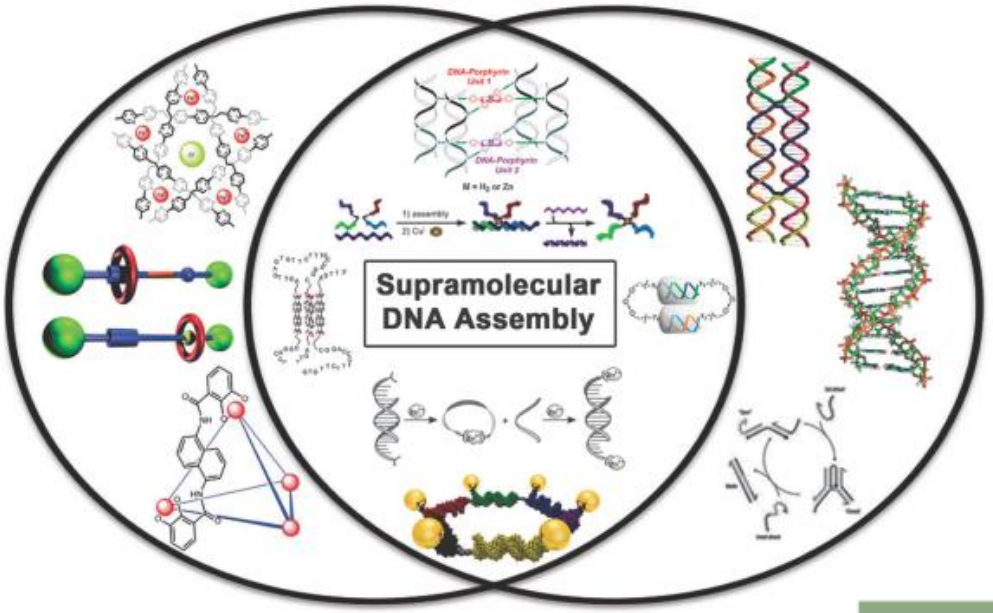
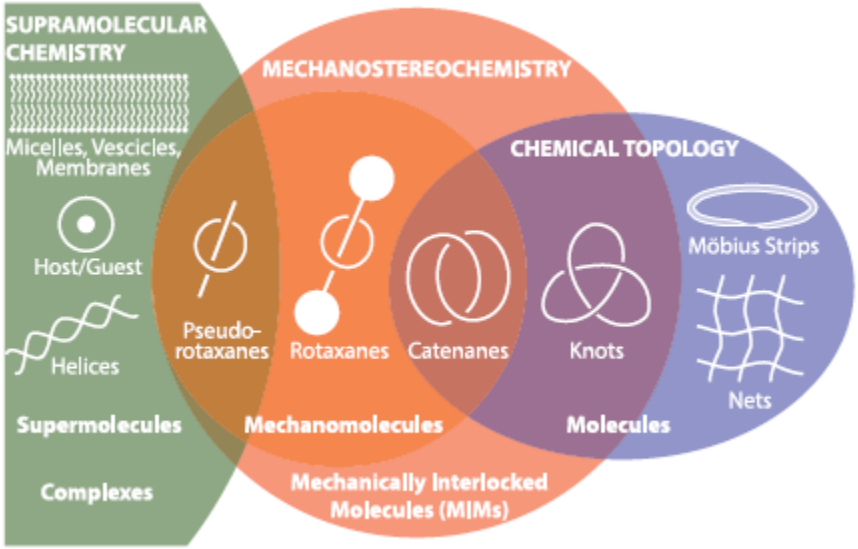
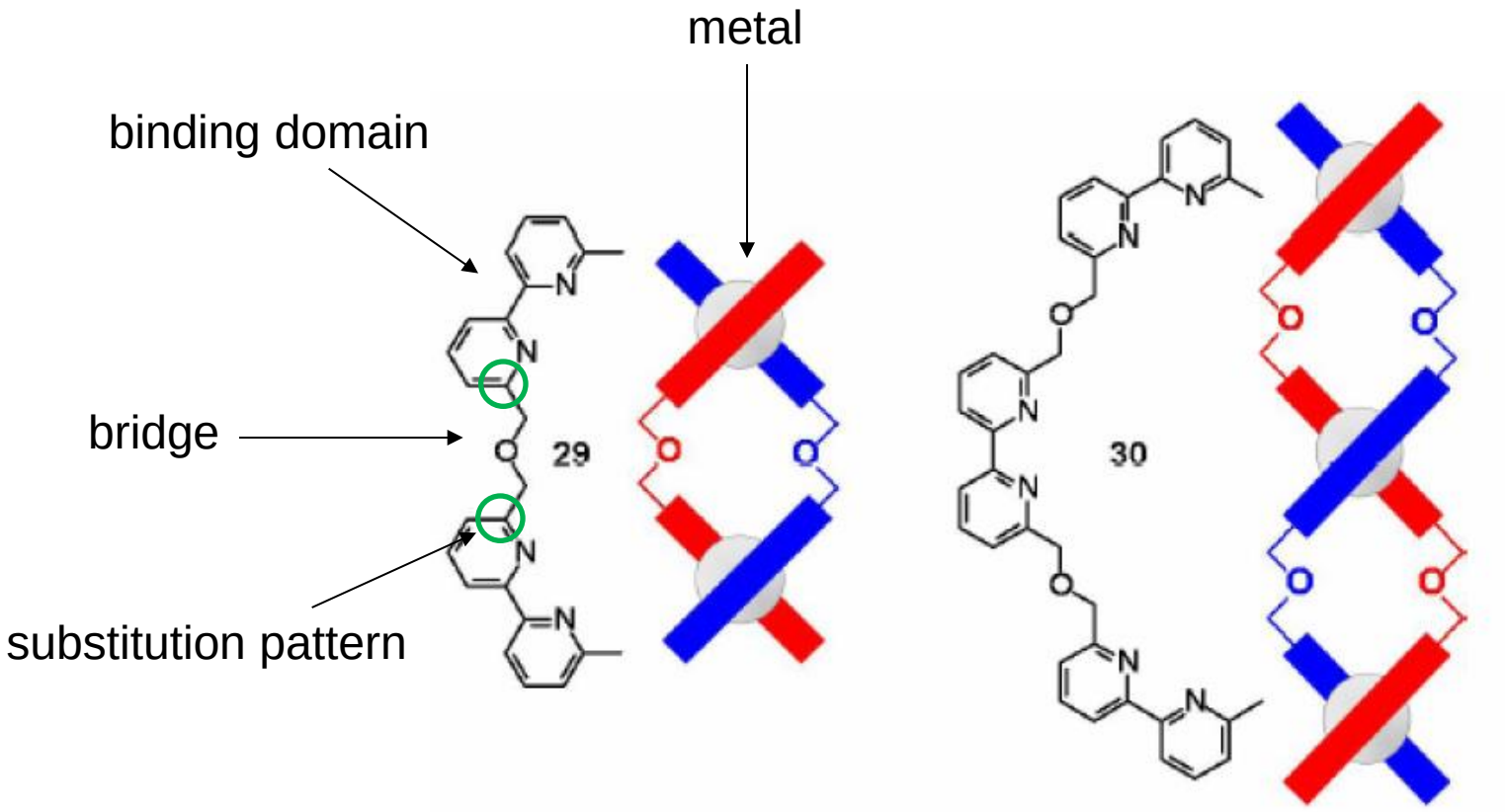
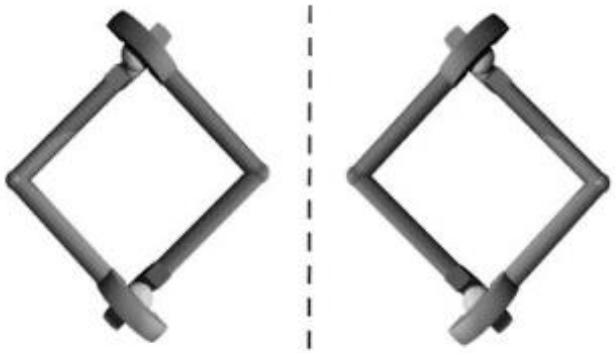

Supramolecular
DNA Assembly


SUPRAMOLECULAR CHEMISTRY
Micelles, Vescicles, Membranes
Host/Guest
Helices
Supermolecules
Complexes
MECHANOSTEREOCHEMISTRY
Pseudo-rotaxanes
Rotaxanes
Catenanes
Mechanomolecules
Mechanically Interlocked Molecules (MIMs)
CHEMICAL TOPOLOGY
Knots
Möbius Strips
Nets
Molecules

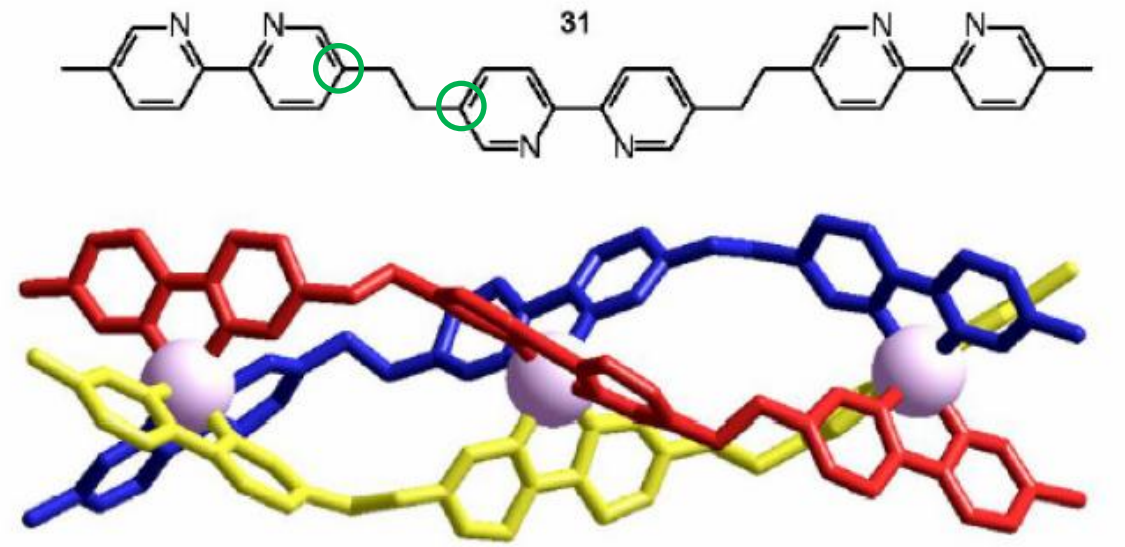
Double stranded helicates



Chirality

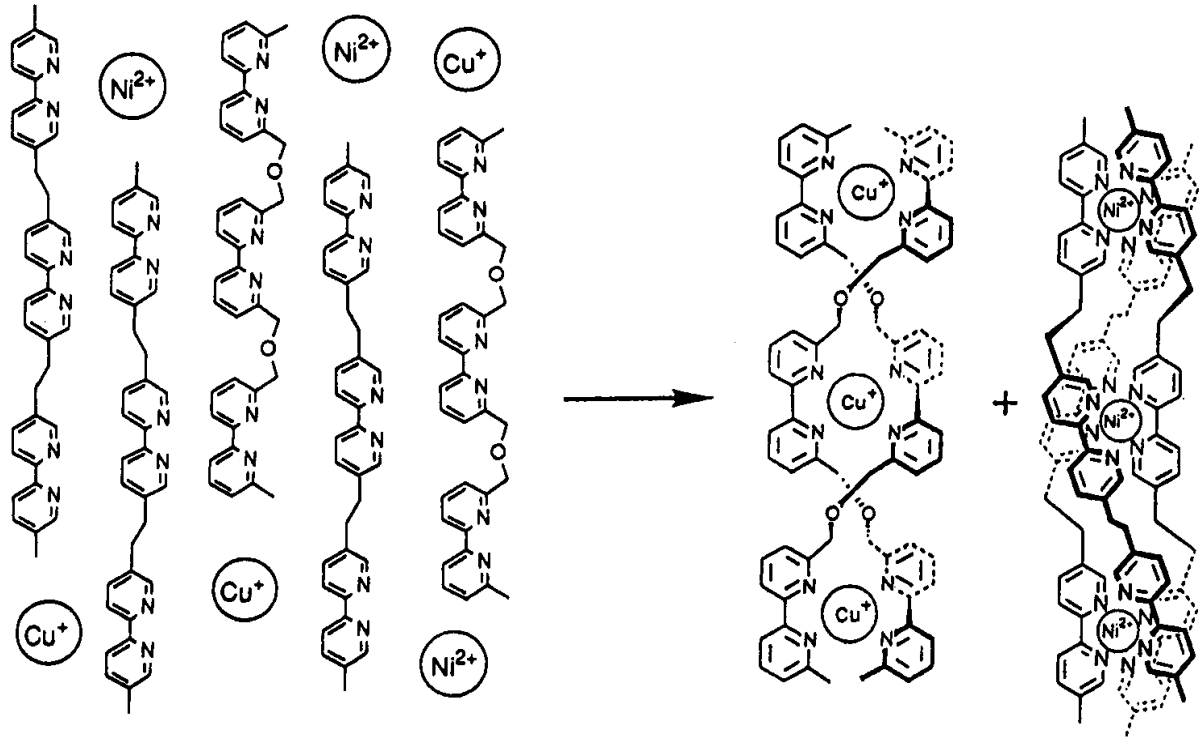


Triple stranded helicates

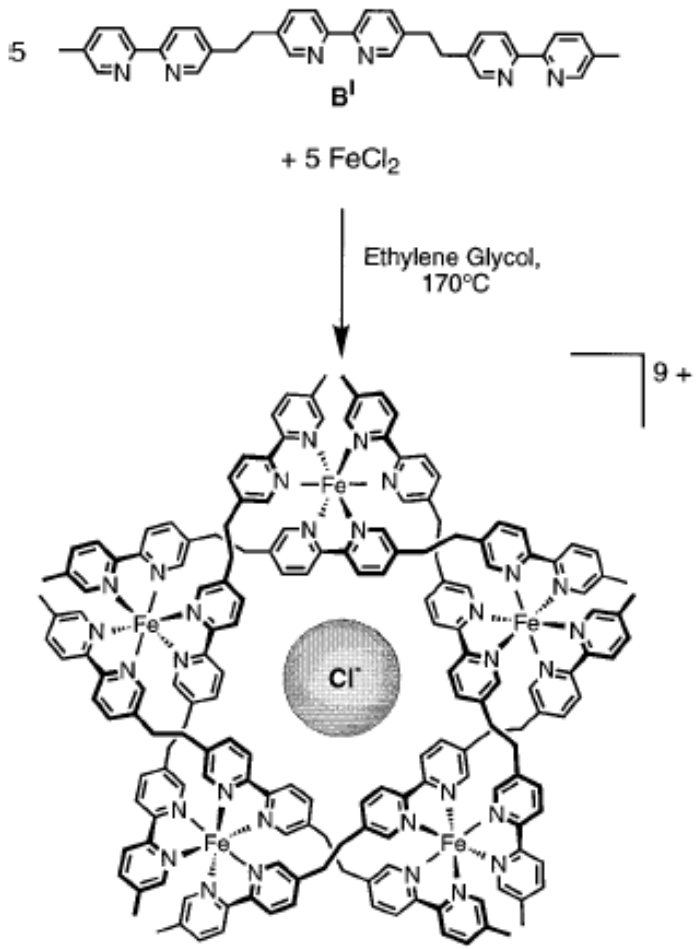


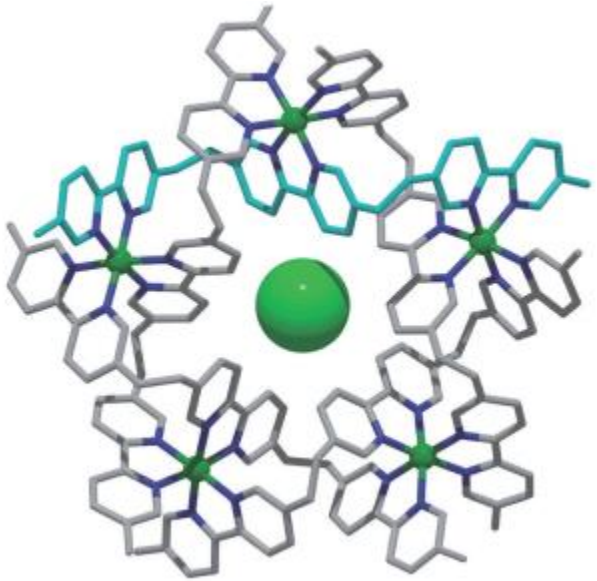
- Ni(II) : octahedral geometry
- one ligand can not wrap around one Ni(II) cation : trimerization
- other metals: Co(II), Fe(II), lanthanides

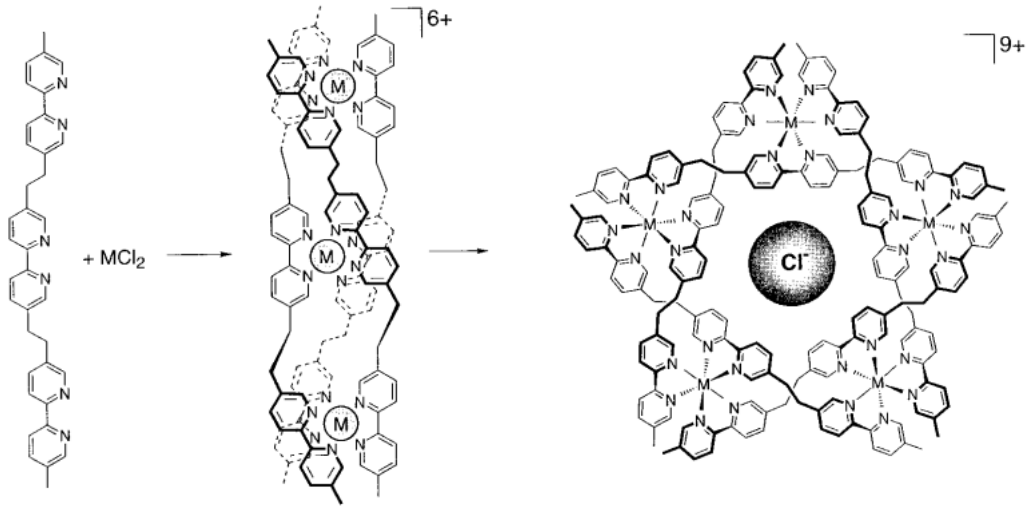
Double and Triple Helicates: an example of Self-sorting



Cyclic Helicates





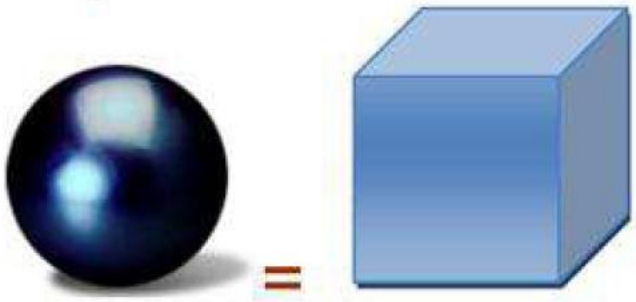


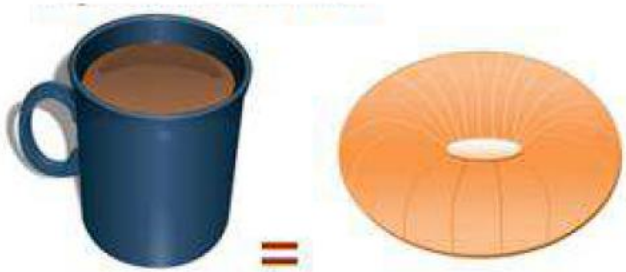
^{1}H-NMR

ESI-MS

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

Topological chemistry

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

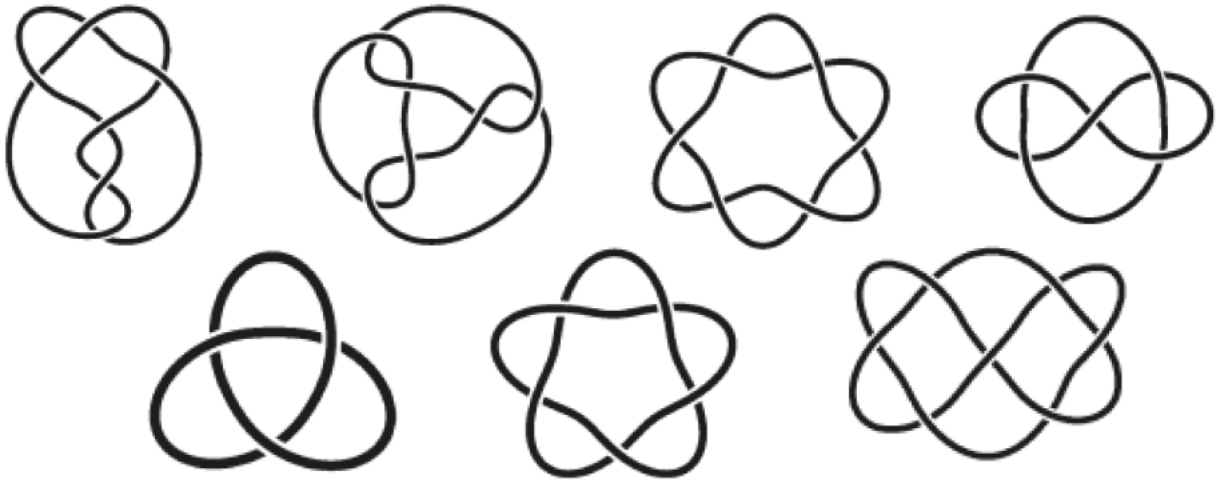
a is an isomer of **b** and **c**.
b and **c** are topological enantiomers.

Molecular graph

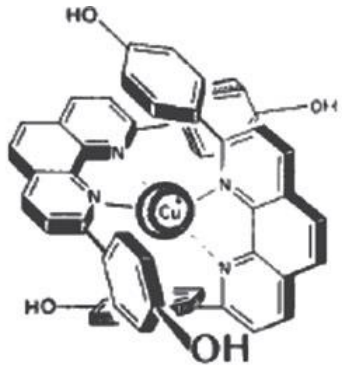
non-planar graph

No possible conformation with no crossing in 2D representation

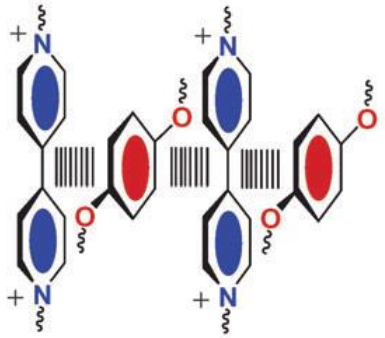
topological chemistry is the chemistry of molecules having a non planar graph



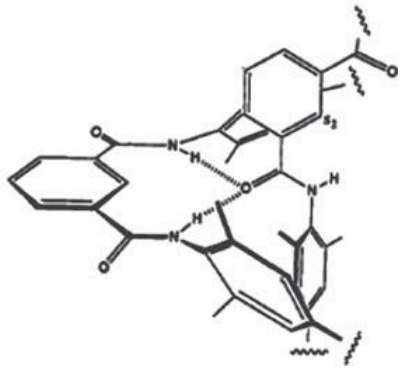
1



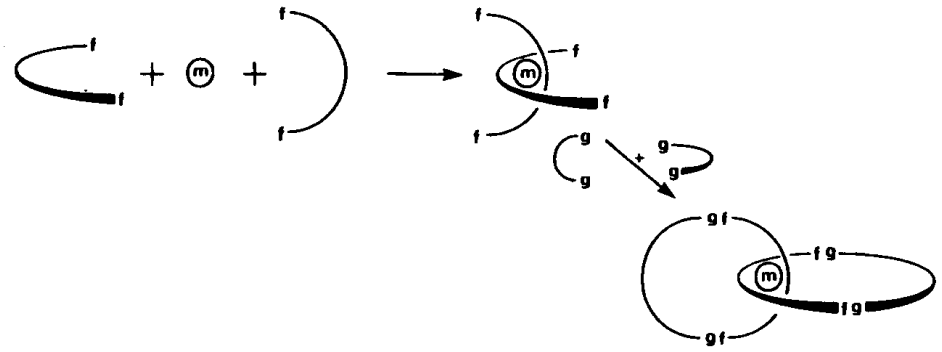
2

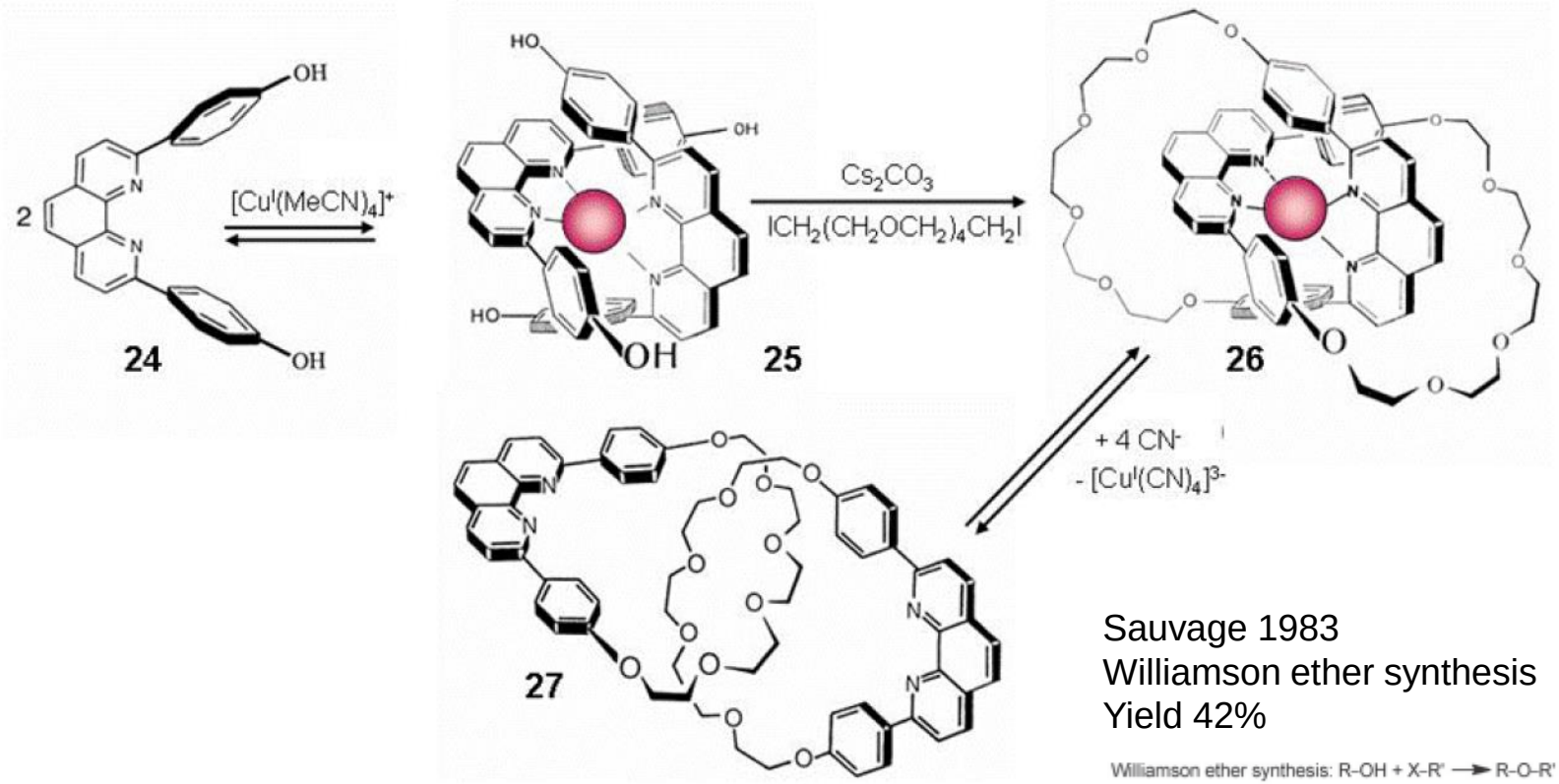


3



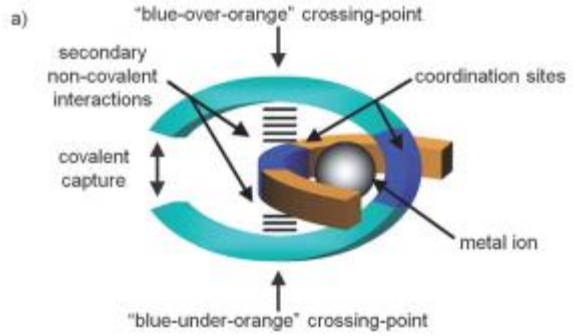
[*n*]Catenani

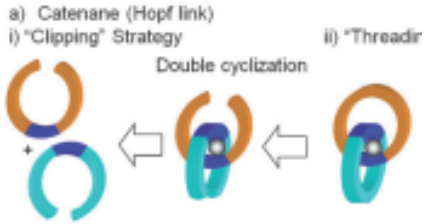


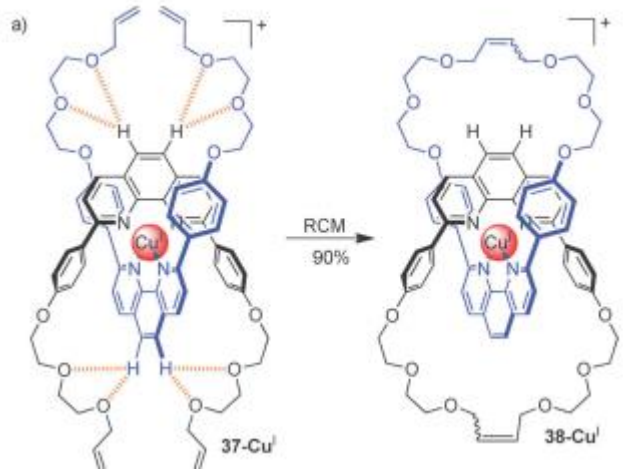


Sauvage 1983
Williamson ether synthesis
Yield 42%

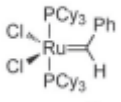
Williamson ether synthesis: R–OH + X–R' ⟶ R–O–R'

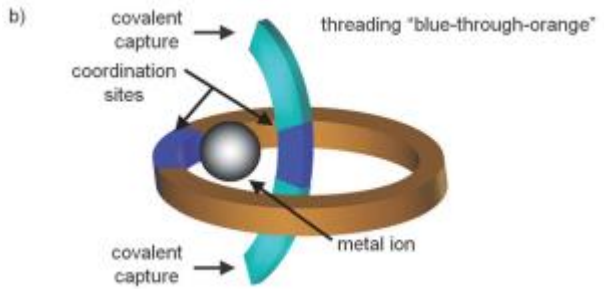




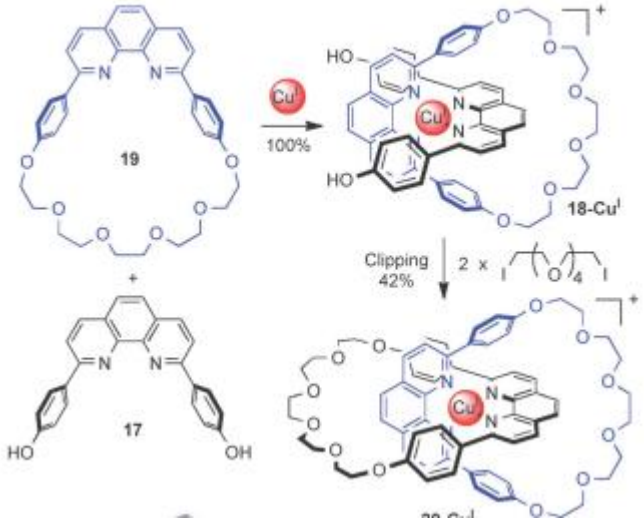


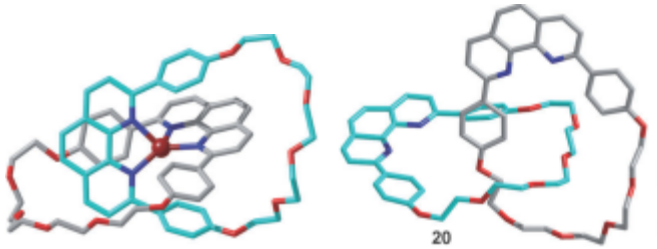
Ring closing metathesis (RCM): 2 x 

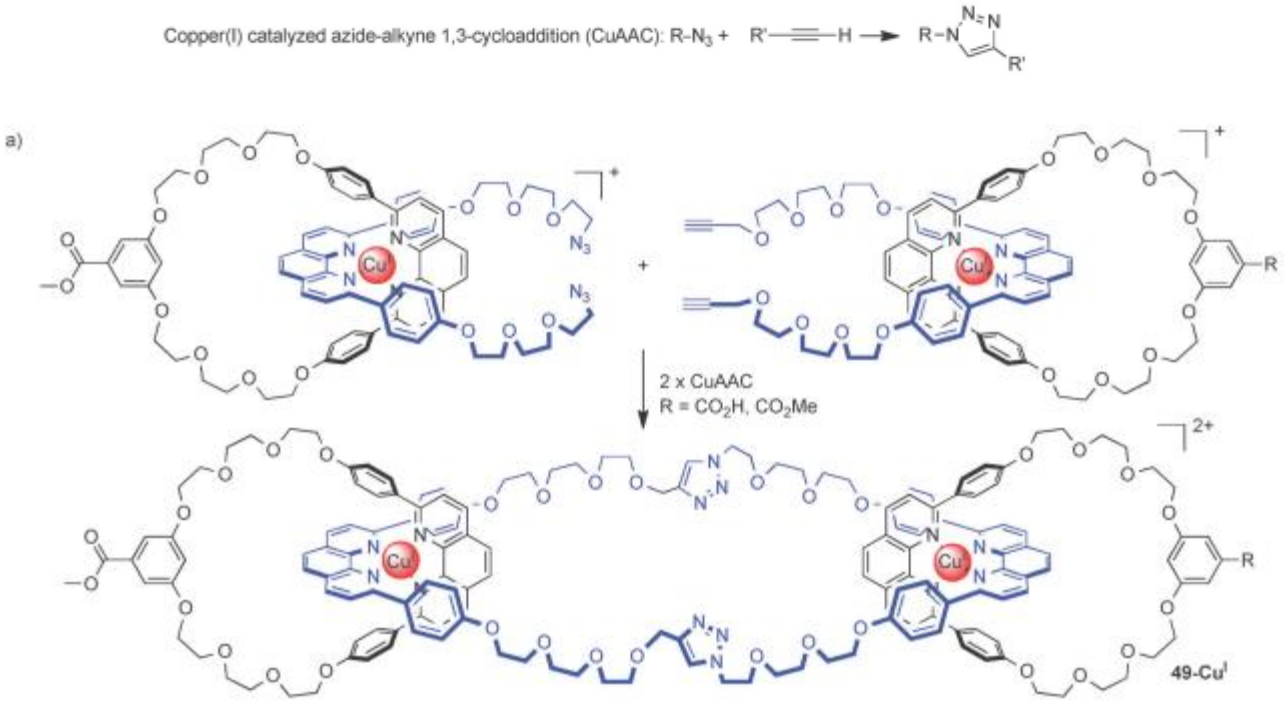


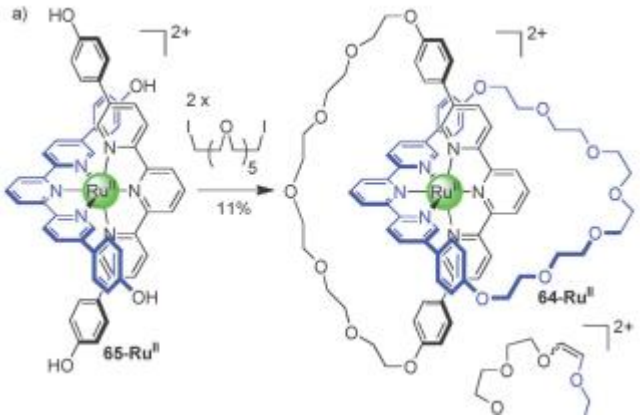

b)
covalent capture
coordination sites
threading "blue-through-orange"
metal ion
covalent capture

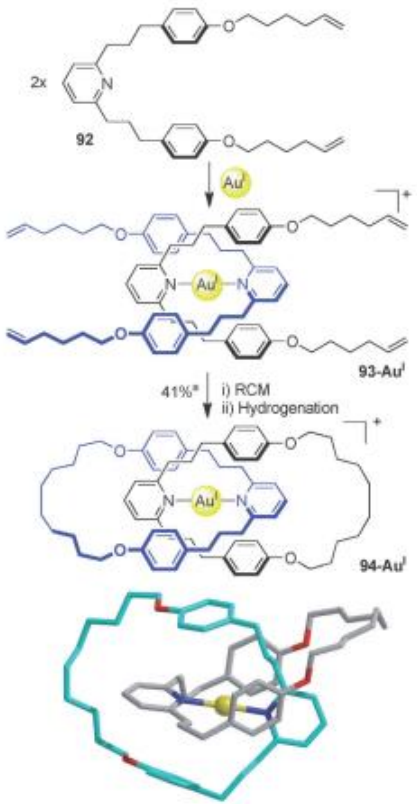

ii) "Threading-followed-by-clipping" strategy
Single cyclization

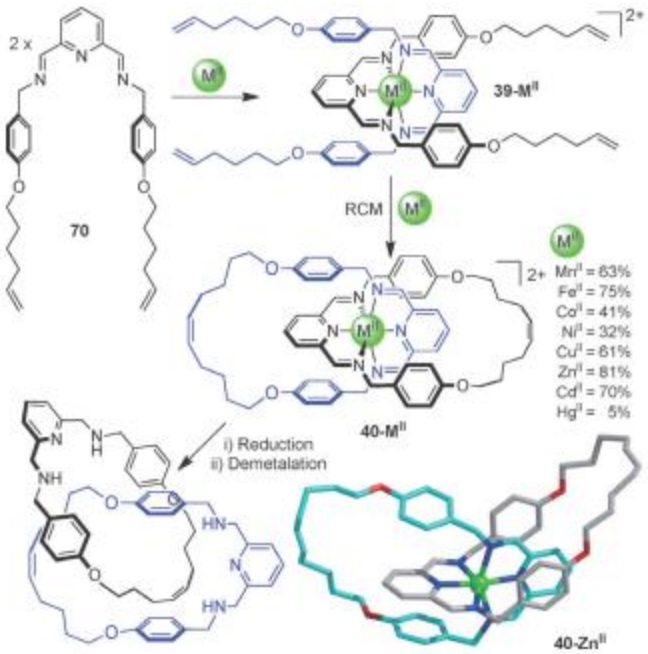

19
17
HO
OH
Cu^{I}
100%
HO
HO
18-Cu^{I}
Clipping
42%
2 x


20

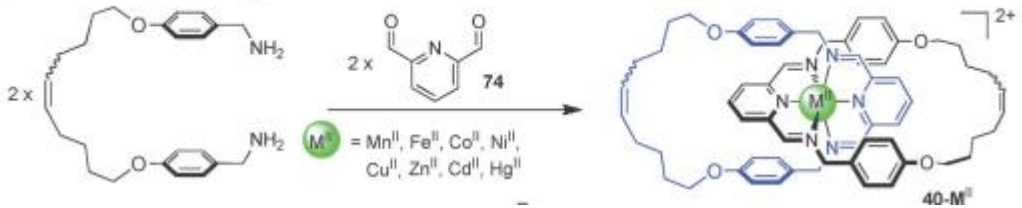

Copper(I) catalyzed azide-alkyne 1,3-cycloaddition (CuAAC): R-N3 +
a)
2 x CuAAC
R = CO2H, CO2Me
49-Cu


a)
HO
OH
OH
HO
2+
Ru
N
65-Ru^{II}
2 x
O
5
11%
64-Ru^{II}

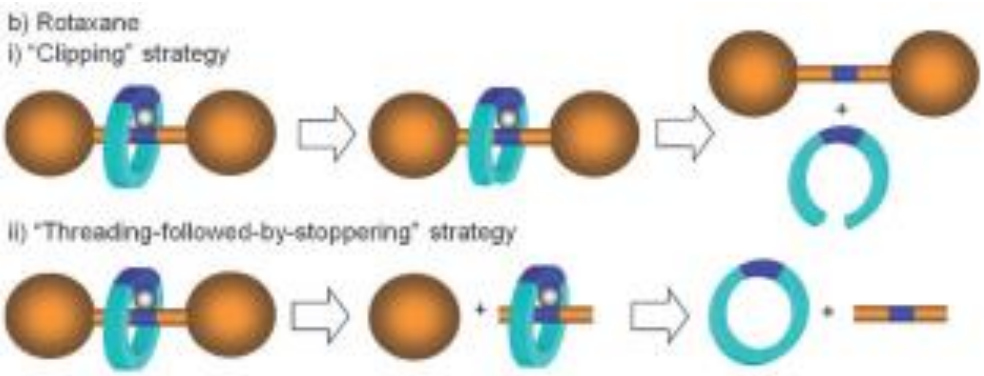

2x
N
92
Au^{I}
93-Au^{I}
41%*
i) RCM
ii) Hydrogenation
94-Au^{I}

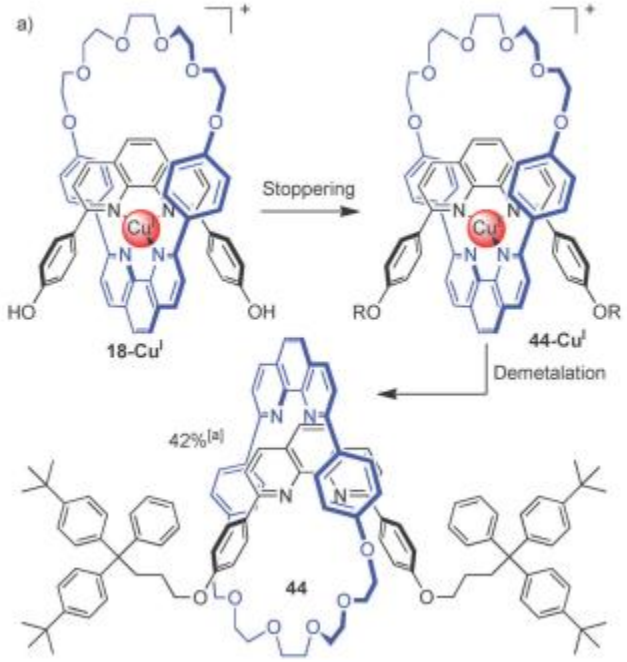


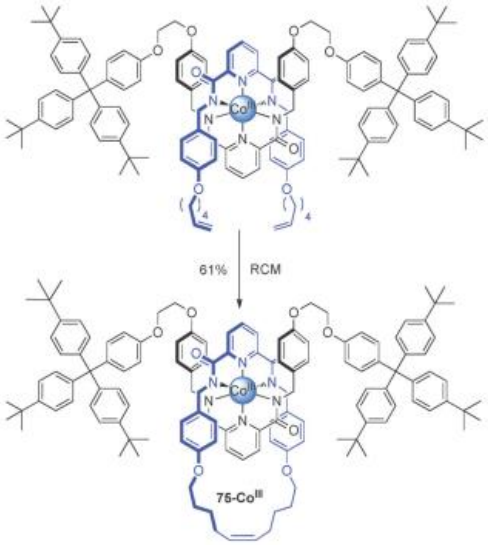
c) Imine bond formation: $R\text{-}NH_2 + R'\text{-}CHO \longrightarrow R\text{-}N{=}CH\text{-}R'$

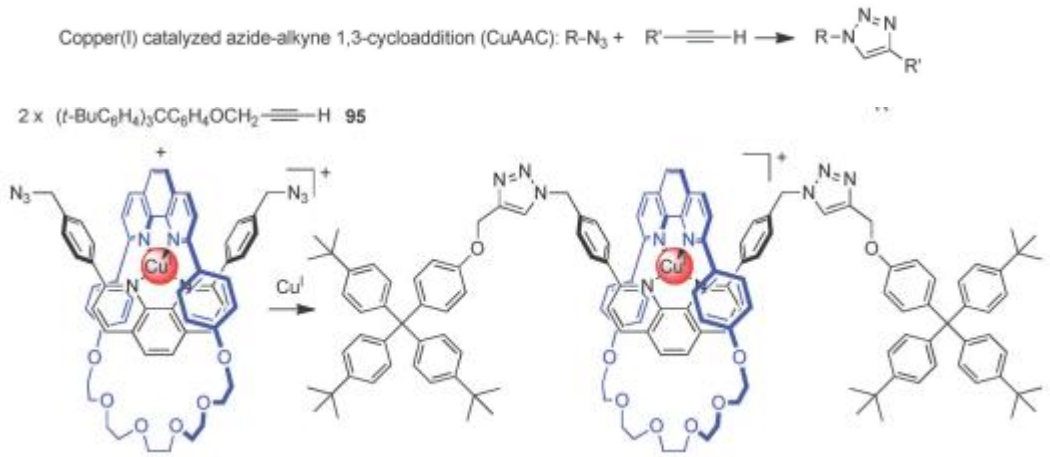


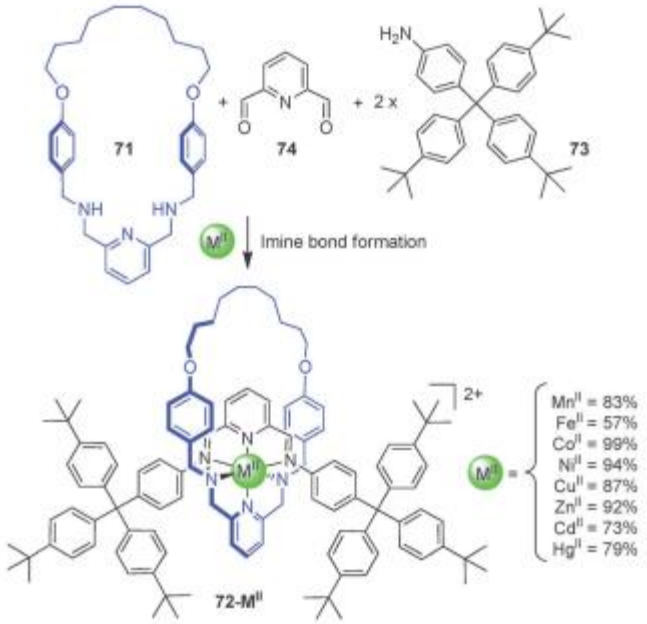
[2]Rotaxani

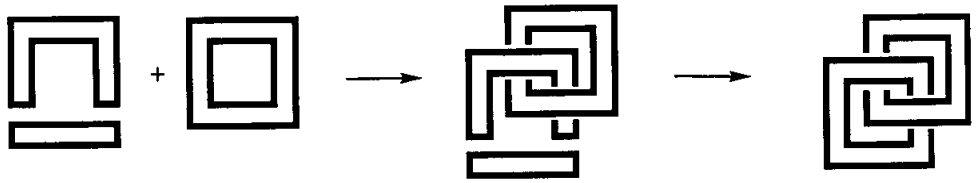

b) Rotaxane
i) "Clipping" strategy
ii) "Threading-followed-by-stoppering" strategy


a)
Stoppering
HO
OH
RO
OR
18-Cu^I
44-Cu^I
Demetalation
42%[a]
44

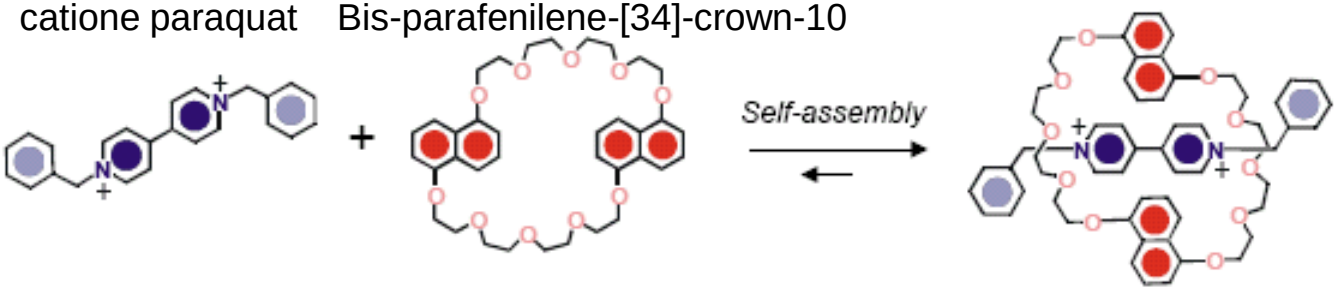

61%
RCM
75-Co^III

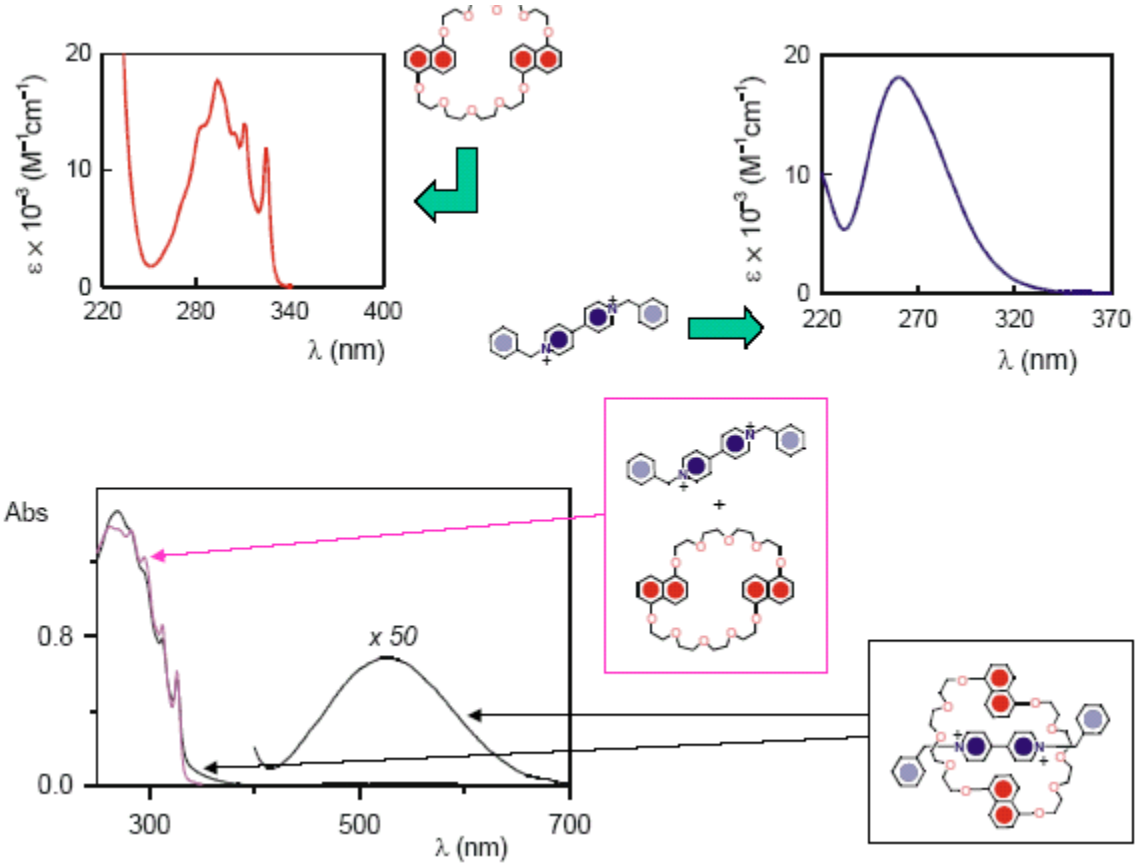

Copper(I) catalyzed azide-alkyne 1,3-cycloaddition (CuAAC): R-N3 + R'—≡—H → R-N(N=N)-CH=C(R')
2 x (t-BuC6H4)3CC6H4OCH2—≡—H 95
Cu
Cu^I

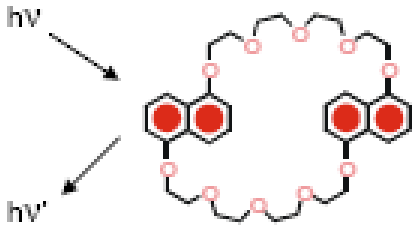

71
74
73
2 x
M^II
Imine bond formation
72-M^II
Mn^II = 83%
Fe^II = 57%
Co^II = 99%
Ni^II = 94%
Cu^II = 87%
Zn^II = 92%
Cd^II = 73%
Hg^II = 79%

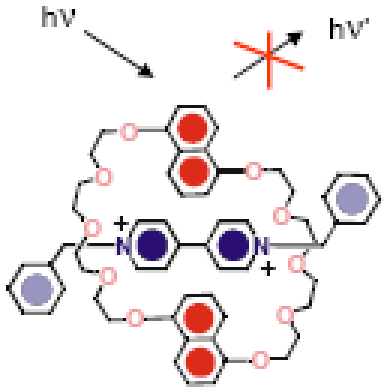


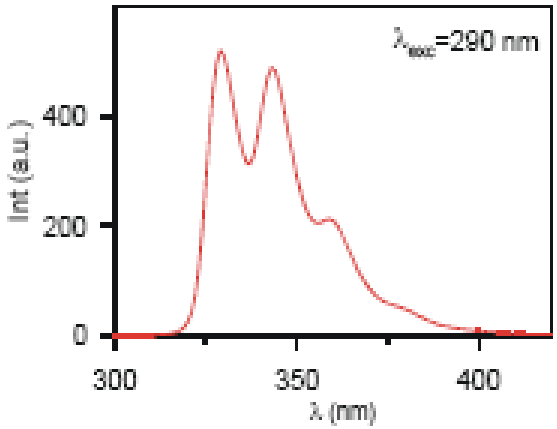
catione paraquat Bis-parafenilene-[34]-crown-10

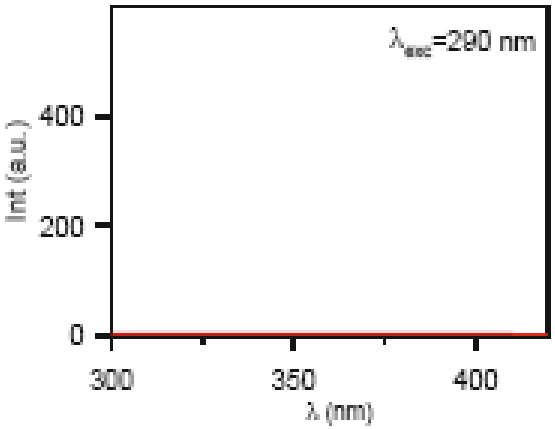


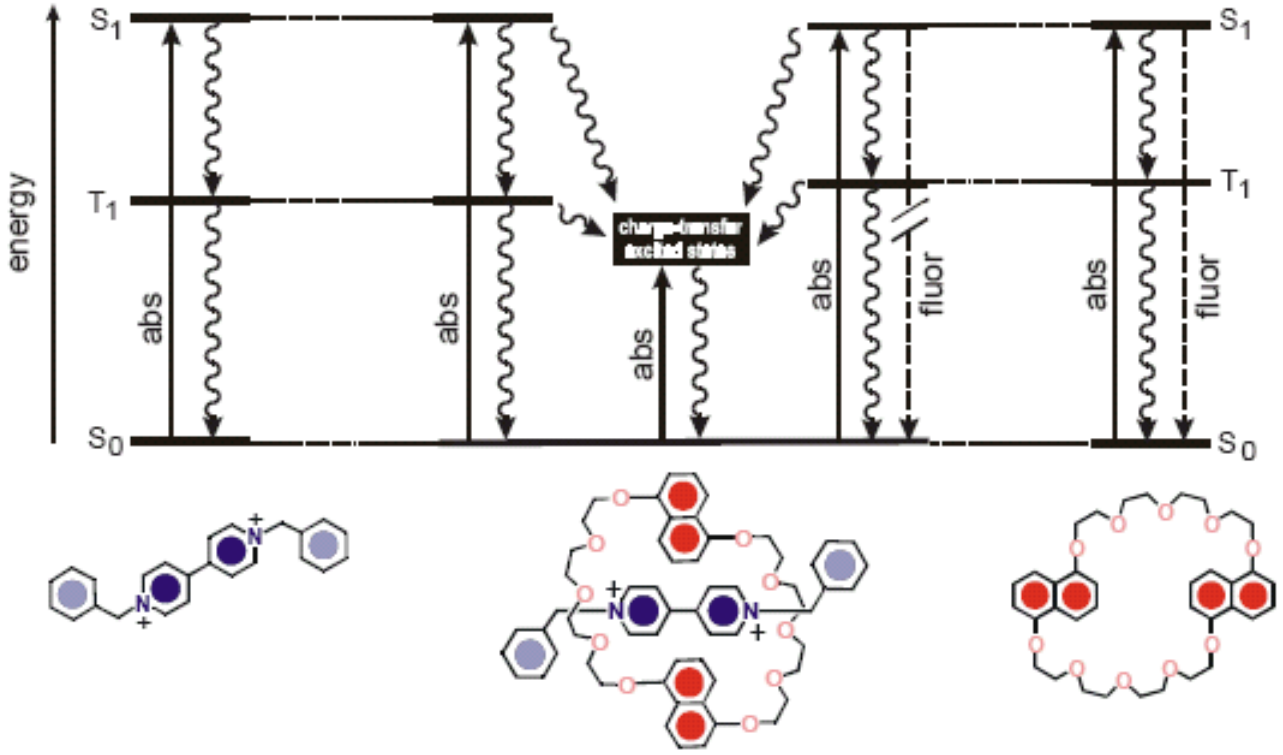

20
10
0
ε x 10^-3 (M^-1cm^-1)
220
280
340
400
λ (nm)
20
10
0
ε x 10^-3 (M^-1cm^-1)
220
270
320
370
λ (nm)
Abs
0.8
0.0
x 50
300
500
700
λ (nm)

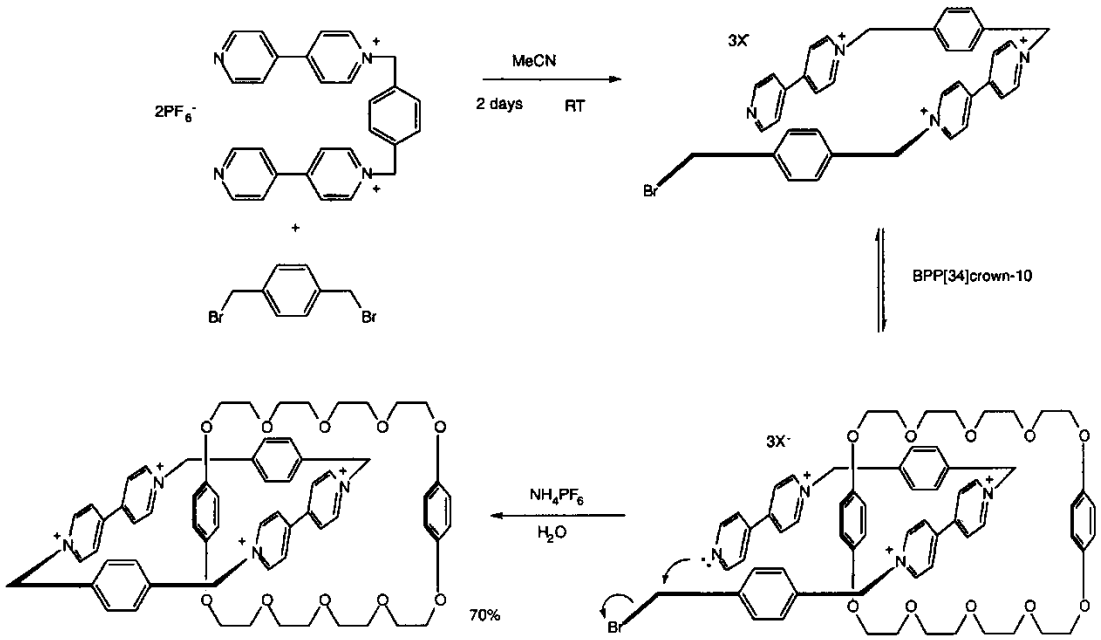

hν
hν'

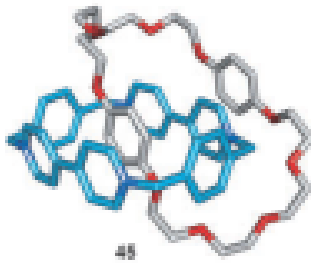

hν
hν'
N
N
+
+


λexc=290 nm
Int (a.u.)
400
200
0
300
350
400
λ (nm)

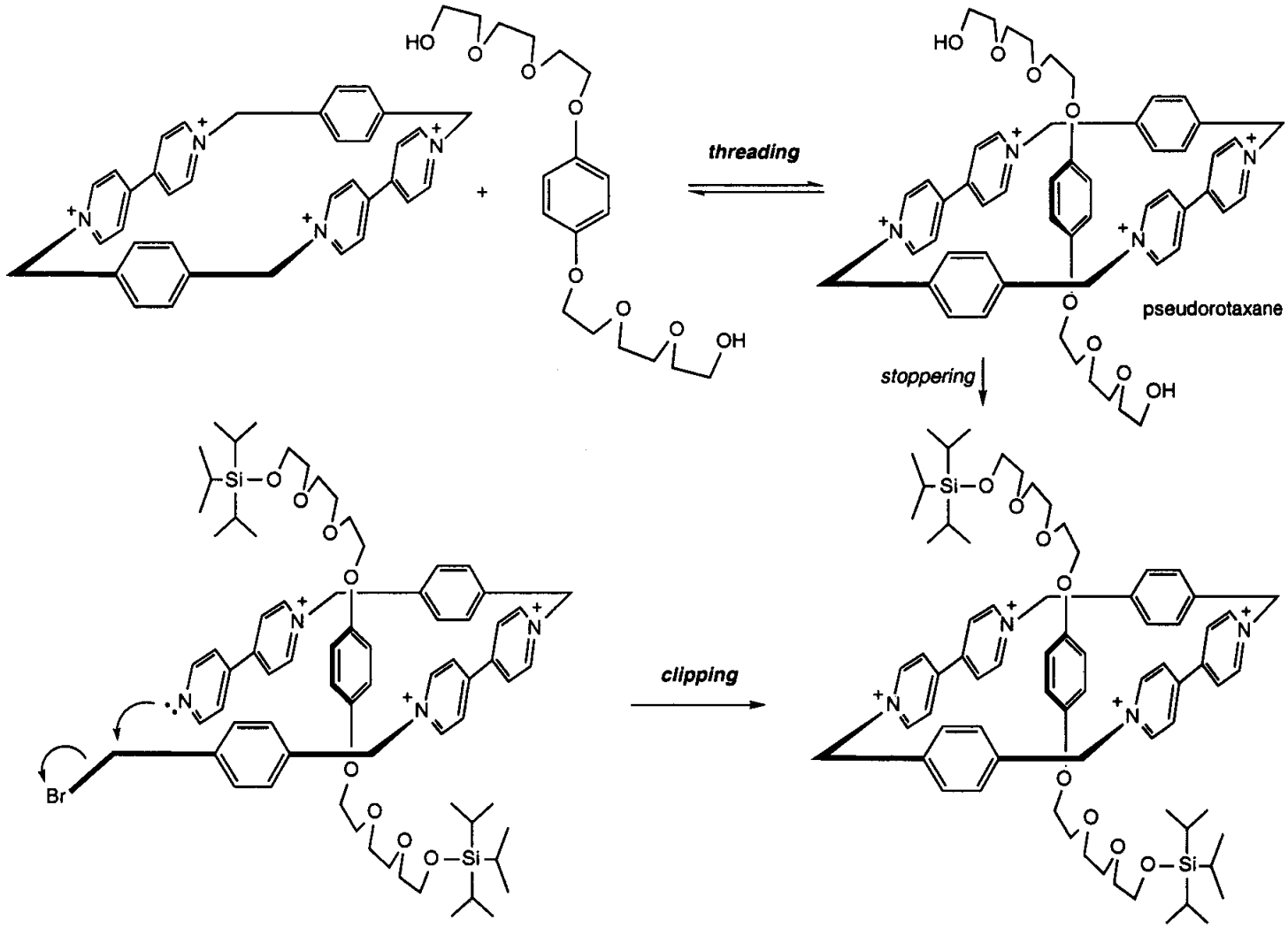

λexc=290 nm
Int (a.u.)
400
200
0
300
350
400
λ (nm)


energy
S1
T1
S0
abs
abs
abs
charge-transfer excited states
abs
fluor
abs
fluor
S1
T1
S0

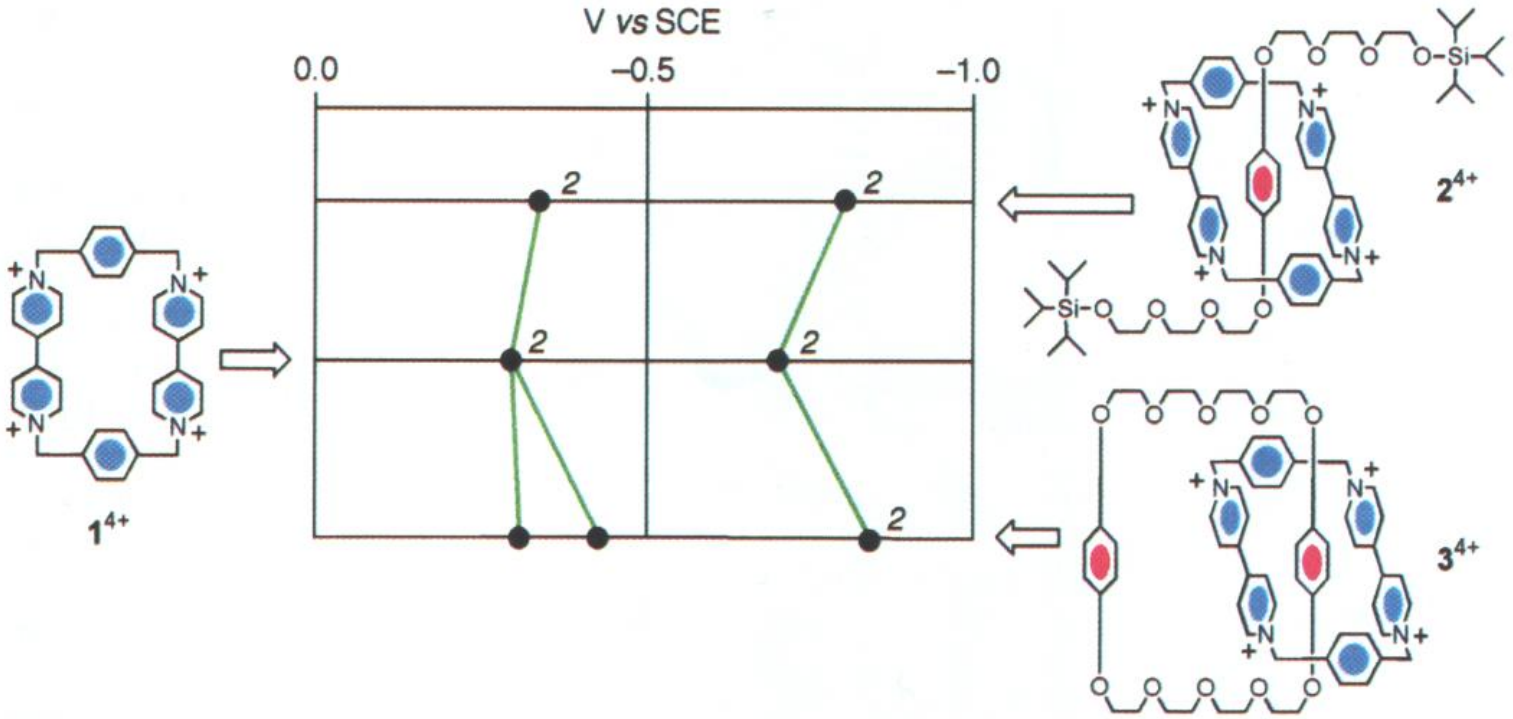


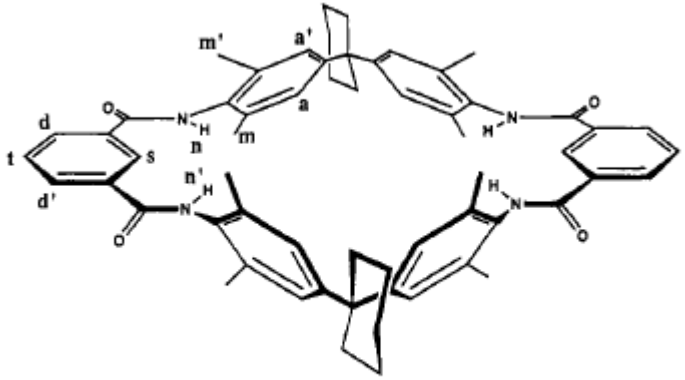


45

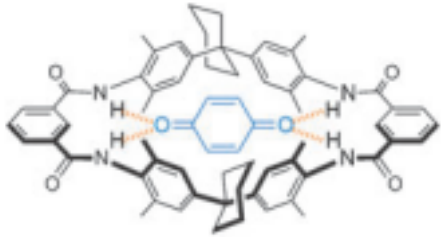


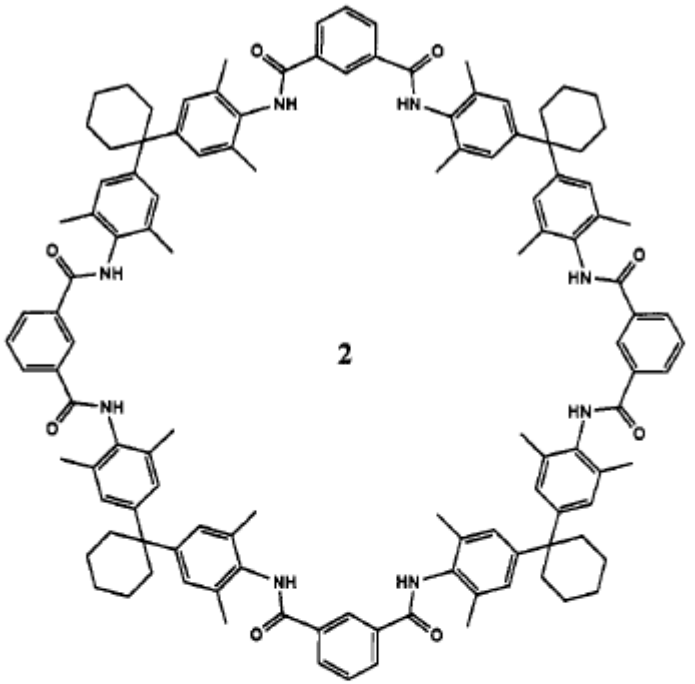
Synthesis of a rotaxane by two different routes: threading and clipping.


V vs SCE
0.0
–0.5
–1.0
2
2
2
2
2
1^{4+}
2^{4+}
3^{4+}

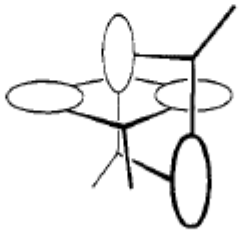


1

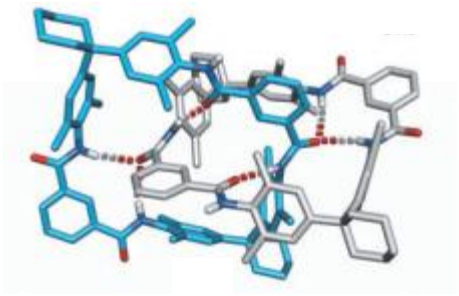


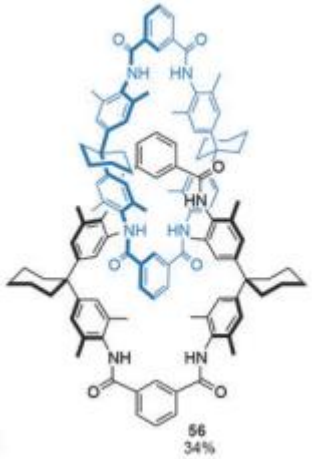


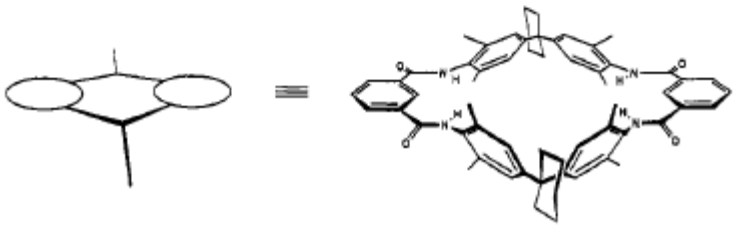
2



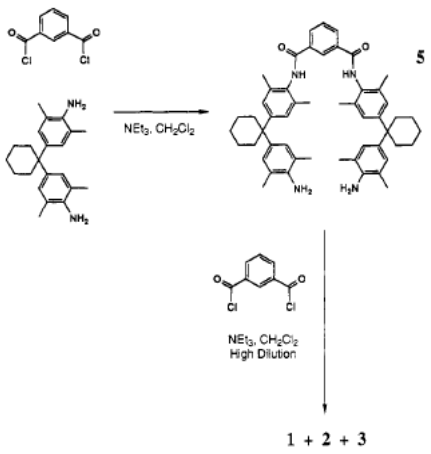
3







Scheme II

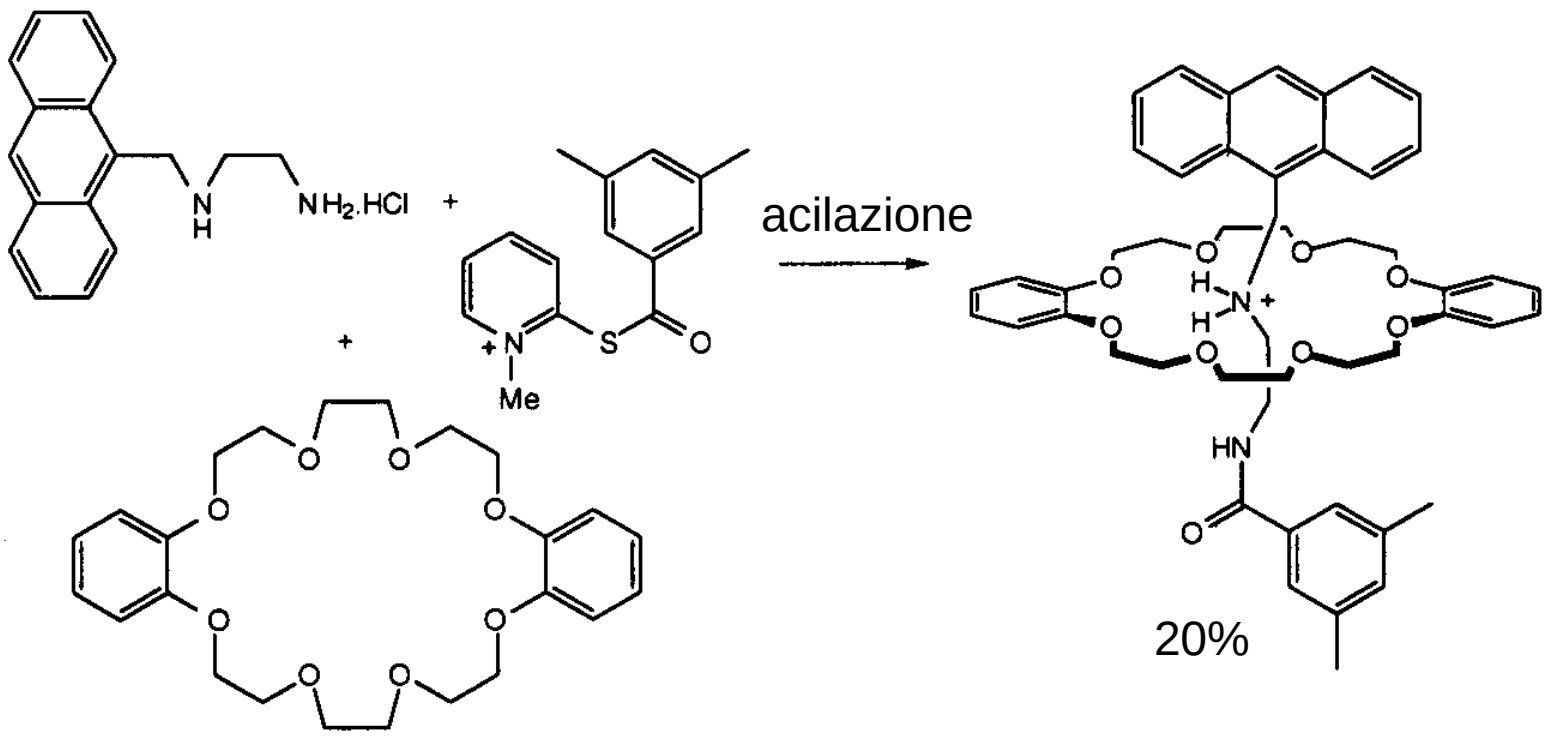


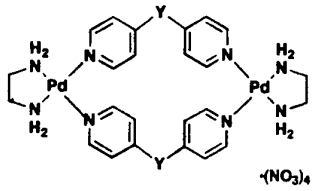
Cyclic Dimer 1, Cyclic Tetramer 2, and Catenane 3 (Scheme II). **5**, 1 g, and 0.4 mL of triethylamine were dissolved in 250 mL of dry dichloromethane and transferred to a dropping funnel. Isophthaloyl dichloride (0.26 g) was similarly dissolved in 250 mL of dry dichloromethane and transferred to an identical dropping funnel. These two solutions were added dropwise to 1200 mL of dry dichloromethane over a period of 4 h with stirring under nitrogen. The reaction mixture was then stirred for a further 12 h. The precipitate was filtered off and the solvent evaporated under reduced pressure. The products were chromatographed on silica with chloroform–ethanol eluant. Fraction A was eluted with chloroform. Fraction B was eluted with chloroform–ethanol (99:1). Fraction C was eluted with chloroform–ethanol (98:2). All three fractions were recrystallized from chloroform–pentane.

Fraction A was obtained as a white crystalline solid (400 mg, 34%). The NMR data are discussed in the main text. m/z 1806 (MH^+); $C_{120}H_{128}N_8O_8$ requires $M^+ = 1808$.

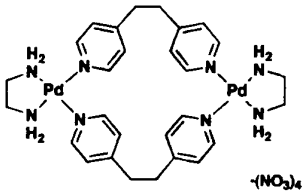
Fraction B was obtained as a white powder (600 mg, 51%). Spectroscopic data were as for the cyclic dimer **1** from Scheme I.

Fraction C was obtained as a white powder (50 mg, 5%). NMR ($CDCl_3/CD_3OD$) δ 8.41 (4 H, s), 7.98 (8 H, d), 7.43 (4 H, t), 6.96 (16 H, s), 2.21 (16 H, br), 2.10 (48 H, s), 1.52 (24 H, br). m/z 1806 (MH^+); $C_{120}H_{128}N_8O_8$ requires $M^+ = 1808$.


NH2.HCl
+
+
N
Me
S
O
acilazione
H
N
HN
20%



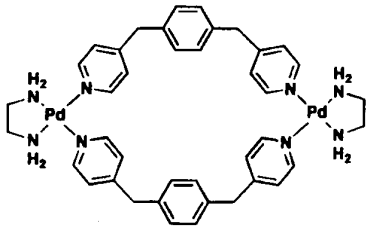
$\cdot(NO_3)_4$

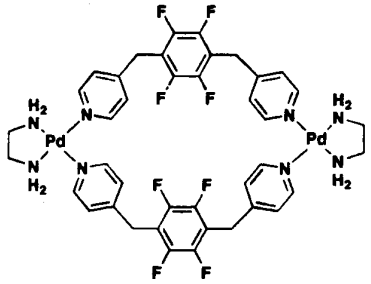


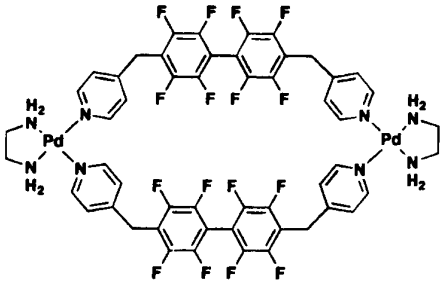
$\cdot(NO_3)_4$

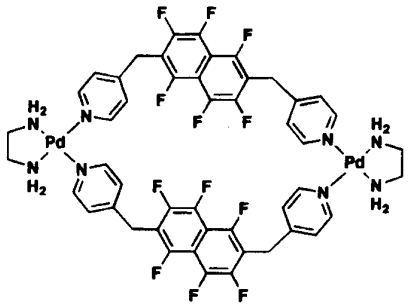
Y = CH_2

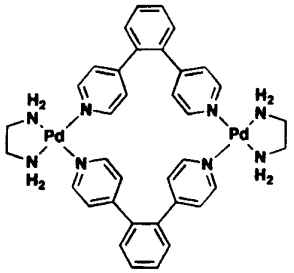
Y = $C(OH)_2$

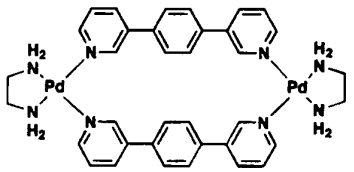




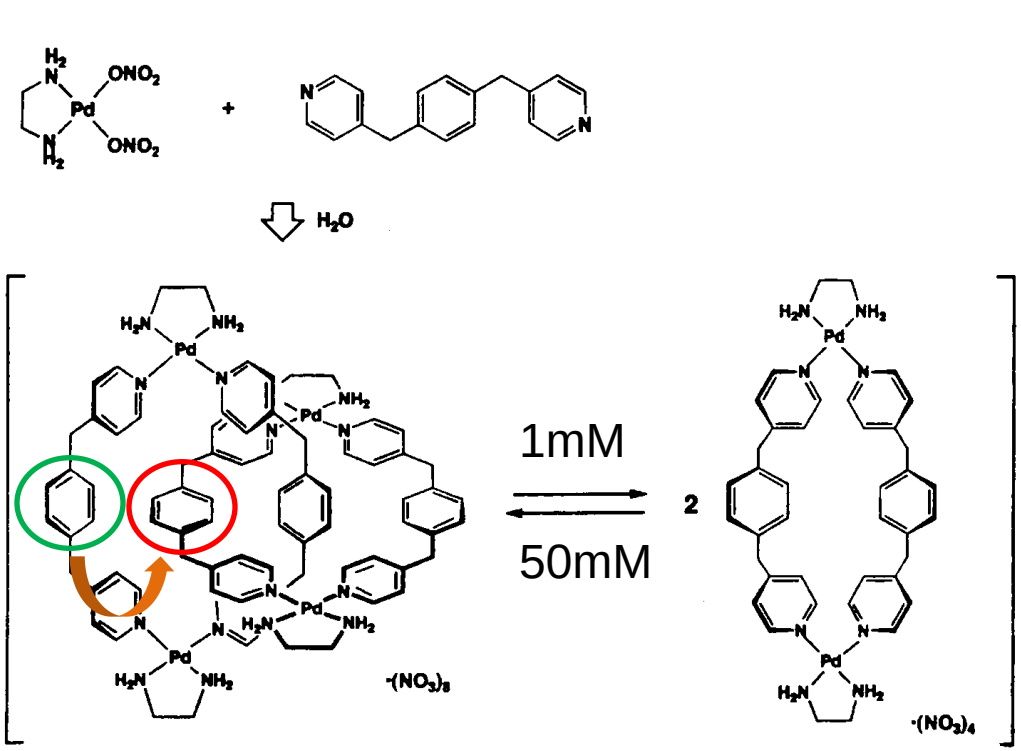


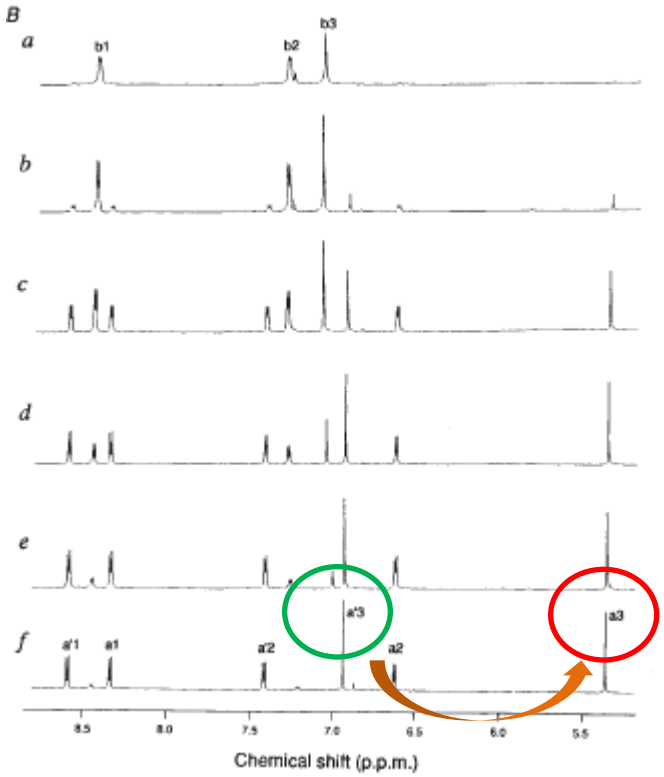


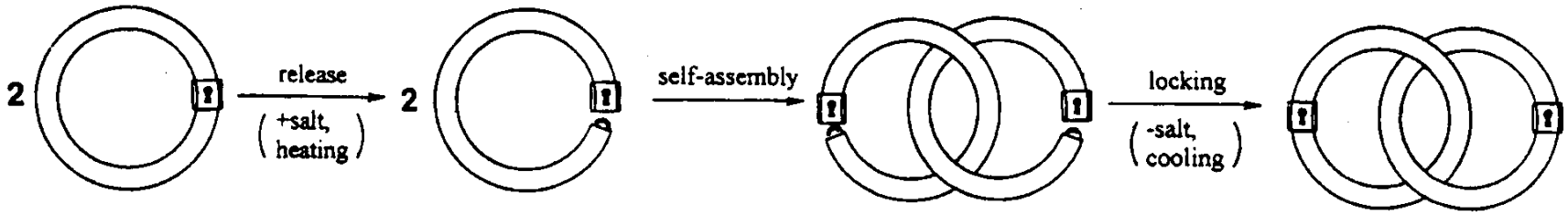


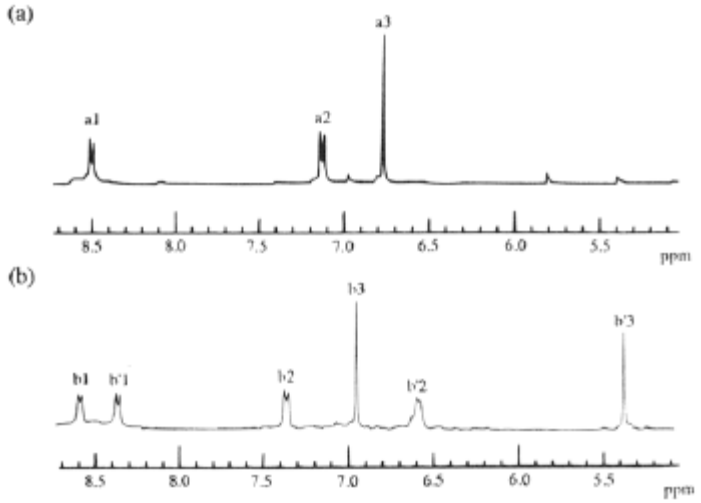


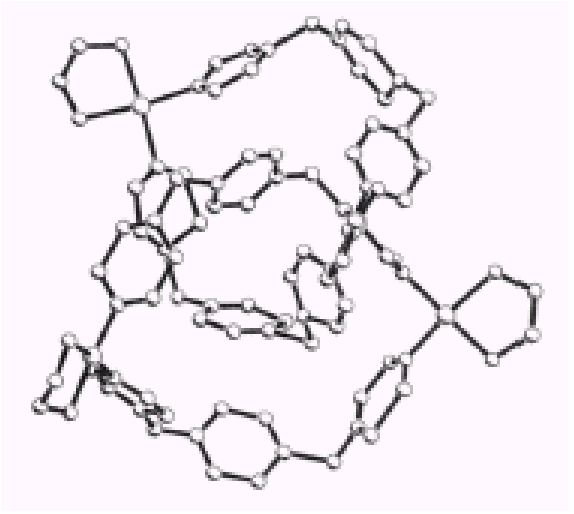
Catenani


H2O
1mM
50mM
2
·(NO3)8
·(NO3)4


B
a
b
c
d
e
f
b1
b2
b3
a'3
a3
a'1
a1
a'2
a2
Chemical shift (p.p.m.)


2
release
(+salt, heating)
2
self-assembly
locking
(-salt, cooling)


(a)
a1
a2
a3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
ppm
(b)
b1
b'1
b2
b3
b'2
b'3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
ppm

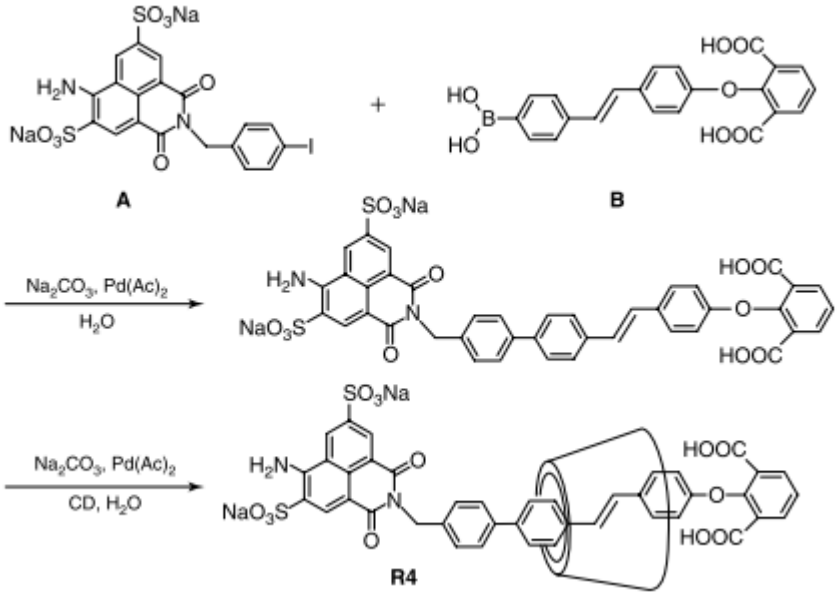


Molecular Borromean Rings

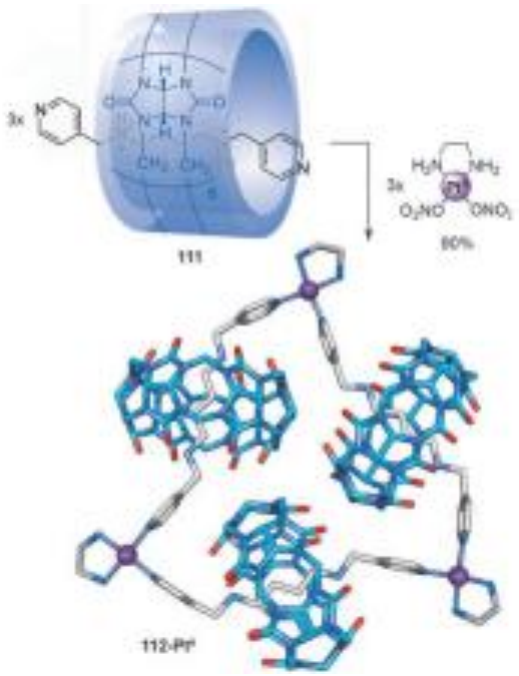
Kelly S. Chichak,[1] Stuart J. Cantrill,[1] Anthony R. Pease,[1]
Sheng-Hsien Chiu,[1] Gareth W. V. Cave,[2] Jerry L. Atwood,[2]
J. Fraser Stoddart[1*]

28 MAY 2004 VOL 304 SCIENCE www.sciencemag.org

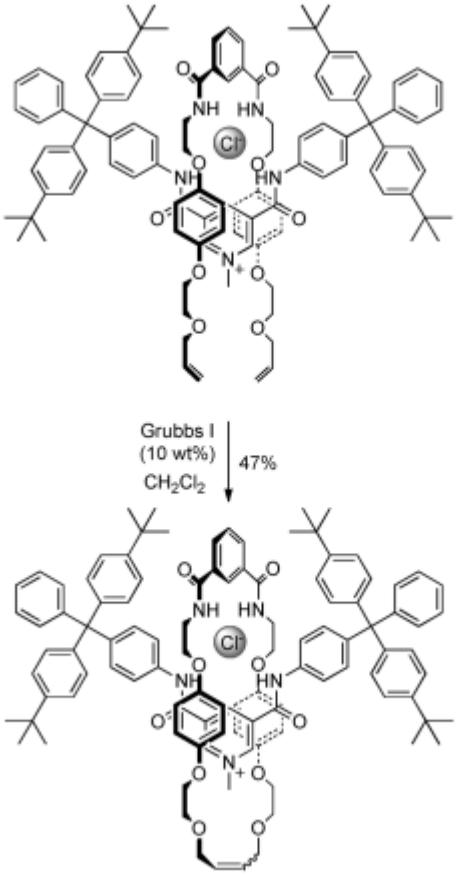
Hydrophobic effect



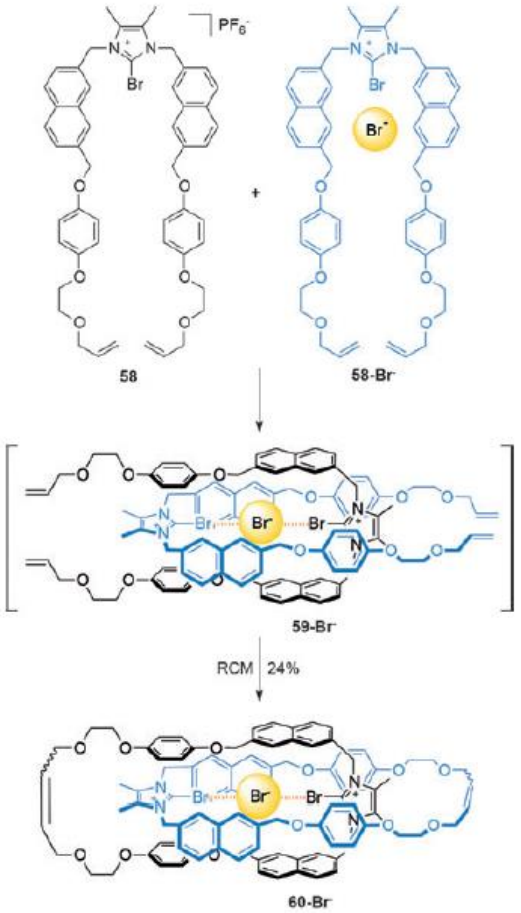
Hydrophobic effect



Anion templating



Halogen bond templating



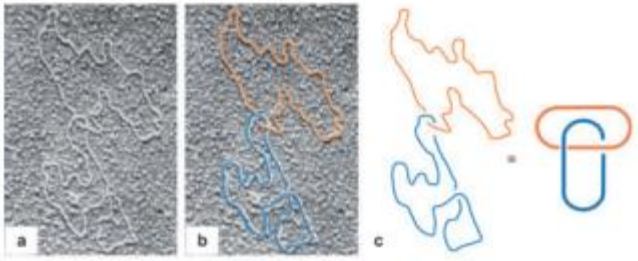
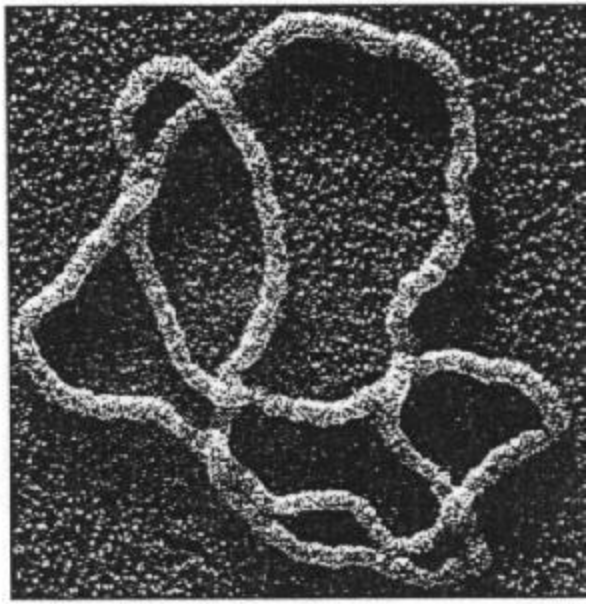


Figure 4. a) Electron micrograph of circular DNA revealing a catenane topology. b,c) Highlighting the two component rings of the DNA catenane as a Hopf link. Modified from Ref. [23] with permission.



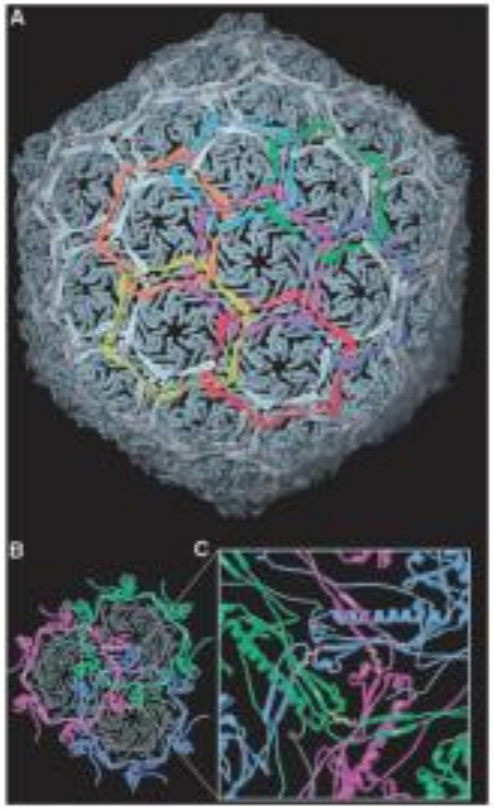


Figure 5. The "chainmail" arrangement of proteins found in bacteriophage HK97s capsid (colored sections highlight the individual protein rings). a) The repeating pattern of interlocking proteins which constitute the spherical capsid. b) A cross-section of the capsid in which three protein rings interlock with one another. c) Magnified view of the position at which protein rings overlap (cross-linking isopeptide bonds are highlighted). Reprinted from Ref. [28] with permission.

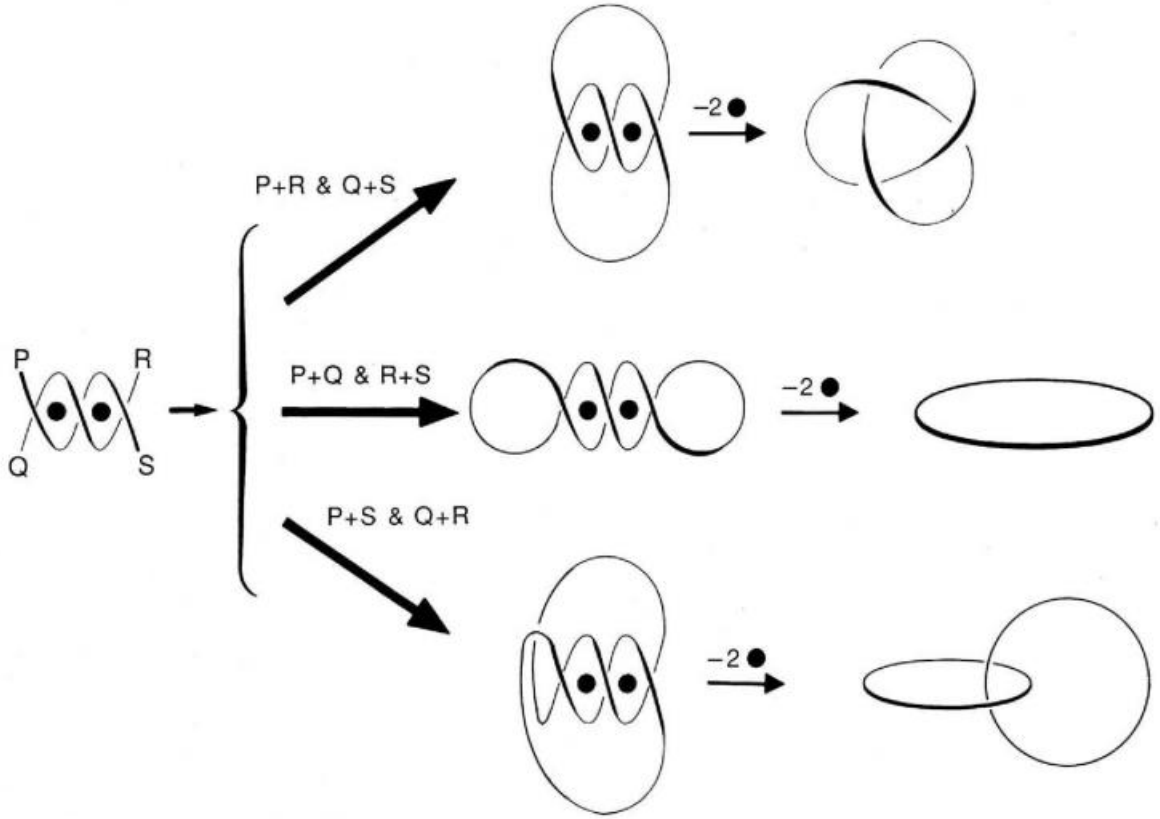
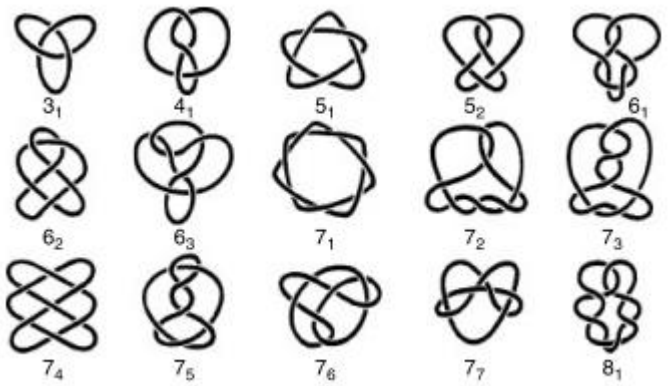


Figure 23. A guide for demonstrating the synthesis of topologically different molecules from the precursor to the trefoil knot.

Nodi Molecolari e Links



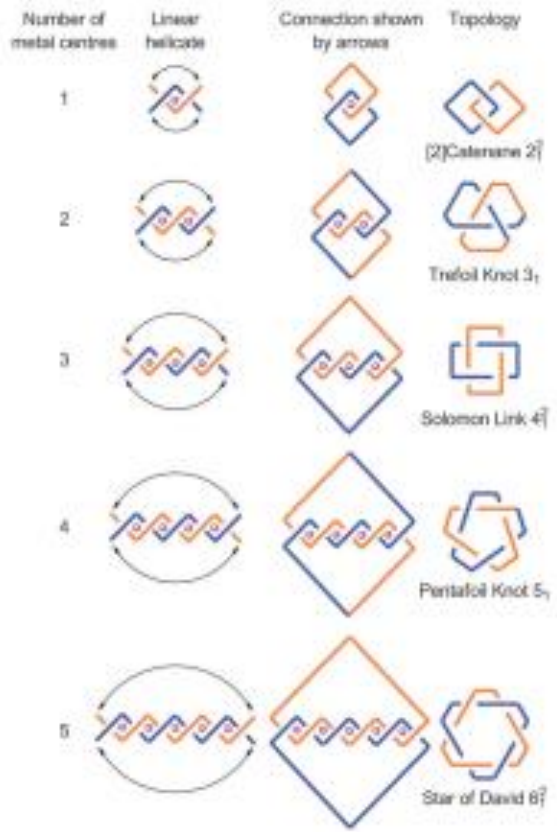


Fig. 3 The linear helicate strategy to interlocked molecules introduced by Sauvage.[48] To date the first three entries of this table have been realised experimentally using this strategy, generating catenanes,[4] trefoil knots[38] and doubly-interlocked [2]catenanes (Solomon links)[47] using one, two and three metal centres, respectively. The synthesis of a pentafoil knot or triply-interlocked [2]catenane (the 'Star of David' topology) from a linear helicate has thus far proved unsuccessful.[48]

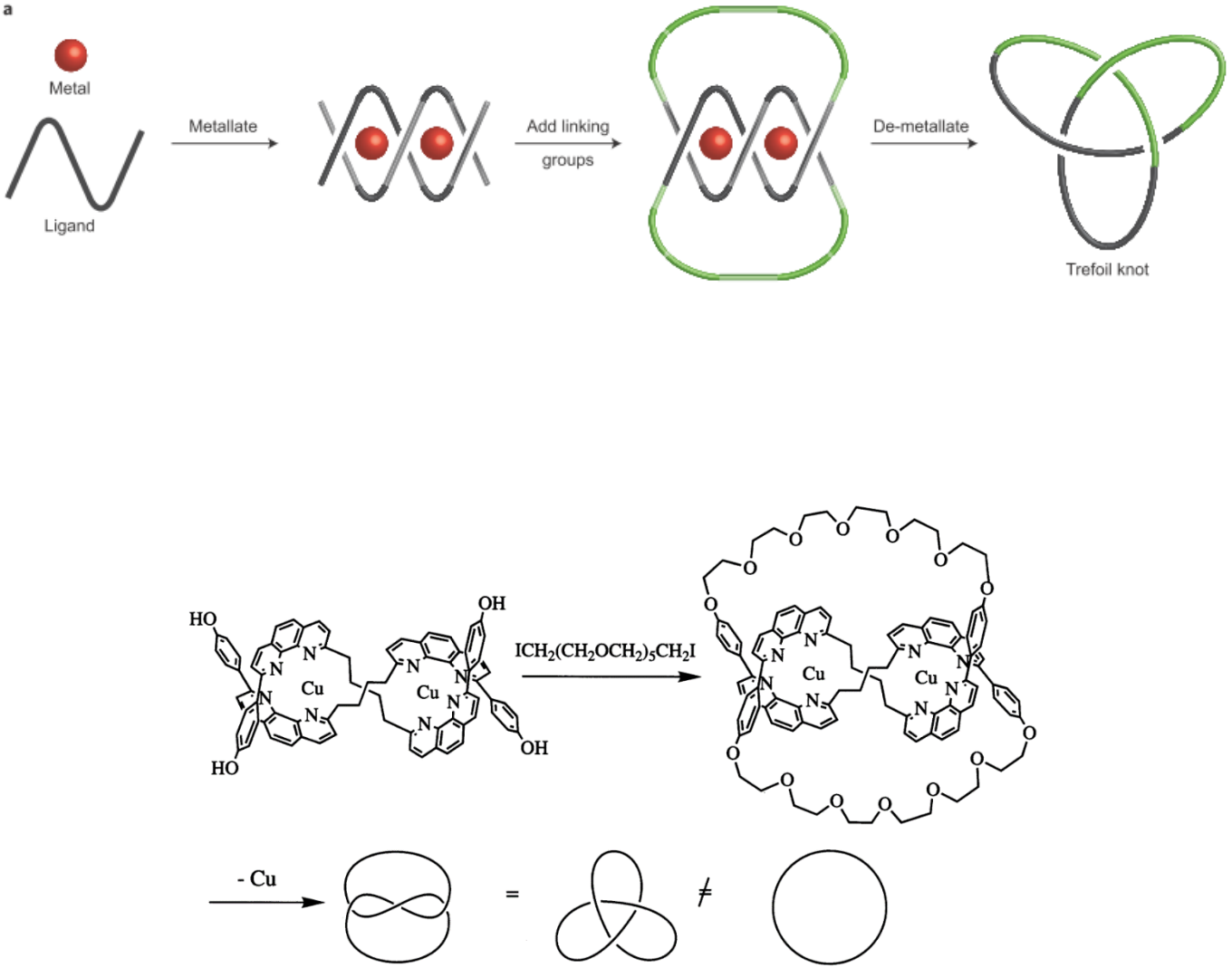


Fig. 8. Synthesis of the first trefoil knot using a two-anchor helical template.

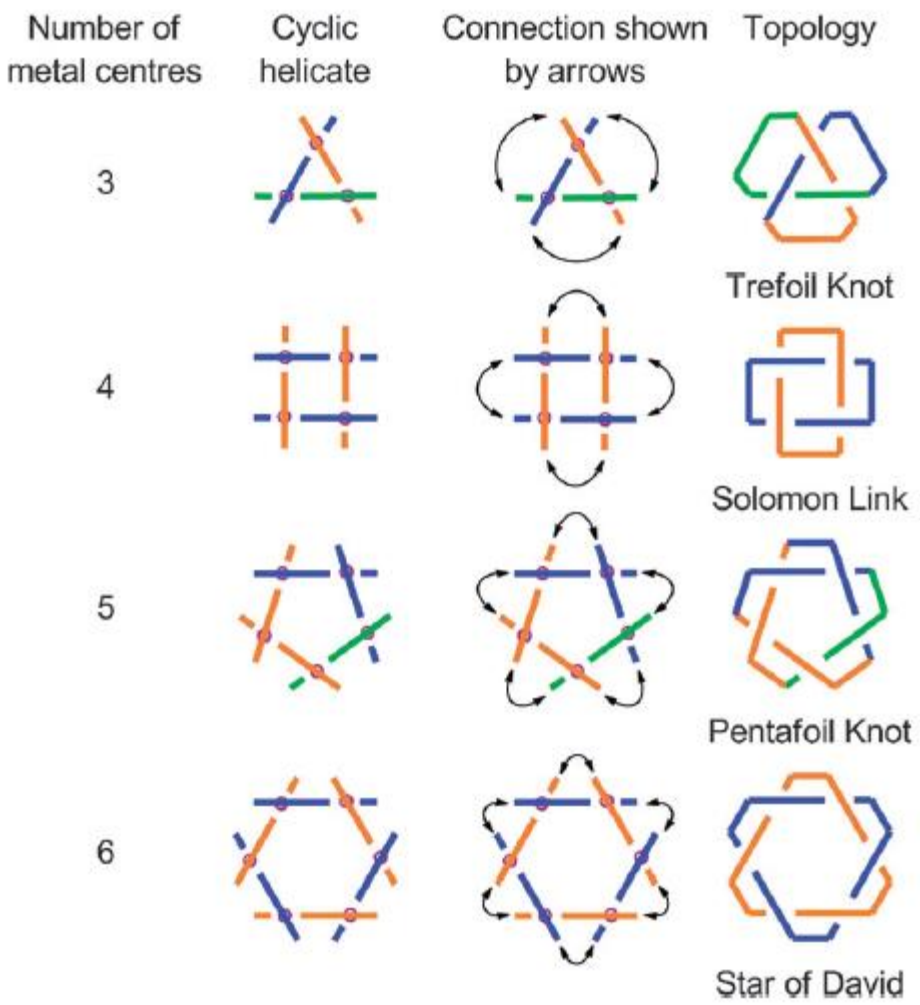


Fig. 5 The potential of circular metal helicates to form molecular knots and links by connecting adjacent end-groups. To date only a pentafoil knot has been prepared through this strategy.[73]

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A synthetic molecular pentafoil knot

Jean-François Ayme[1], Jonathon E. Beves[1], David A. Leigh[1]*, Roy T. McBurney[1], Kari Rissanen[2] and David Schultz[1]

Interlocked Molecules

DOI: 10.1002/anie.201007963

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*

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Template synthesis of molecular knots†

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

Catenanes

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Catenanes: Fifty Years of Molecular Links

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

Angew. Chem. Int. Ed. **2015**, *54*, 6110 – 6150

Nobel Laureate in Chemistry 2016: Jean-Pierre Sauvage, University of Strasbourg, France.
The Nobel Committee for Chemistry. From: The Nobel Lectures 2016, 2016-12-08

https://www.youtube.com/watch?v=voihgqHlU_4

http://www.catenane.net/pages/2017_819knot.html