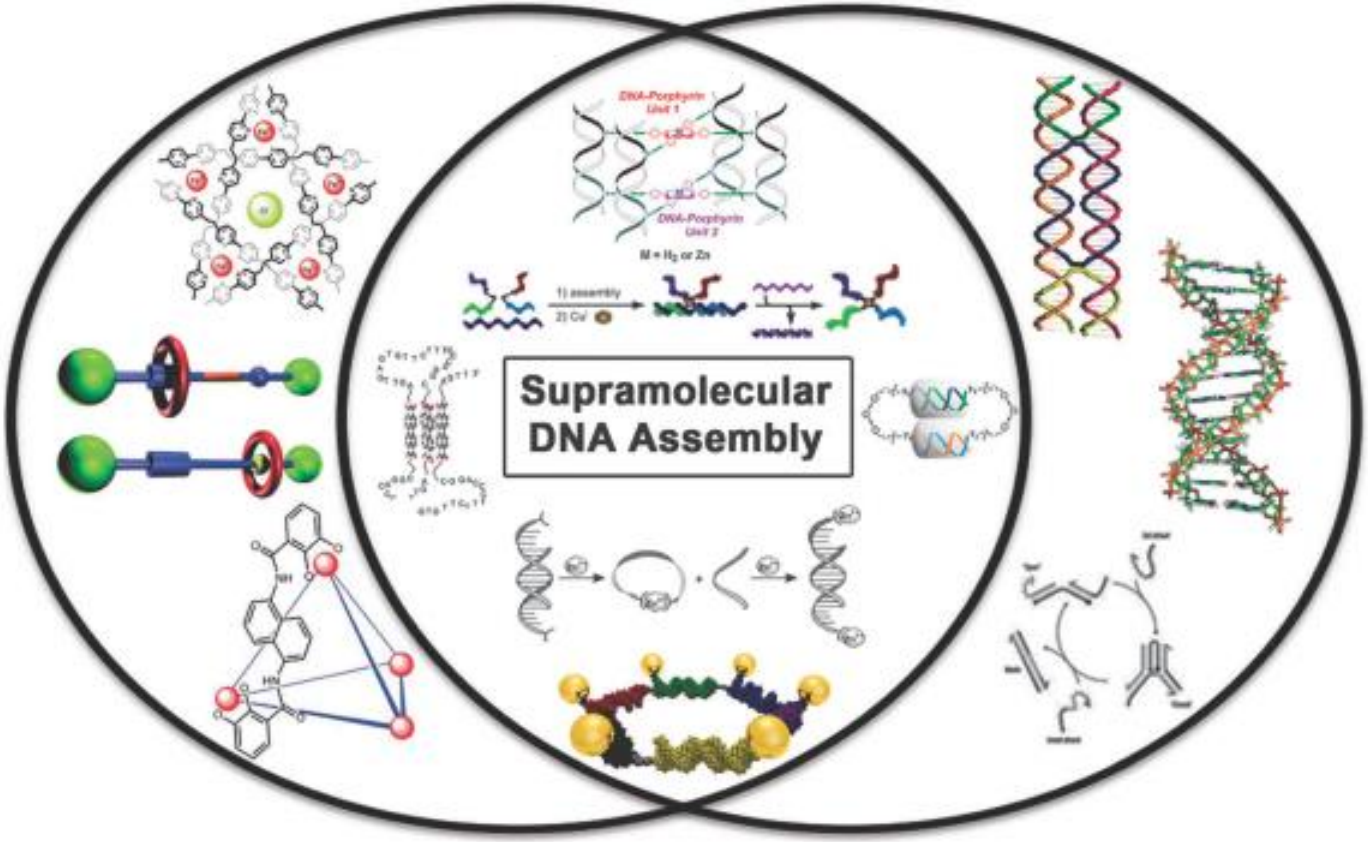
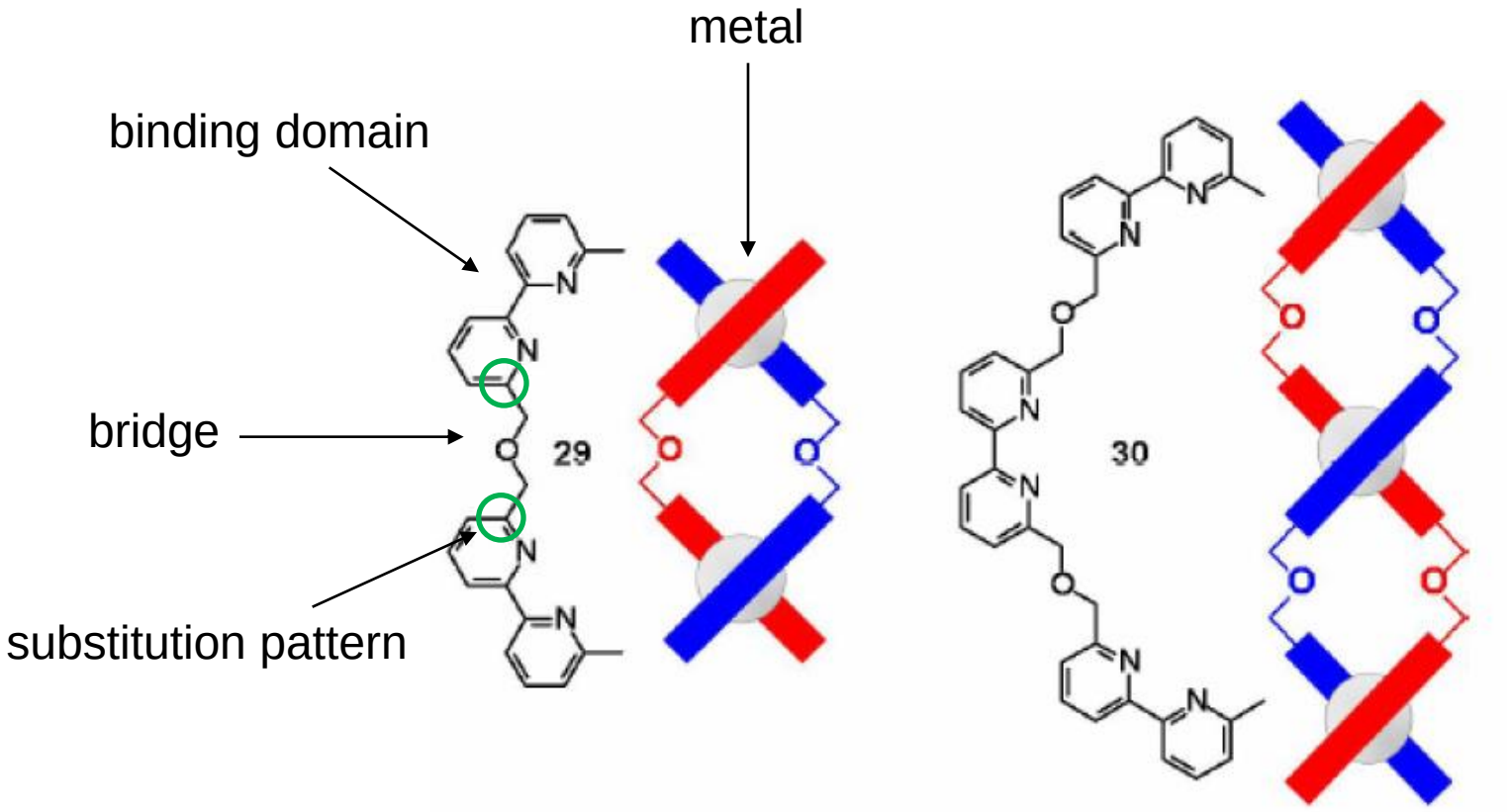
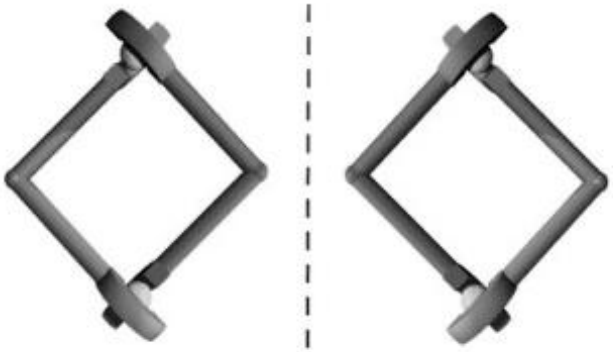
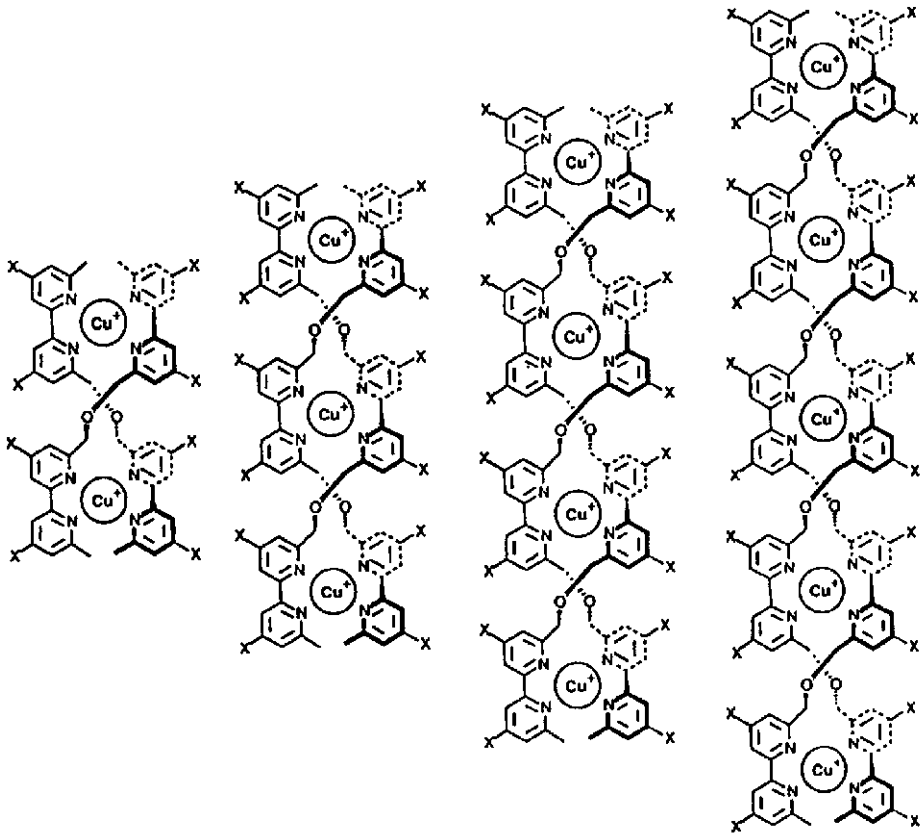

DNA-Porphyrin Unit 1
DNA-Porphyrin Unit 2
M = H2 or Zn
1) assembly
2) Cu2+
Supramolecular DNA Assembly

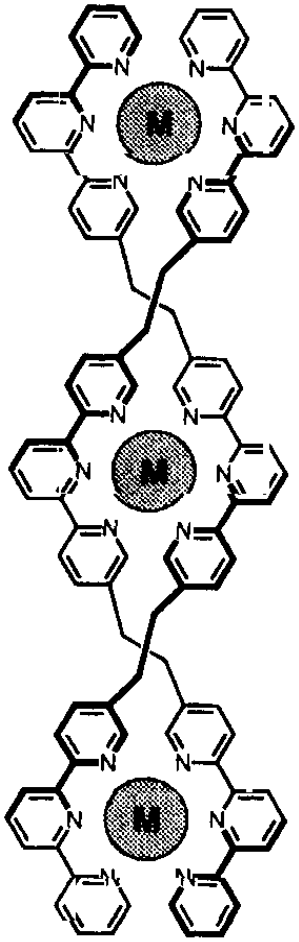
Double stranded helicates



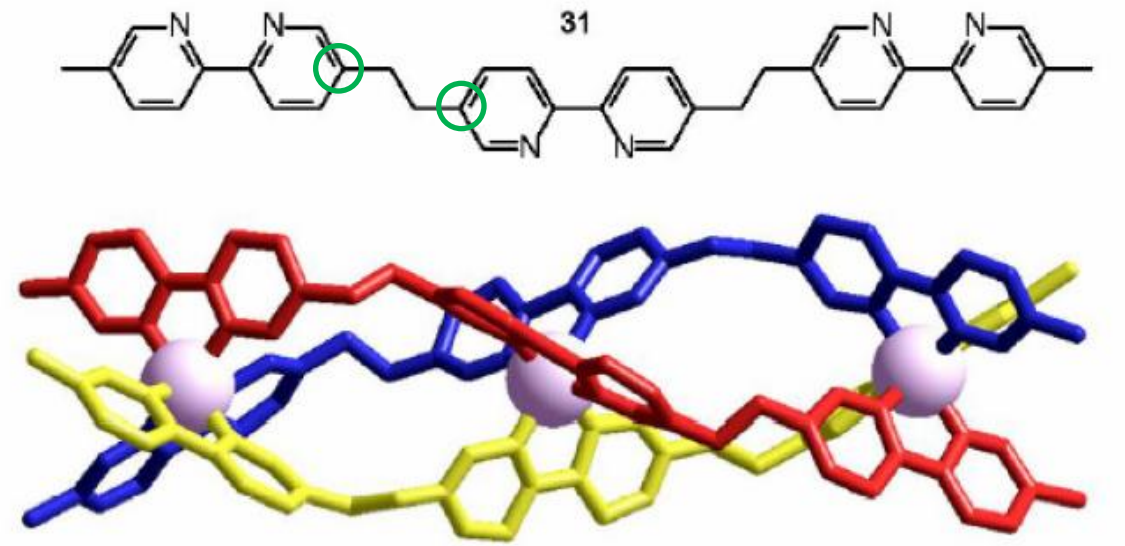


Double helicates



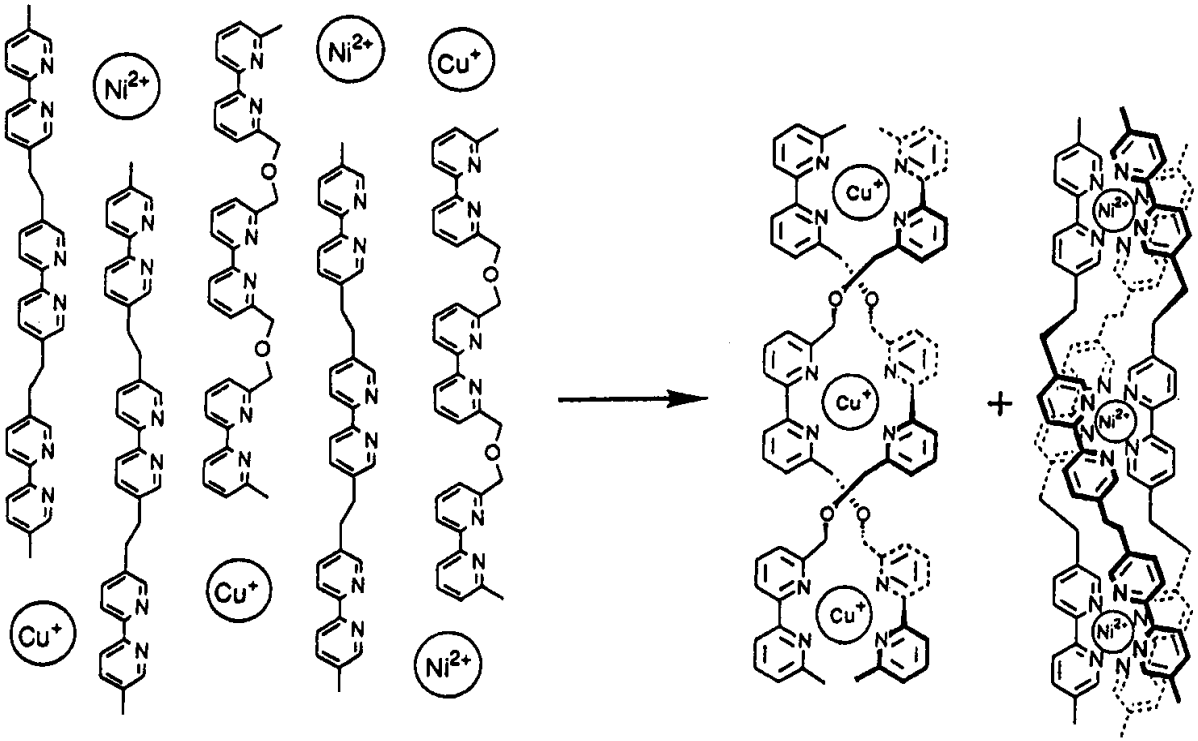

M
M
M

Triple stranded helicates

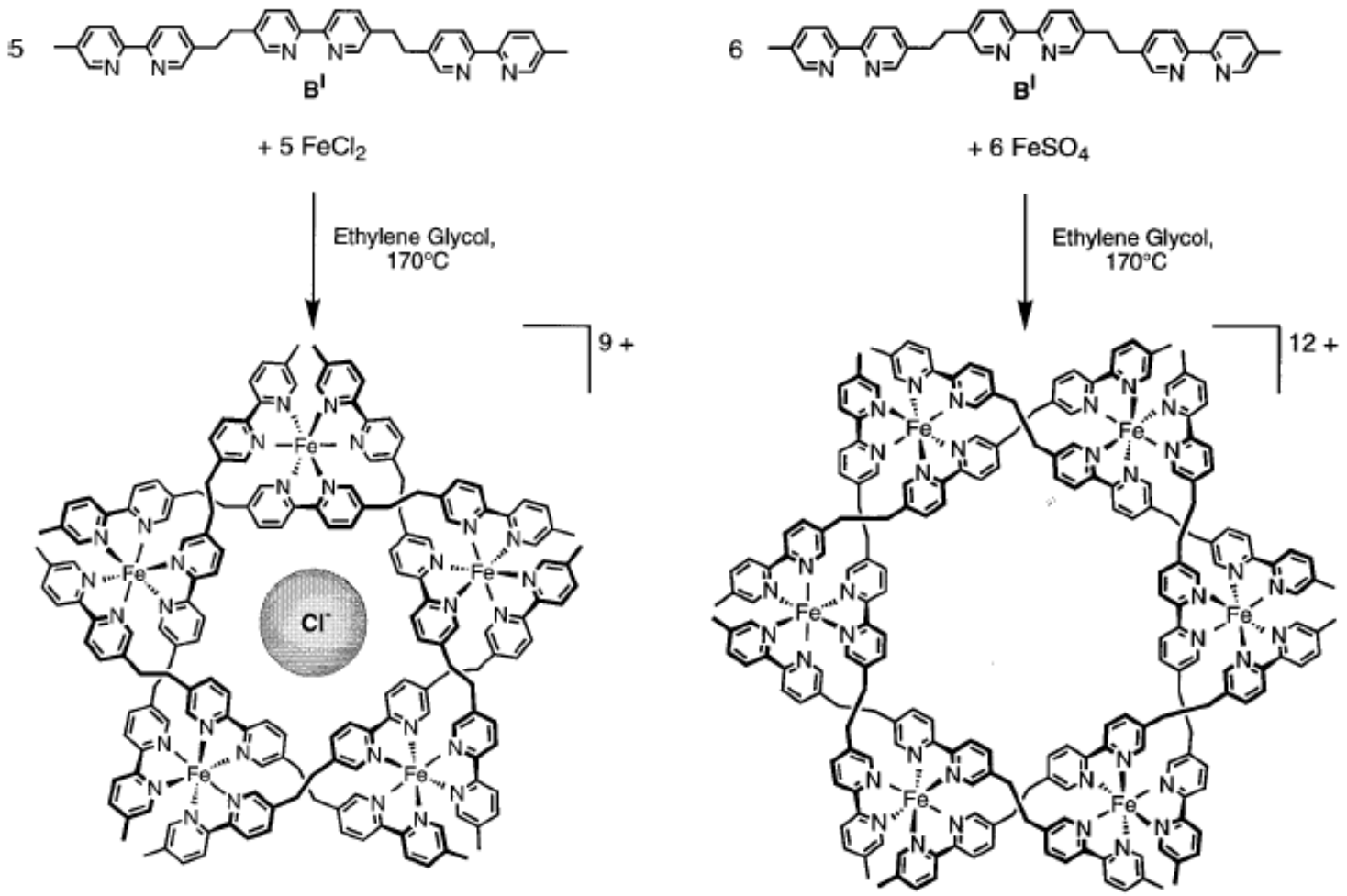


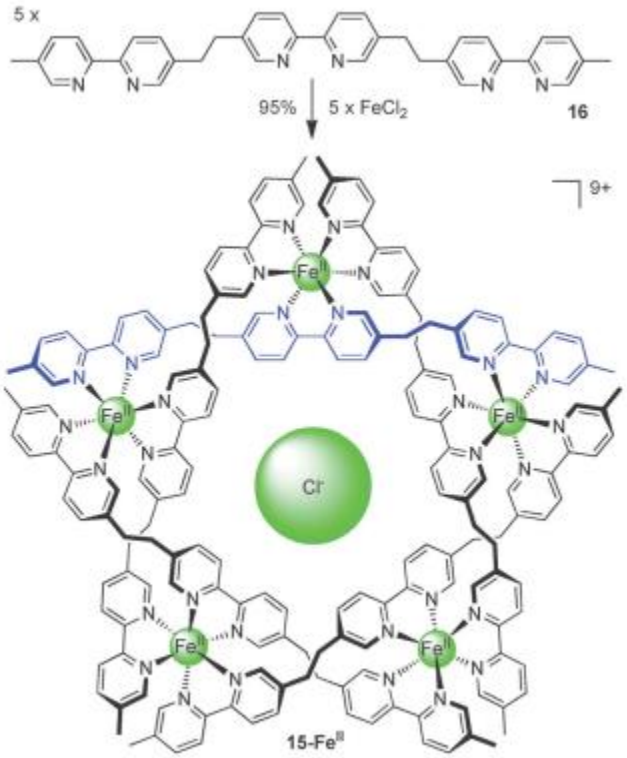
- Ni(II) : octahedral geometry
- one ligand can not wrap around one Ni(II) cation : trimerization
- other metals: Co(II), Fe(II), lanthanides

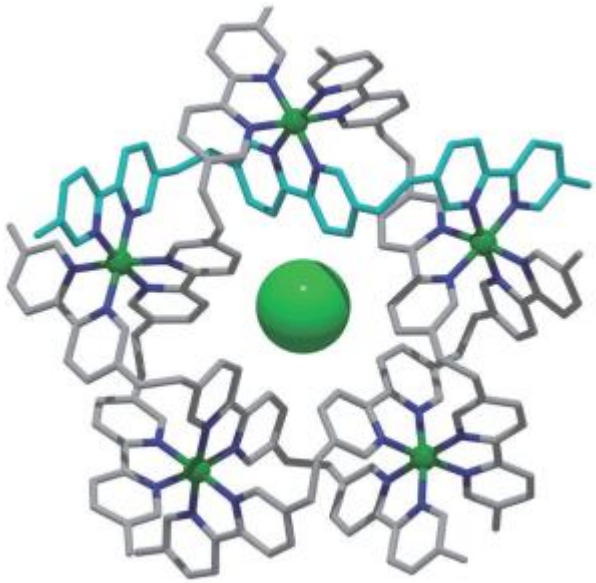
Double and Triple Helicates: an example of Selective-Recognition



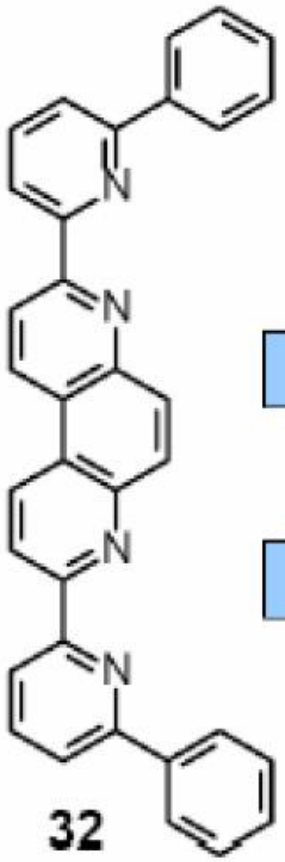
Cyclic Helicates



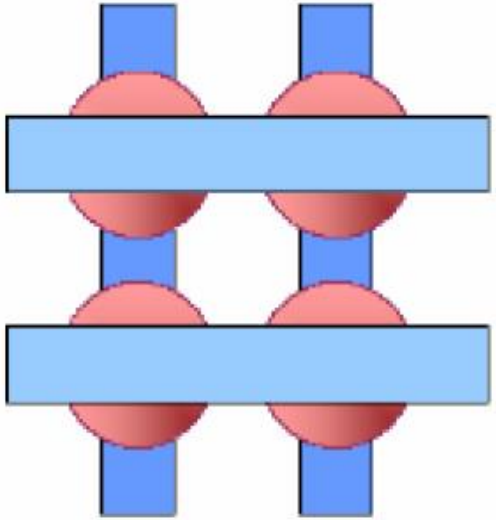

5 x
95%
5 x FeCl2
16
9+
Fe
Cl
15-Fe



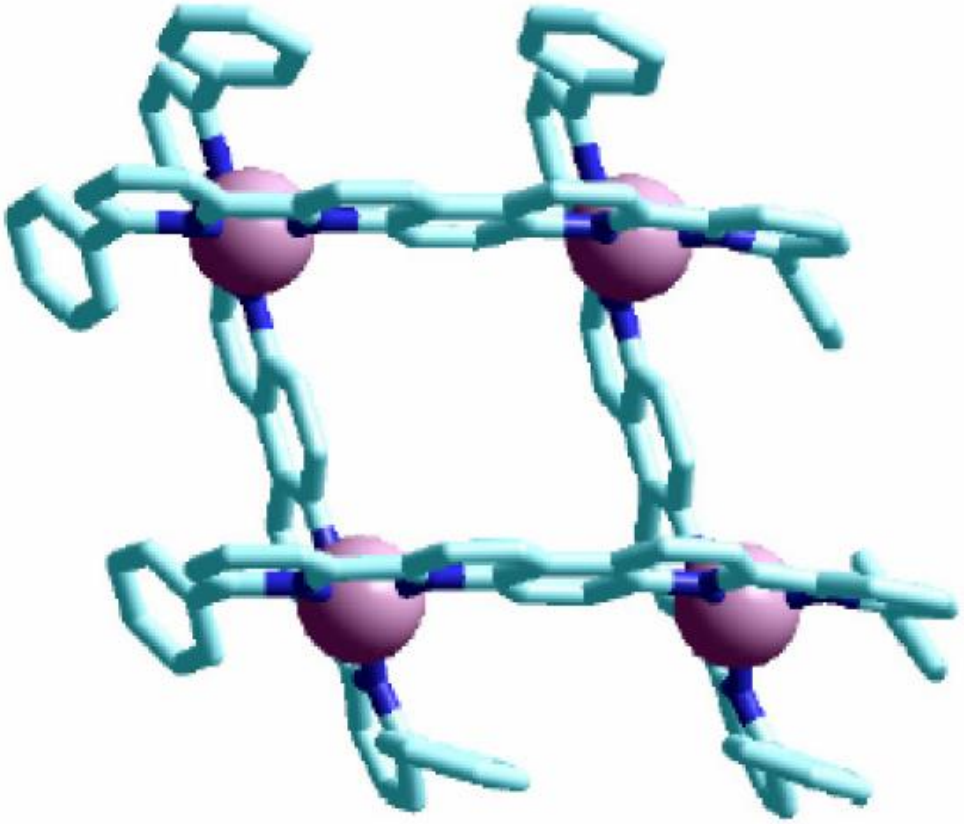
Molecular Grids

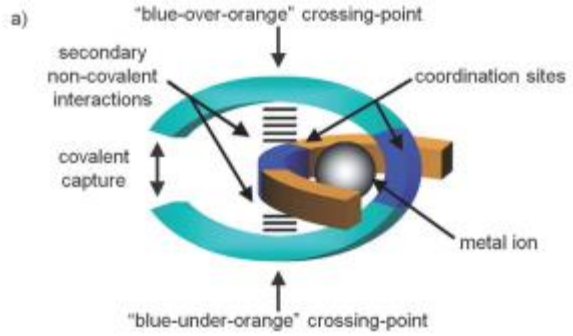


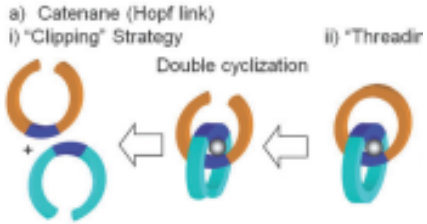
32

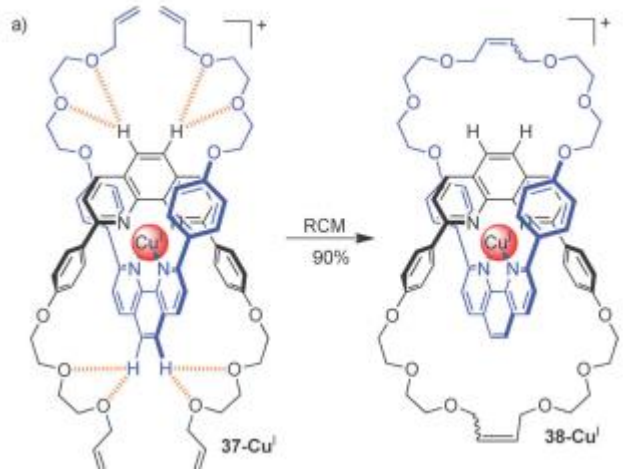


2X2 Cu(I) grid

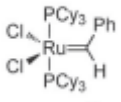


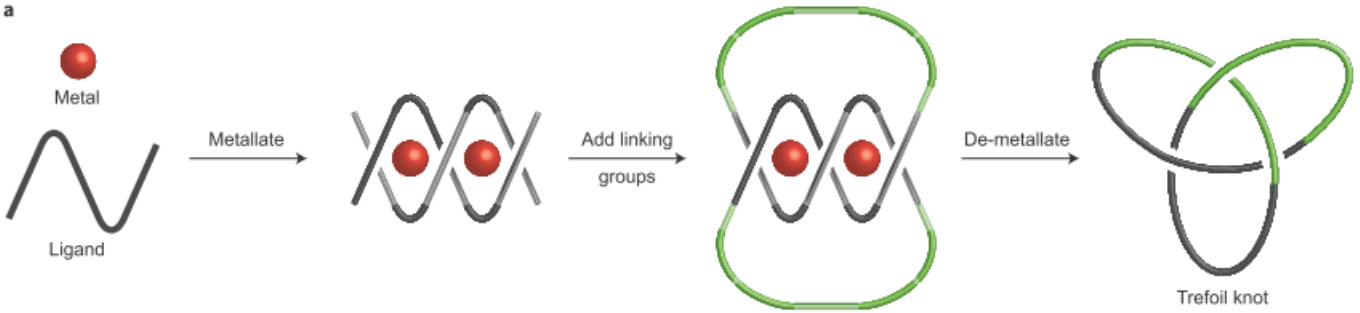


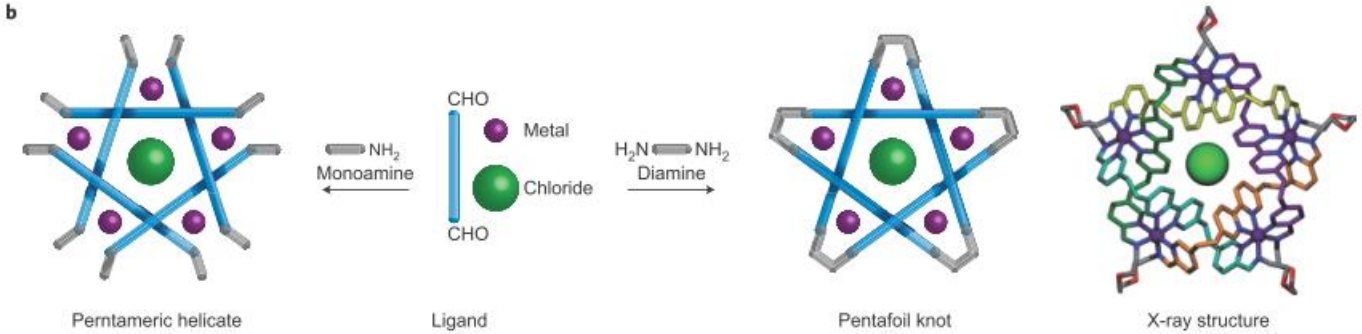




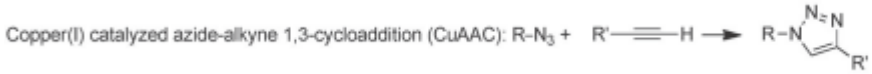
Ring closing metathesis (RCM): 2 x 

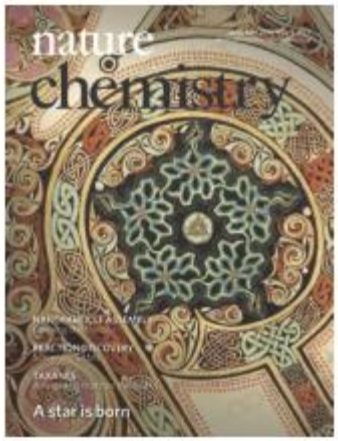



a
Metal
Ligand
Metallate
Add linking
groups
De-metallate
Trefoil knot


b
NH2
Monoamine
CHO
Metal
Chloride
CHO
H2N
NH2
Diamine
Perntameric helicate
Ligand
Pentafoil knot
X-ray structure

Reaction	year	A		B		h/c	catalyst
Glaser	1869	RC≡CH	sp	RC≡CH	sp	homo	Cu
Ullmann	1901	Ar-X	sp^2	Ar-X	sp^2	homo	Cu
Sonogashira	1975	RC≡CH	sp	R-X	sp^3 sp^2	cross	Pd and Cu
Negishi	1977	R-Zn-X	sp^3, sp^2, sp	R-X	sp^3 sp^2	cross	Pd or Ni
Stille	1978	R-SnR_3	sp^3, sp^2, sp	R-X	sp^3 sp^2	cross	Pd
Suzuki	1979	R-$B(OR)_2$	sp^2	R-X	sp^3 sp^2	cross	Pd
Hiyama	1988	R-SiR_3	sp^2	R-X	sp^3 sp^2	cross	Pd
Buchwald-Hartwig	1994	R_2N-R SnR_3	sp	R-X	sp^2	cross	Pd

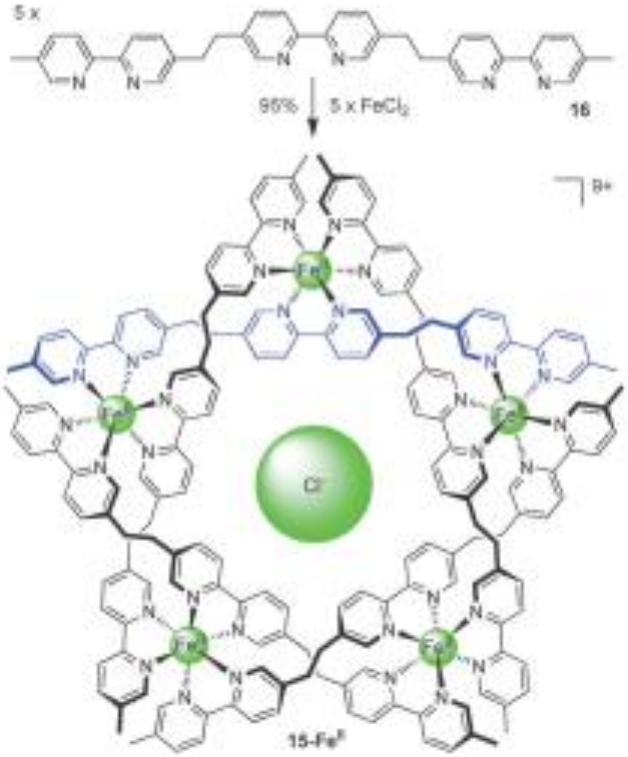


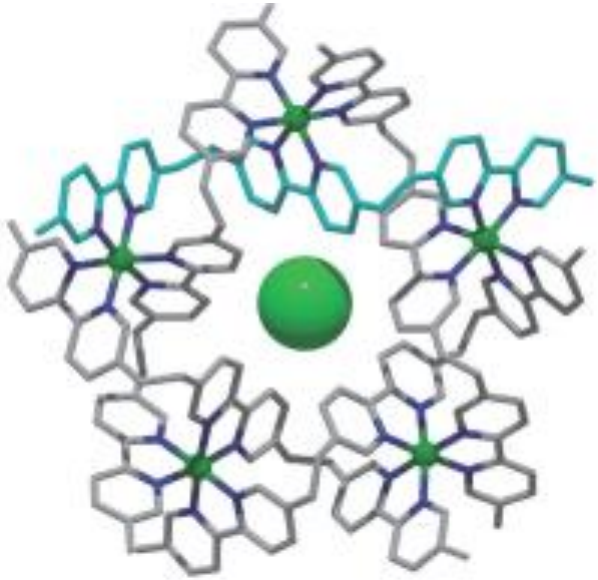


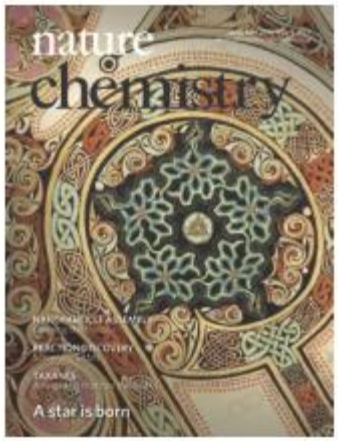
COVER IMAGE

The cover image features the interlaced 'rho' character from Matthew 1:18 in the Lindisfarne Gospels as a backdrop for the X-ray crystal structure of the most complex non-DNA molecular knot synthesized so far. A team led by David Leigh prepared the 160-atom-long pentafoil knot in a one-step reaction from ten organic building blocks and five iron(II) cations. They use a single chloride anion as a template, which, in the solid-state structure, is located at the centre of the pentafoil knot and exhibits ten **CH···Cl**$^-$ hydrogen bonds.

Article p15; News & Views p7







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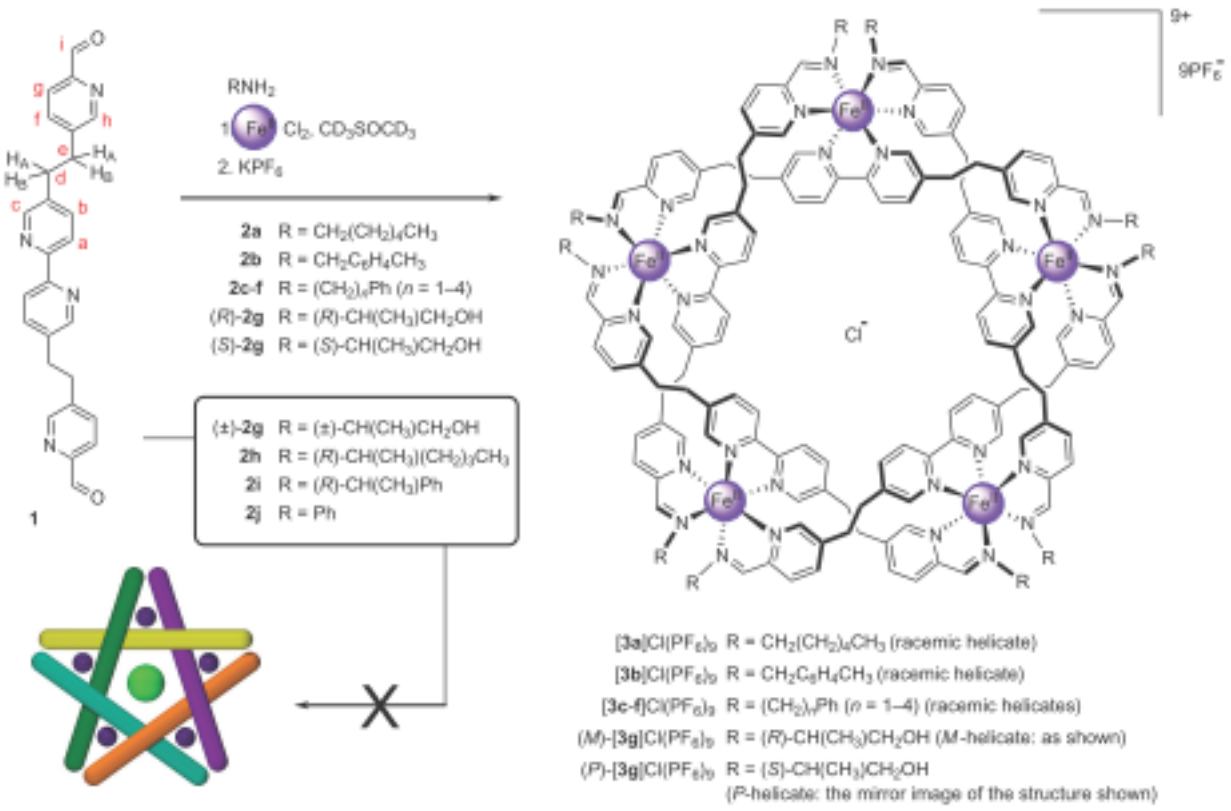
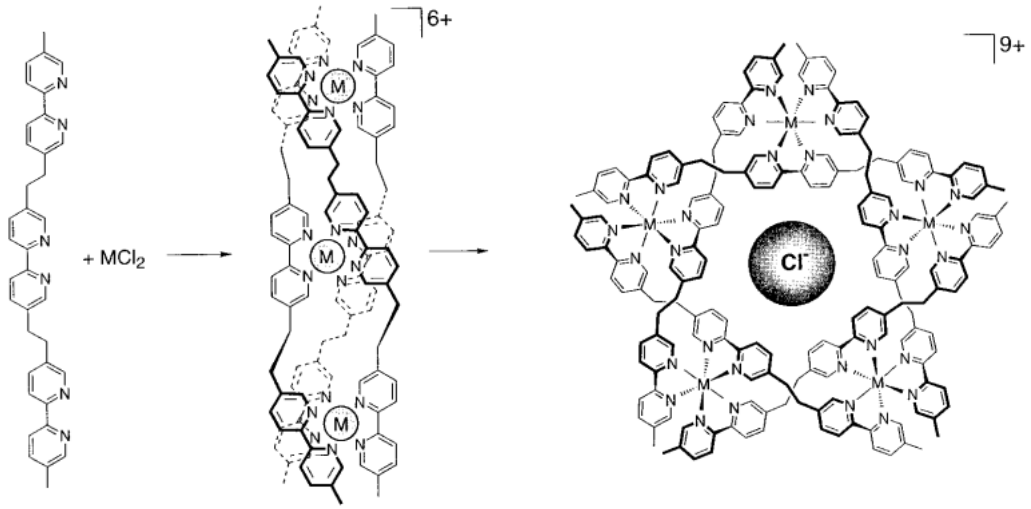
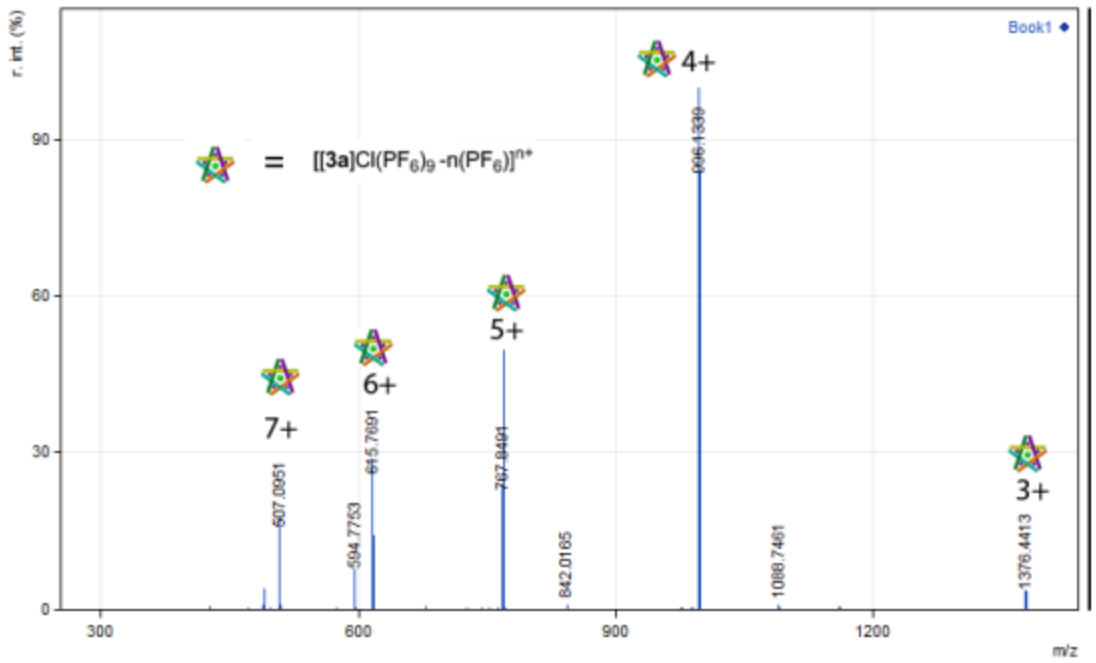
Article p15; News & Views p7

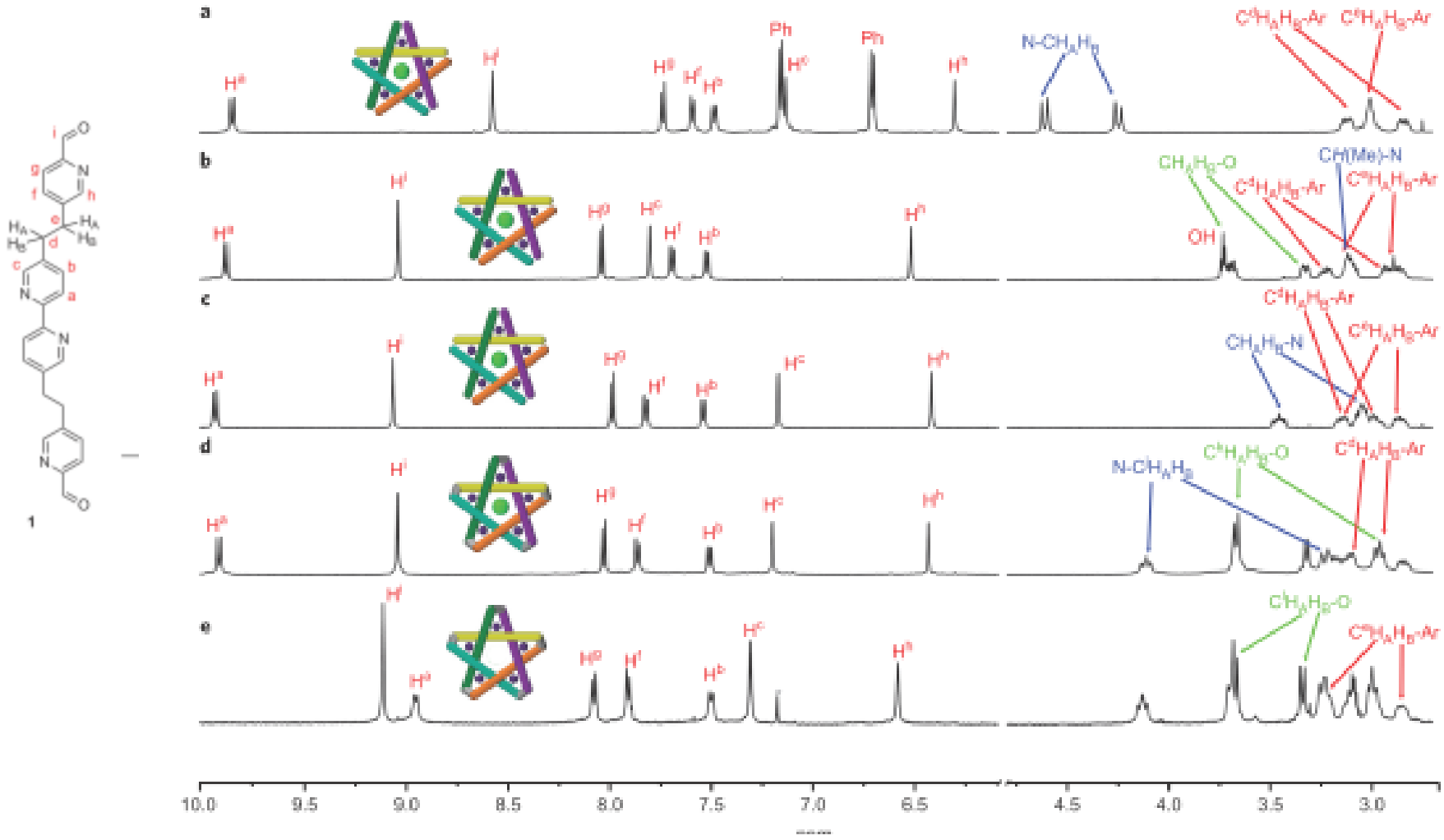




^{1}H-NMR

ESI-MS


Book1
r. int. (%)
90
60
30
0
300
600
900
1200
m/z
= [[3a]Cl(PF6)9 -n(PF6)]n+
4+
5+
6+
7+
3+
996.1339
767.8491
615.7691
607.0951
594.7753
842.0165
1088.7461
1376.4413


a
b
c
d
e
Ph
Ph
N-CHAHB
CAHB-Ar
CAHB-Ar
CH(Me)-N
CHAHB-O
OH
CHAHB-N
CHAHB-O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
4.5
4.0
3.5
3.0

1

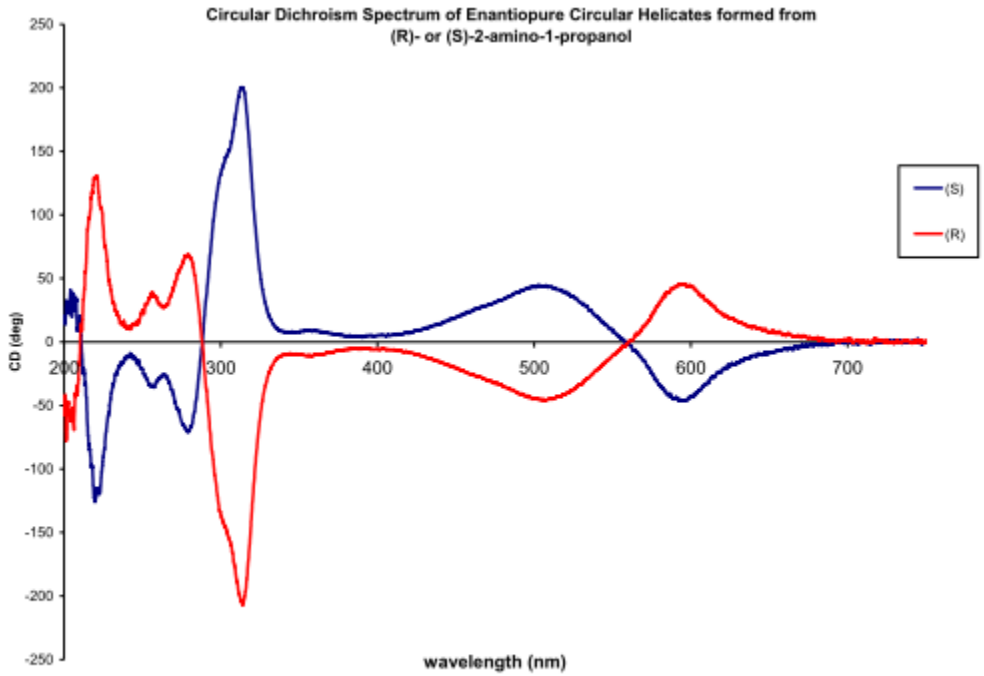
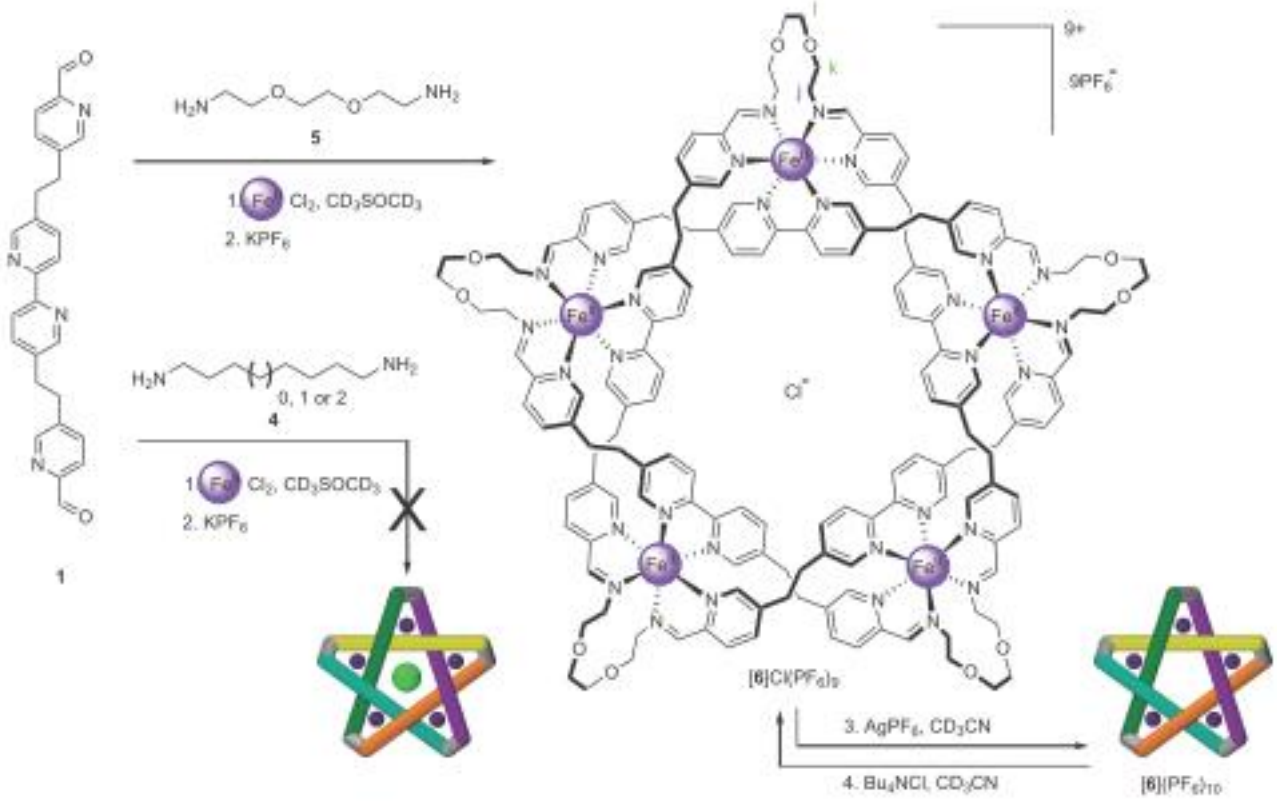


Figure S8 Circular dichroism spectra of (*R*)-[**3g**]Cl$(PF_6)_9$ and (*S*)-[**3g**]Cl$(PF_6)_9$ in MeCN.


1
5
1. Fe2+ Cl2, CD3SOCD3
2. KPF6
4
0, 1 or 2
1. Fe2+ Cl2, CD3SOCD3
2. KPF6
9+
9PF6-
Cl-
[6]Cl(PF6)9
3. AgPF6, CD3CN
4. Bu4NCl, CD3CN
[6](PF6)10

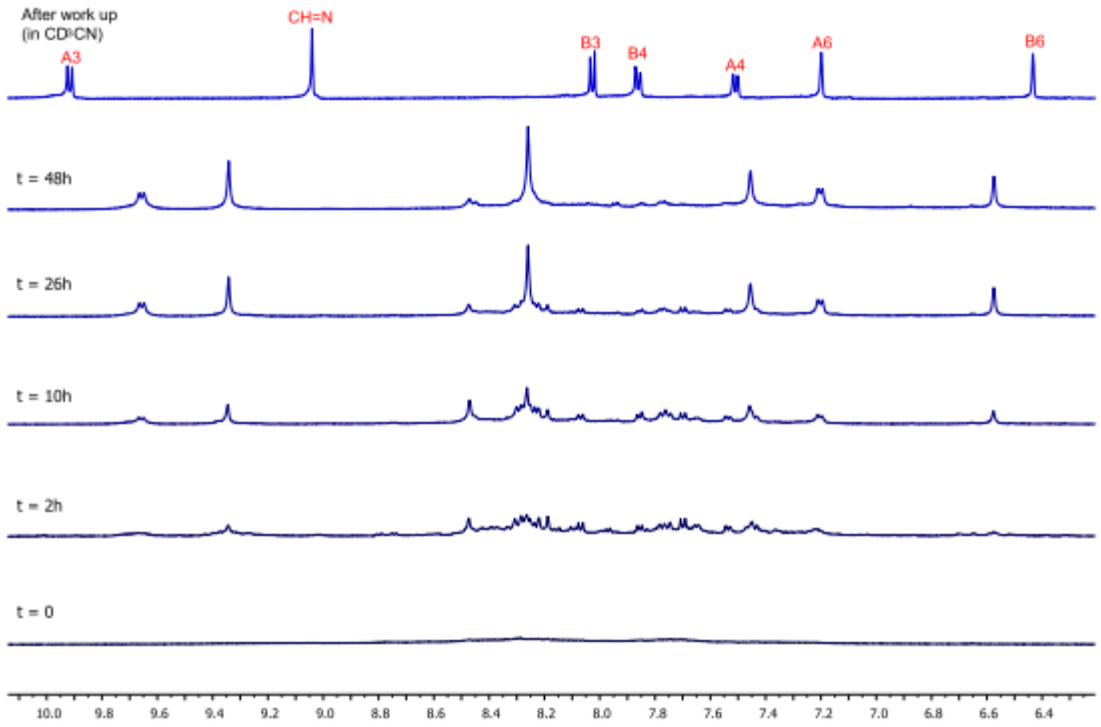
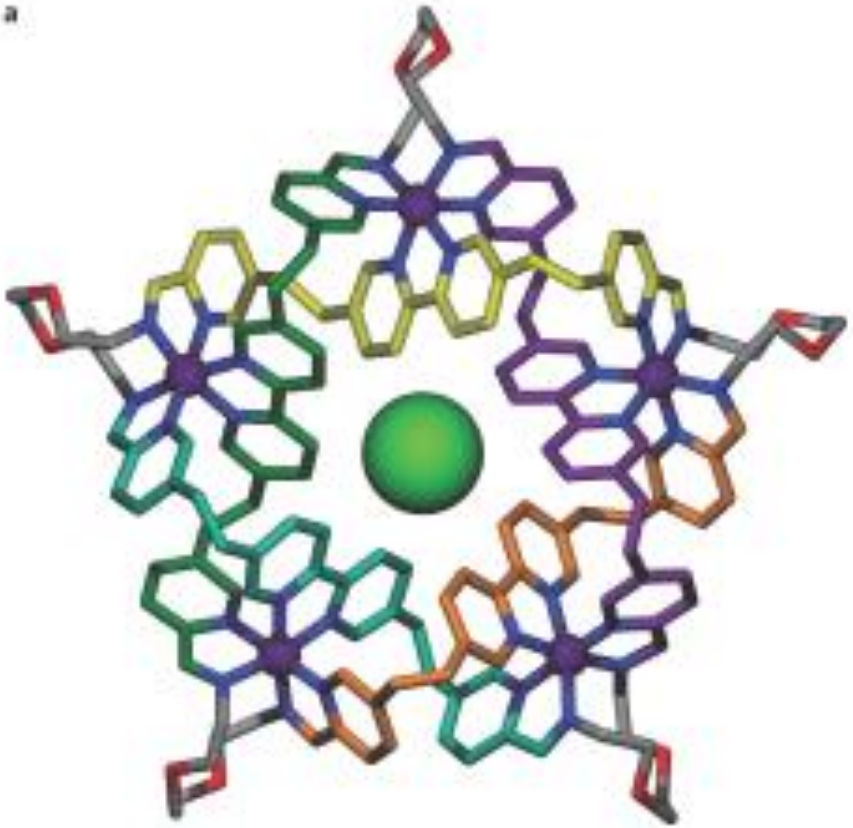
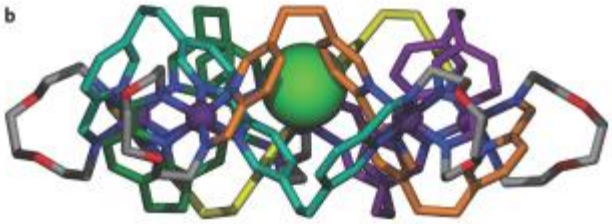


Figure S9 Formation of pentafoil knot $[\mathbf{6}]^{10+}$ monitored by ^{1}H NMR (DMSO-d_6, 500 MHz), aromatic region of spectrum shown. Spectra were collected of the crude reaction mixture after t = 0 (bottom), 2h, 10h, 26h and 48h. The top spectra is of the same sample after work-up (^{1}H NMR in CD_3CN) with ^{1}H NMR assignments indicated.

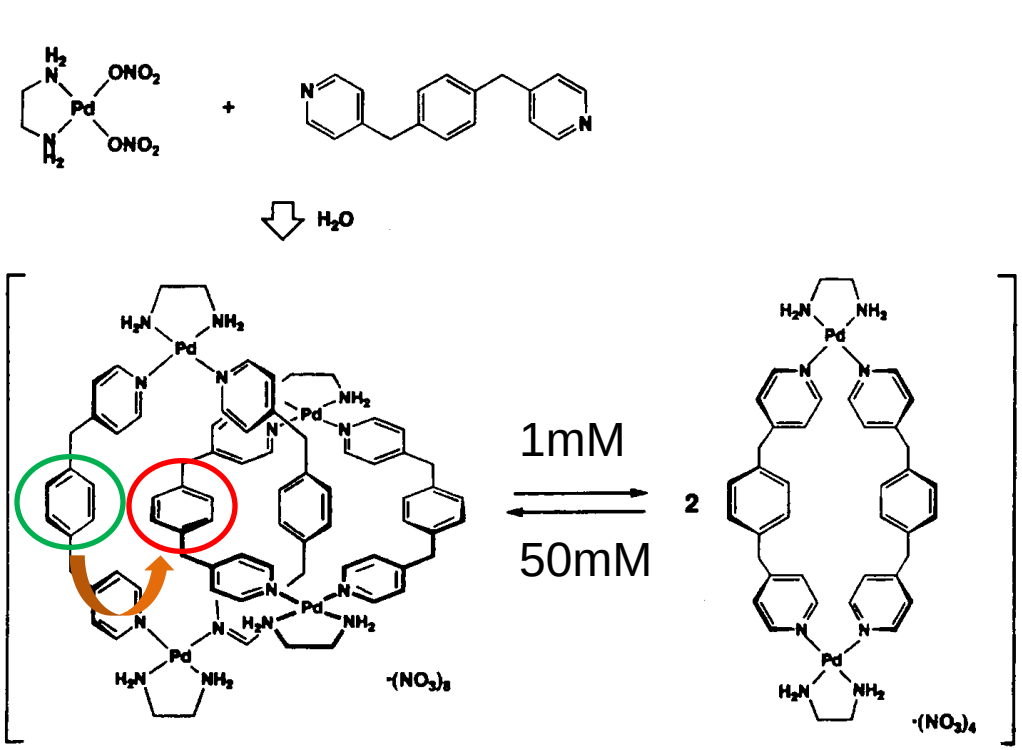
a

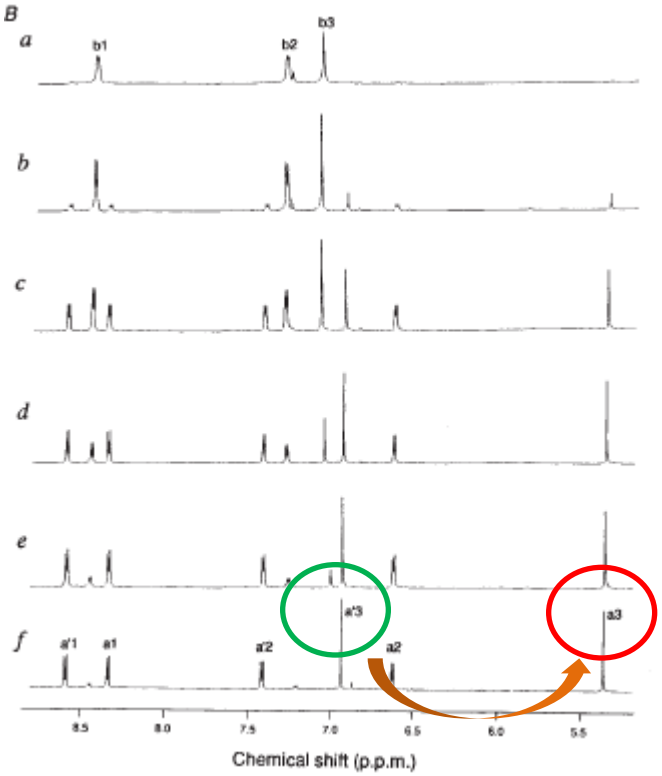


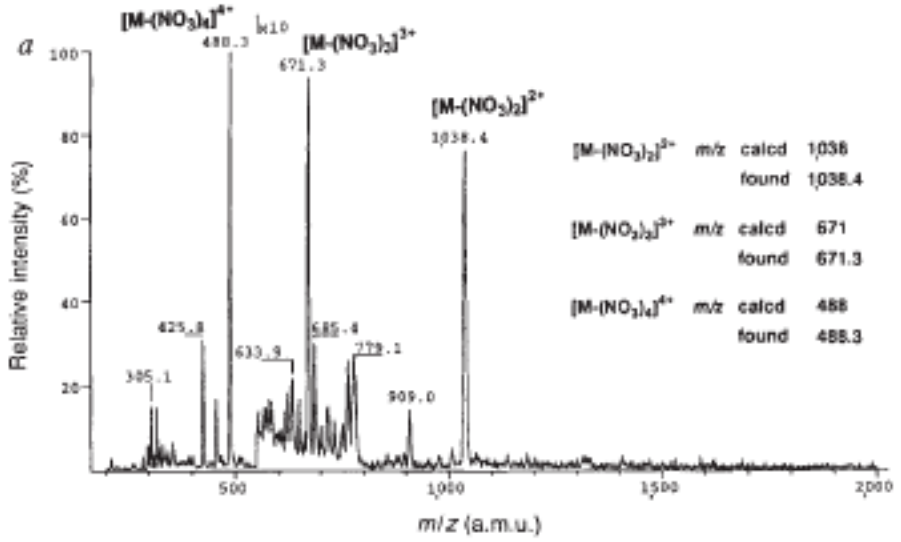
b

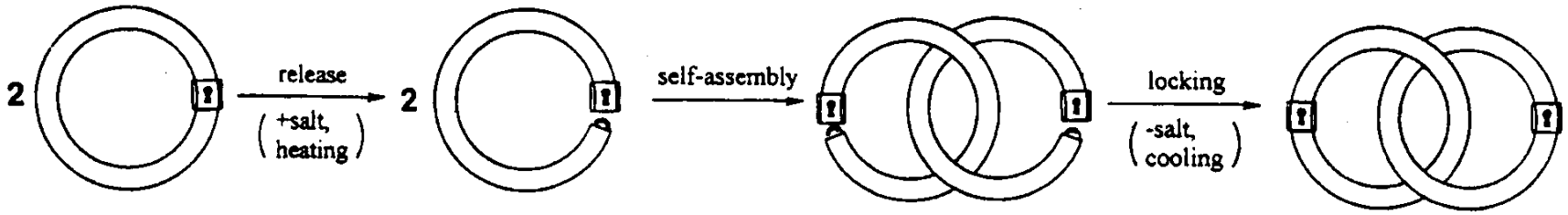


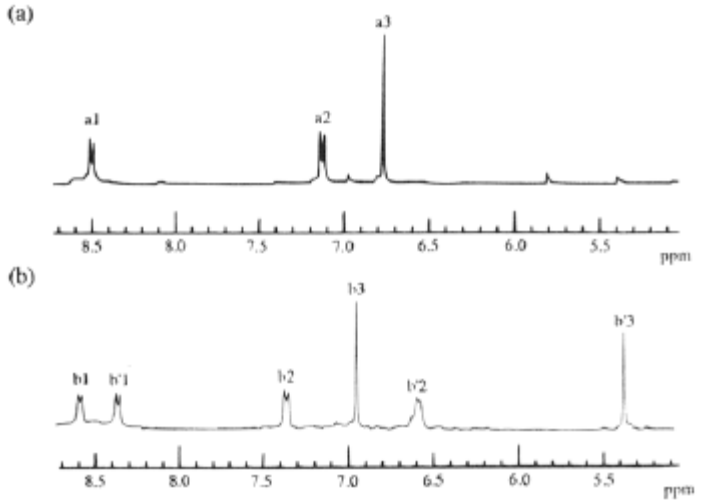
Catenani

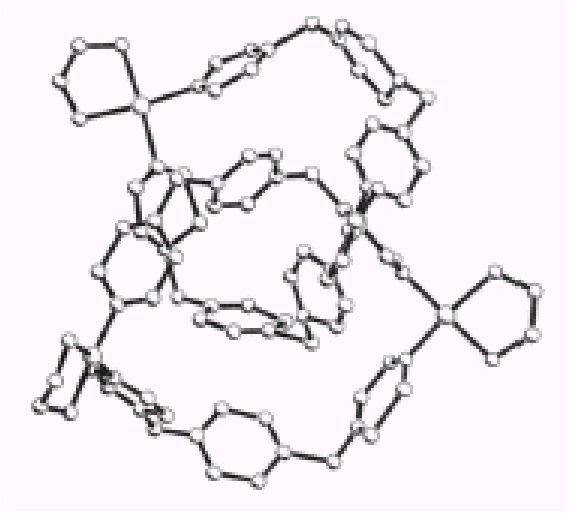

H2
N
Pd
ONO2
ONO2
N
H2
+
N
N
H2O
H2N
NH2
Pd
N
N
Pd
NH2
N
N
Pd
NH2
H2N
N
N
Pd
NH2
H2N
NH2
·(NO3)8
1mM
50mM
2
H2N
NH2
Pd
N
N
Pd
H2N
NH2
·(NO3)4


B
a
b1
b2
b3
b
c
d
e
f
a'3
a3
a'1
a1
a'2
a2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
Chemical shift (p.p.m.)

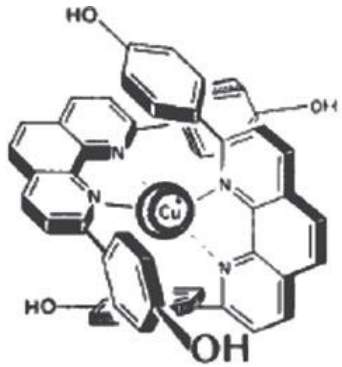

a
[M-(NO3)4]4+
488.3
x10
[M-(NO3)3]3+
671.3
[M-(NO3)2]2+
1038.4
425.8
633.9
585.4
729.1
385.1
909.0
Relative intensity (%)
100
80
60
40
20
500
1000
1500
2000
m/z (a.m.u.)
[M-(NO3)2]2+ m/z calcd 1,038
found 1,038.4
[M-(NO3)3]3+ m/z calcd 671
found 671.3
[M-(NO3)4]4+ m/z calcd 488
found 488.3


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

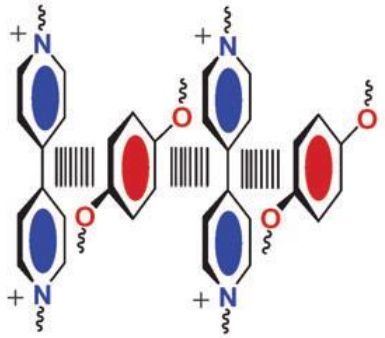

(a)
a1
a2
a3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
ppm
(b)
b1
b'1
b2
b3
b'2
b'3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
ppm



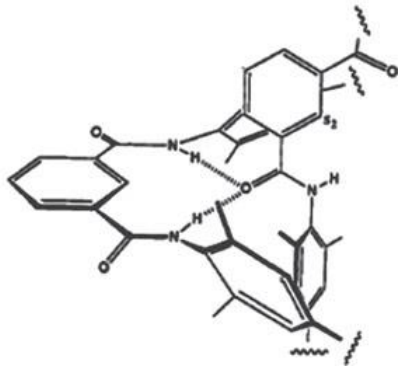
1

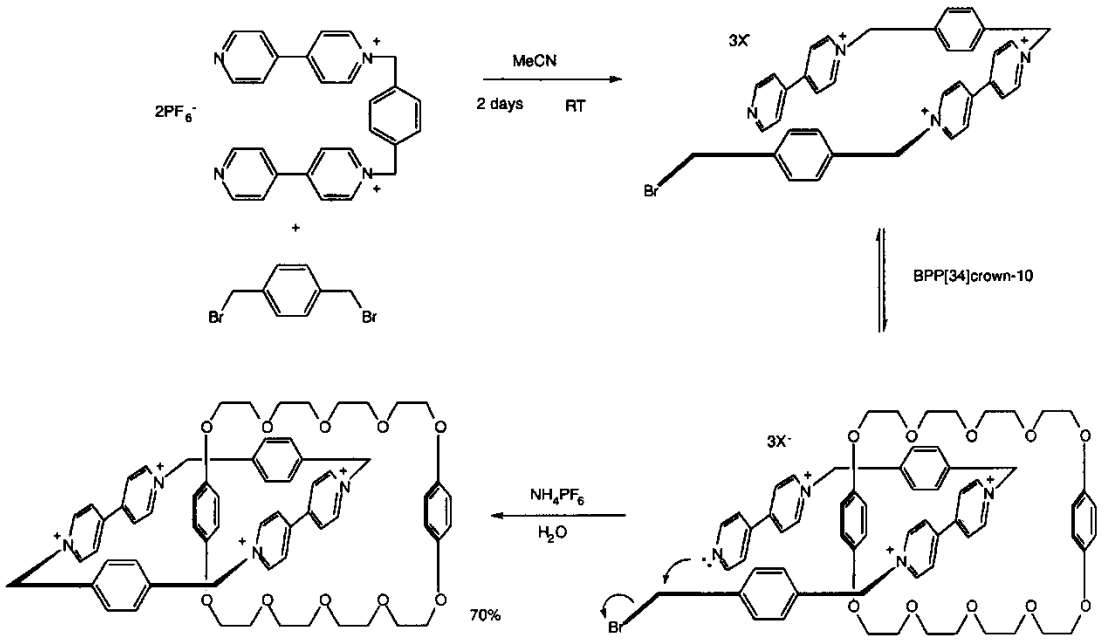


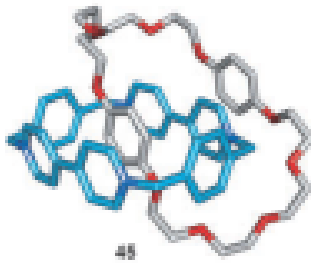
2



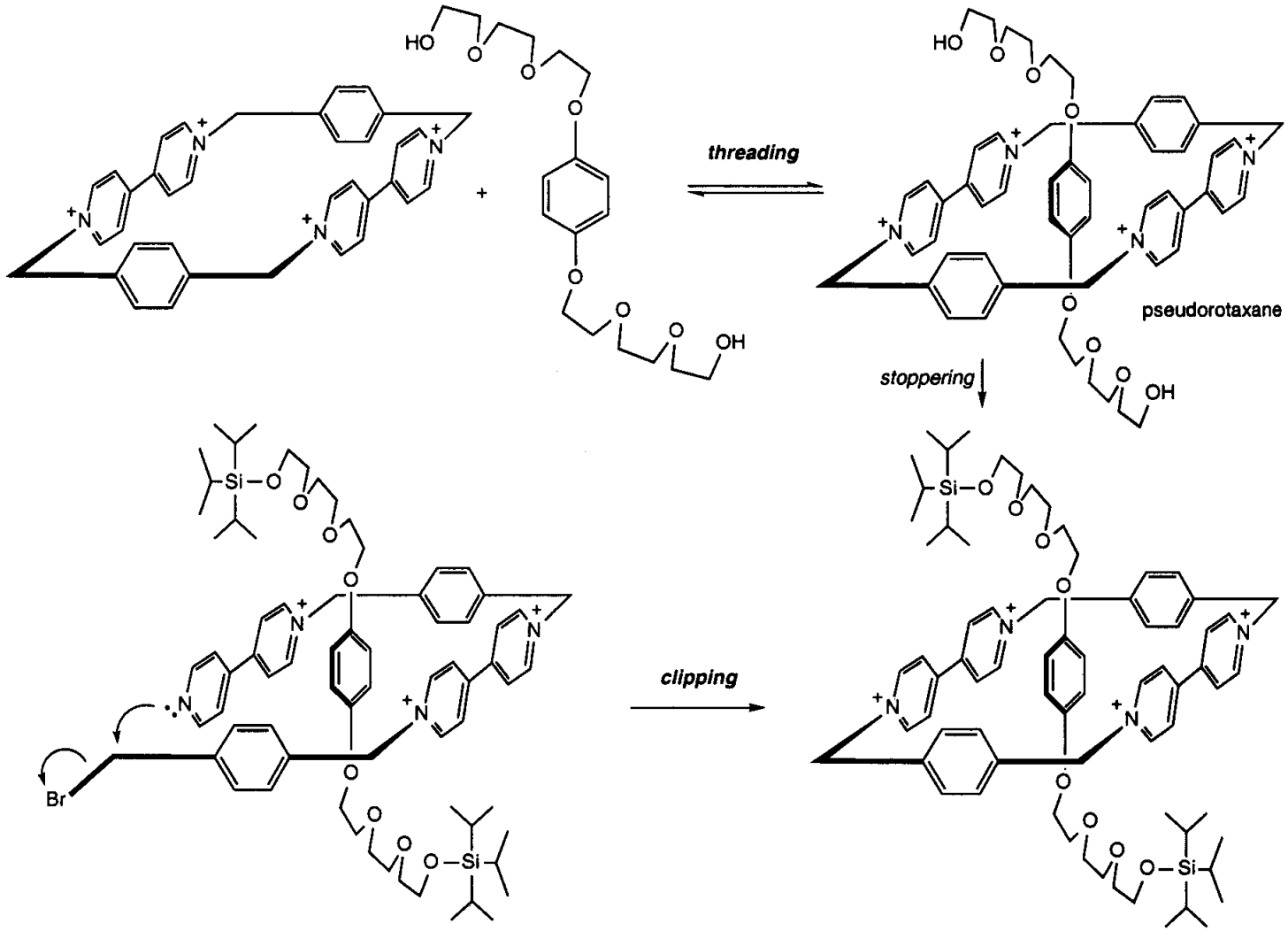
3



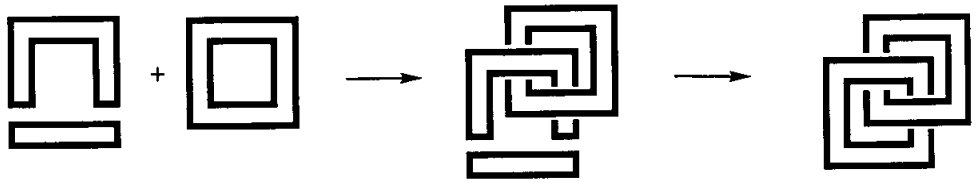




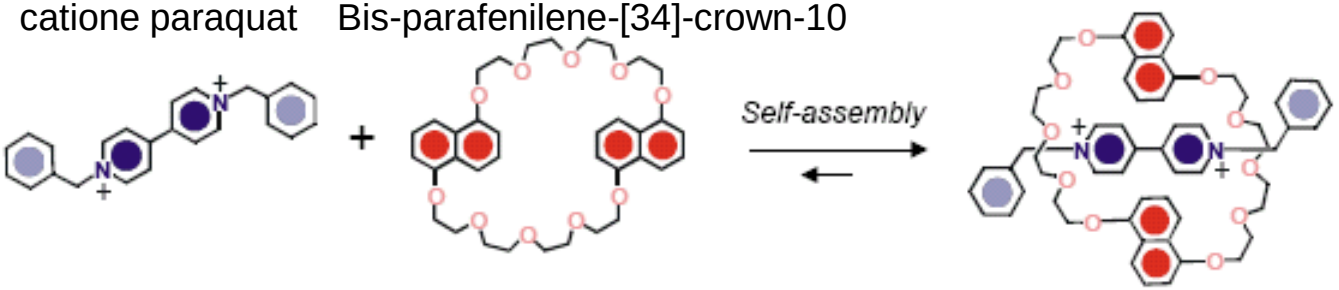
45

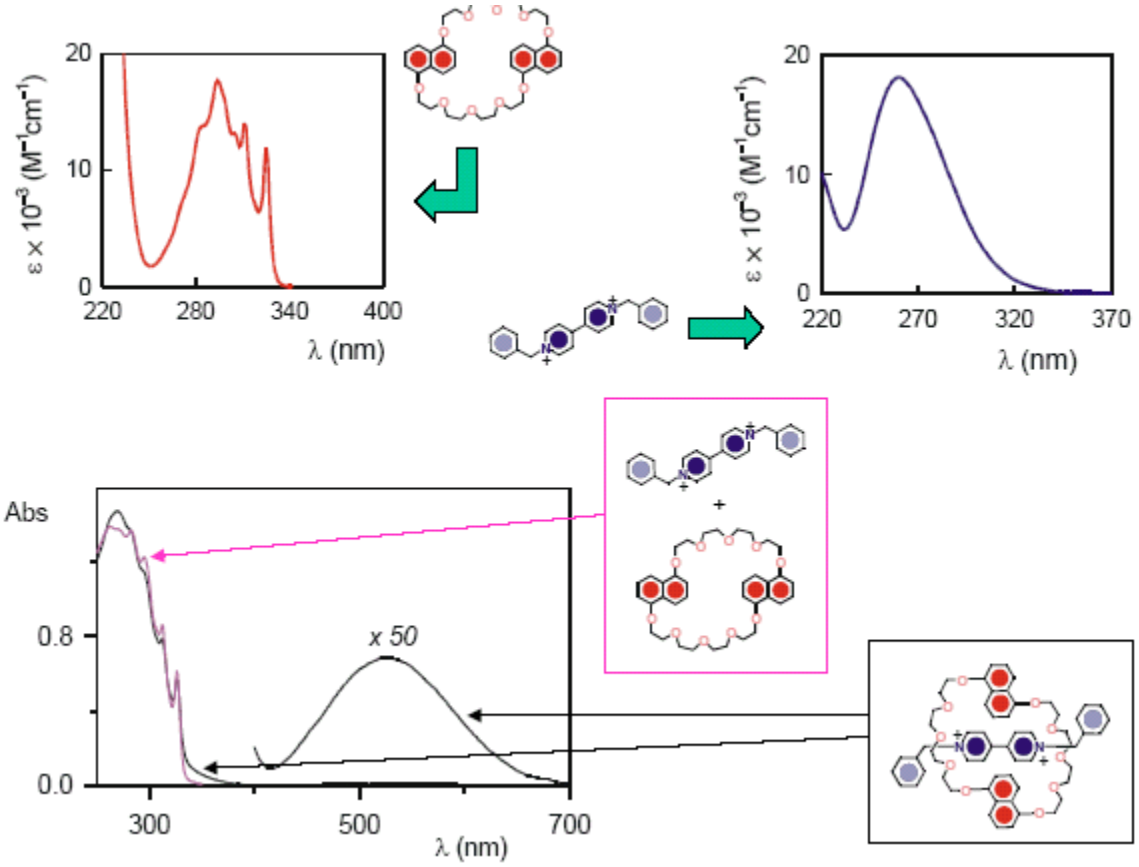


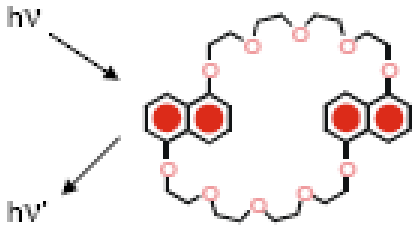
Synthesis of a rotaxane by two different routes: threading and clipping.

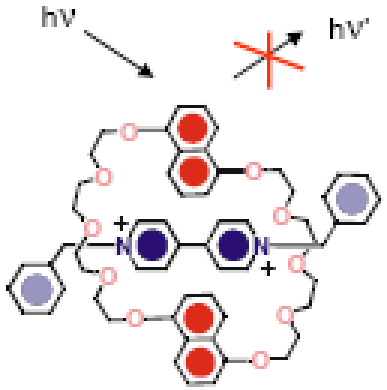


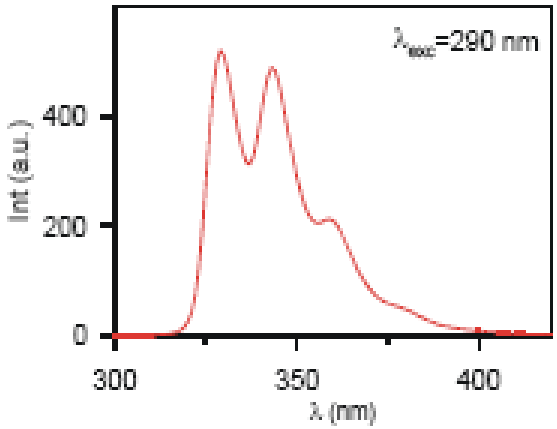
catione paraquat Bis-parafenilene-[34]-crown-10

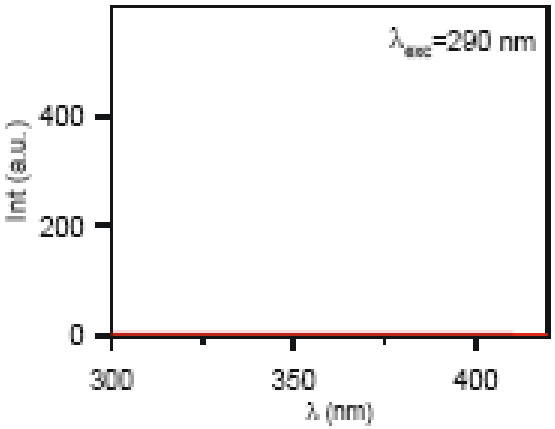


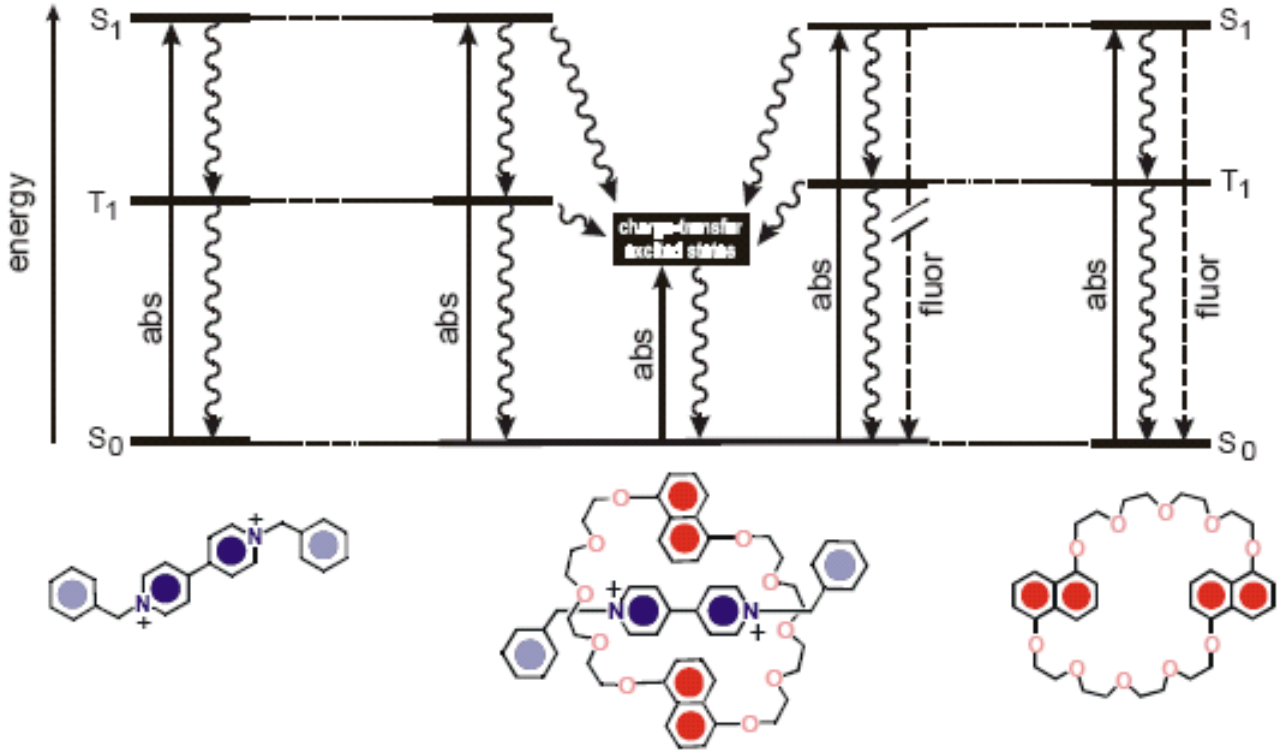

20
10
0
ε x 10^-3 (M^-1cm^-1)
220
280
340
400
λ (nm)
20
10
0
ε x 10^-3 (M^-1cm^-1)
220
270
320
370
λ (nm)
Abs
0.8
0.0
x 50
300
500
700
λ (nm)

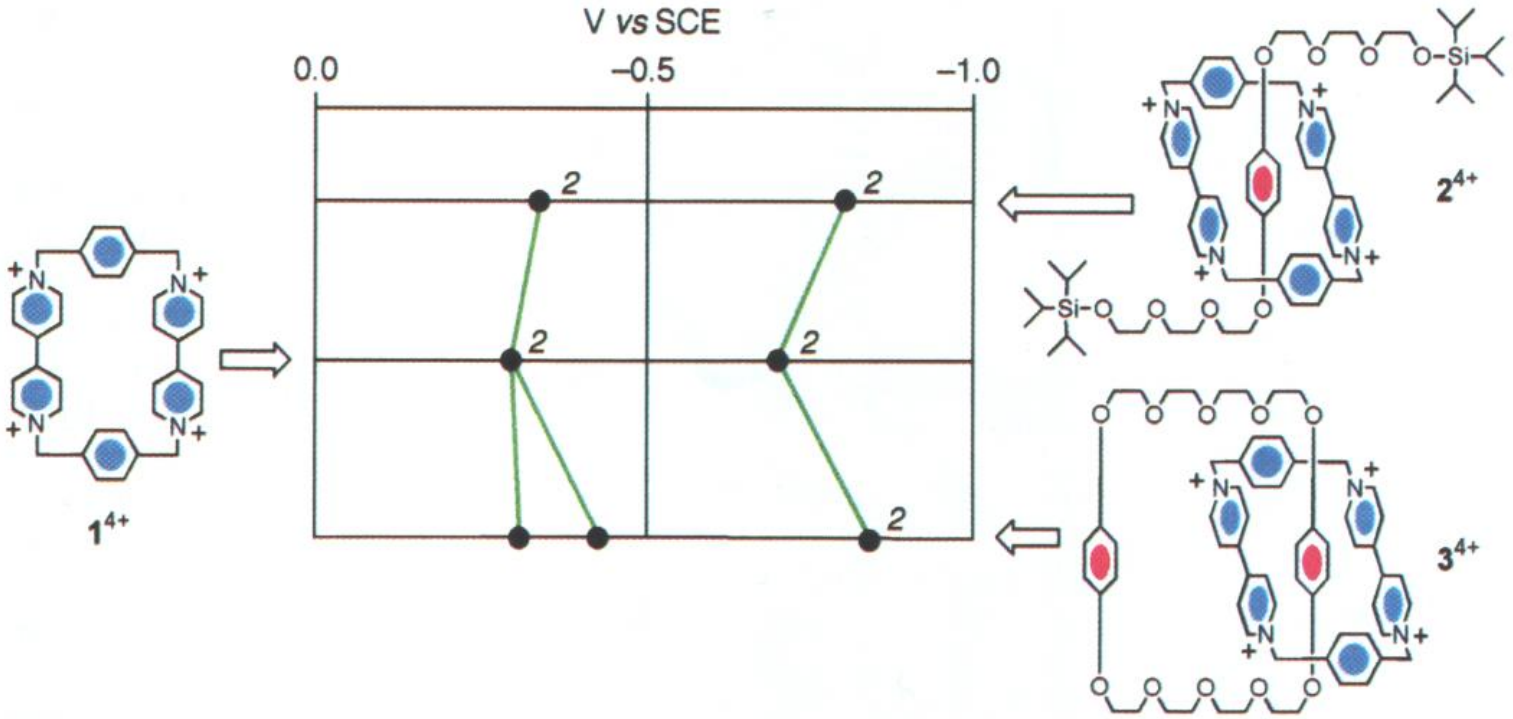

hν
hν'

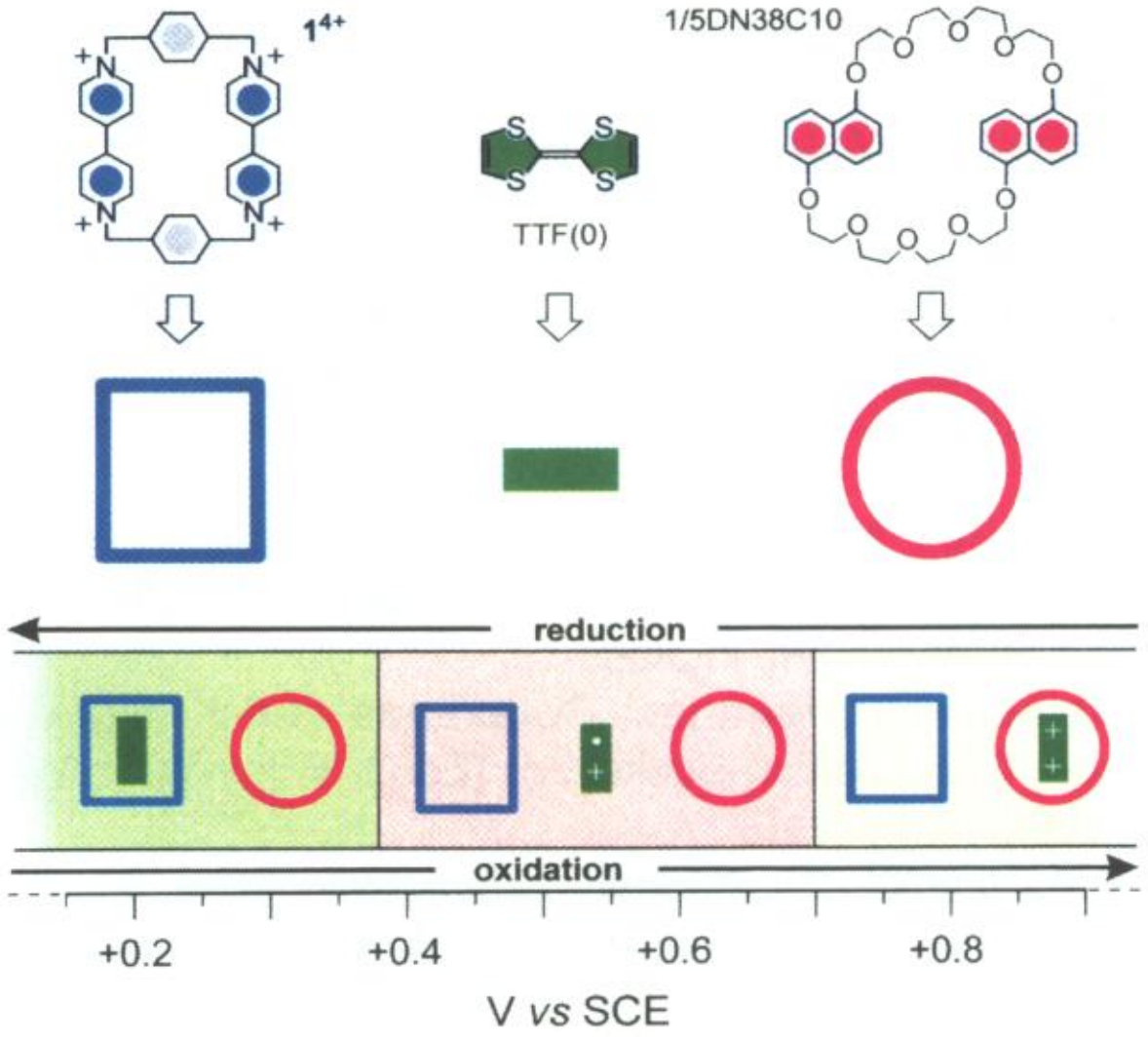

hν
hν'
N
N
+
+

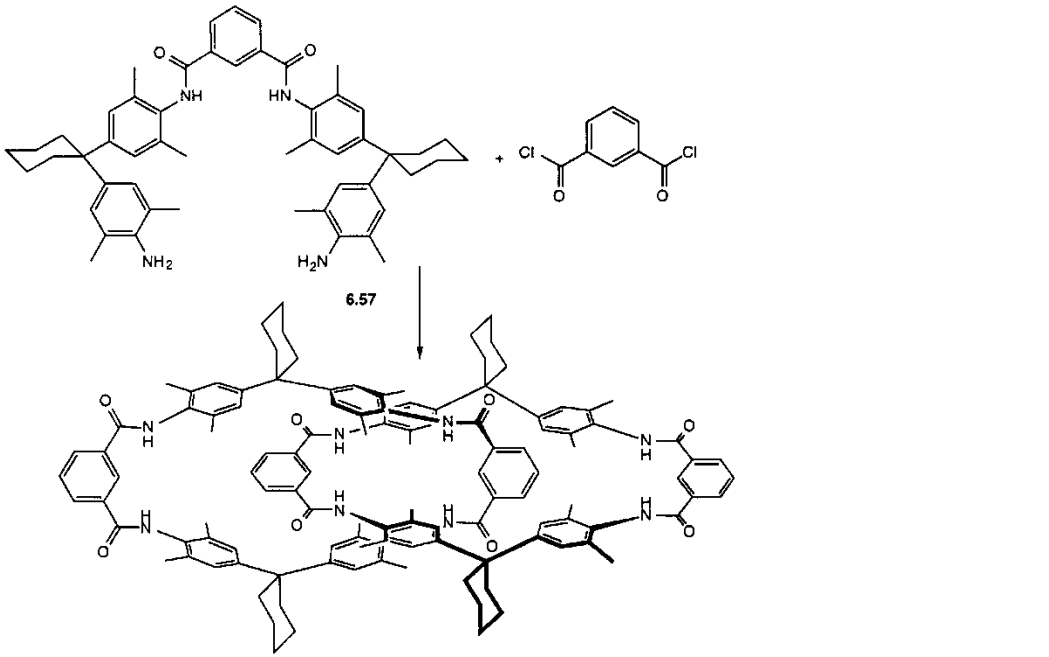

λexc=290 nm
Int (a.u.)
400
200
0
300
350
400
λ (nm)

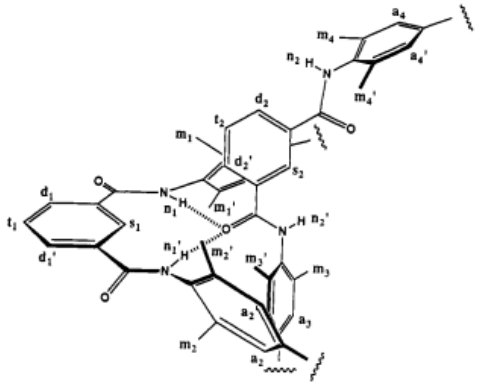

λexc=290 nm
Int (a.u.)
400
200
0
300
350
400
λ (nm)

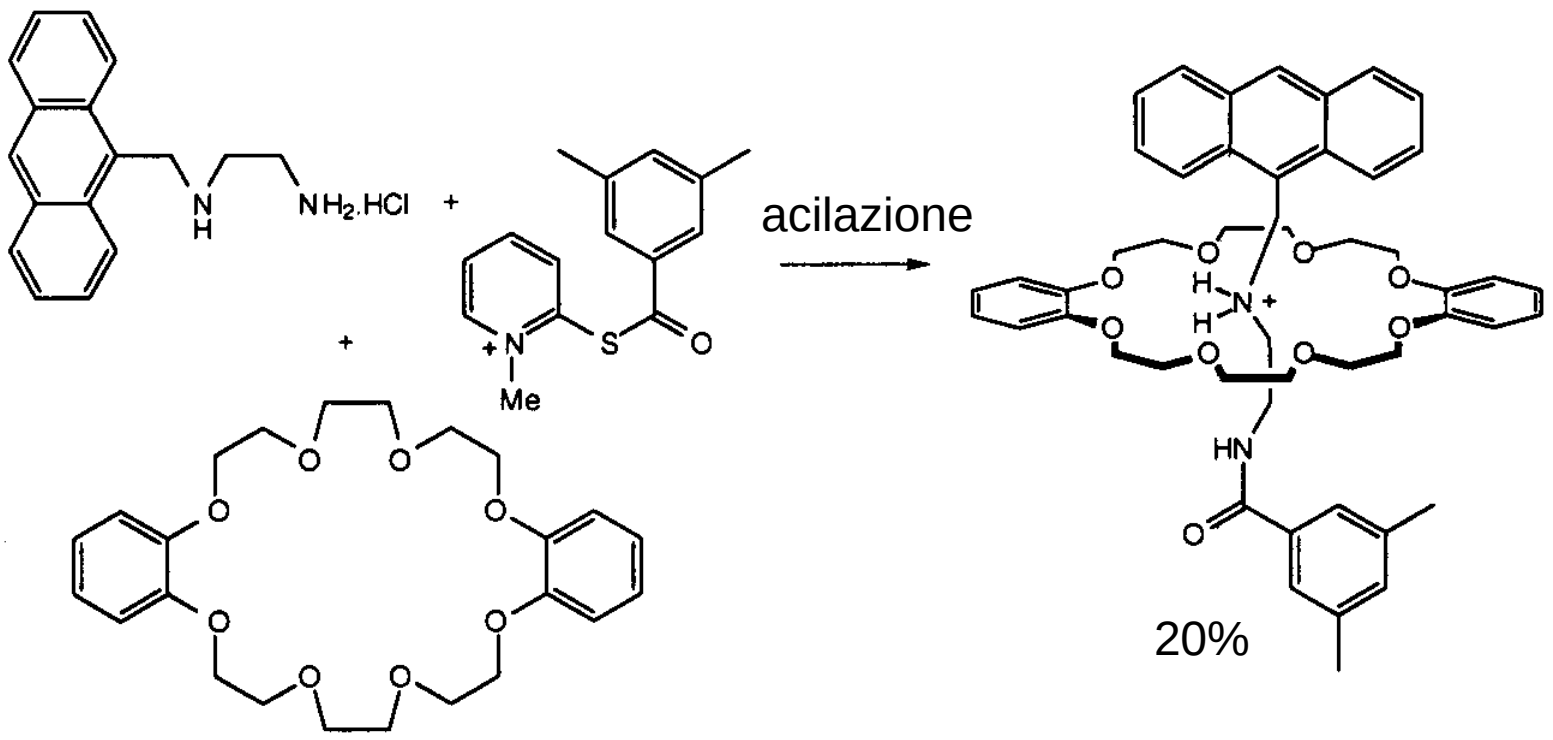

energy
S1
T1
S0
abs
abs
abs
charge-transfer excited states
abs
fluor
abs
fluor
S1
T1
S0

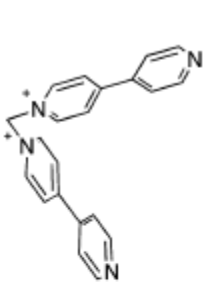

V vs SCE
0.0
–0.5
–1.0
2
2
2
2
2
1^{4+}
2^{4+}
3^{4+}


1^4+
1/5DN38C10
TTF(0)
reduction
oxidation
+0.2
+0.4
+0.6
+0.8
V vs SCE

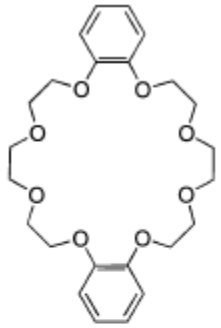

6.57



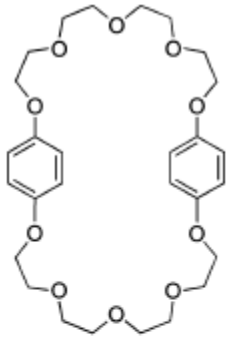

NH2.HCl
+
+
N
Me
S
O
acilazione
H
N
HN
20%



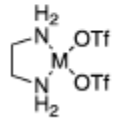
1·2PF_6



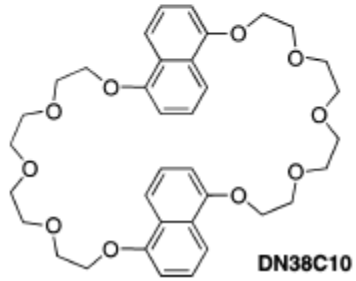
DB24C8



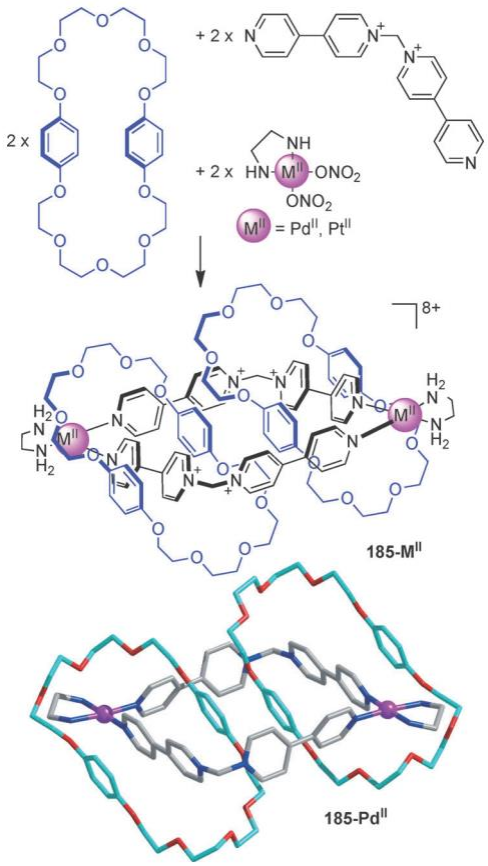
BPP34C10



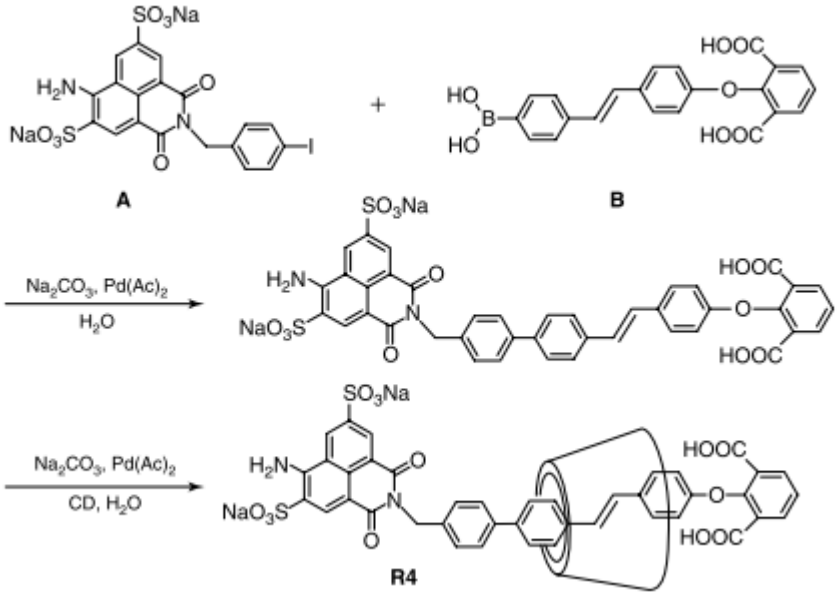
2a M = Pd
2b M = Pt



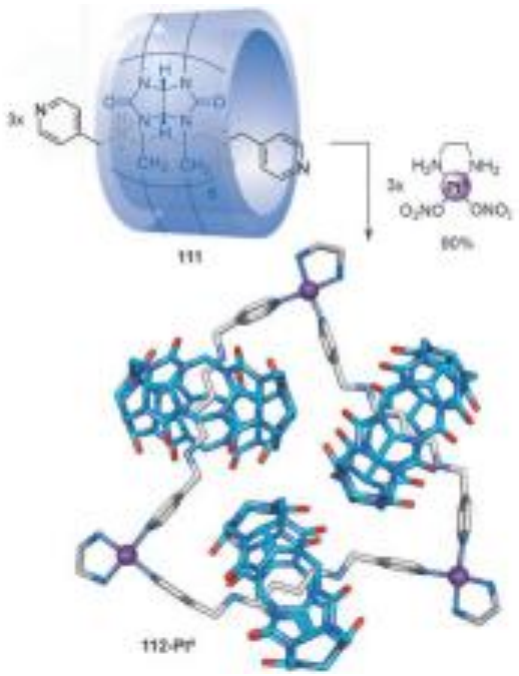
DN38C10


2 x
+ 2 x
+ 2 x
NH
HN
M^II
ONO2
ONO2
M^II = Pd^II, Pt^II
8+
185-M^II
185-Pd^II

Hydrophobic effect



Hydrophobic effect



Halogen bond templating