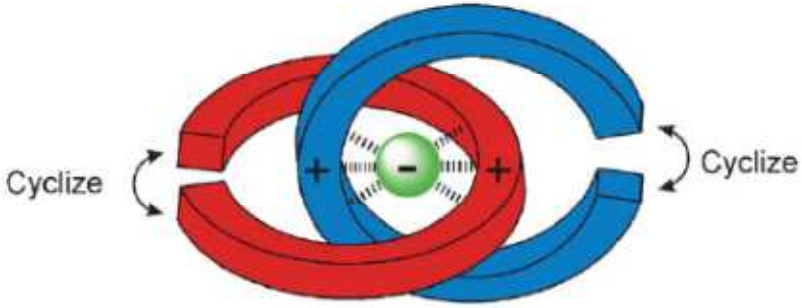
R=OMe Vögtle, 1992
R=H Hunter, 1992



Hydrophobic effect, Fujita, 1994

Catenane: other template syntheses

Sauvage's strategy transposed to an anion template:



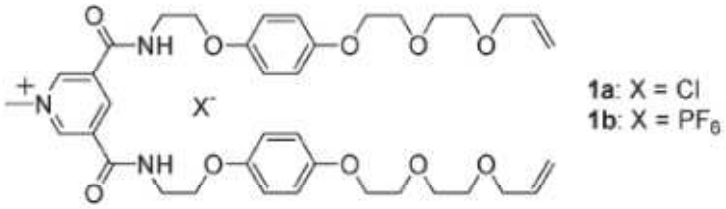


Fig. 2 Structure of the catenane precursor.

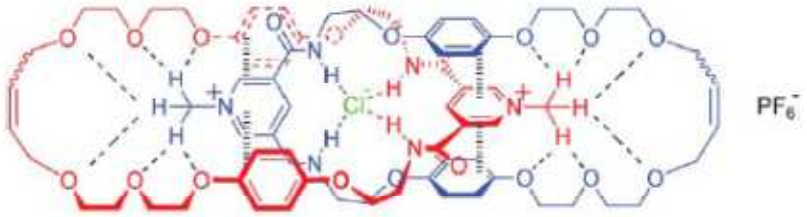
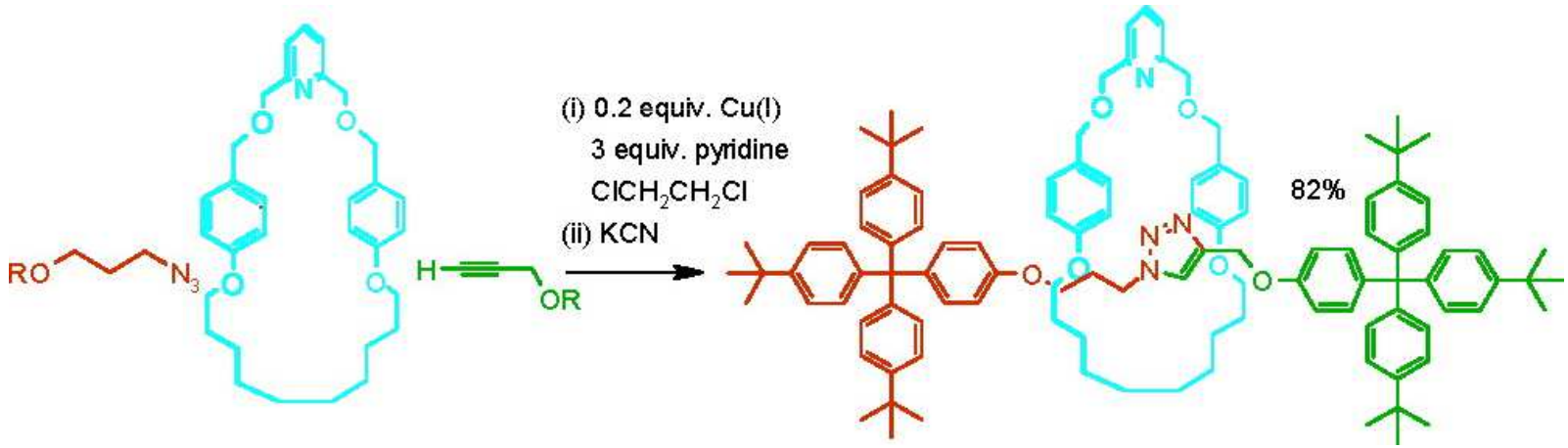


Fig. 3 Structure of the [2]catenane $2^{2+}(Cl^-)(PF_6^-)$.

Beer et al. *Chem. Commun.*, **2006**, 3676

Rotaxane: active template synthesis

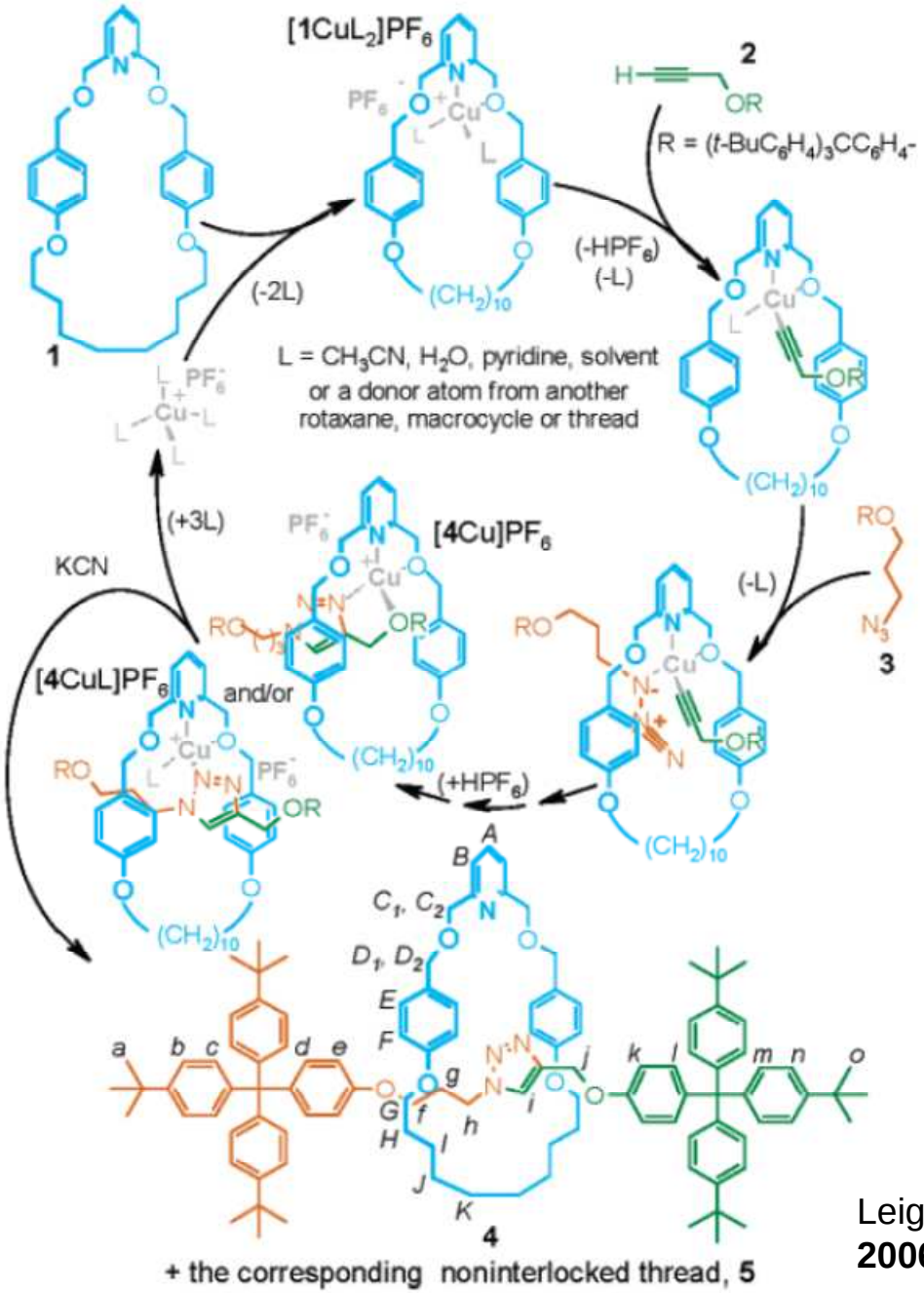
A new template reaction under kinetic control: *active template synthesis*.
The template is not only used for thermodynamic stabilization of a transient species but also for its role in bond formation.



Leigh et al. *J. Am. Chem. Soc.*, **2006**, 128, 2186

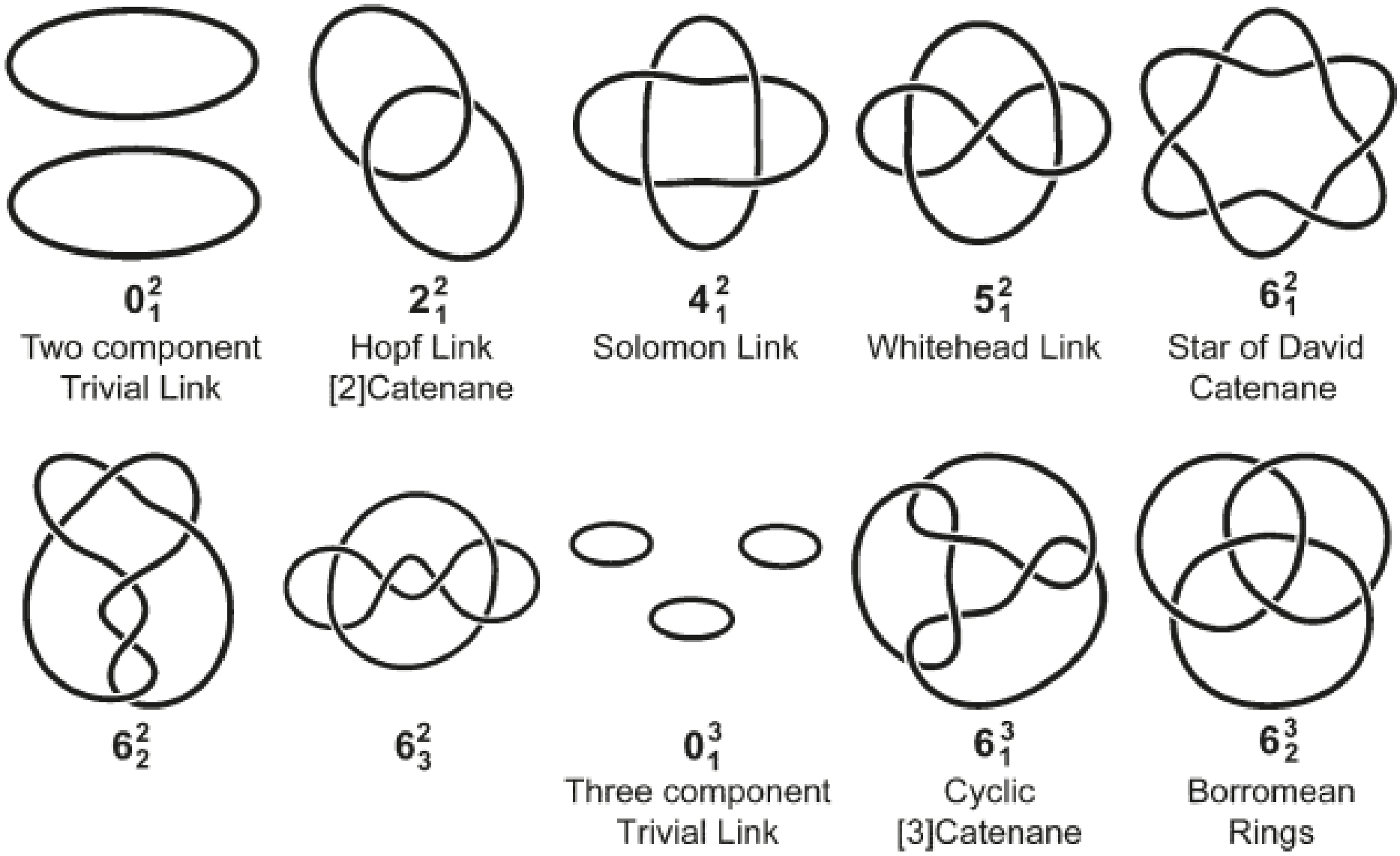
- Many other metal-catalyzed reactions have been employed (Pd(II), Ni(II)…)
- This strategy can also be used for the synthesis of catenane

Scheme 1. Proposed Catalytic Cycle for the Cu(I)-Template Synthesis of [2]Rotaxane **4** from **1**, **2**, and **3** (ref 9)



Leigh et al. *J. Am. Chem. Soc.*, **2006**, 128, 2186

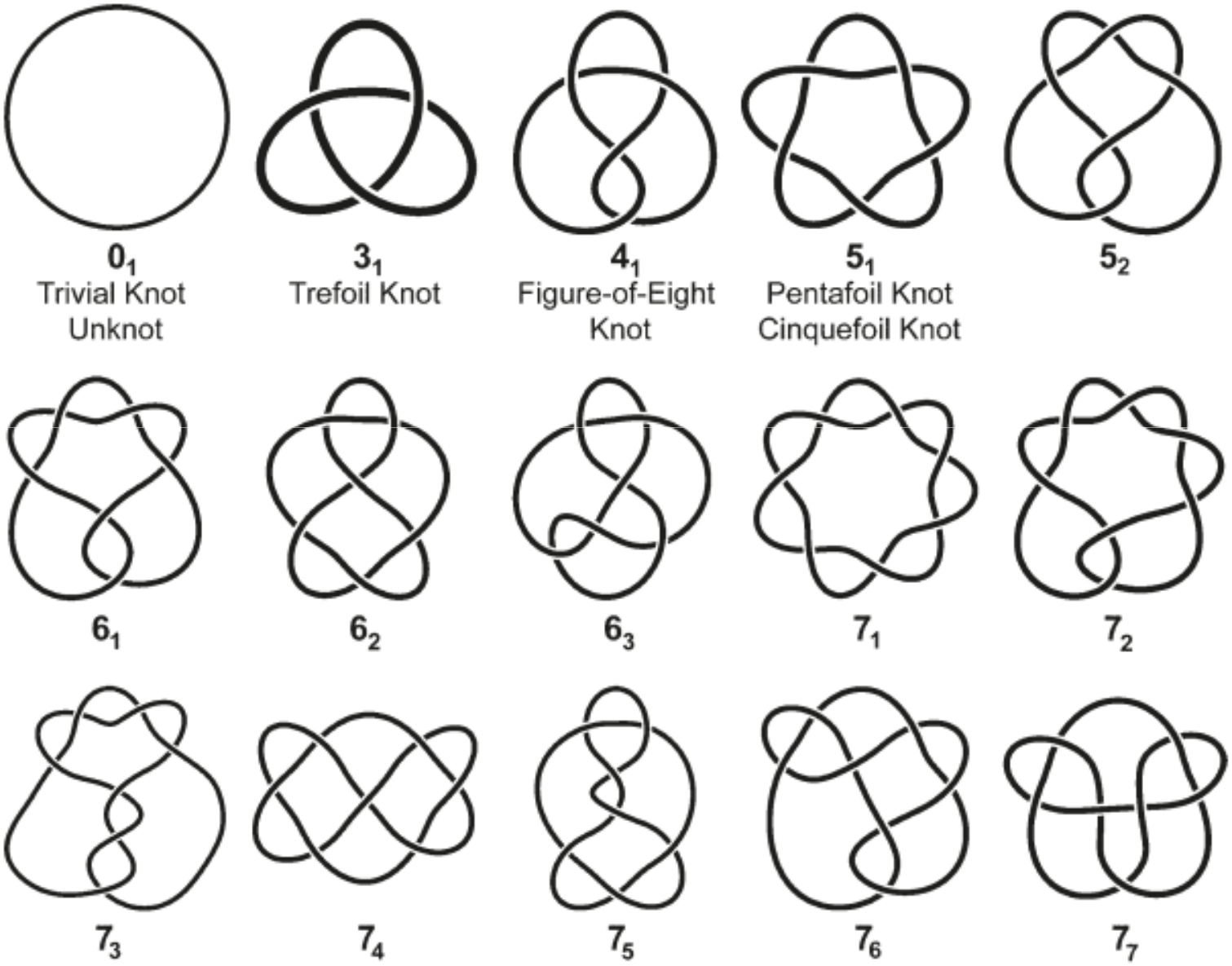
Beyond the simplest catenane



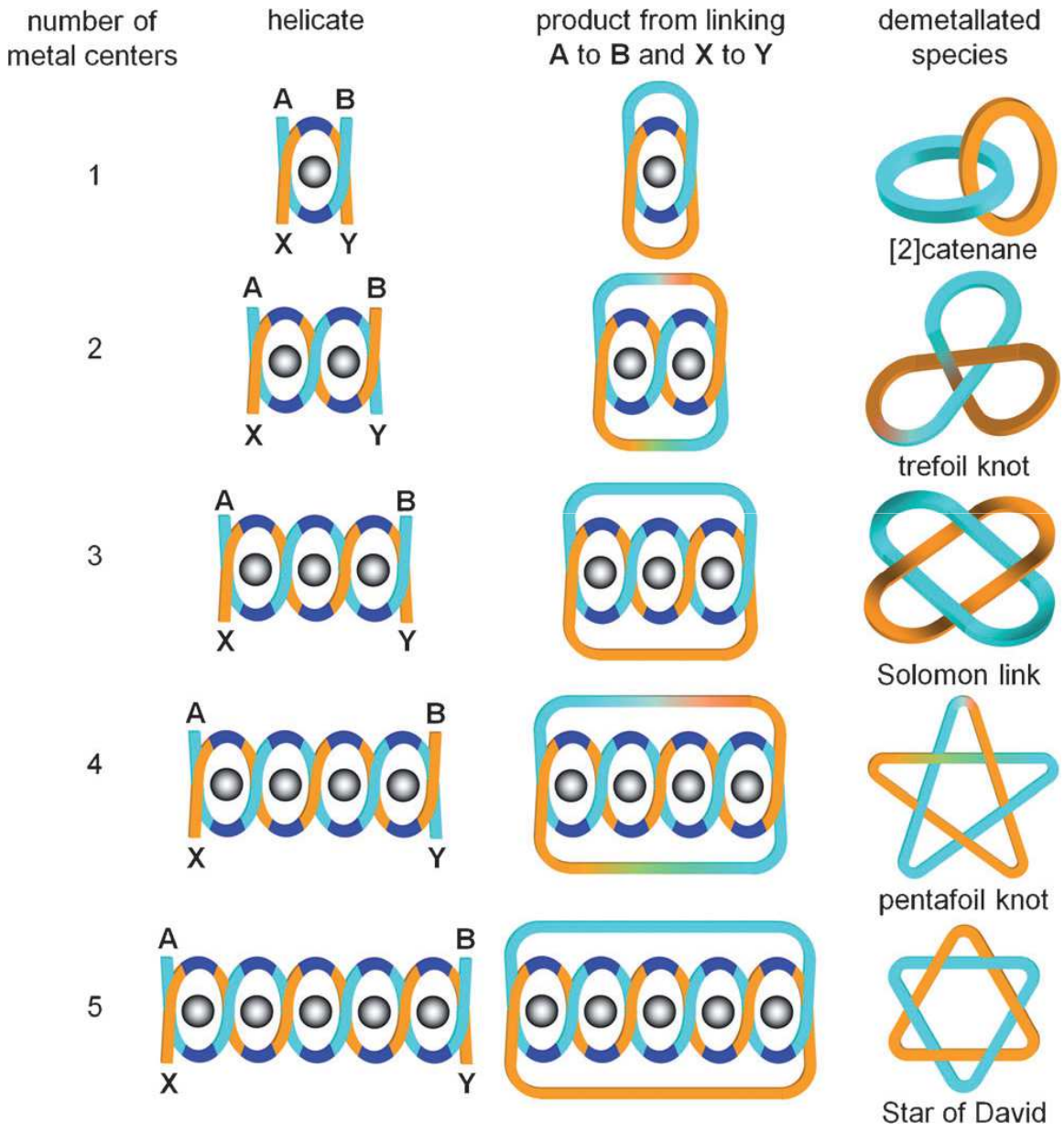
X^y_z: Alexander-Briggs notation

X = minimum crossing points; y = number of components; z = order of the knot

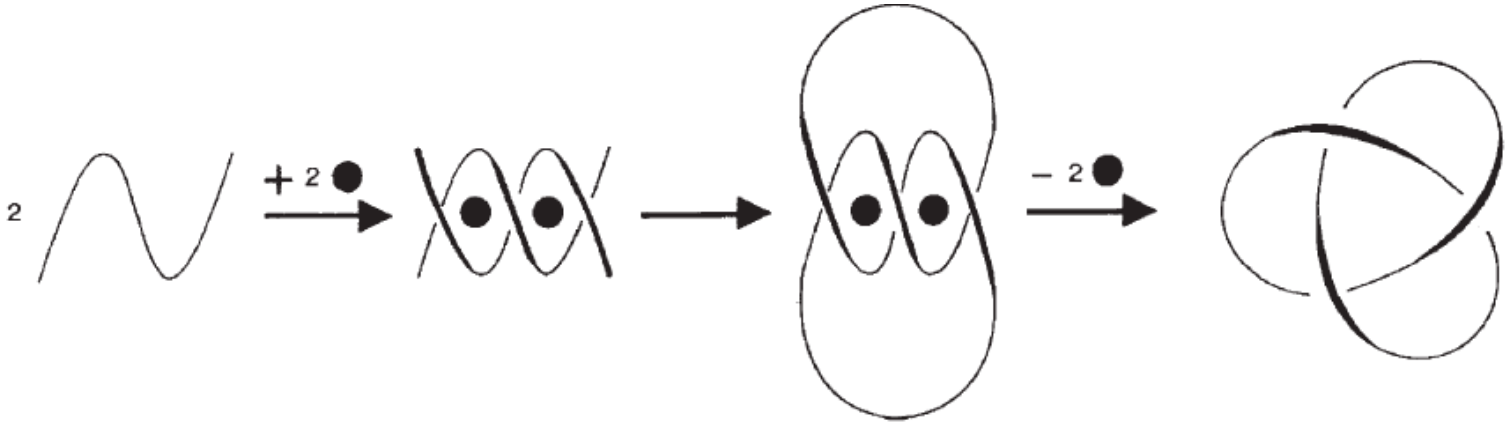
Molecular knots



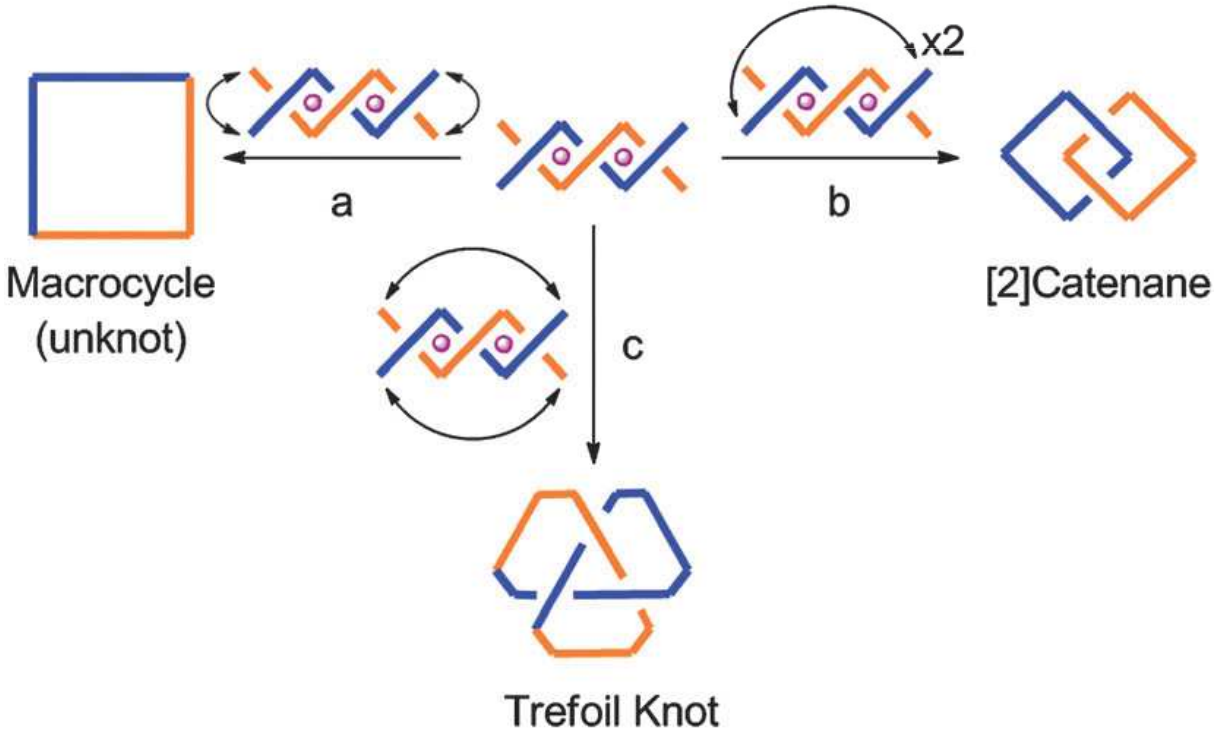
Sauvage's strategy



Molecular trefoil knot

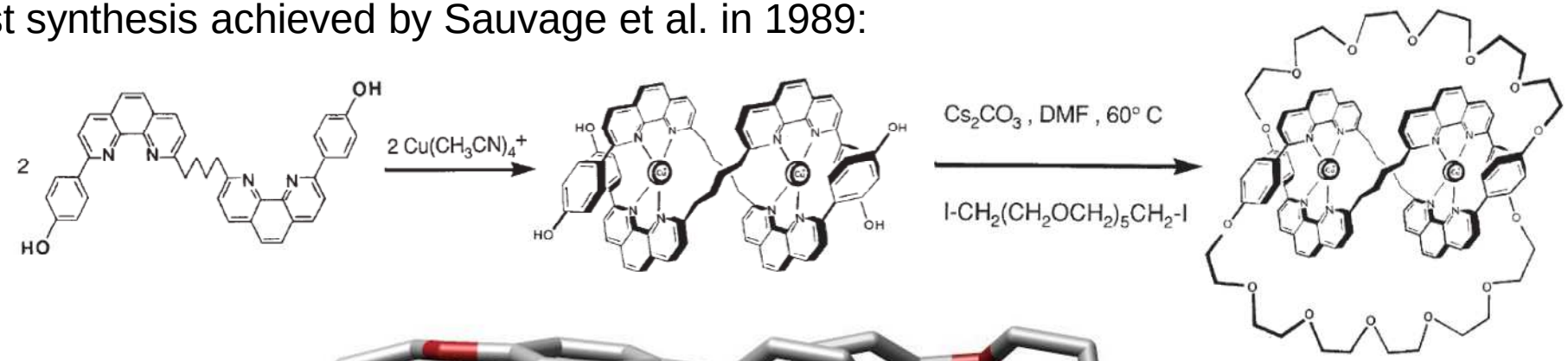


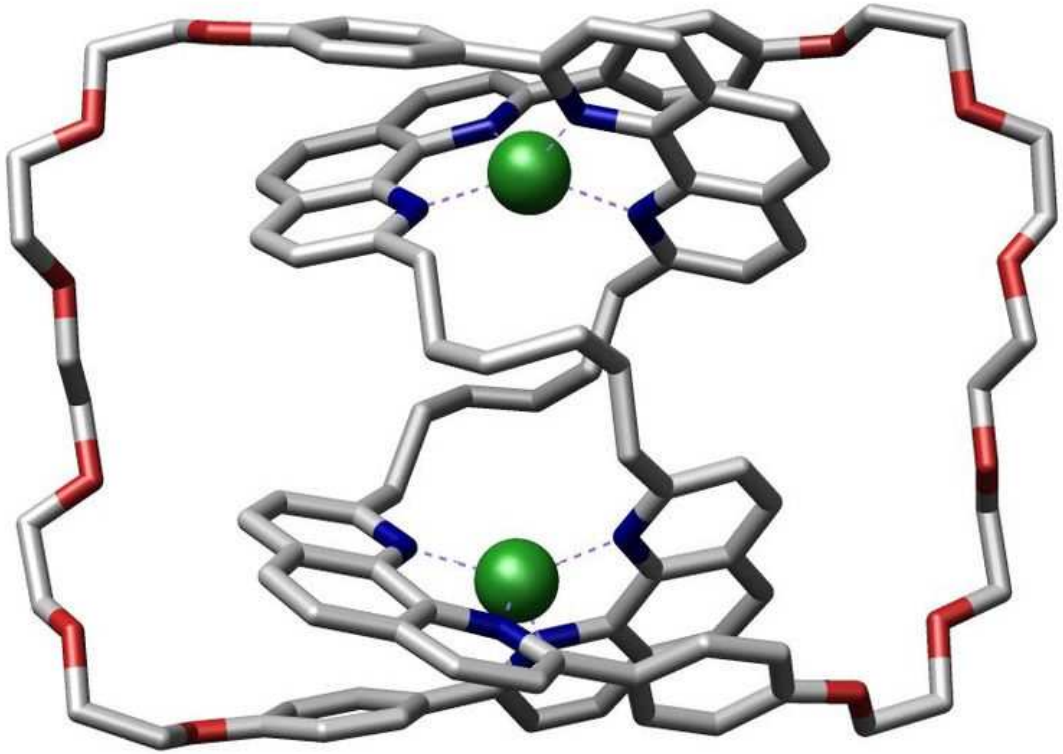
-Design: find the good connection



Molecular trefoil knot

First synthesis achieved by Sauvage et al. in 1989:



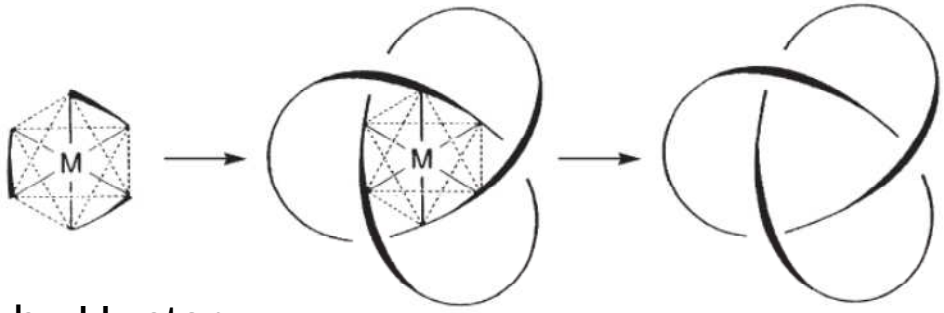


X-ray structure

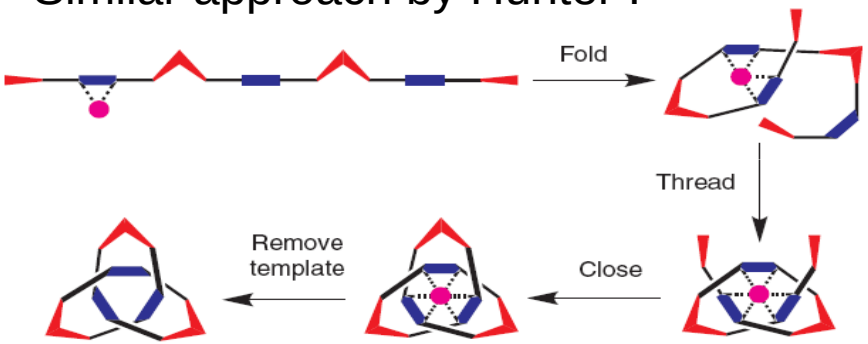
Sauvage et al. *Angew. Chem. Int. Ed.,* **1989**, 28, 189

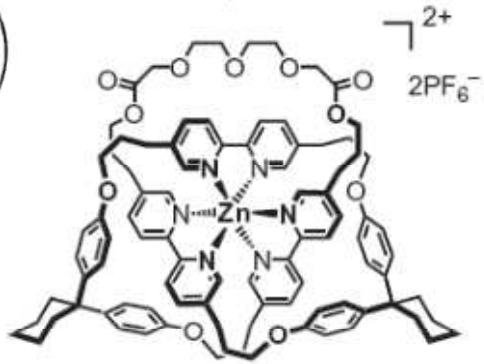
Molecular Knot

- Another strategy proposed by Sokolov in 1973:

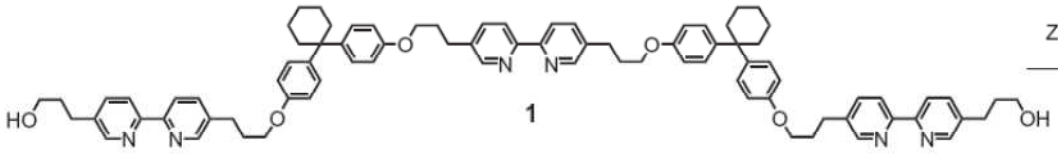


- Similar approach by Hunter :



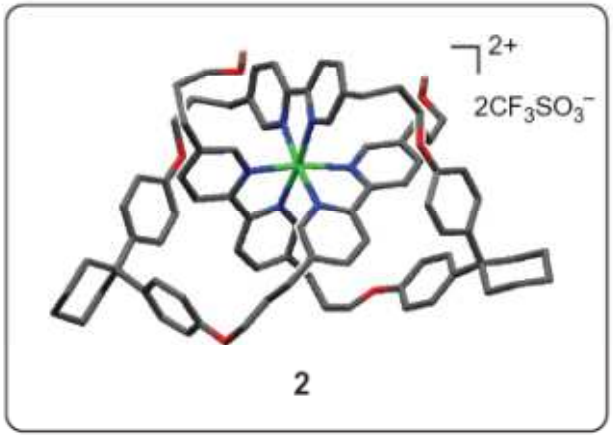


3 (25%)



1

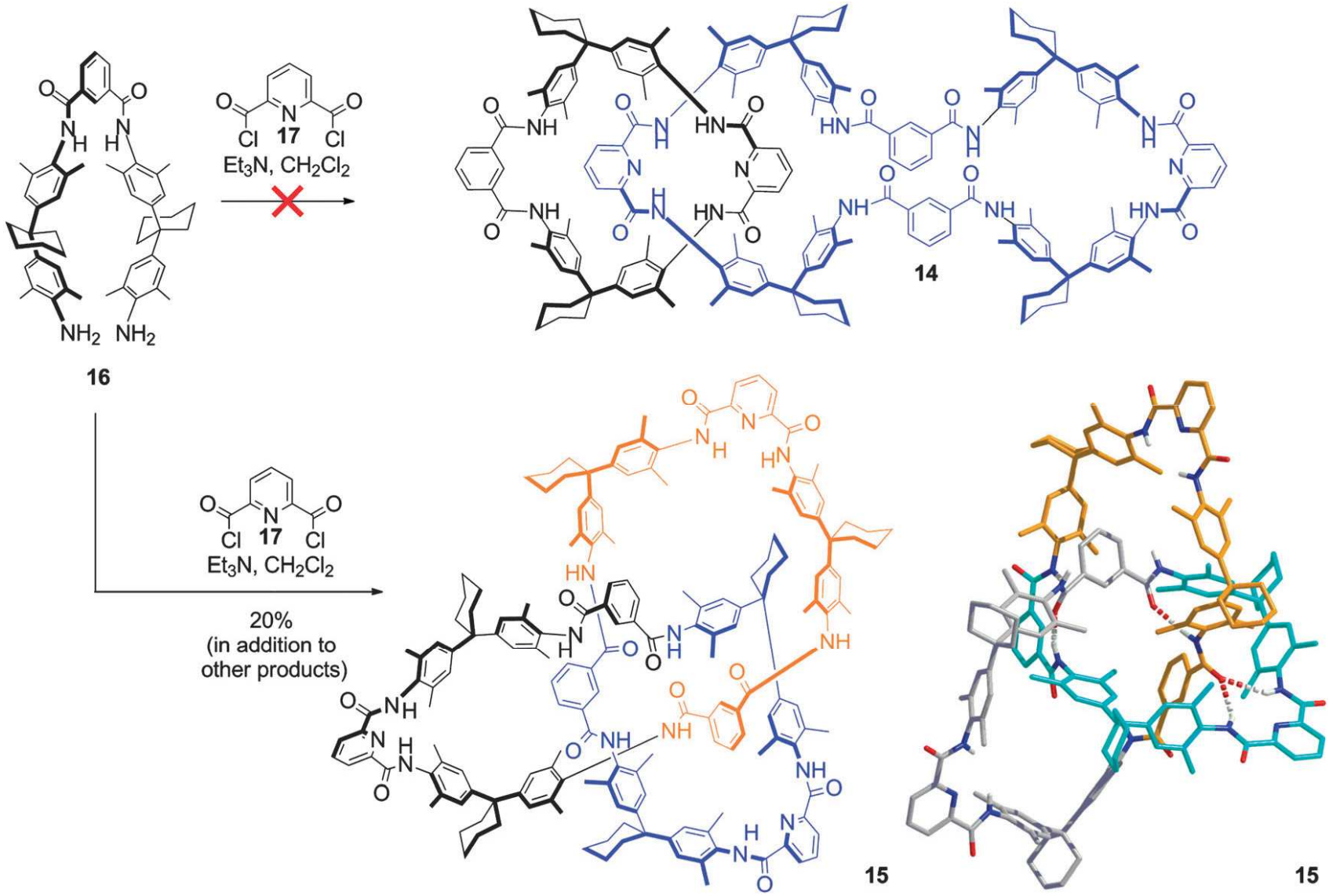
$Zn(CF_3SO_3)_2$



2

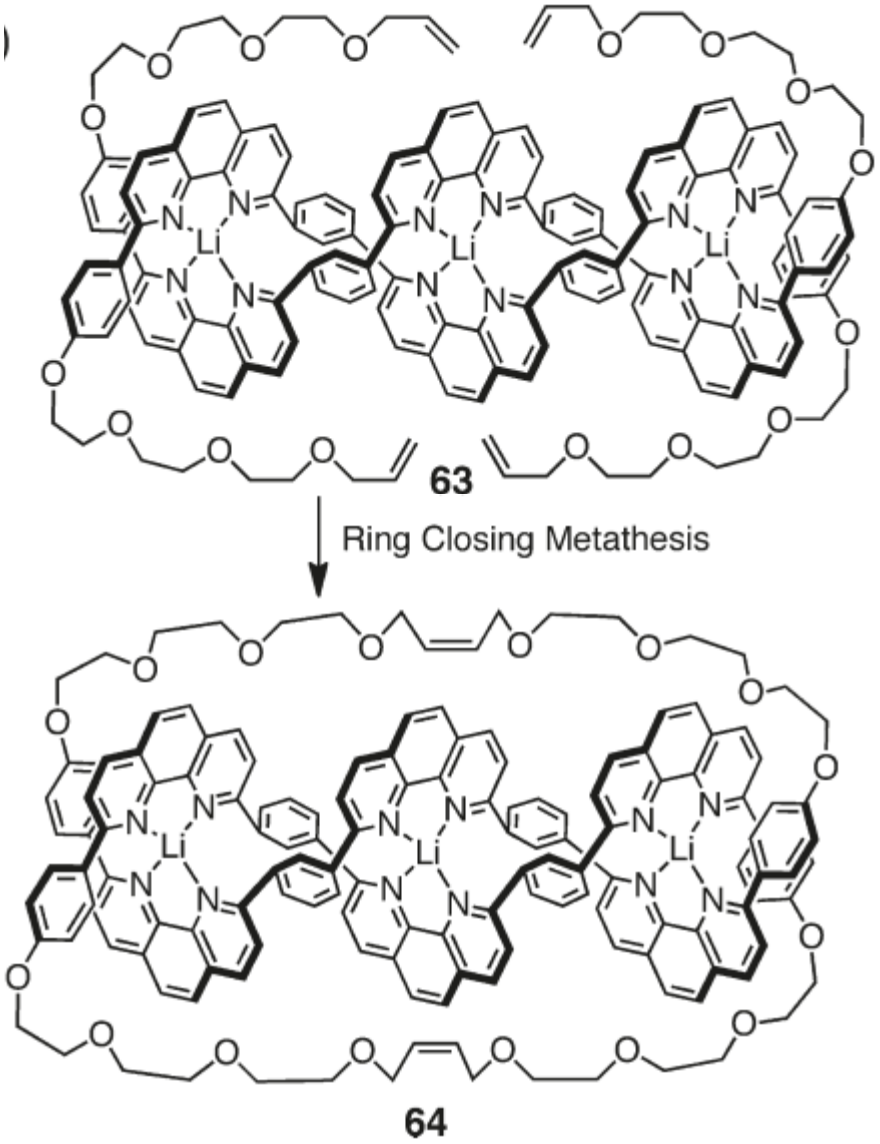
Hunter et al. *Nature. Chem.,* **2010**, 2, 218

H-bonding template synthesis of a molecular trefoil knot



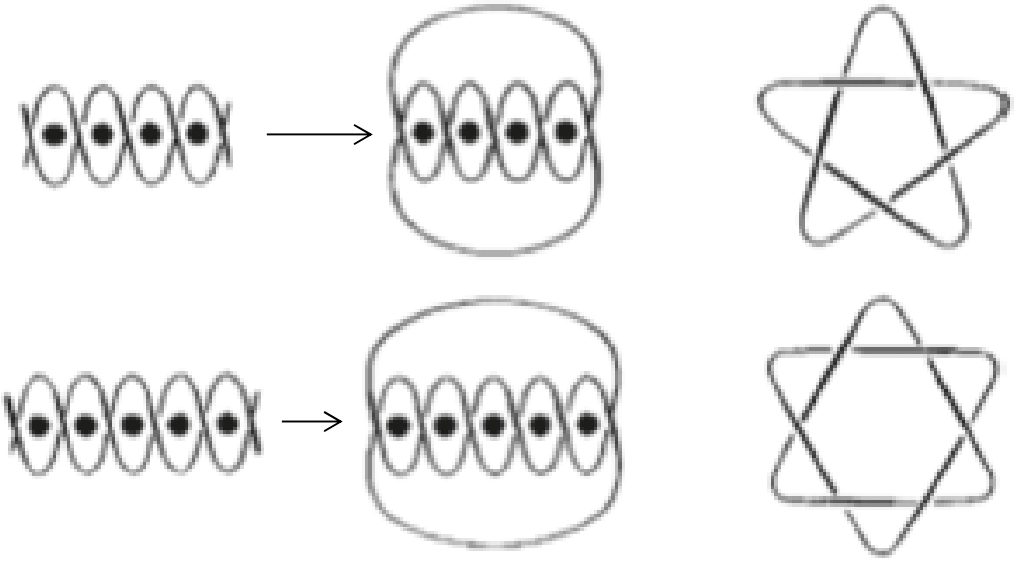
Vögtle et al., *Angew. Chem., Int. Ed.*, **2000**, *39*, 1616

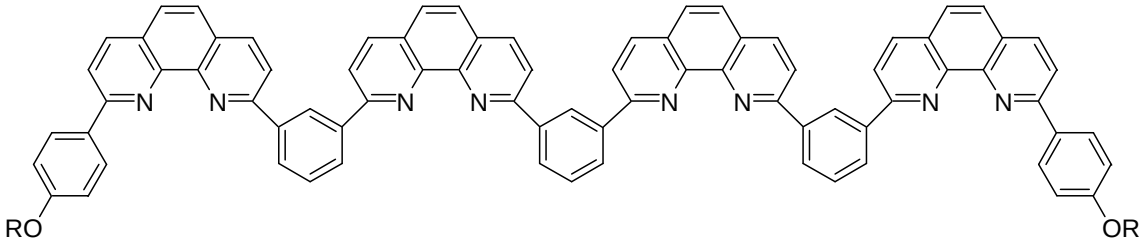
Doubly interlocked [2]catenane – Solomon link

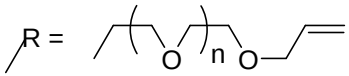


Sauvage et al. *Chem Commun.,* **1999**, 615.

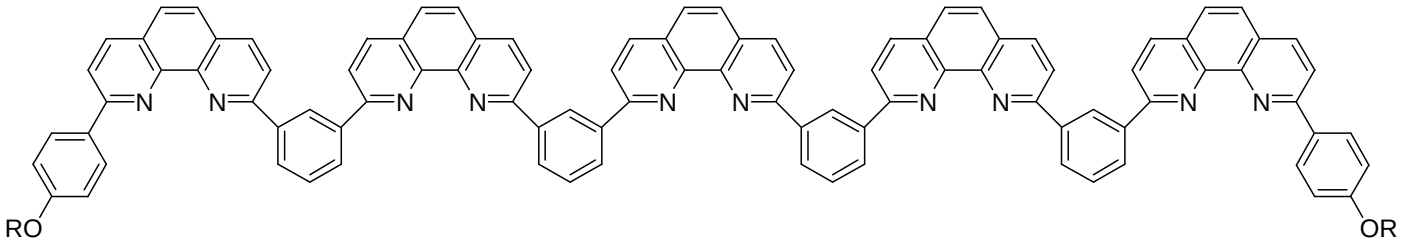
Limit to the strategy based on linear double helices







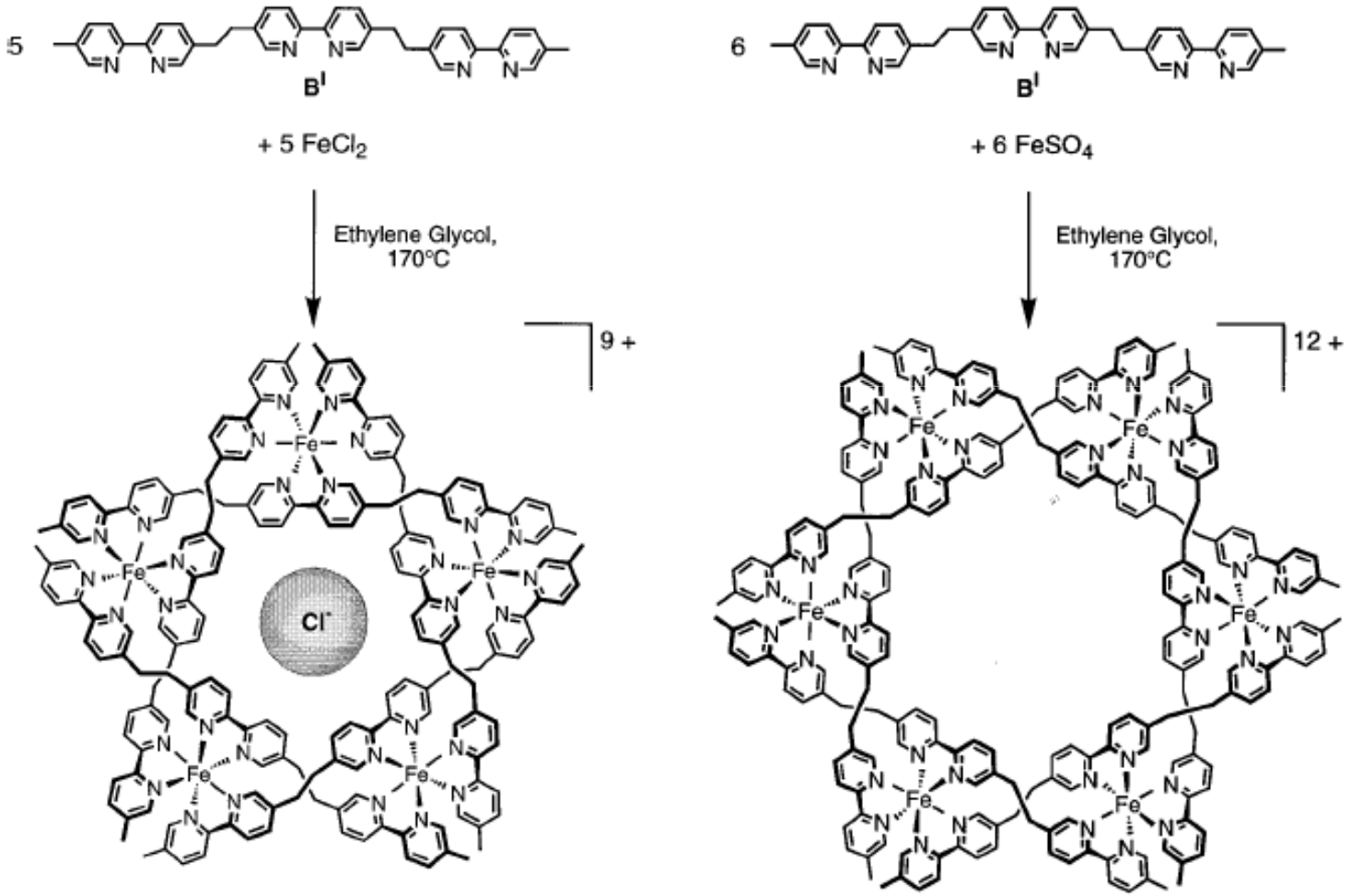
1: n=3
2: n=4



Sauvage et al. *Chem. Eur. J.* **2005**, 11, 4374

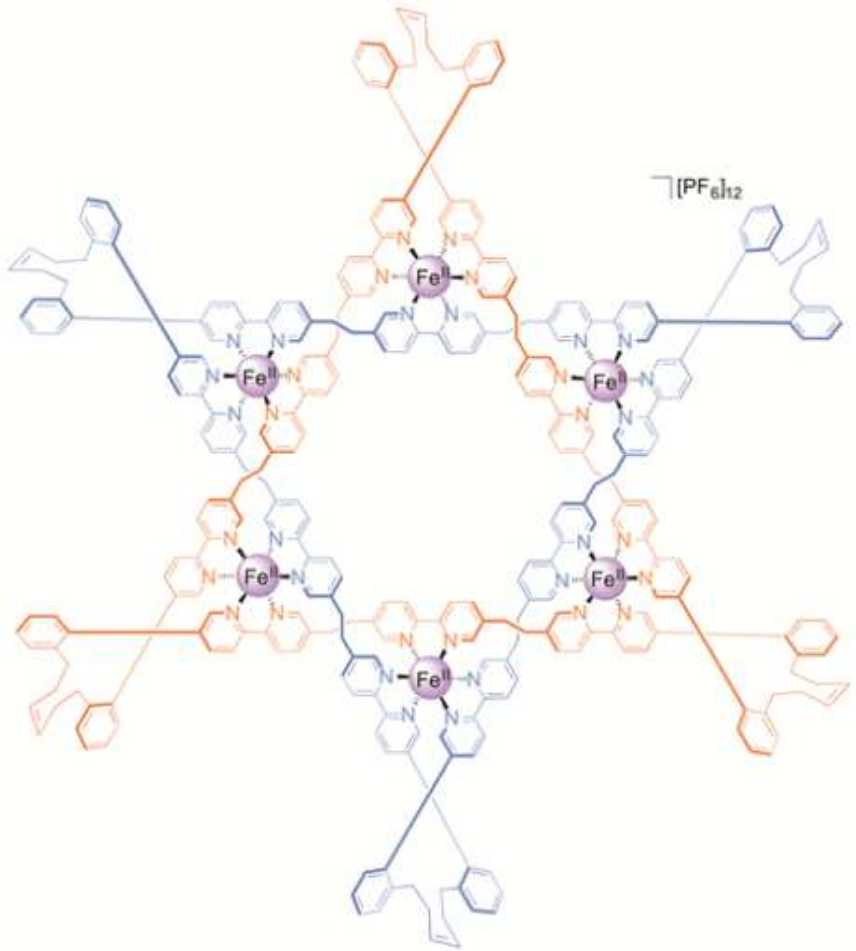
Circular helix strategy

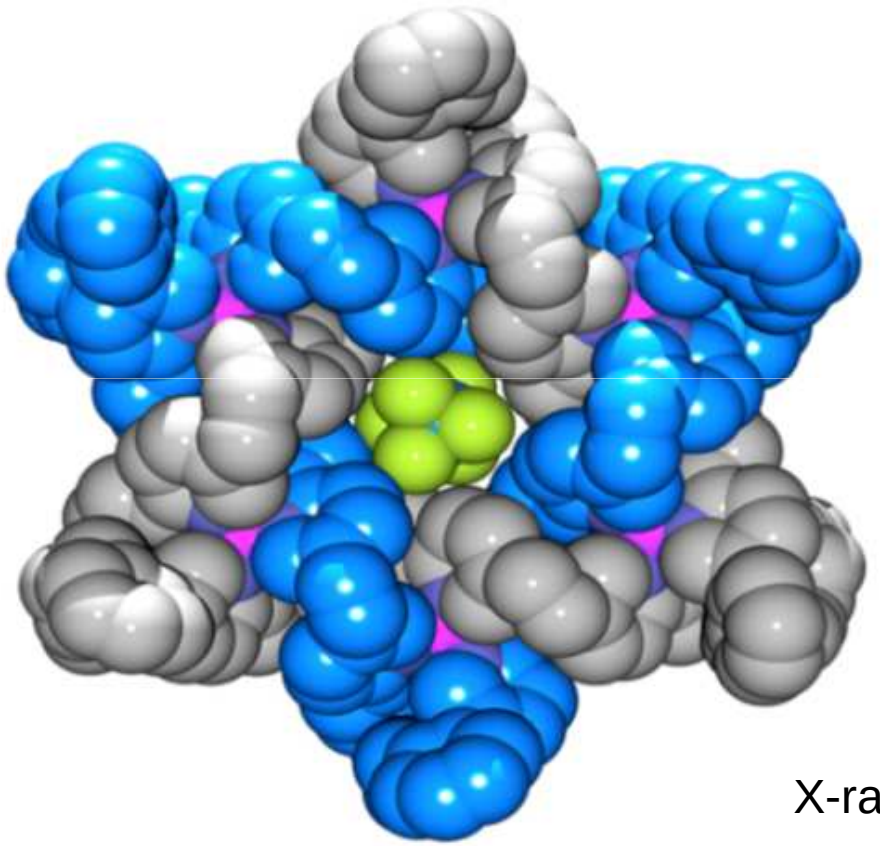
Inspiration from Lehn's work



Lehn al. *J. Am. Chem. Soc.*, **1997**, 119, 10956

Leigh's triply interlocked [2]catenane - star of David

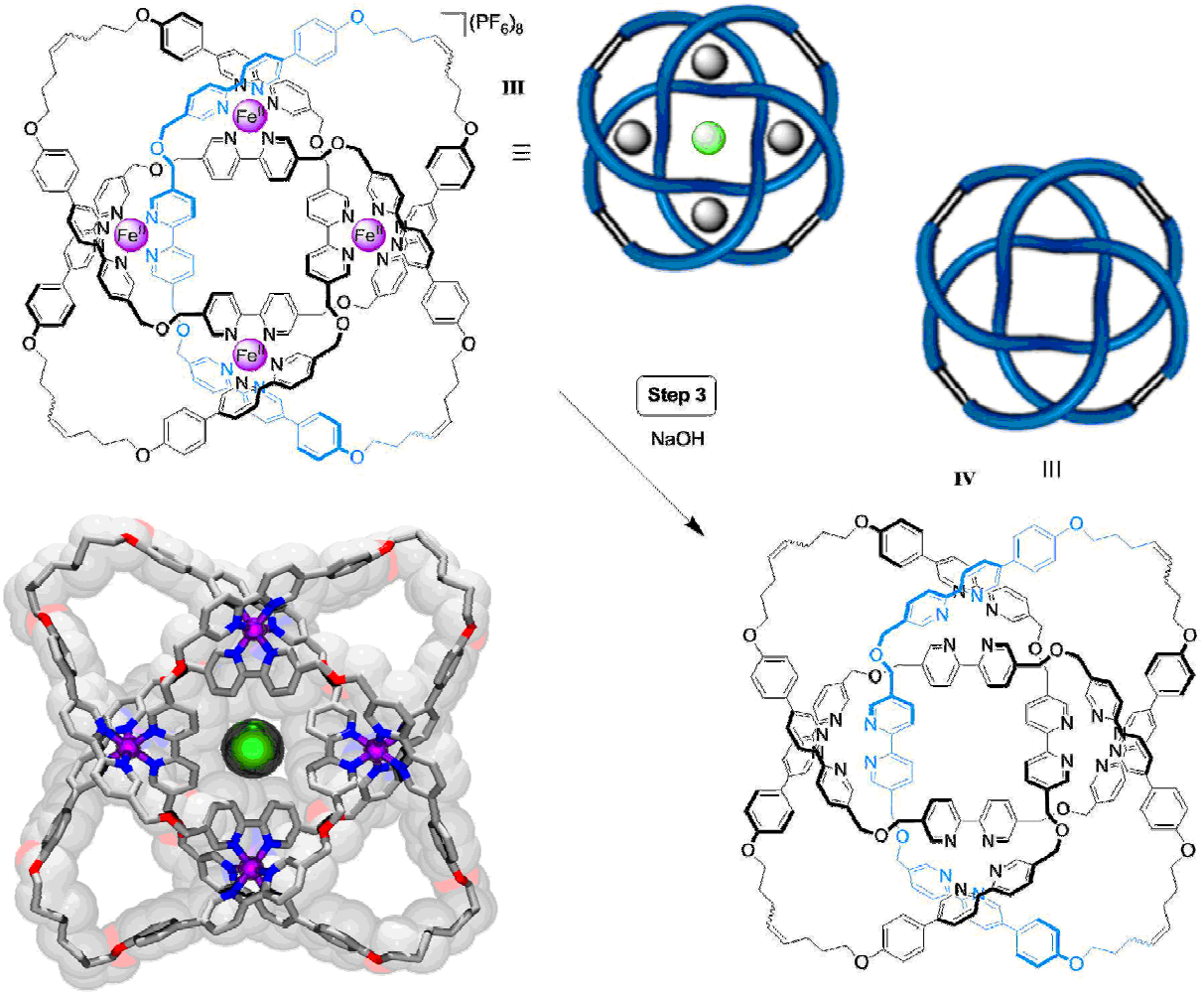




X-ray

Leigh et al., *Nature Chem*, **2014**, *6*, 978

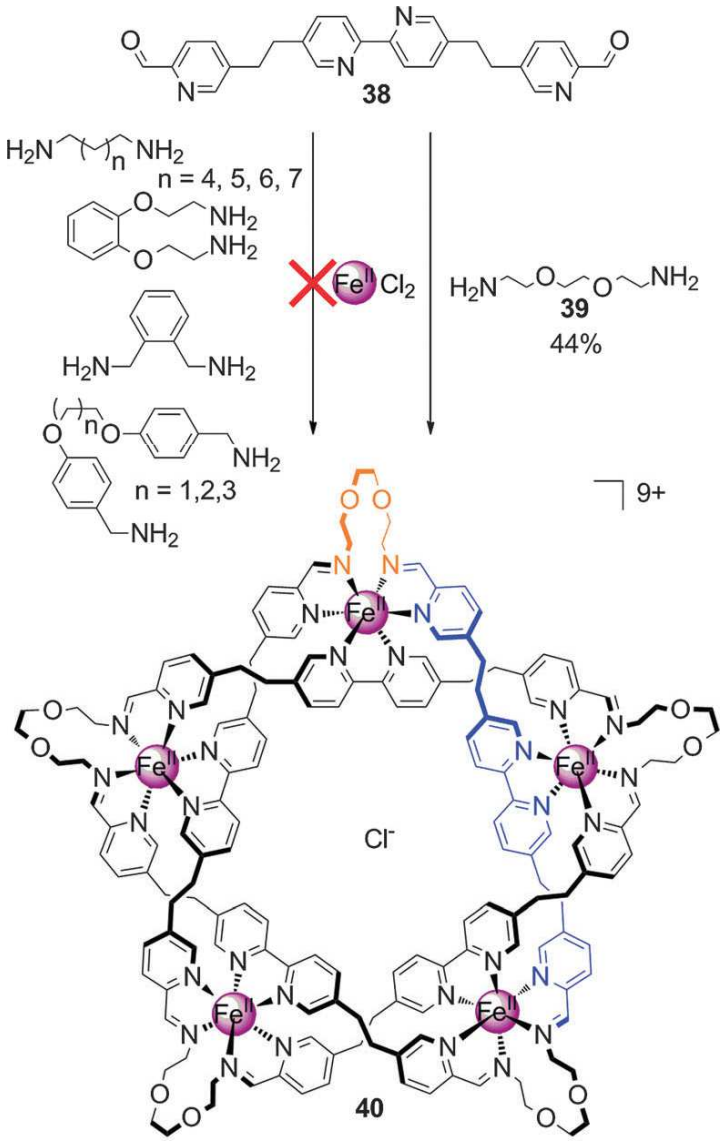
Leigh's 8_{19} knot

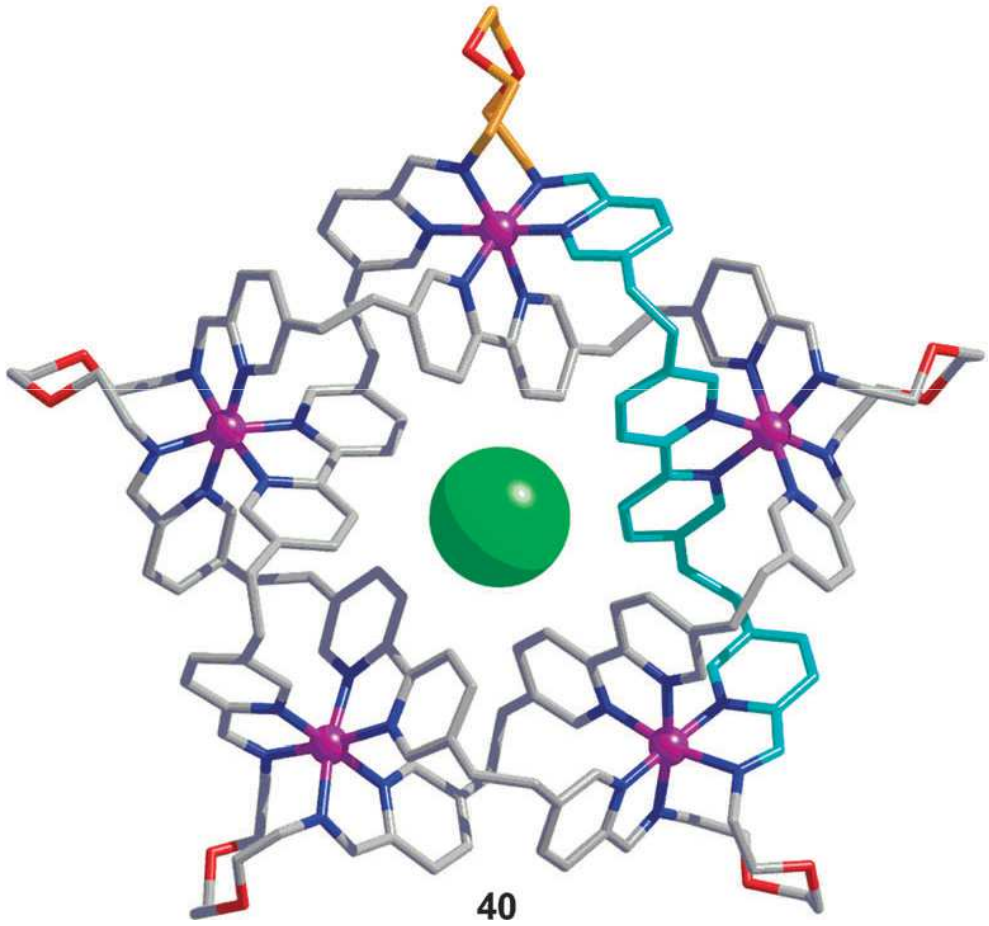


Leigh et al., *Science*, **2017**, *355*, 159

Leigh's pentafoil knot

Dynamic covalent bond-metal template and anion template



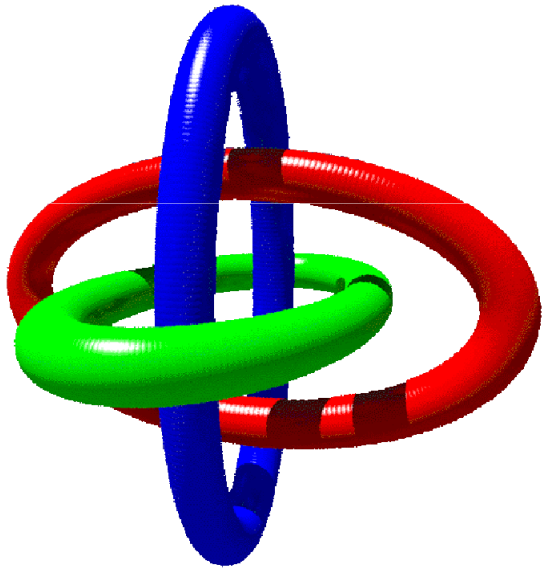


X-ray

Leigh et al., *Nature Chem*, **2012**, *4*, 15

Borromean Rings

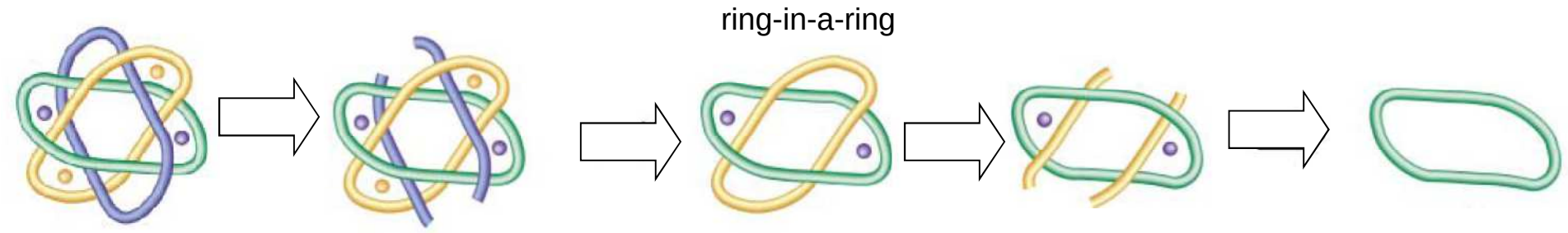
One of the most impressive achievement in topological chemistry

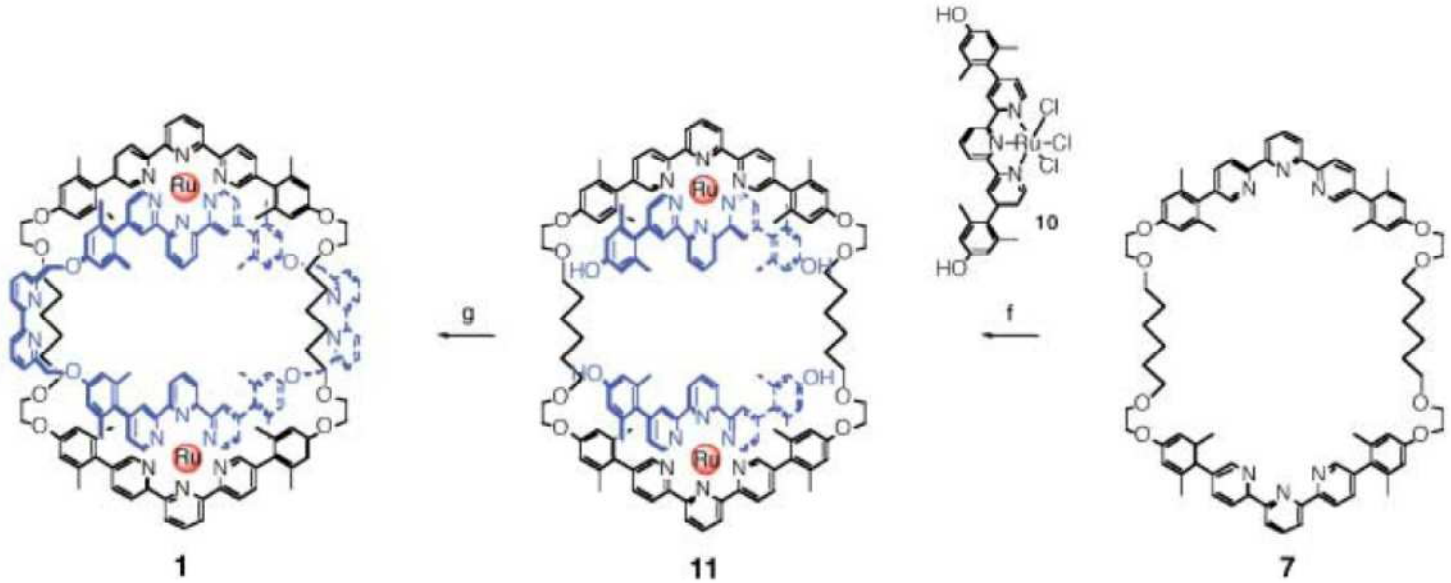


Three identical rings. Each ring is inside a second one and outside the third one. No catenation.

Borromean Rings

Ring-by-ring synthesis :





- long synthesis
- Borromean rings were not obtained…

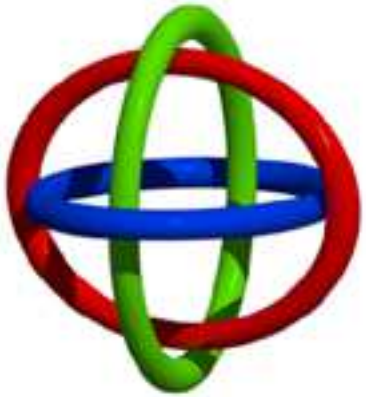
Siegel et al. *Angew. Chem. Int. Ed.,* **2003**, 42, 5702

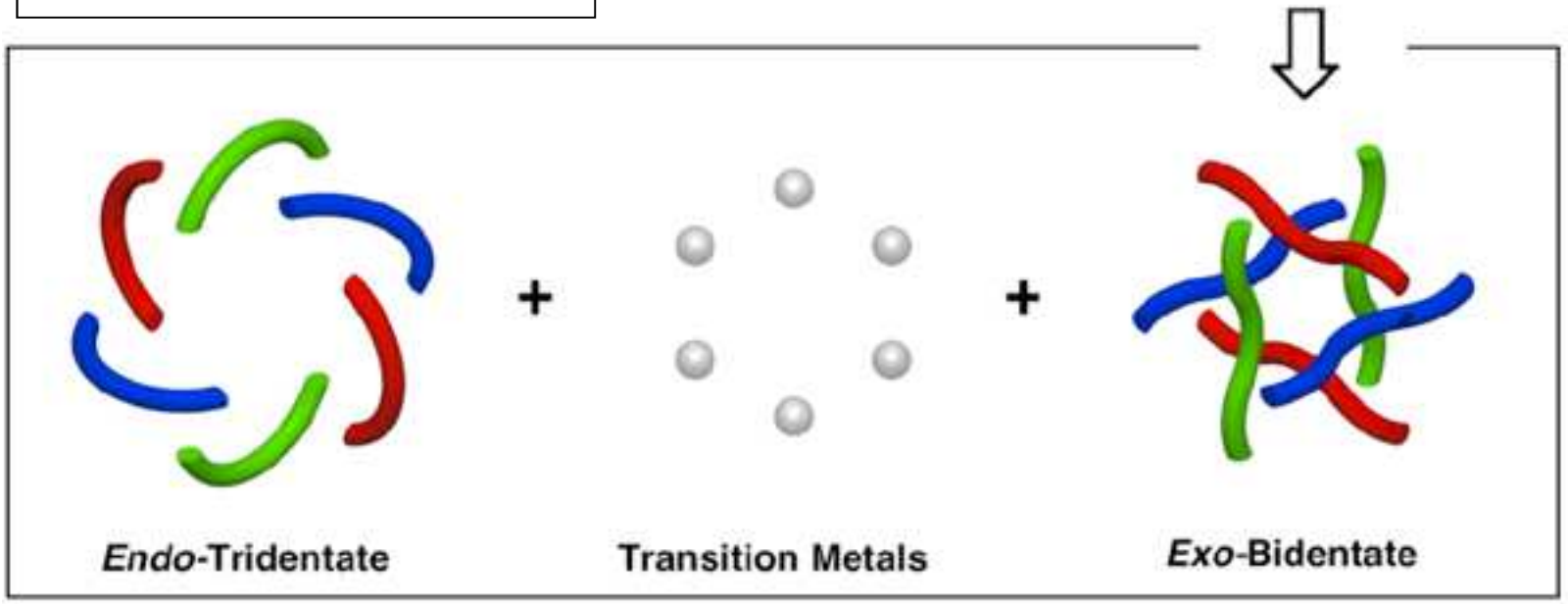
Borromean Rings

- One-step synthesis!!!

control of the synthesis :

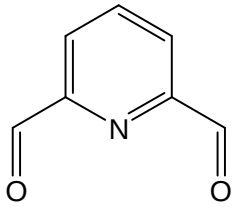
- metal-templated
- imine bond formation
- –Π–stacking
- geometry and size of the ligand



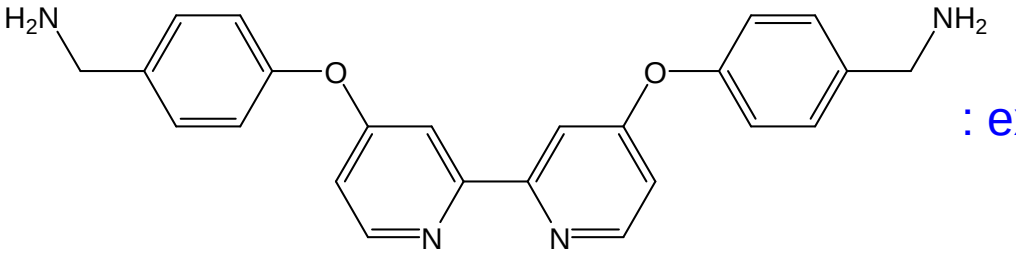


Stoddart et al. *Science,* **2004**, 304, 1308

Borromean Rings

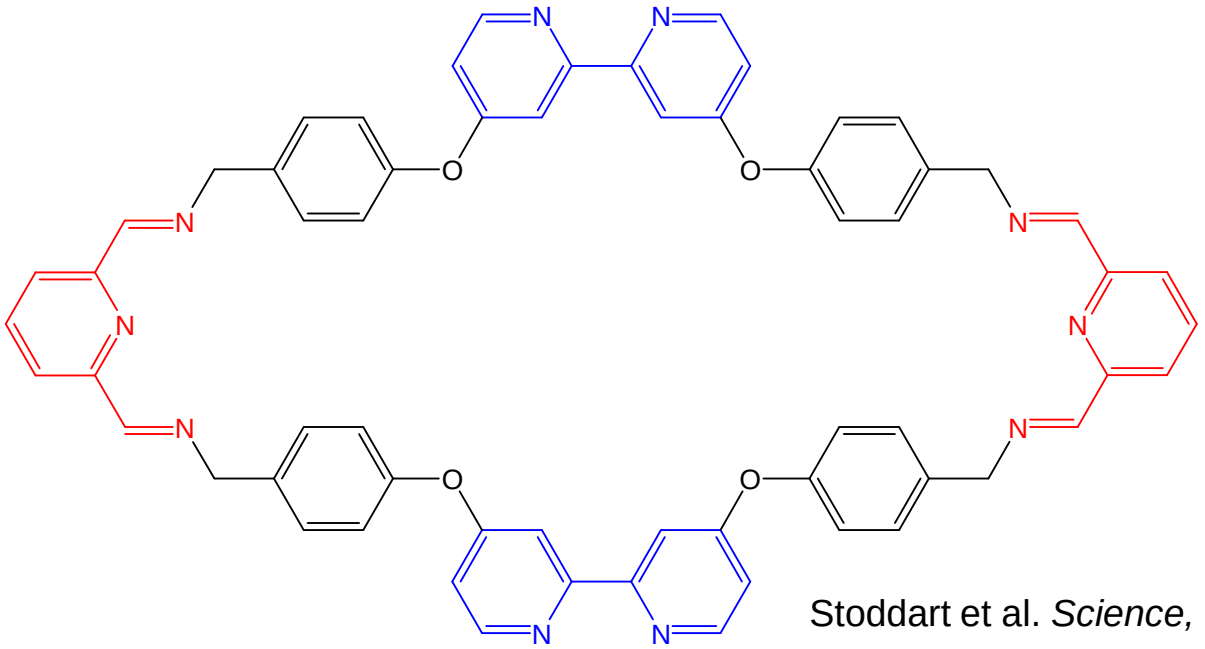


: endo-tridentate



: exo-bidentate

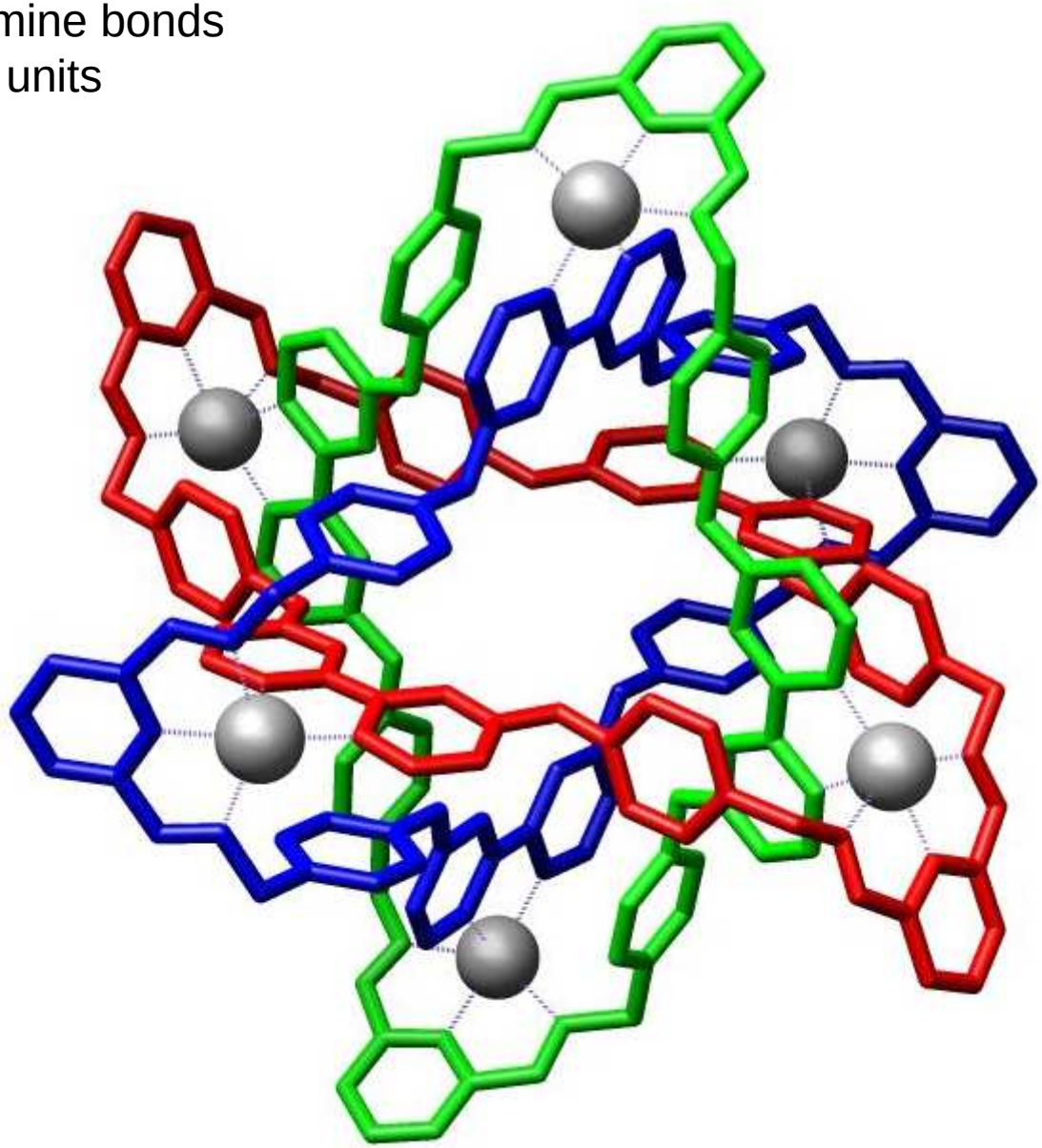
5-coordinated metal
Zn(II)



Stoddart et al. *Science,* **2004**, 304, 1308

Borromean Rings

Formation of 12 imine bonds
Association of 18 units

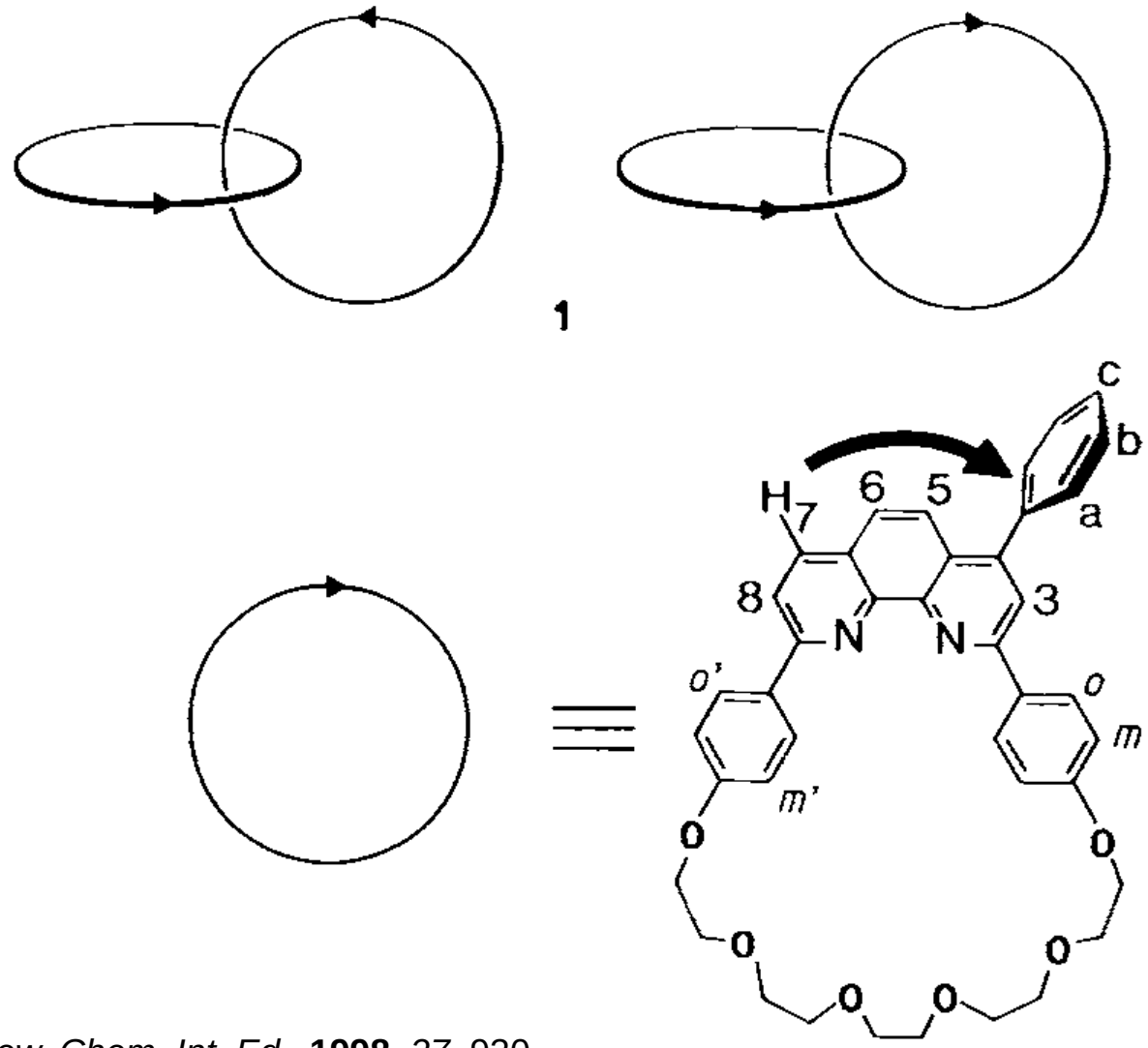


X-Ray structure

Stoddart et al. *Science,* **2004**, 304, 1308

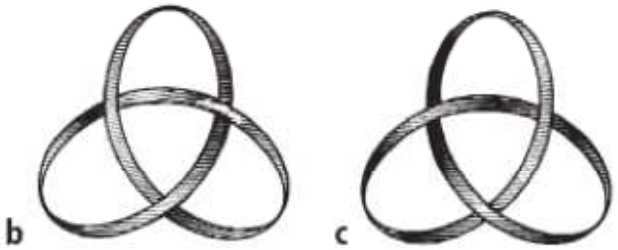
Topological stereochemistry

Catenanes with oriented rings are chiral

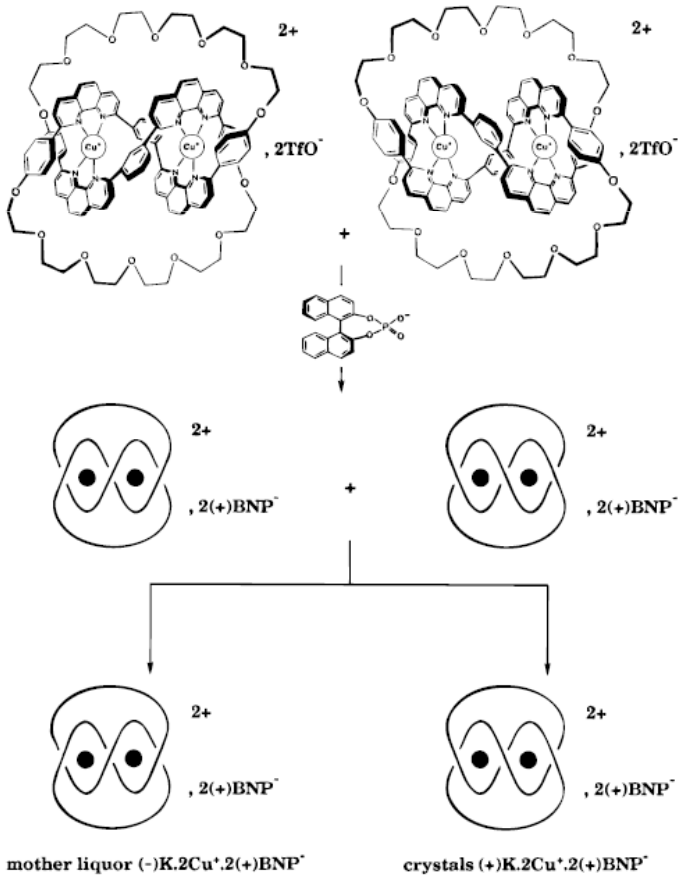


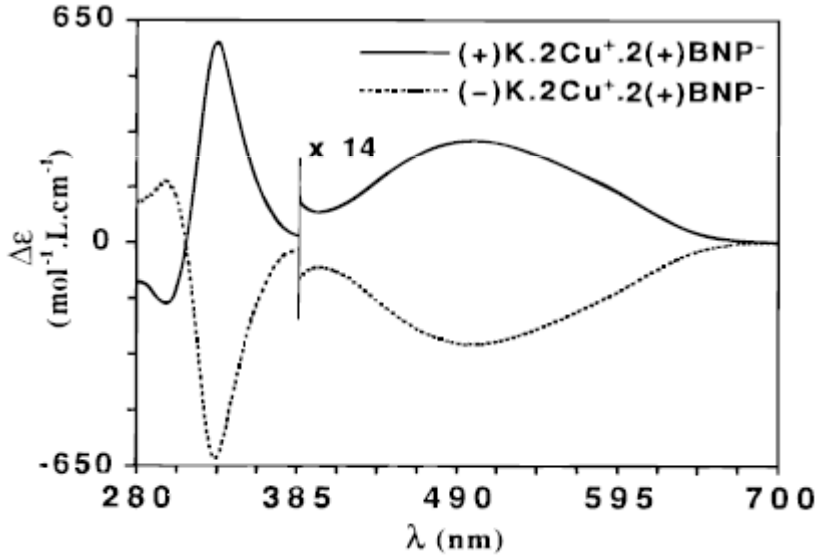
Sauvage et al., *Angew. Chem. Int. Ed.*, **1998**, *27*, 930

Topological stereochemistry



A knot is chiral and can be resolved

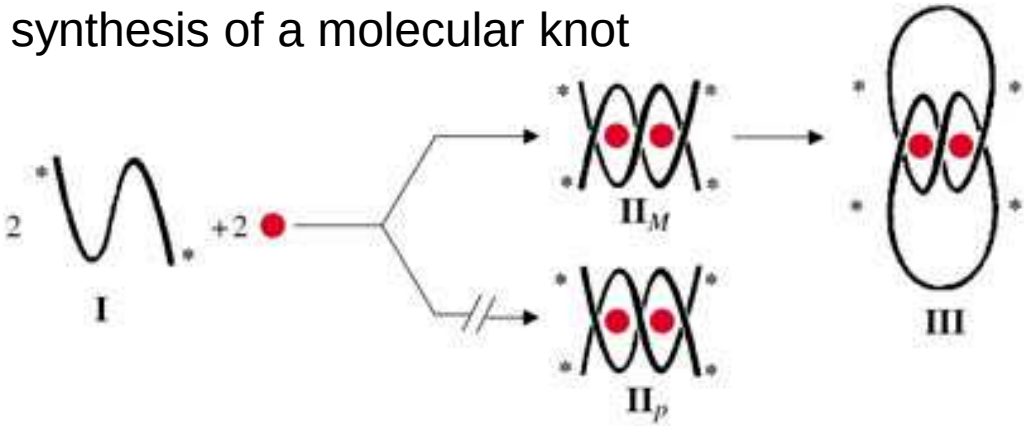


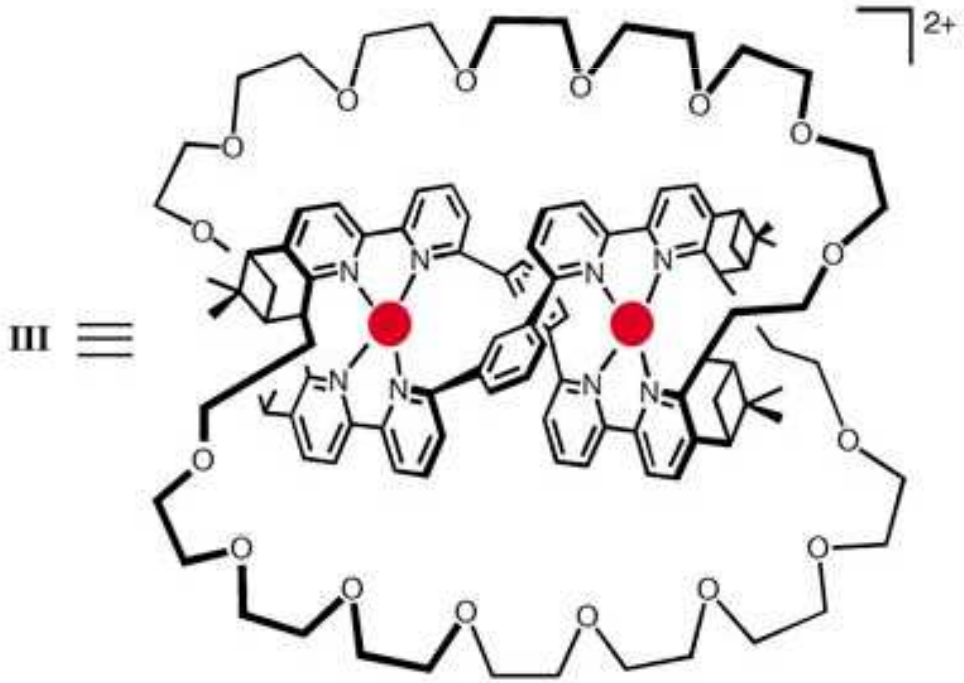


Sauvage et al. *J. Am. Chem. Soc*., **1996**, *118*, 10932

Topological stereochemistry

Diastereoselective synthesis of a molecular knot

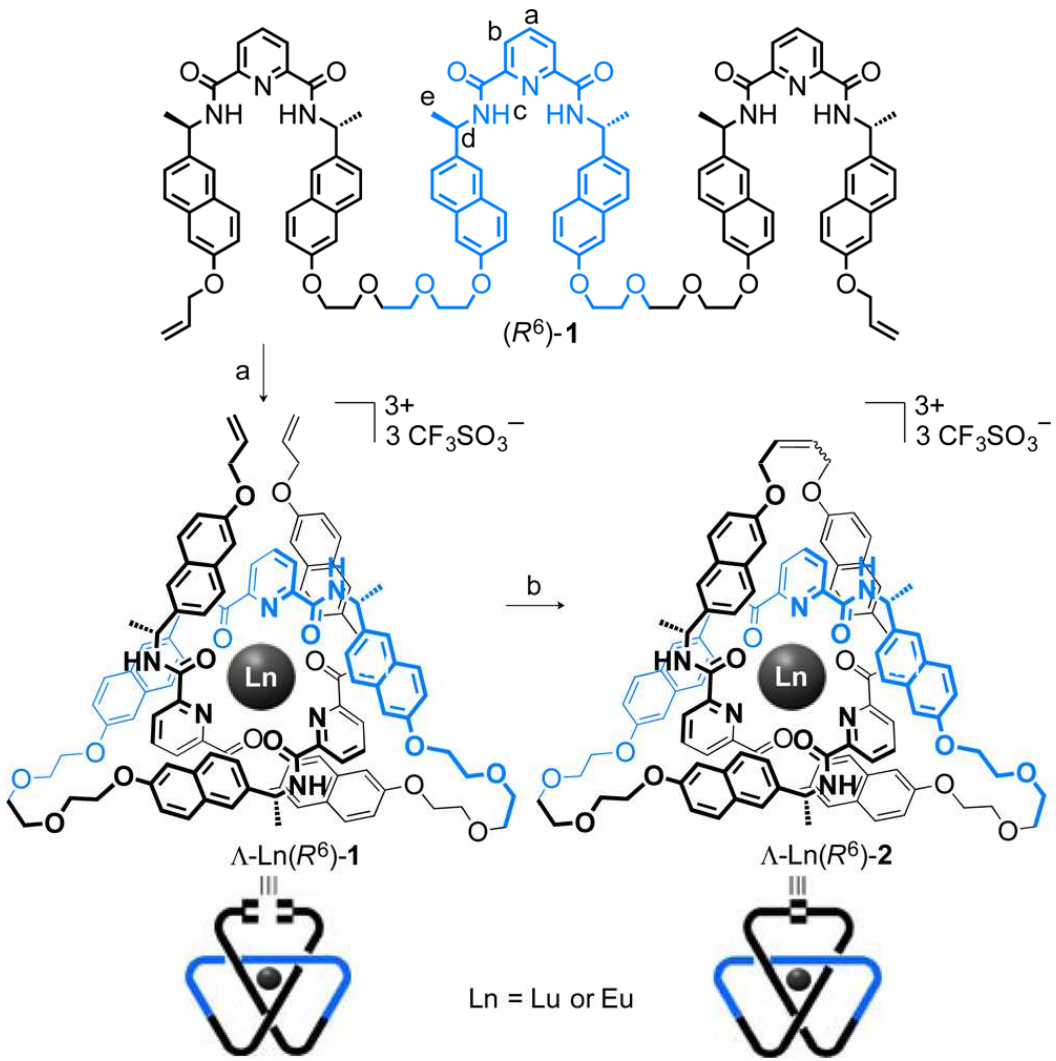


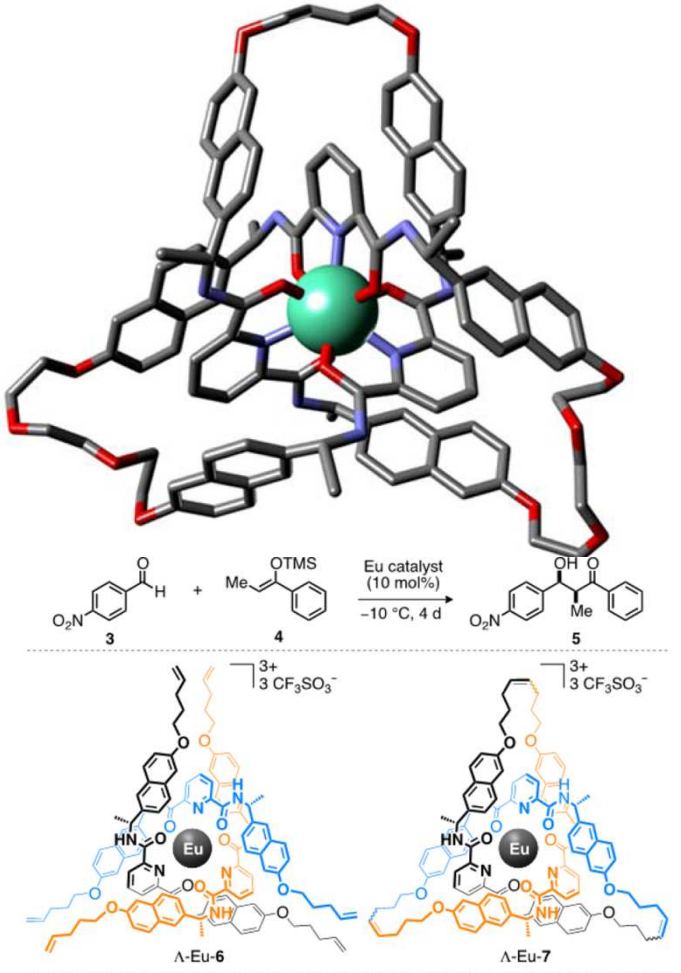


Sauvage, von Zelewsky et al., *Angew. Chem. Int. Ed*., **2004**, *43*, 4482

Topological stereochemistry

Diastereoselective synthesis of a molecular knot





Entry	Catalyst	Solvent	Conv. (%)[a]	*syn*:*anti*[a]	*syn*-er (%)[b]
1	Λ-Eu(R^6)-**2**	MeOH/CH_3CN	61	1 : 1	65:35
2	Λ-Eu-**6**	MeOH/CH_3CN	61	1 : 1	58:42
3	Λ-Eu-**7**	MeOH/CH_3CN	65	1 : 1.4	54:46
4	-	MeOH/CH_3CN	17	1 : 1	-

Leigh et al., *J. Am. Chem. Soc*., **2016**, *138*, 13158

The Nobel Prize in Chemistry 2016

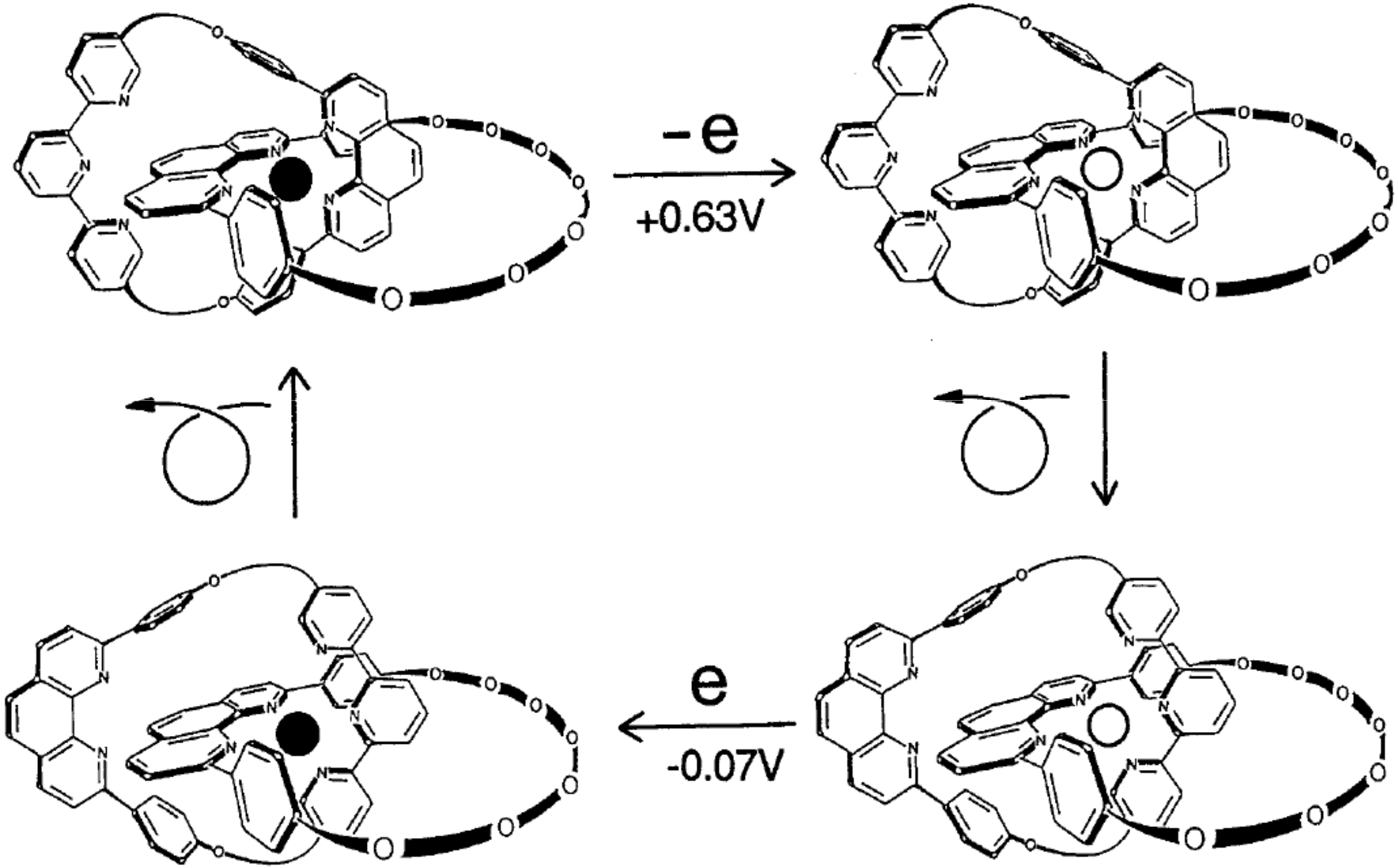
Ill: N. Elmehed. © Nobel Media 2016
Jean-Pierre Sauvage
Prize share: 1/3

Photo: Northwestern University
Sir J. Fraser Stoddart
Prize share: 1/3

Ill: N. Elmehed. © Nobel Media 2016
Bernard L. Feringa
Prize share: 1/3

The Nobel Prize in Chemistry 2016 was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa *"for the design and synthesis of molecular machines"*.

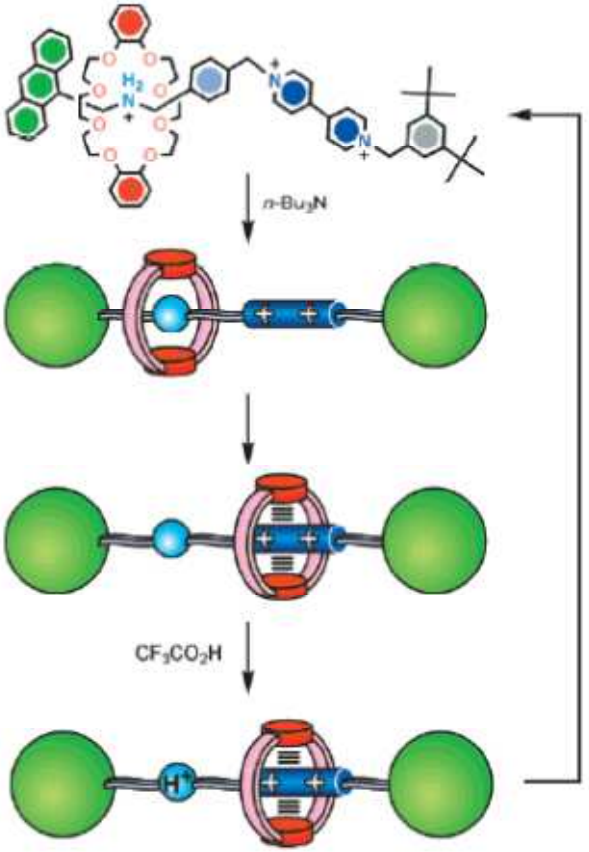
Molecular machine powered by an electrochemical fuel



Sauvage et al. *J. Am. Chem. Soc*., **1994**, 116, 9399

Molecular machine powered by a chemical fuel

Acid-base powered molecular translation of a ring along a thread :



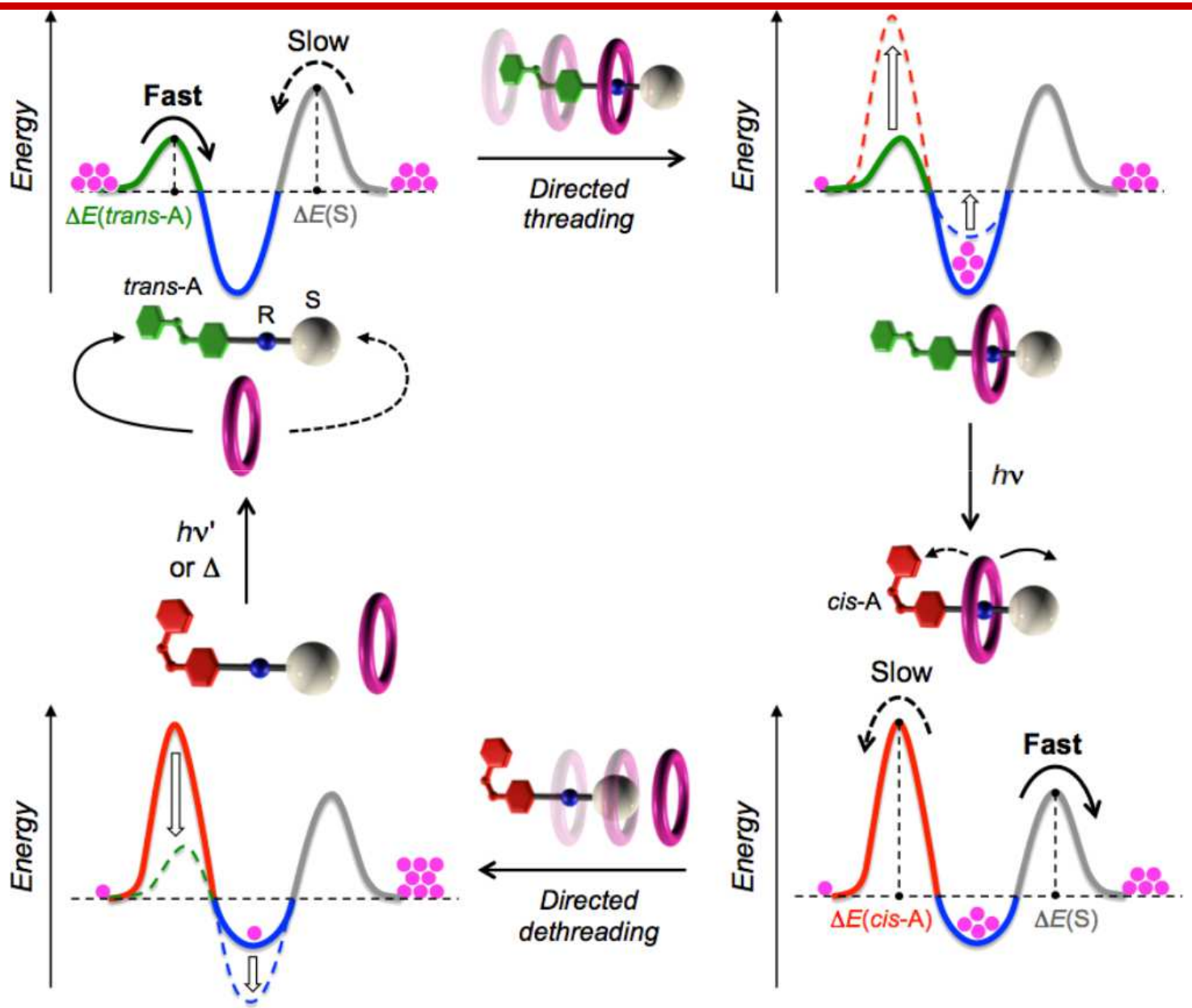
- rotaxane based molecular shuttle
- intramolecular process
- bistable molecule (1 or 0)
- possibility for high density information storage

High complexity of the molecule:

- interlocked system
- two orthogonal binding sites on the thread

Balzani et al. *Acc. Chem. Res*., **2001**, 34, 445

From switches to motors: toward dissipative systems



Credi et al., *Nature Nanotech.*, **2015**, *10*, 70