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*]

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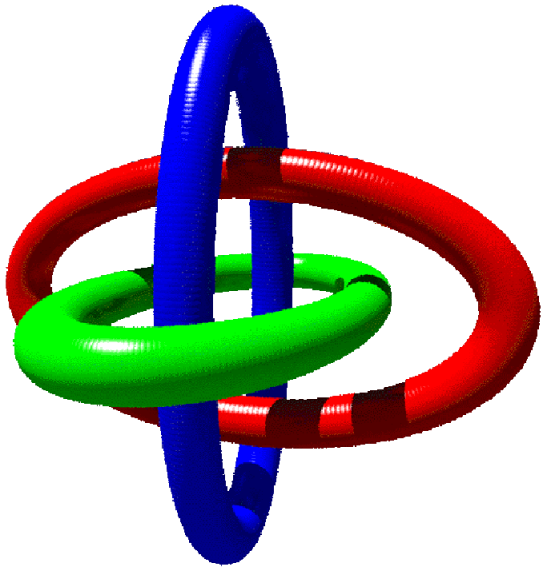
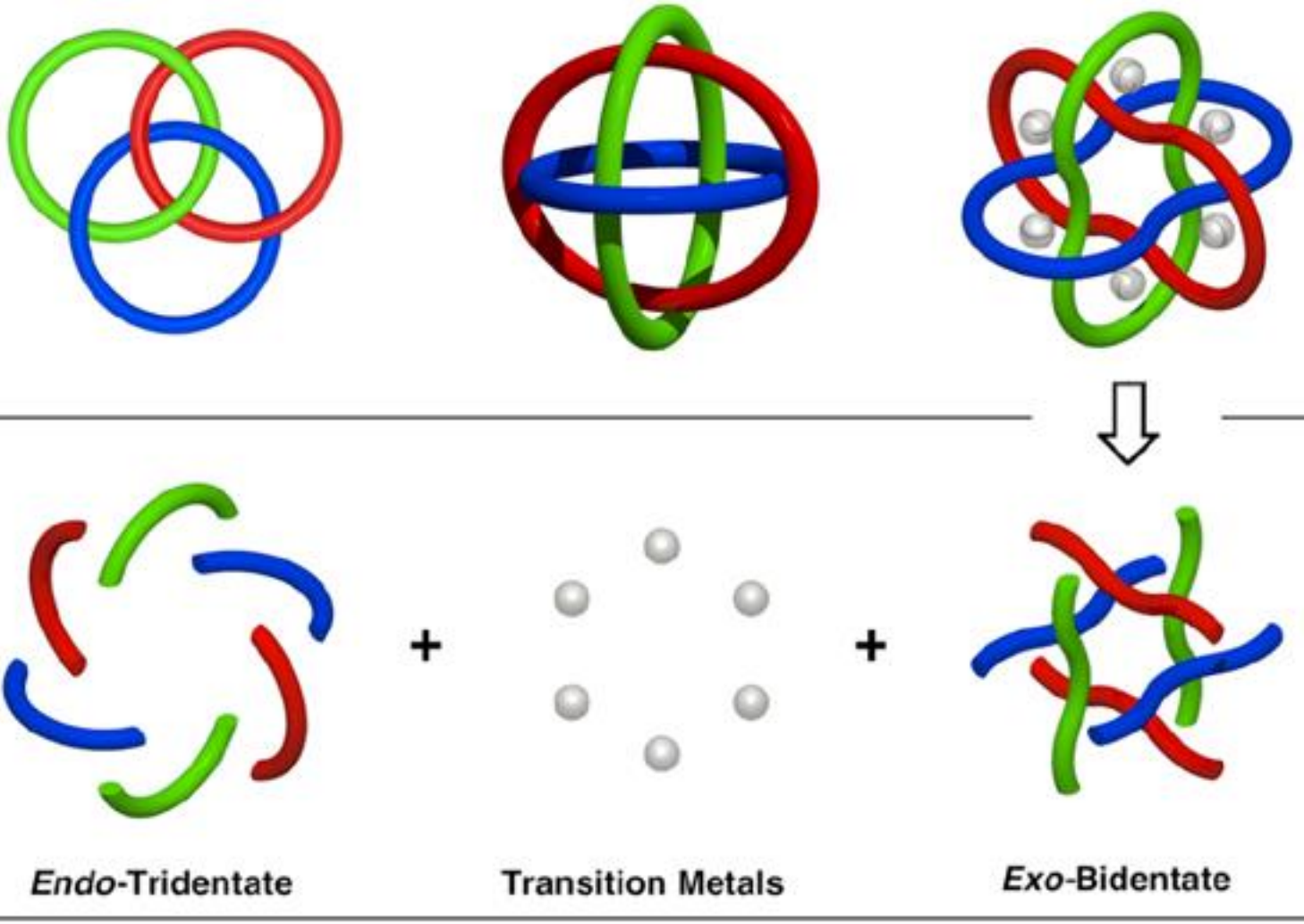
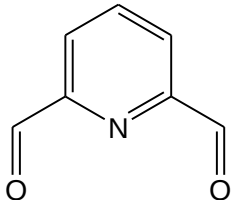
Borromean Rings



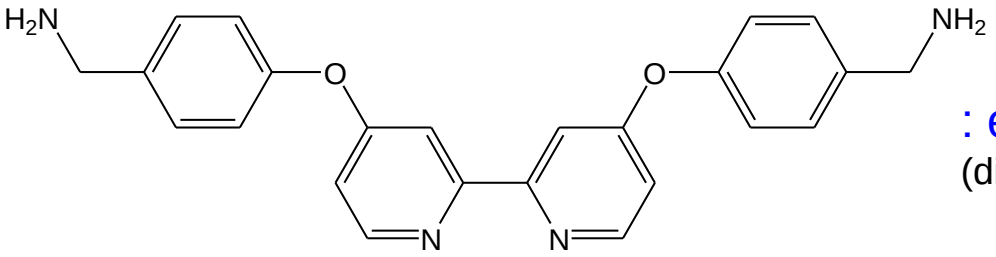
three identical rings. Each ring is inside a second one and outside the third one. No catenation.
4 connections: *endo/eso/endo/eso*

Nodo Borromeo

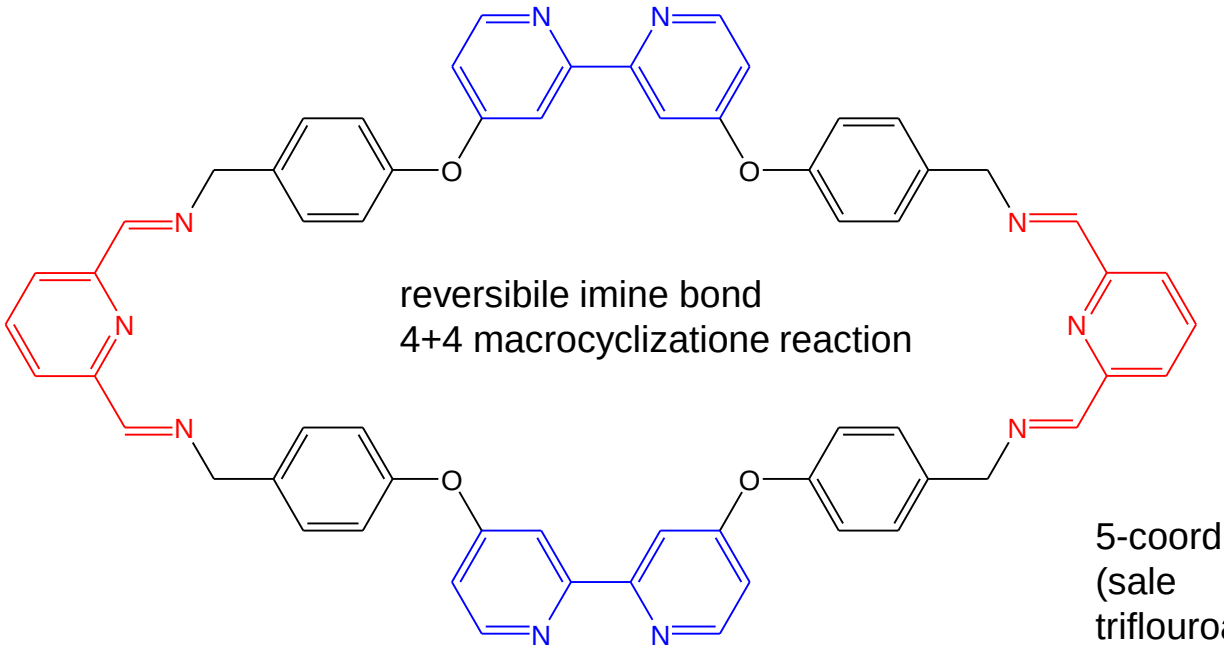




: endo-tridentate (2,6 diformilpyiridine DFP)



: exo-bidentate
(diamminobipyridiyl ligand DAB)



reversibile imine bond
4+4 macrocyclizatione reaction

5-coordinated Zn(II)
(sale
triflouroacetatato)

:

After 2 days 90°C, MeOH
NMR, mass spectrometry (ESI)

Carica: 12^+
Controioni: $12TFA^-$

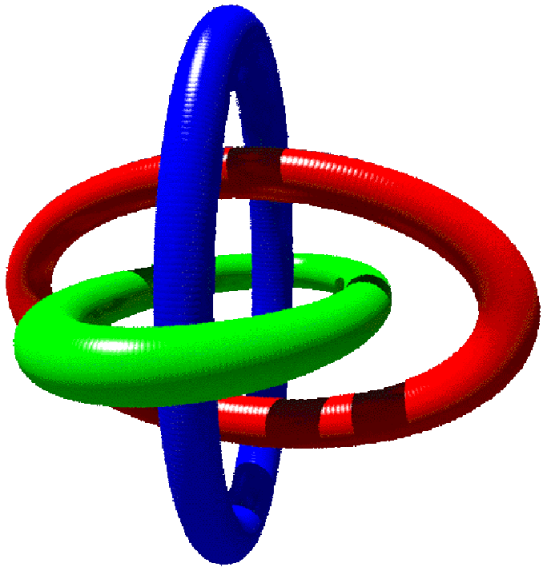
endo-tridentate
2,6 diformilpyiridine (DFP)

exo-bidentate
diamminobipyridiyl ligand (DAB)

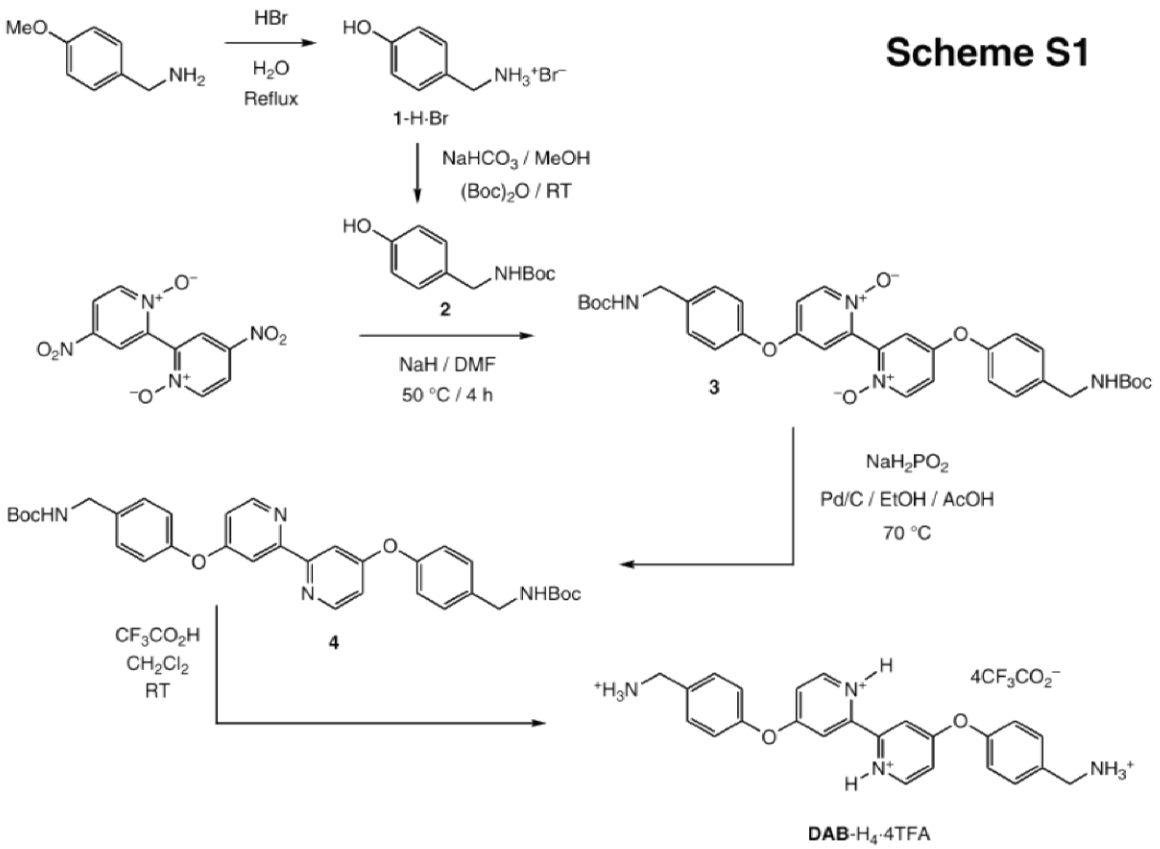
5-coordinated Zn(II)
(sale triflouroacetatato)

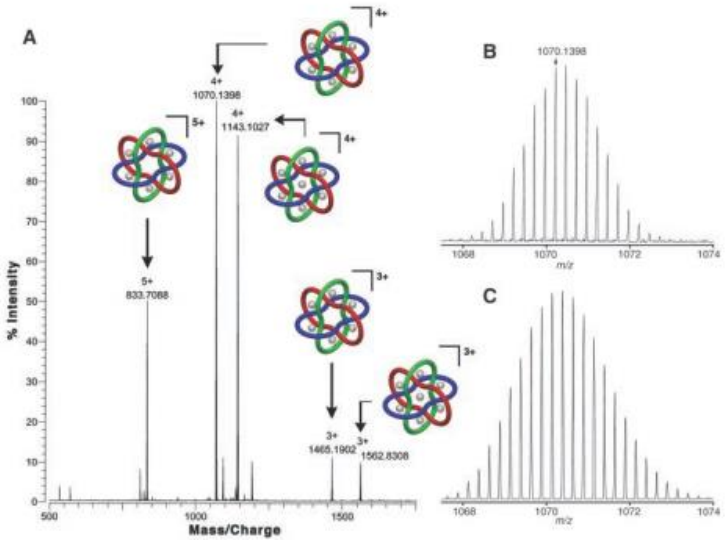
reversibile imine formation

reversible coordination



Scheme S1


MeO
NH2
HBr
H2O
Reflux
HO
NH3+Br−
1-H·Br
NaHCO3 / MeOH
(Boc)2O / RT
HO
NHBoc
2
O2N
NO2
NaH / DMF
50 °C / 4 h
BocHN
NHBoc
3
NaH2PO2
Pd/C / EtOH / AcOH
70 °C
BocHN
NHBoc
4
CF3CO2H
CH2Cl2
RT
+H3N
4CF3CO2−
NH3+
DAB-H4·4TFA



$[M\text{-}3TFA]^{3+}$
$[M\text{-}4TFA]^{4+}$
$[M\text{-}5TFA]^{5+}$

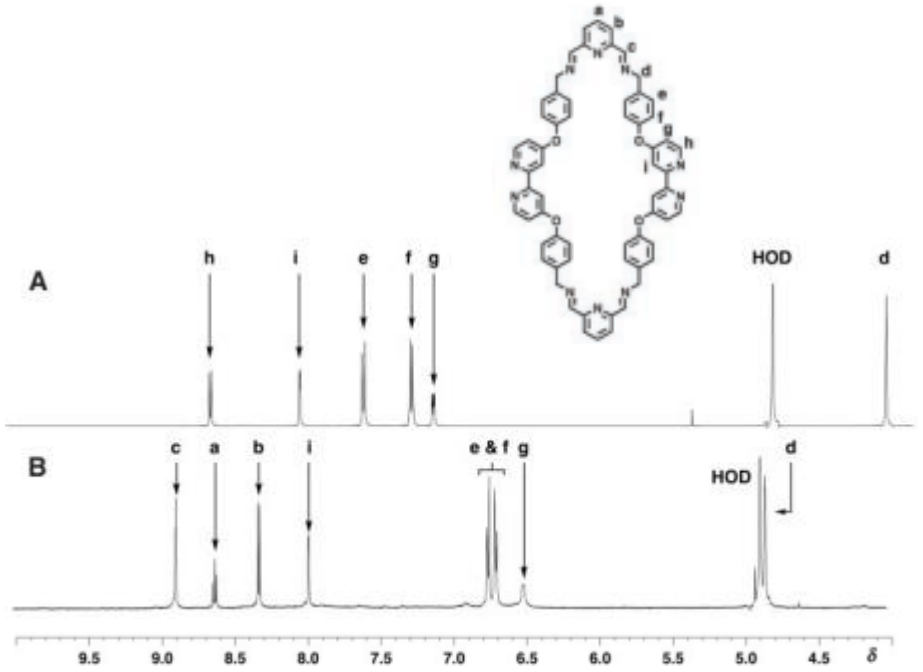
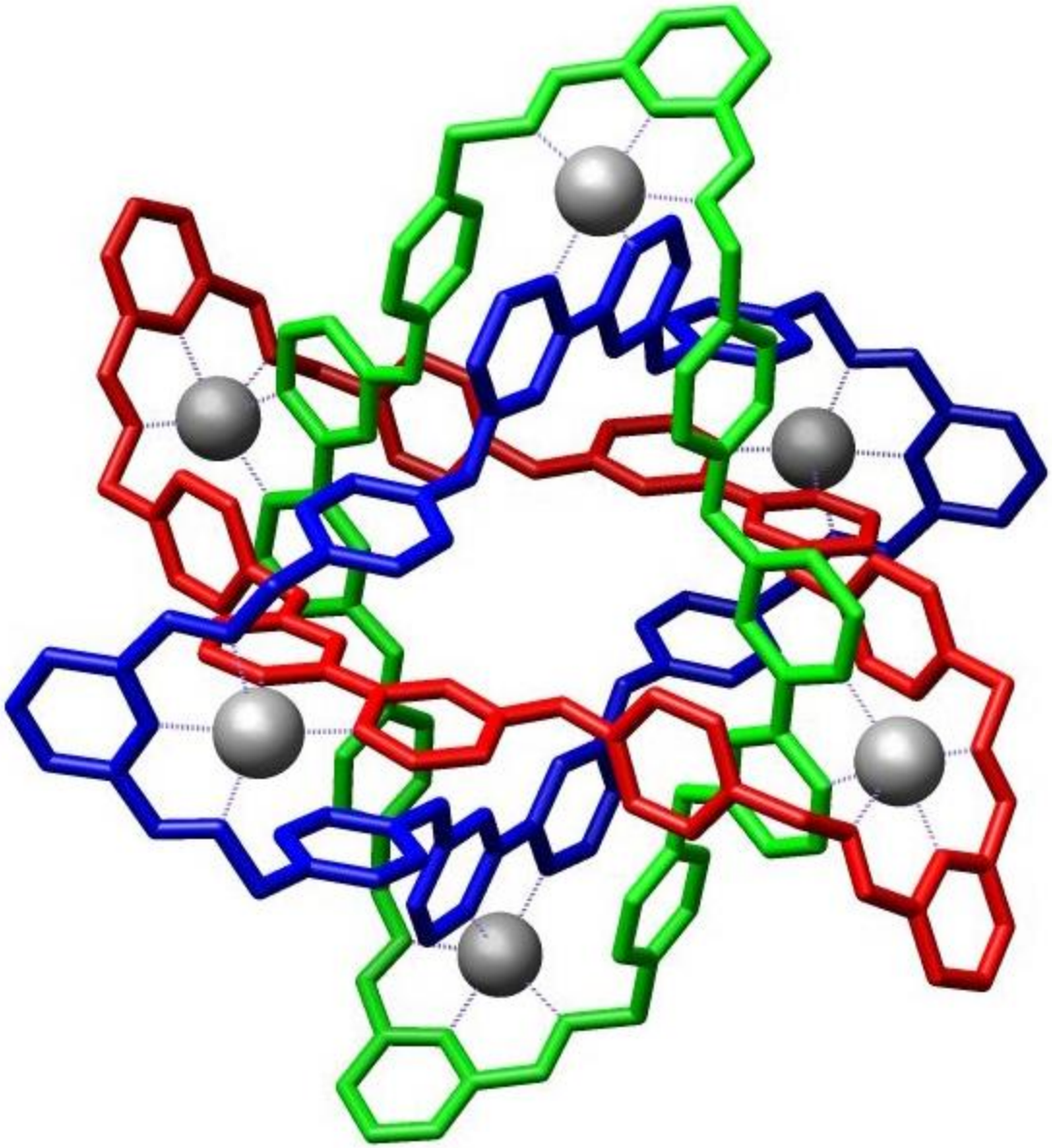
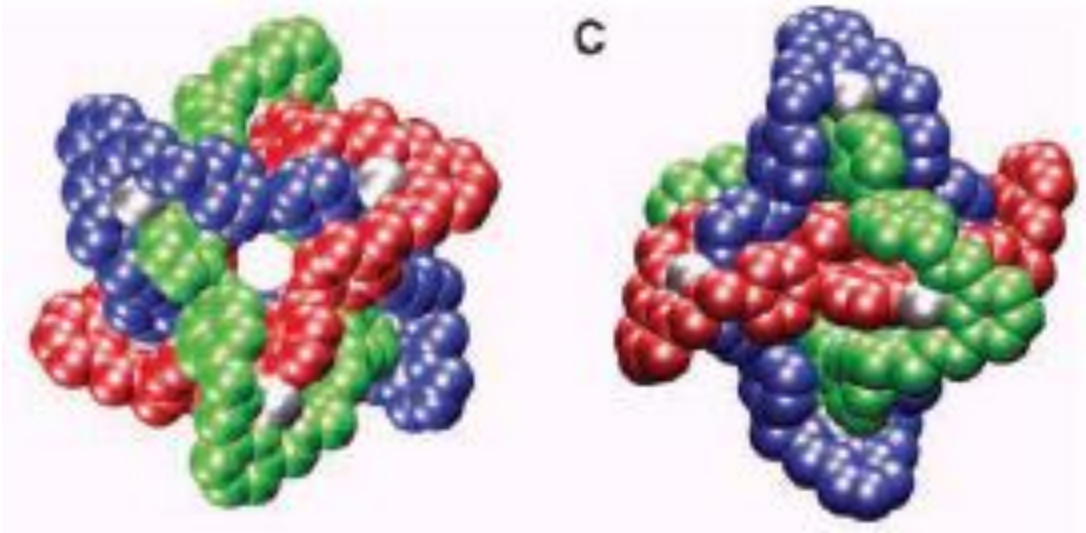
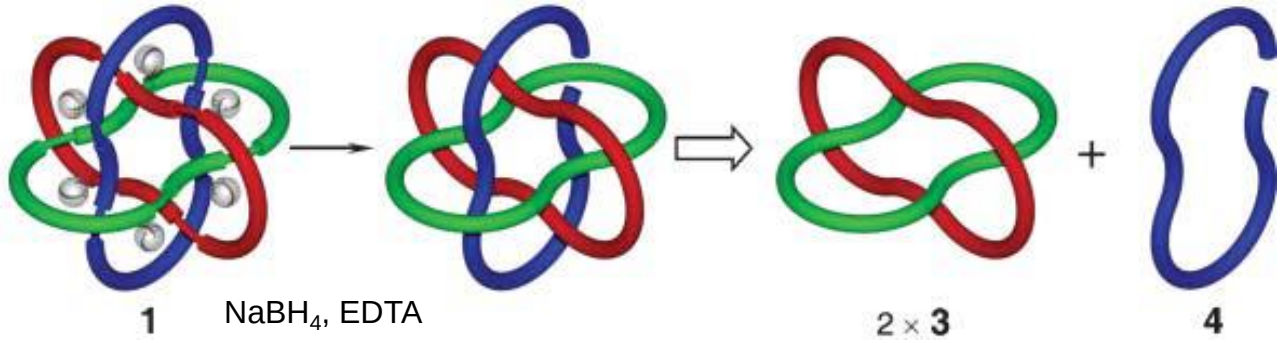


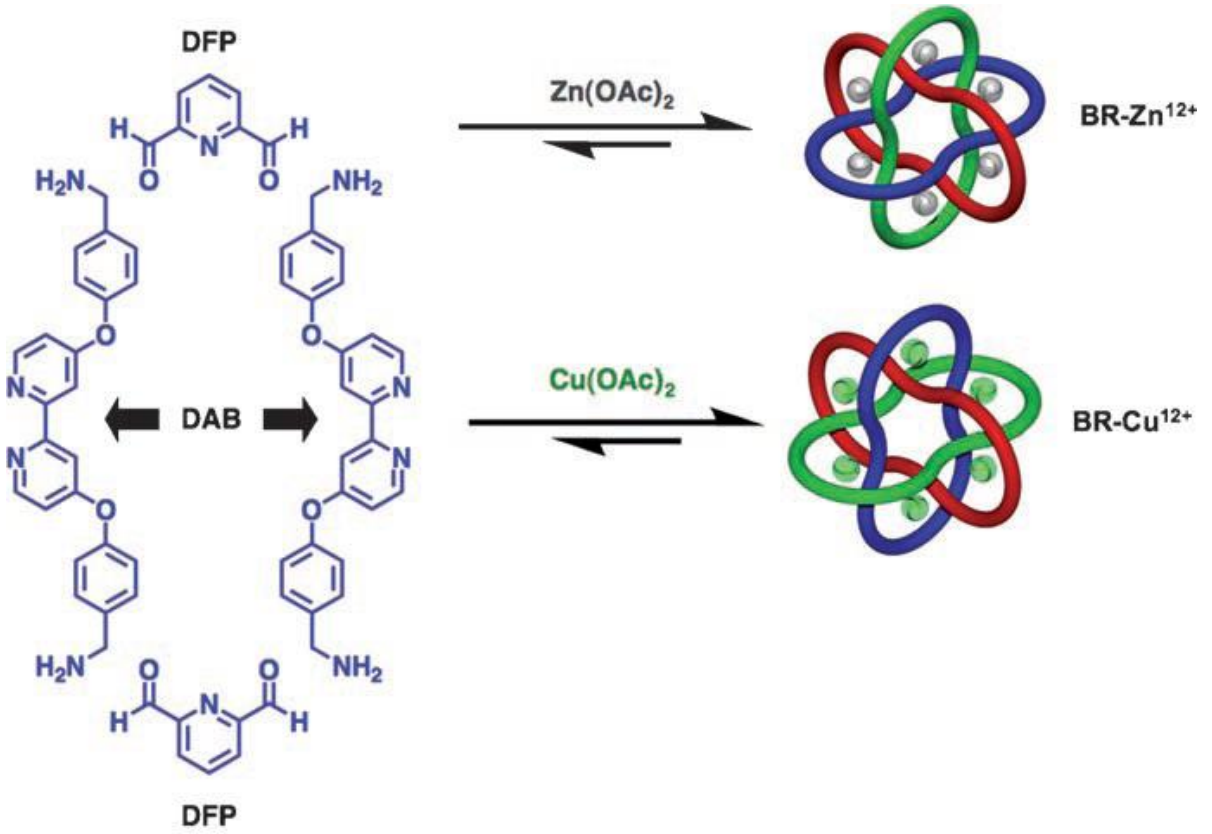
Fig. 2. The ^{1}H NMR spectra (CD_3OD, 298 K) of (**A**) the *exo*-bidentate ligand-containing starting material **DAB**-H_4·4TFA (500 MHz), (**B**) the molecular Borromean rings **BR**·12TFA (600 MHz)





6 Zn(II) bound to one bipy and one dimminopyridine (in the solid state 6th position occupied by triluoroacetate (TFA); S_6 symmetry π-π stacking ech bipy between 2 phenols 3.61-3.66 Å; 12^+


1
NaBH4, EDTA
2 × 3
4


DFP
DAB
DFP
Zn(OAc)2
BR-Zn12+
Cu(OAc)2
BR-Cu12+