Nishinomiya-Yukawa Memorial International Symposium:
What is Life? The Next 100 Years of Yukawa's Dream

Kyoto, Japan
October 15 - 20, 2007

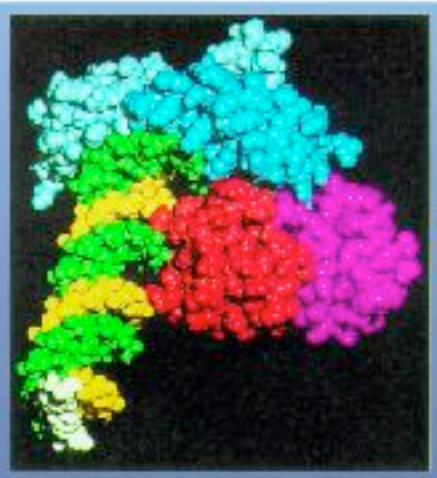
Nanoscopic Molecular Architectures in Supramolecular Science

(Univ. of Tokyo) Mitsuhiko Shionoya

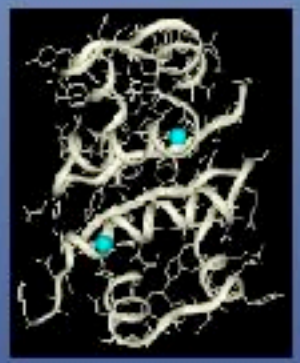
Chemical Bonding

Atoms => bonding => Molecules => self-assembly => Complexes

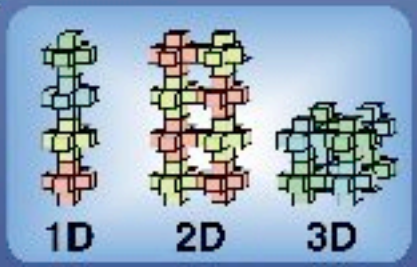
Covalent	***Noncovalent***
Strong & Rigid	Weak but Flexible
Normally irreversible	Reversible
	Distance-dependent
C-C	
366 kJ/mol	Ionic bonds
0.15 nm	Hydrophobic effects
	Hydrogen bonds
	Van-der-Waals
	Dipole-dipole....etc.

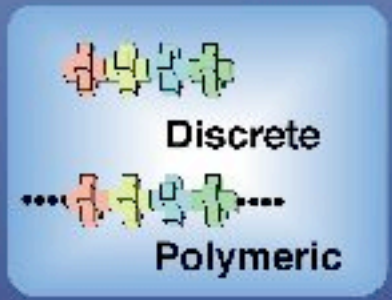


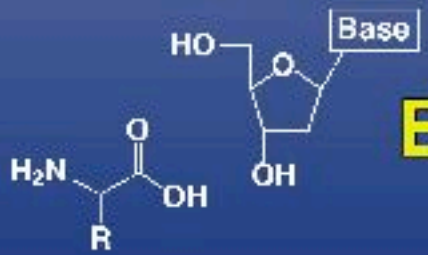
Assembly



Molecules

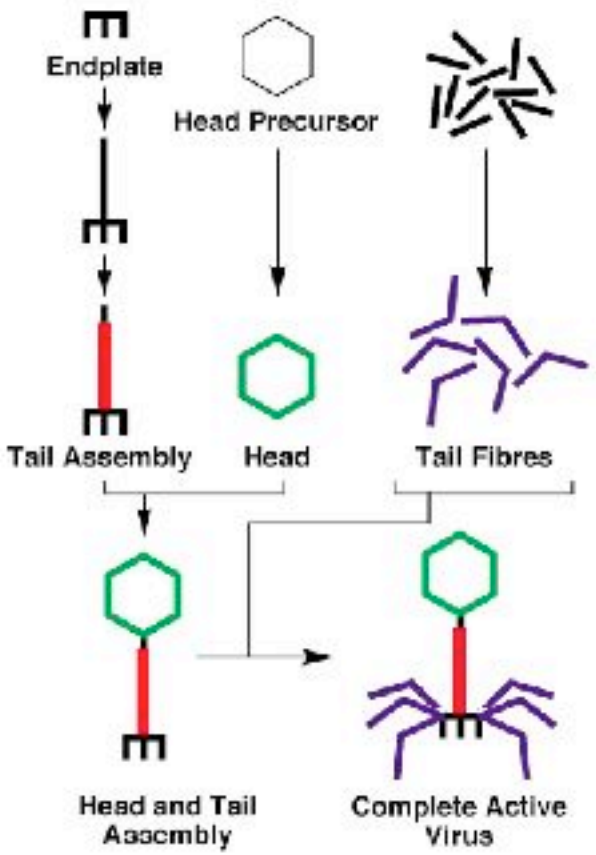




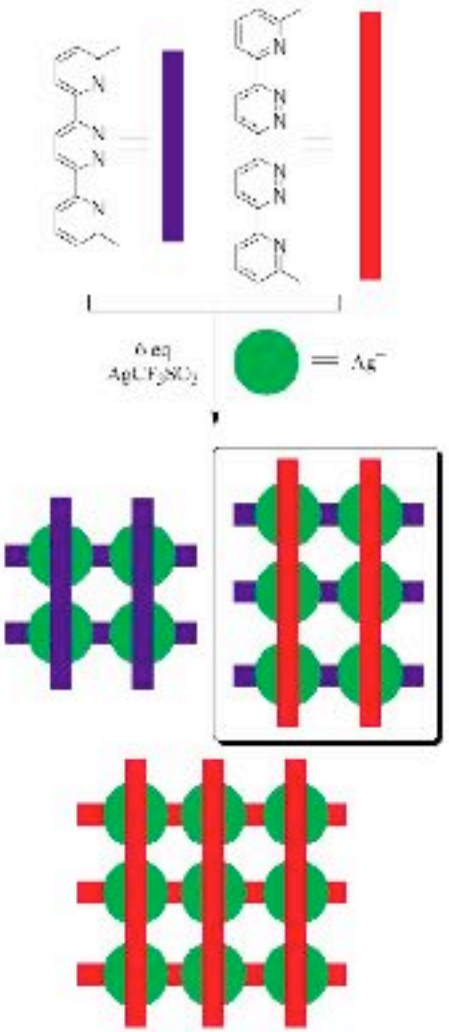


Building Blocks

Self-assembly Protocols
Bio *vs* Artificial

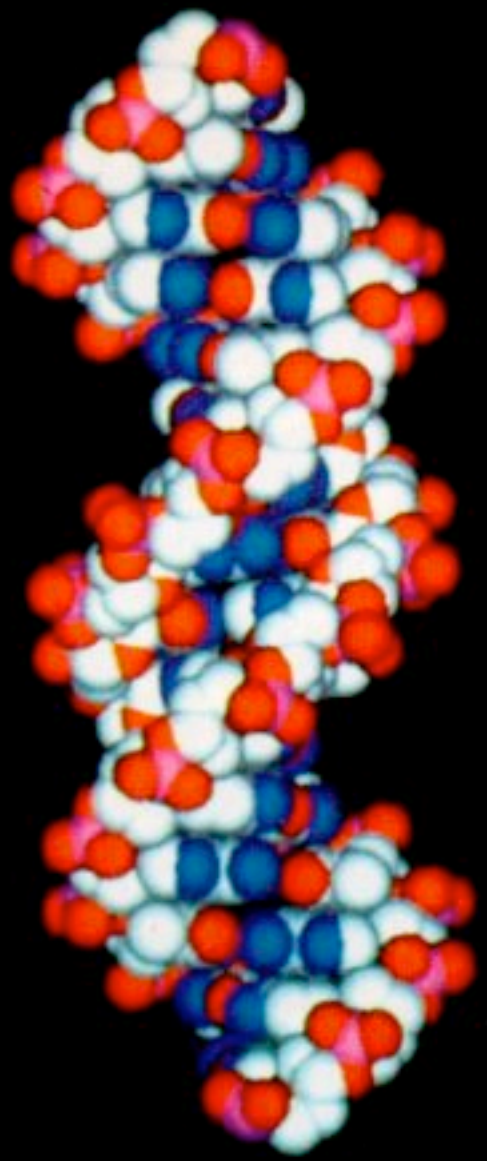


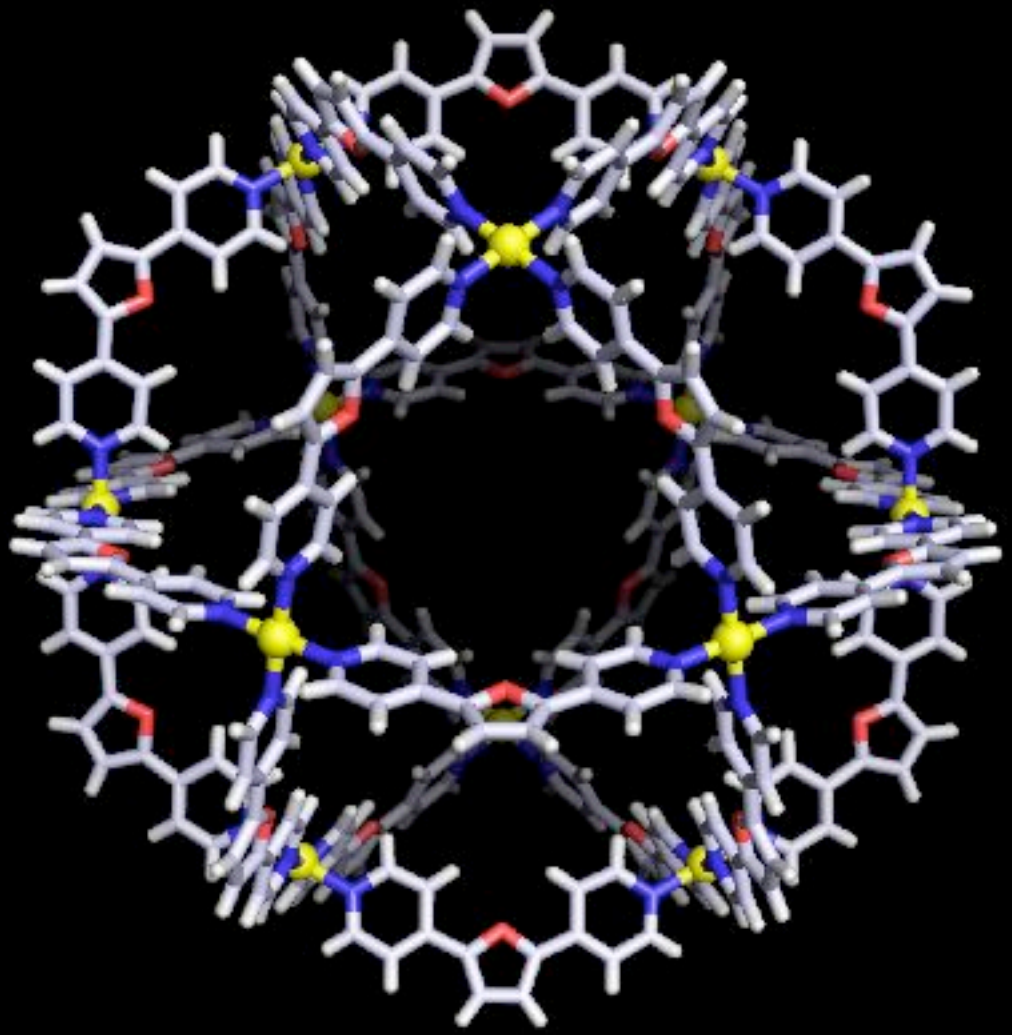
Assembly pathway for T4 bacteriophage



Lehn (*Angew. Chem.*, 1997)

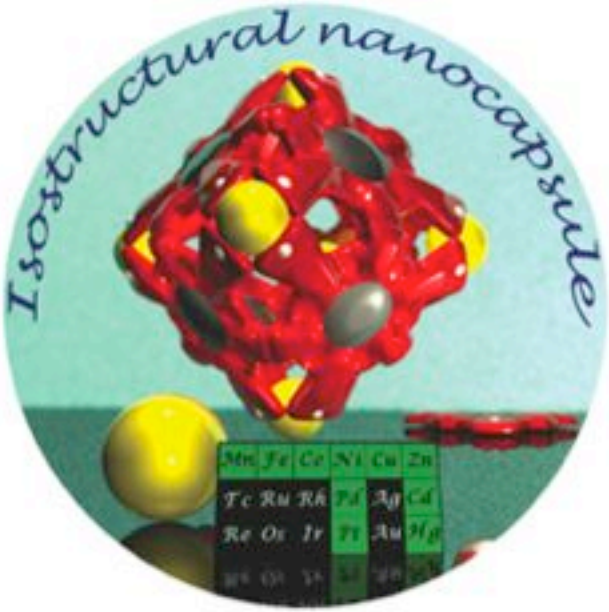
Noncovalent Bonding in Natural & Synthetic Molecules





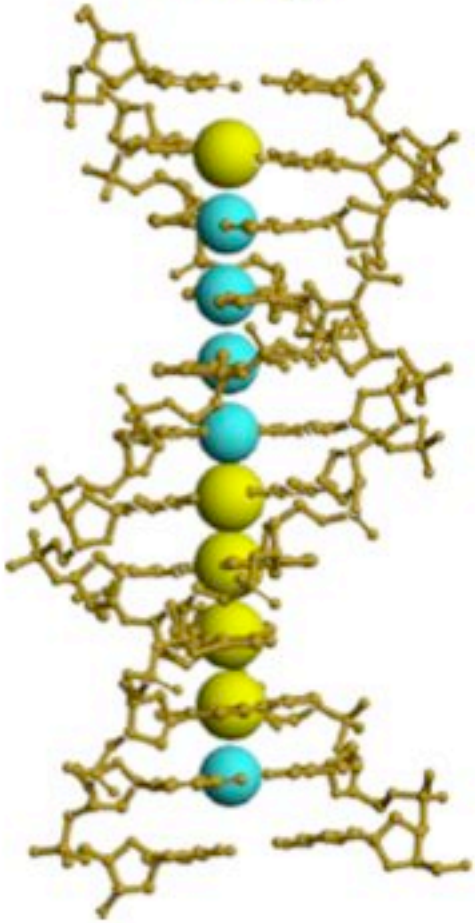
Noncovalent Assemblies

Space



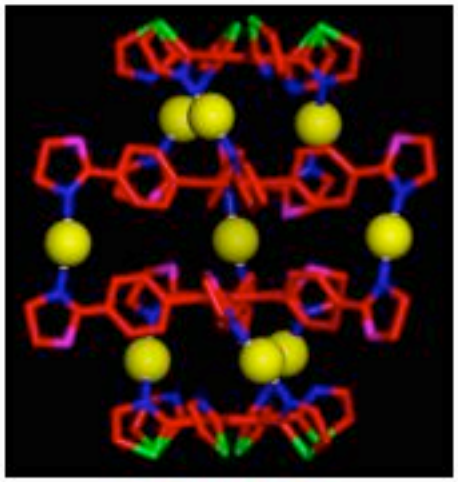
Nanocapsules

Array

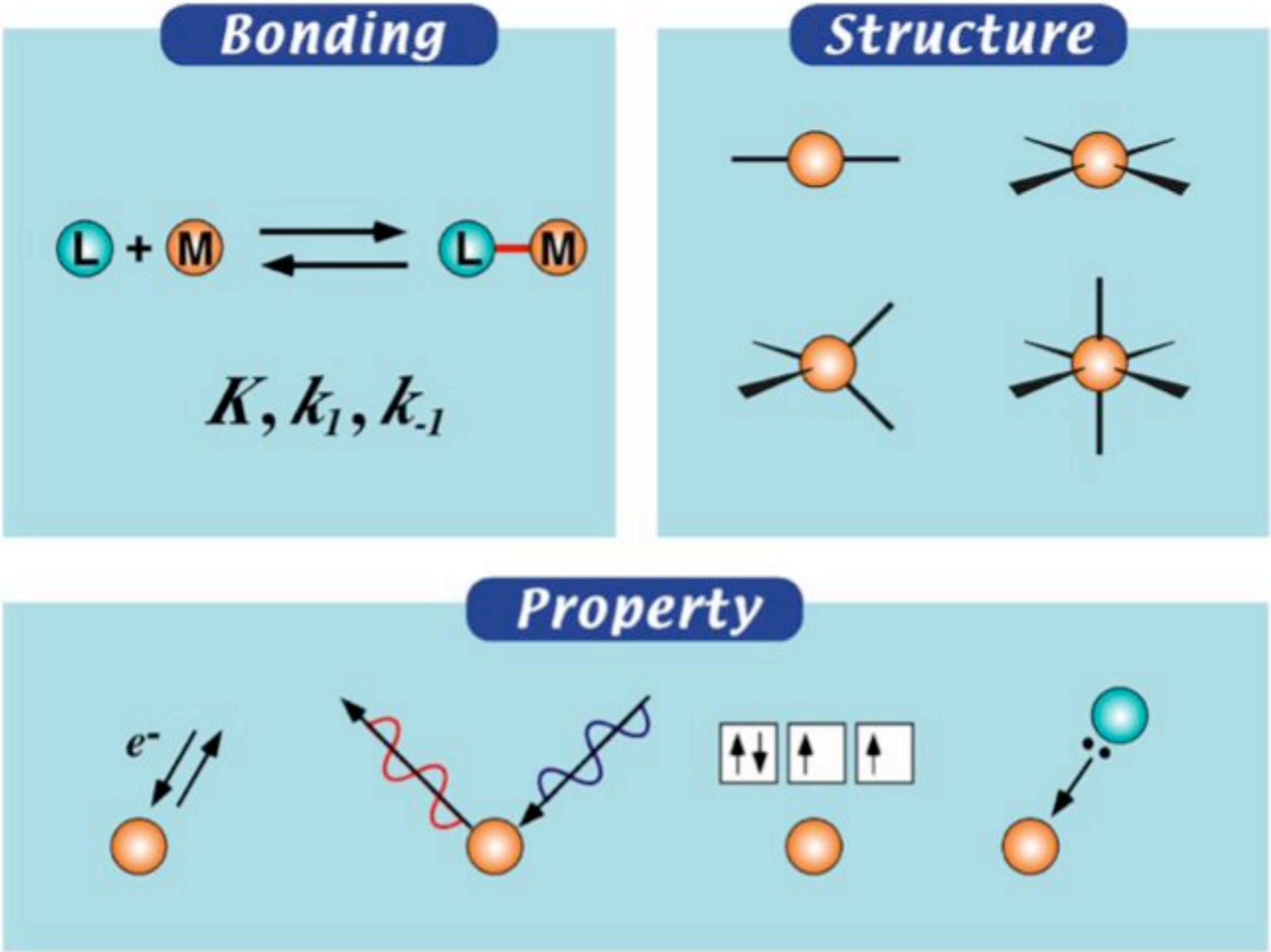


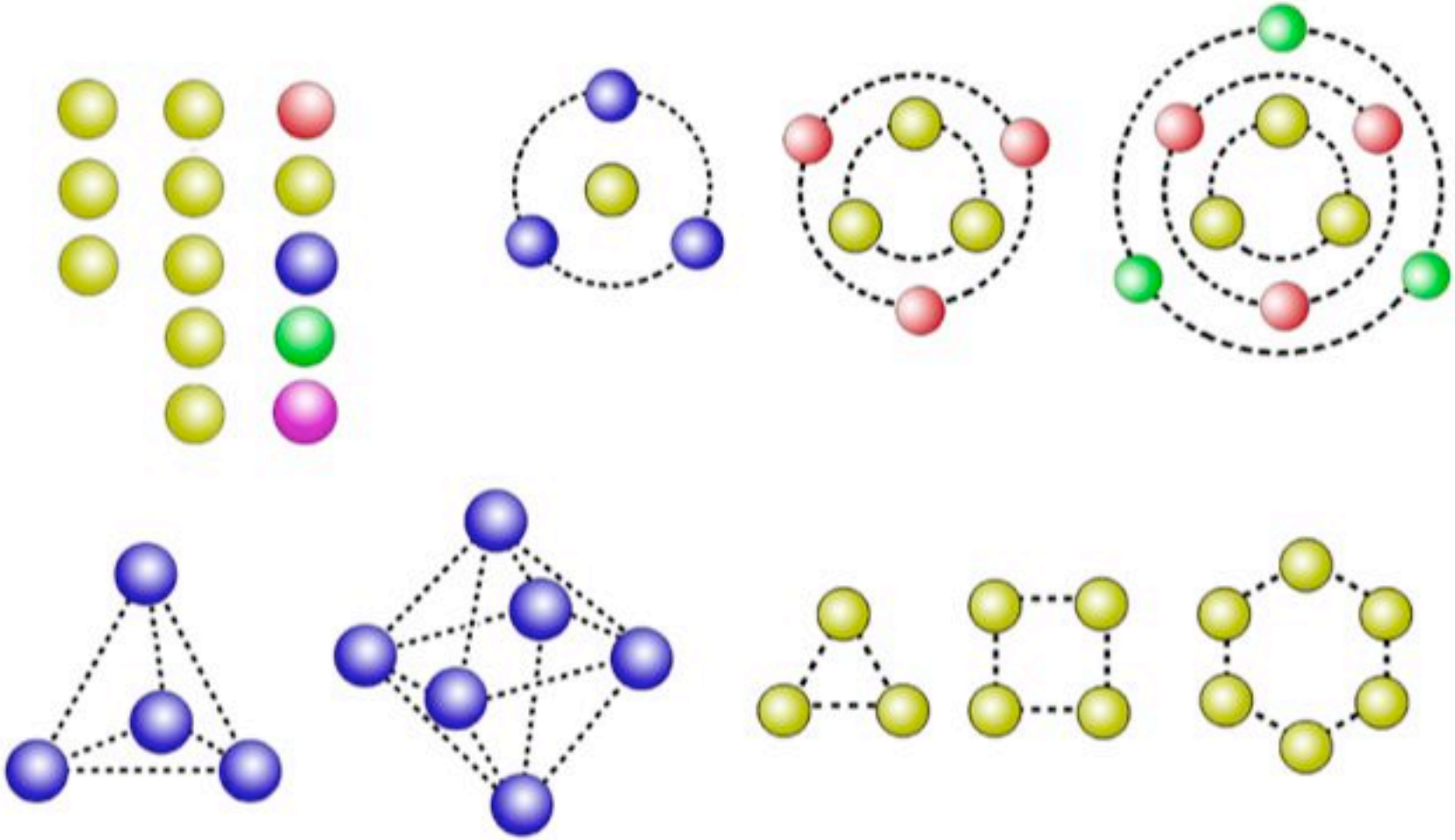
Metallo-DNA

Motion

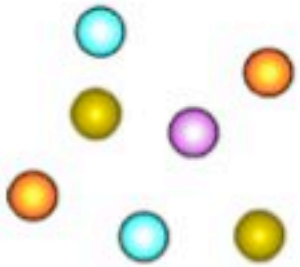


Molecular Machines
(Rotor-Transmitter-Rotor)


Bonding
L + M
L M
K, k_1, k_{-1}
Structure
Property
e-



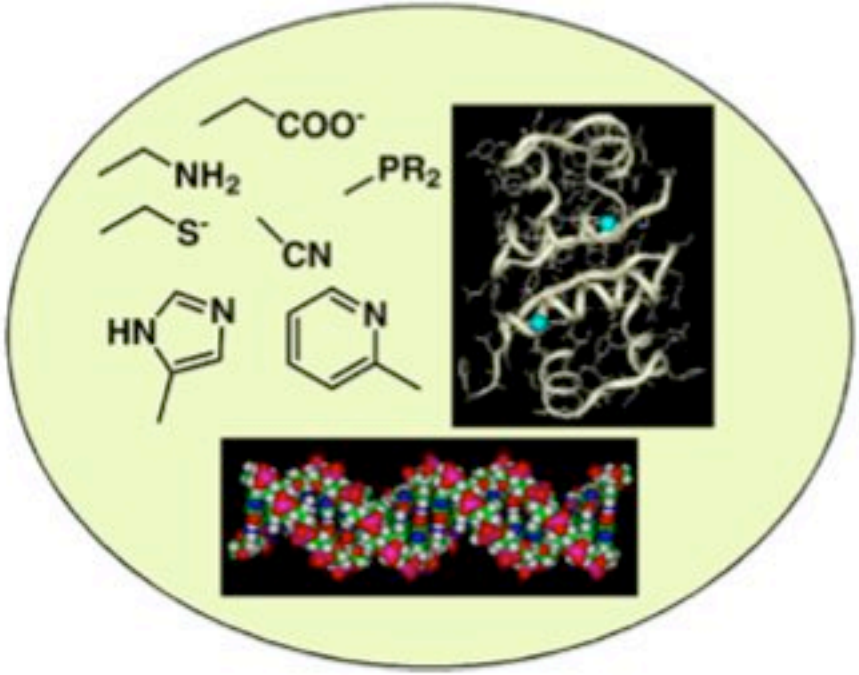
Array



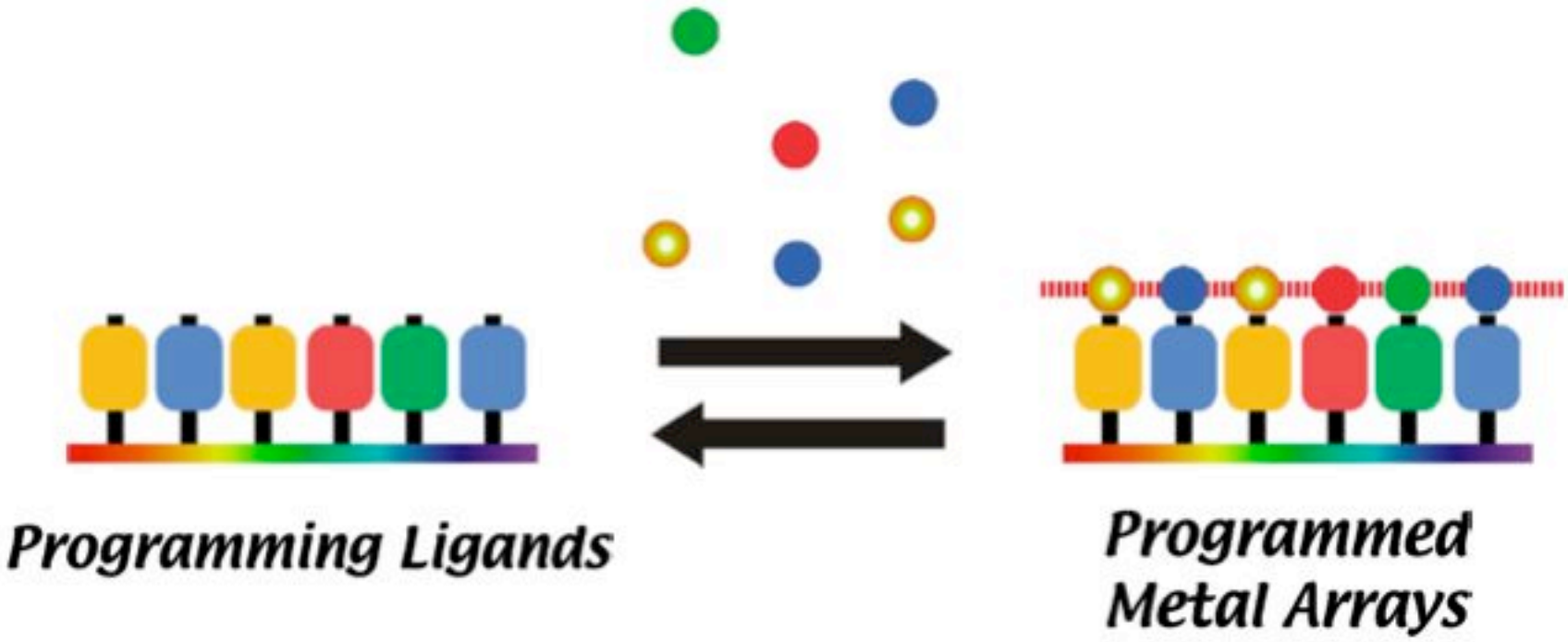
Number
Position
Time

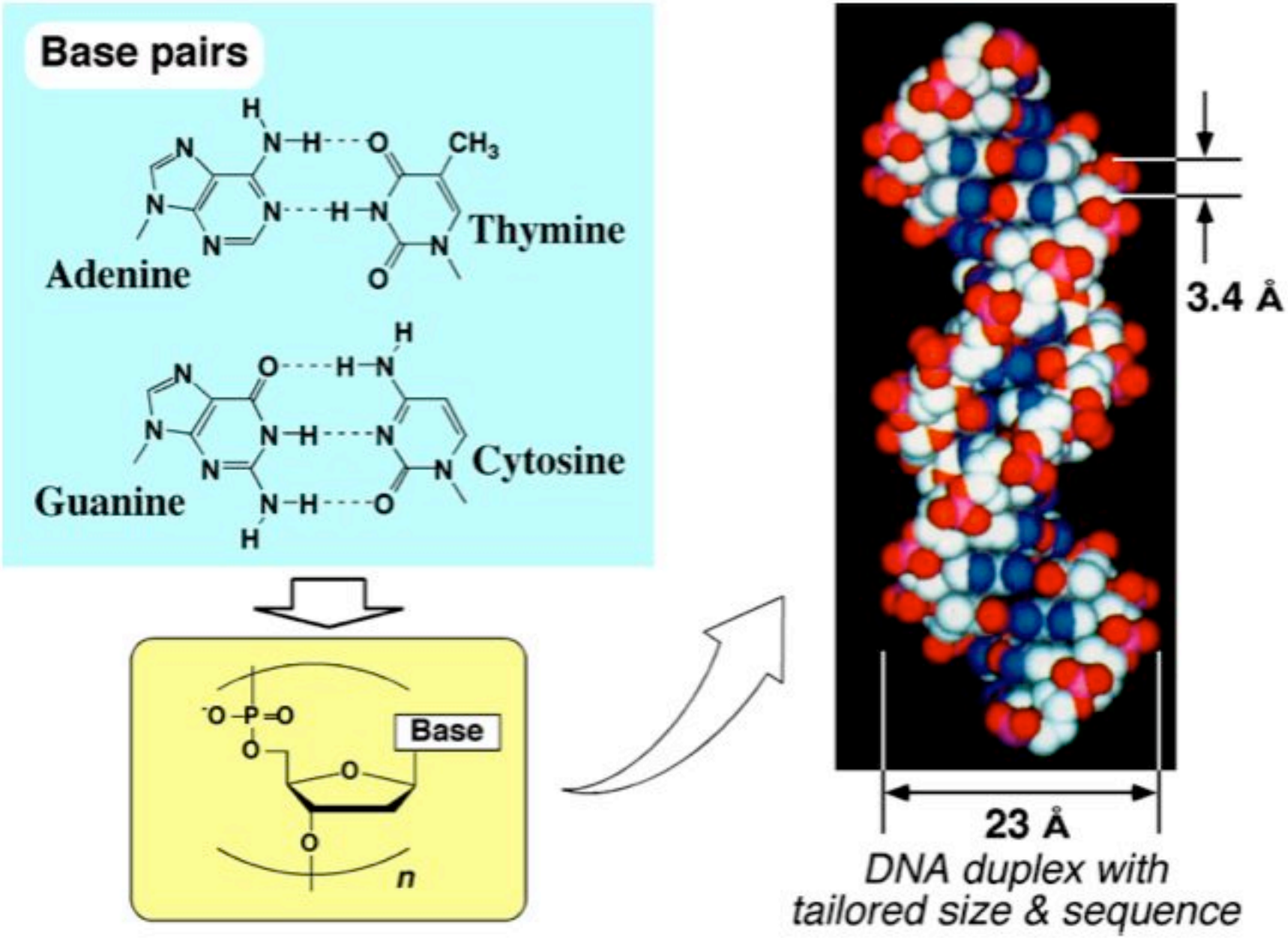
Programming

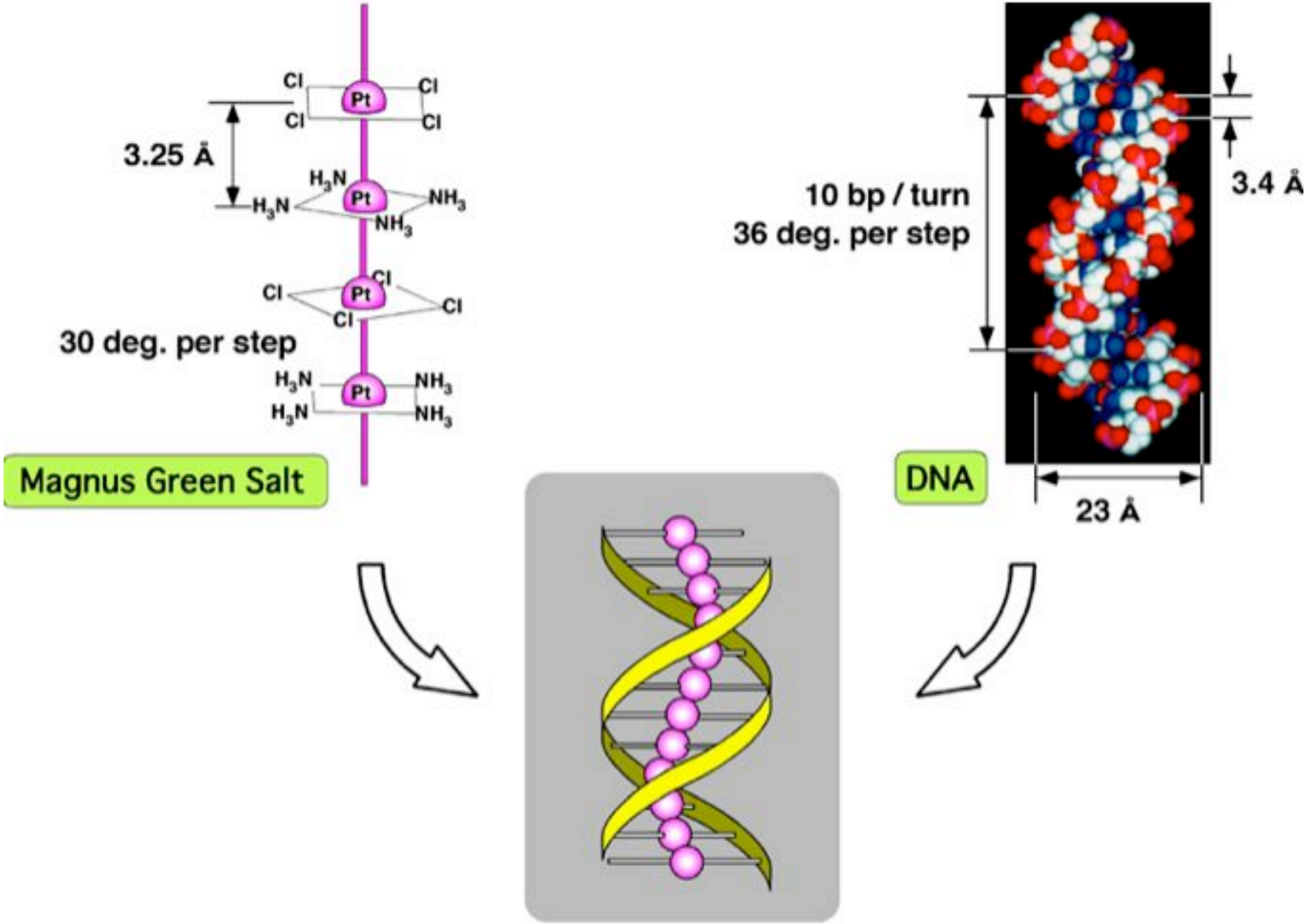
Multi-dimensional Array
Symmetric/Asymmetric Array
Dynamic Array

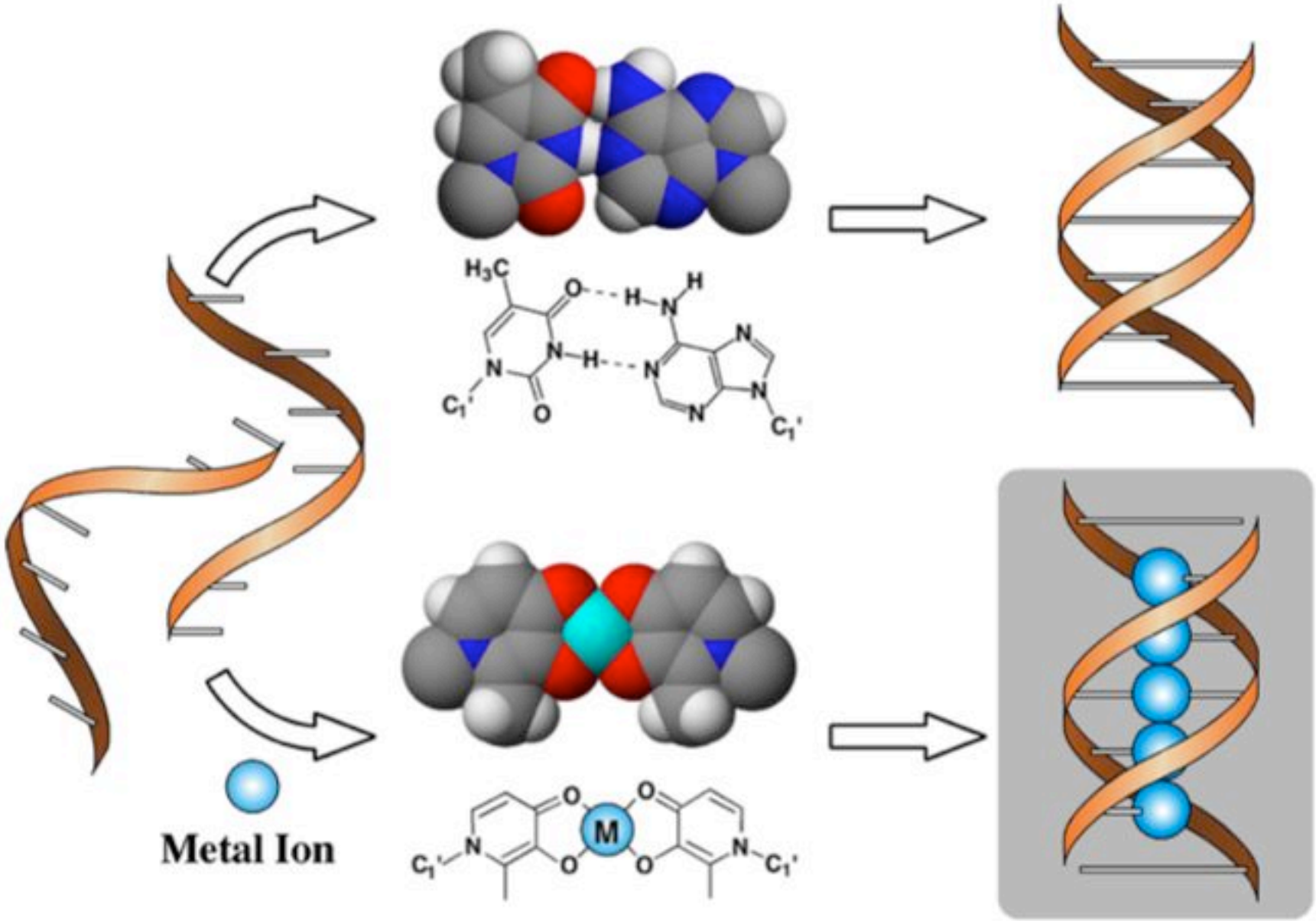


Molecular-scale Programming for Metals

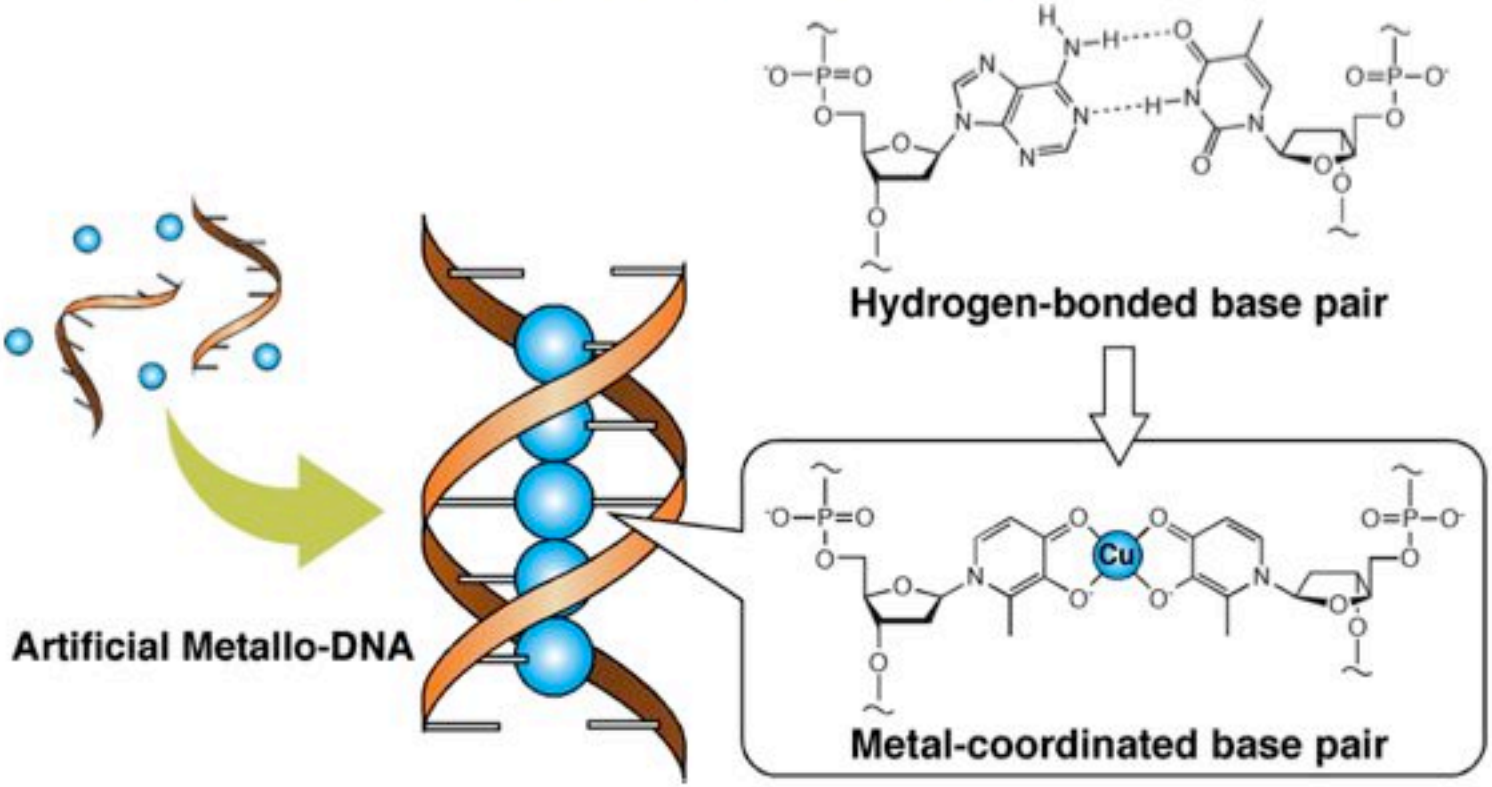



Base pairs
Adenine
Thymine
Guanine
Cytosine
Base
n
3.4 Å
23 Å
DNA duplex with
tailored size & sequence

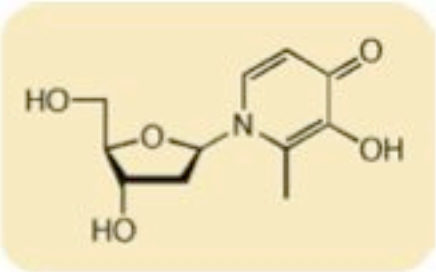

Cl
Pt
Cl
Cl
Cl
3.25 Å
H_3N
Pt
NH_3
H_3N
NH_3
Cl
Pt
Cl
Cl
Cl
30 deg. per step
H_3N
Pt
NH_3
H_3N
NH_3
Magnus Green Salt
10 bp / turn
36 deg. per step
3.4 Å
DNA
23 Å


Metal Ion
M

A Discrete Self-Assembled Metal Array in Artificial DNA

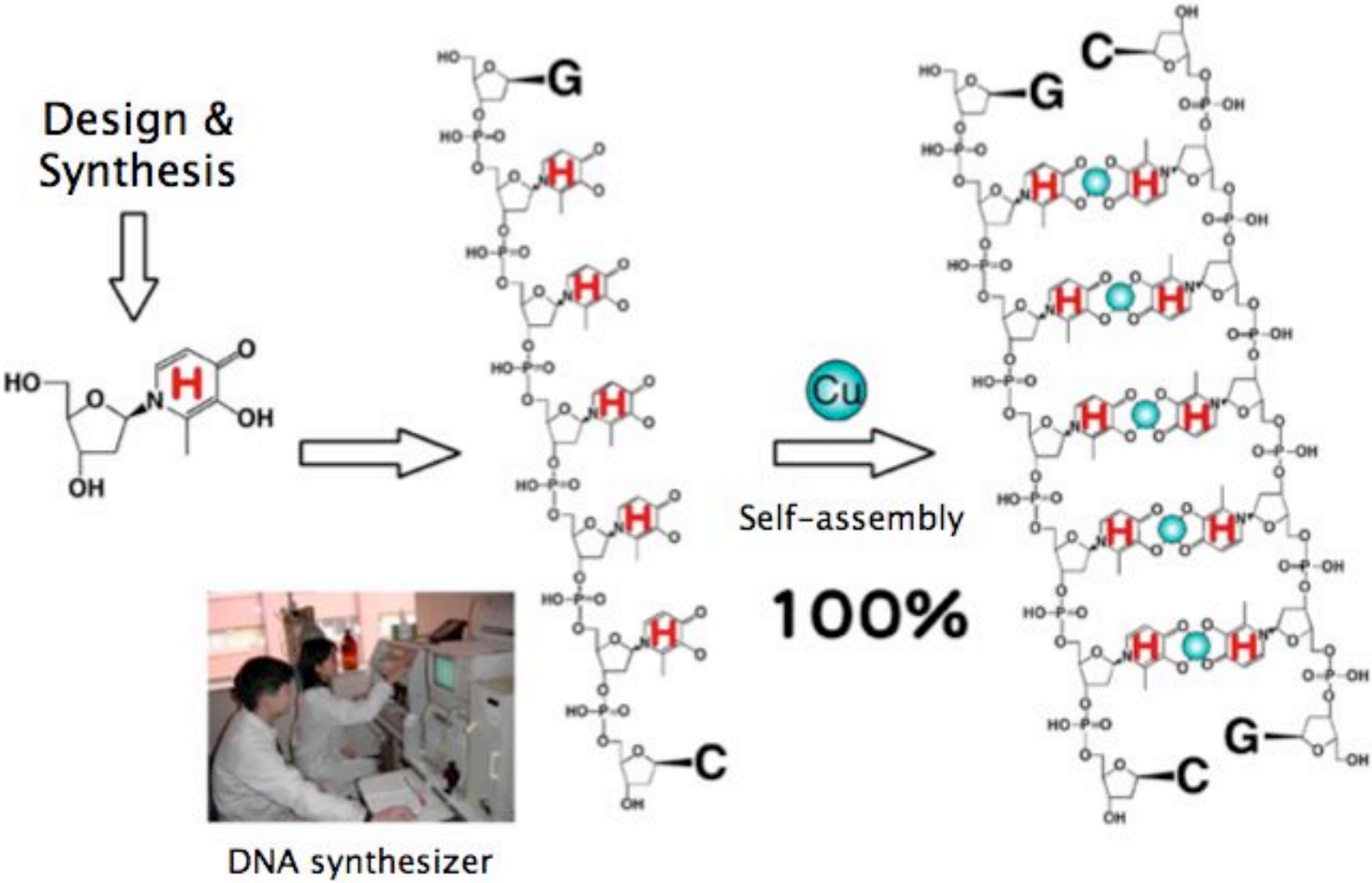


H =

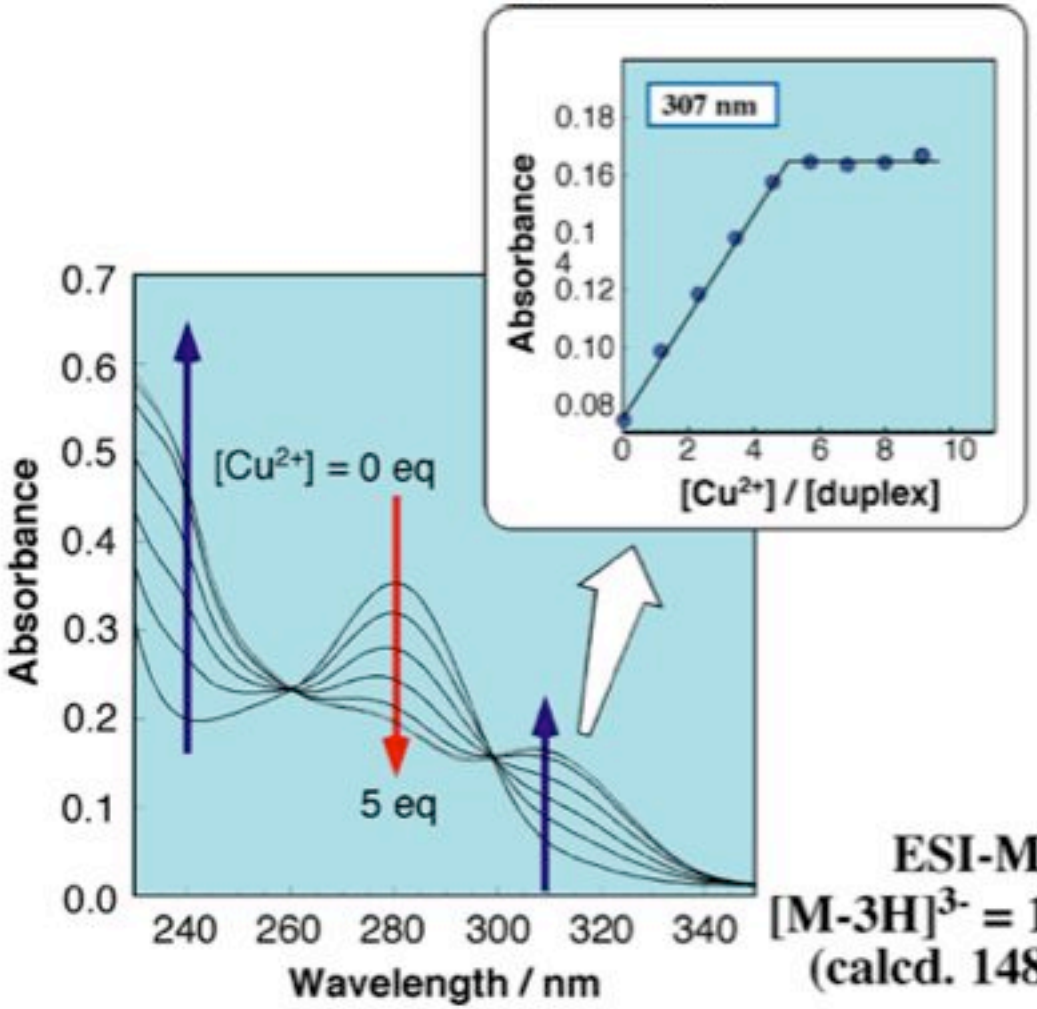


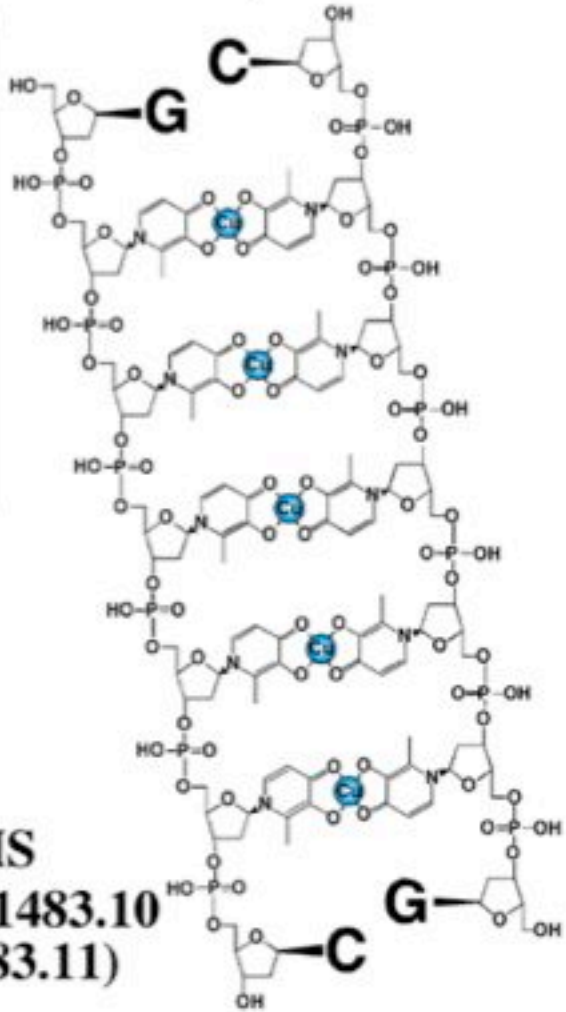
d(5'-G**HHHHH**C-3') d(5'-G**HHHH**C-3')
d(3'-C**HHHHH**G-5') d(3'-C**HHHH**G-5')

d(5'-G**HHH**C-3') d(5'-G**HH**C-3') d(5'-G**H**C-3')
d(3'-C**HHH**G-5') d(3'-C**HH**G-5') d(3'-C**H**G-5')


Design &
Synthesis
HO
OH
OH
H
G
C
Cu
Self-assembly
100%
DNA synthesizer

Pentanuclear Cu^{2+} Complex with Duplex d(5'-GHHHHHHC-3')$_2$

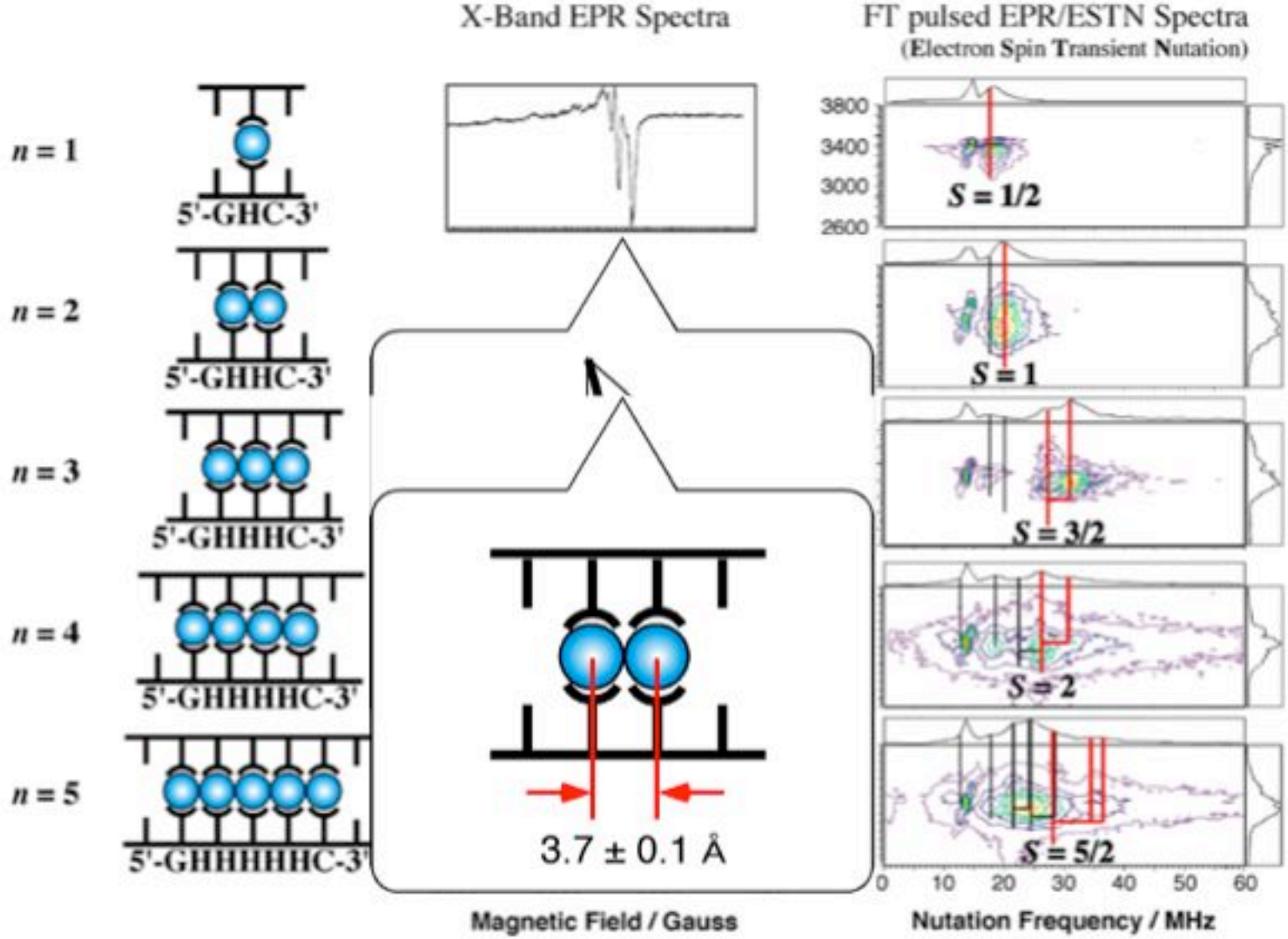




ESI-MS
$[M-3H]^{3-}$ = 1483.10
(calcd. 1483.11)

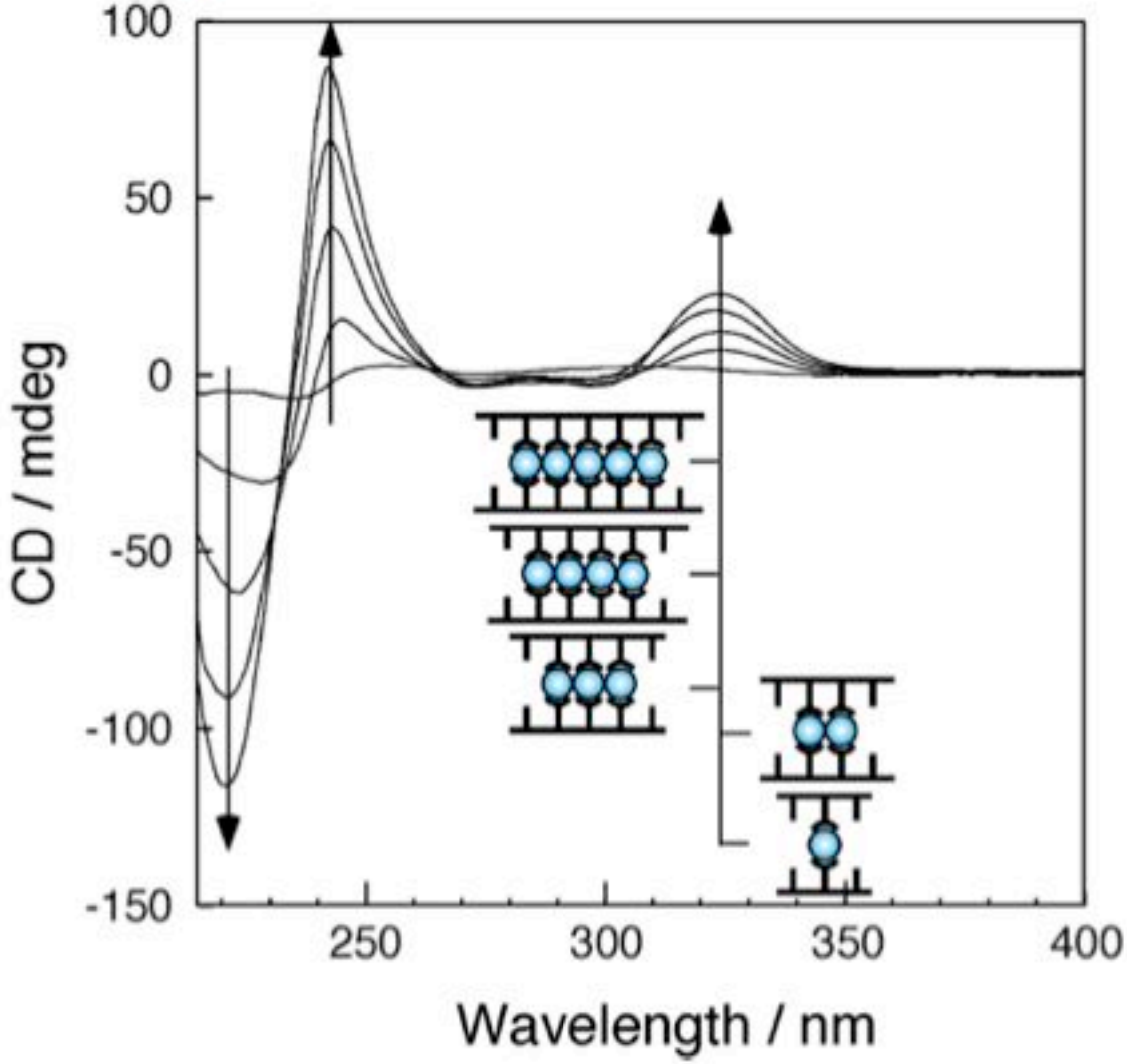
[DNA duplex] = 2.0 μM in 10 mM HEPES (pH 7.0). 50 mM NaCl. 25 °C

Spin-Spin Interactions on Cu^{2+} Ions Aligned in Artificial DNAs



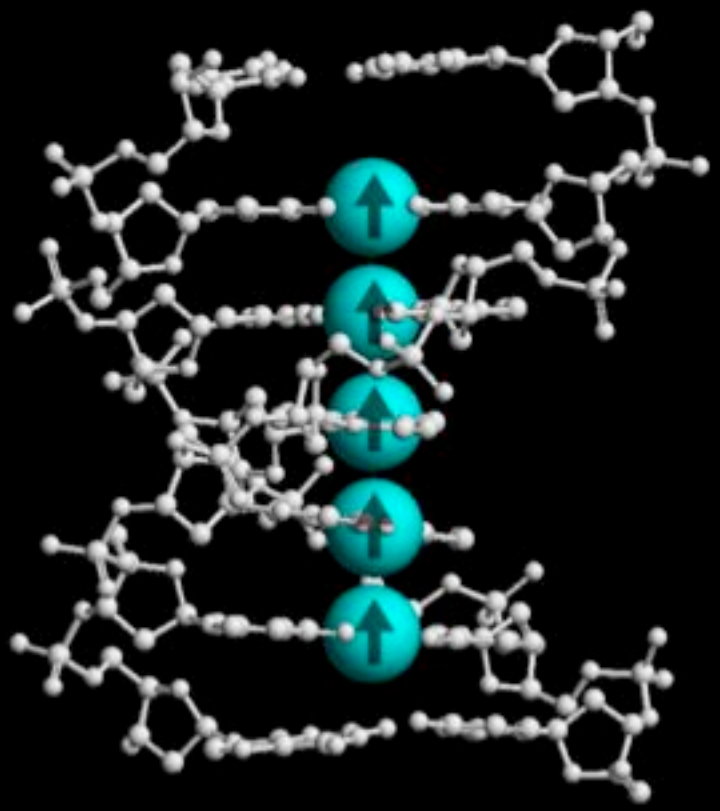
[DNA duplexes] = 100 μM with *n* eq. $CuSO_4$ in 10 mM HEPES (pH 7.0), 50 mM NaCl, at 1.5 K.

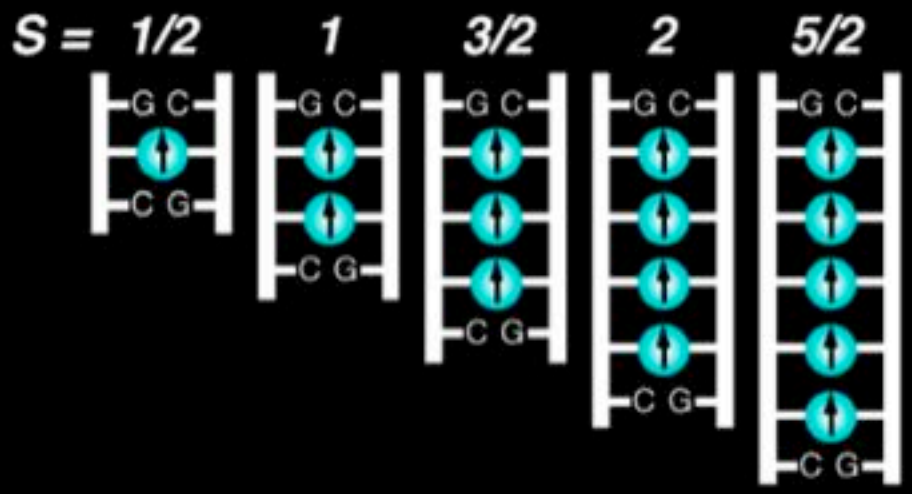
CD Spectra of $Cu^{2+}{}_n \cdot d(5'\text{-}GH_nC\text{-}3')_2$



[DNA duplex] = 8.0 μM in 10 mM HEPES (pH 7.0). 50 mM NaCl. *l* = 1 cm. 25 °C

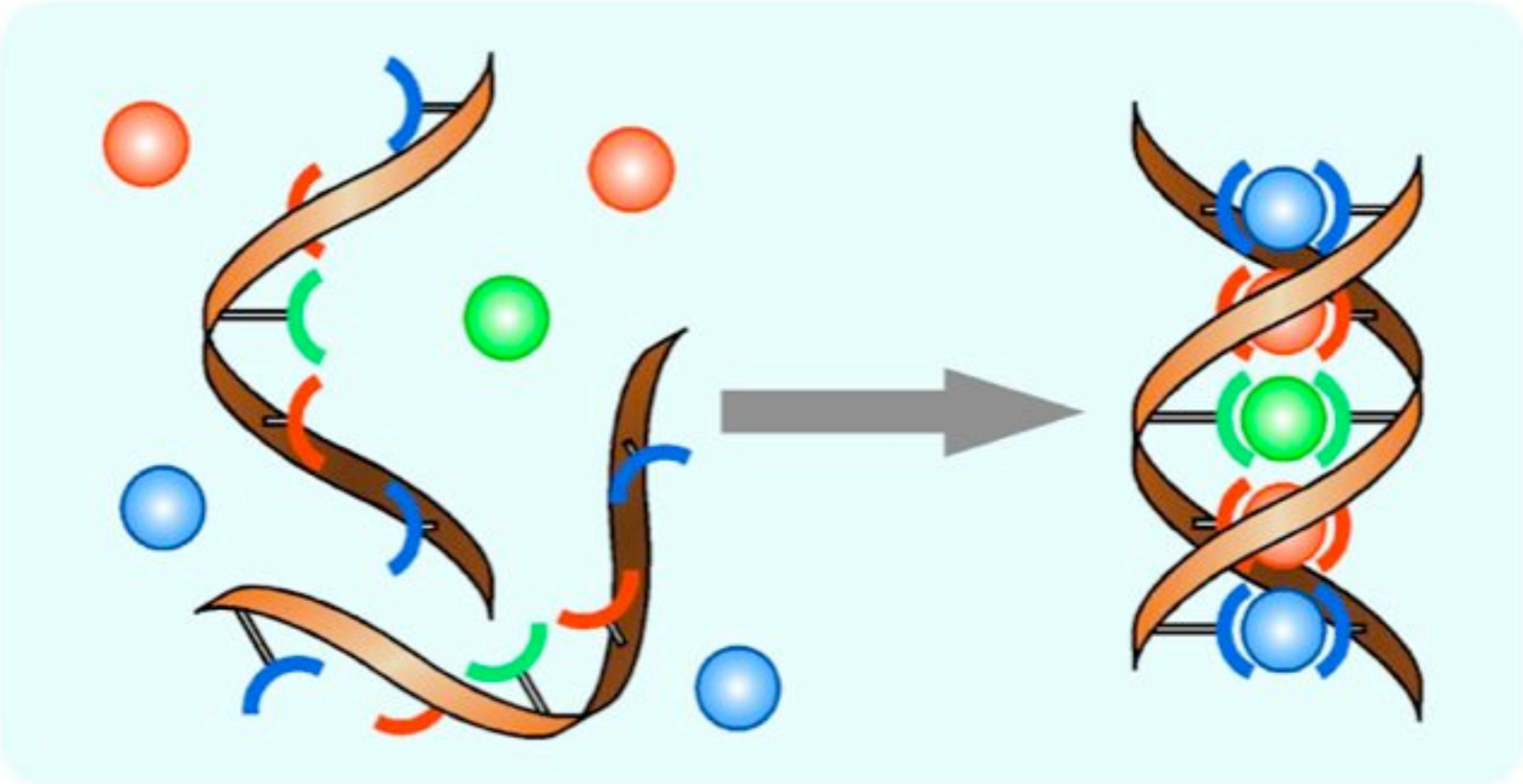
Discrete Metal Arrays in Artificial DNA



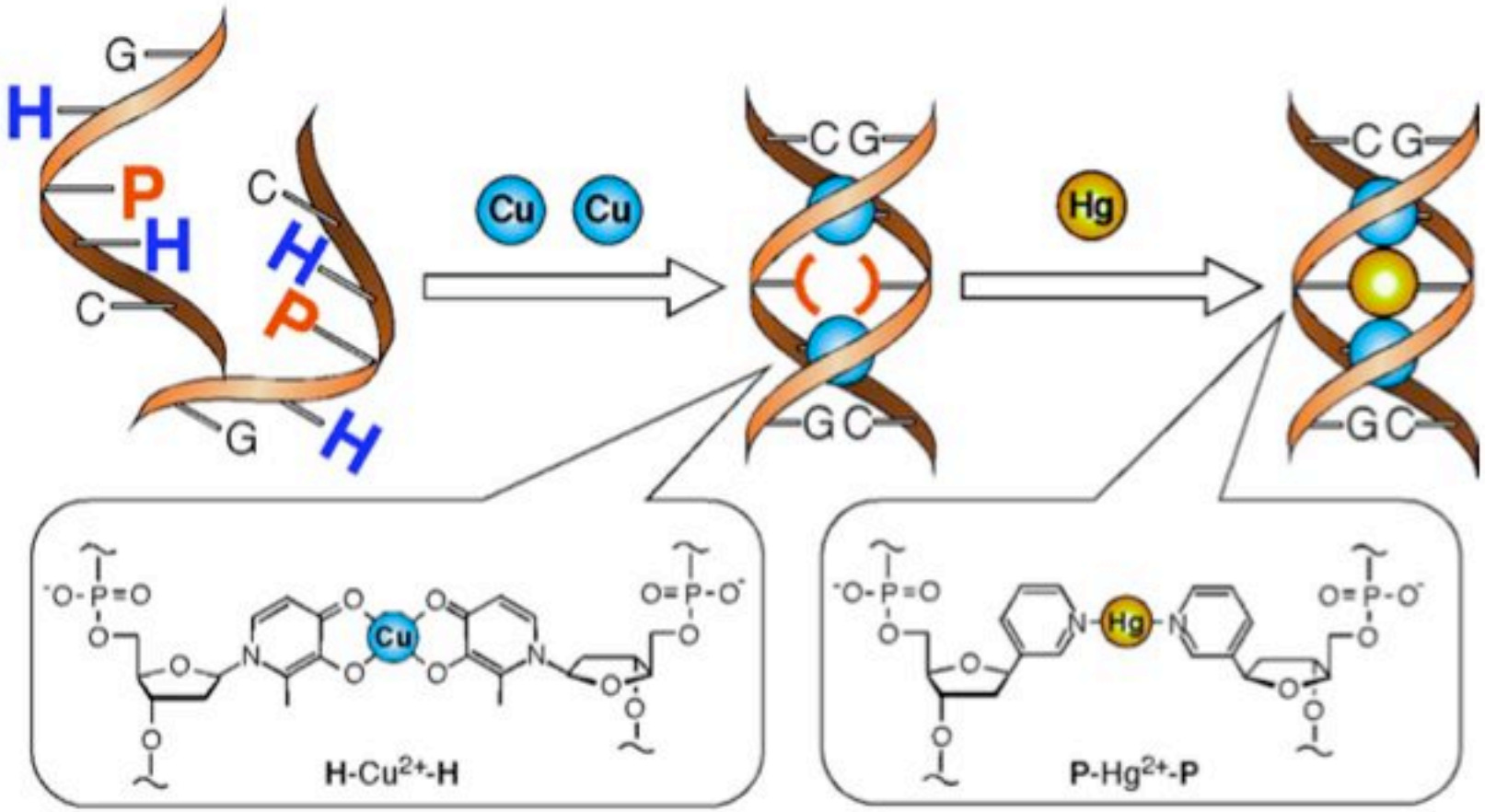


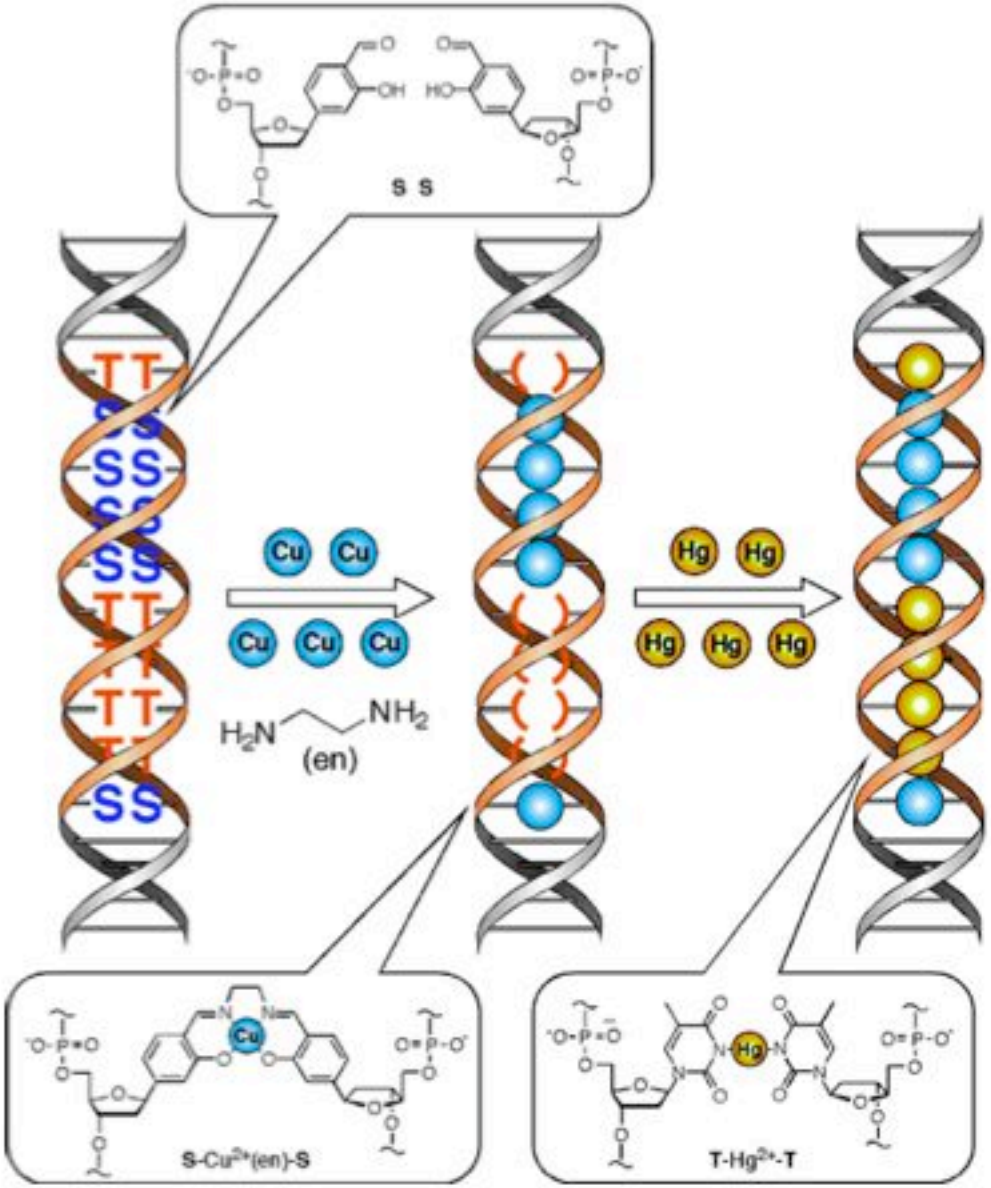
Science, 299, 1212 (2003)

Programmable Heterogeneous Metal Arrays

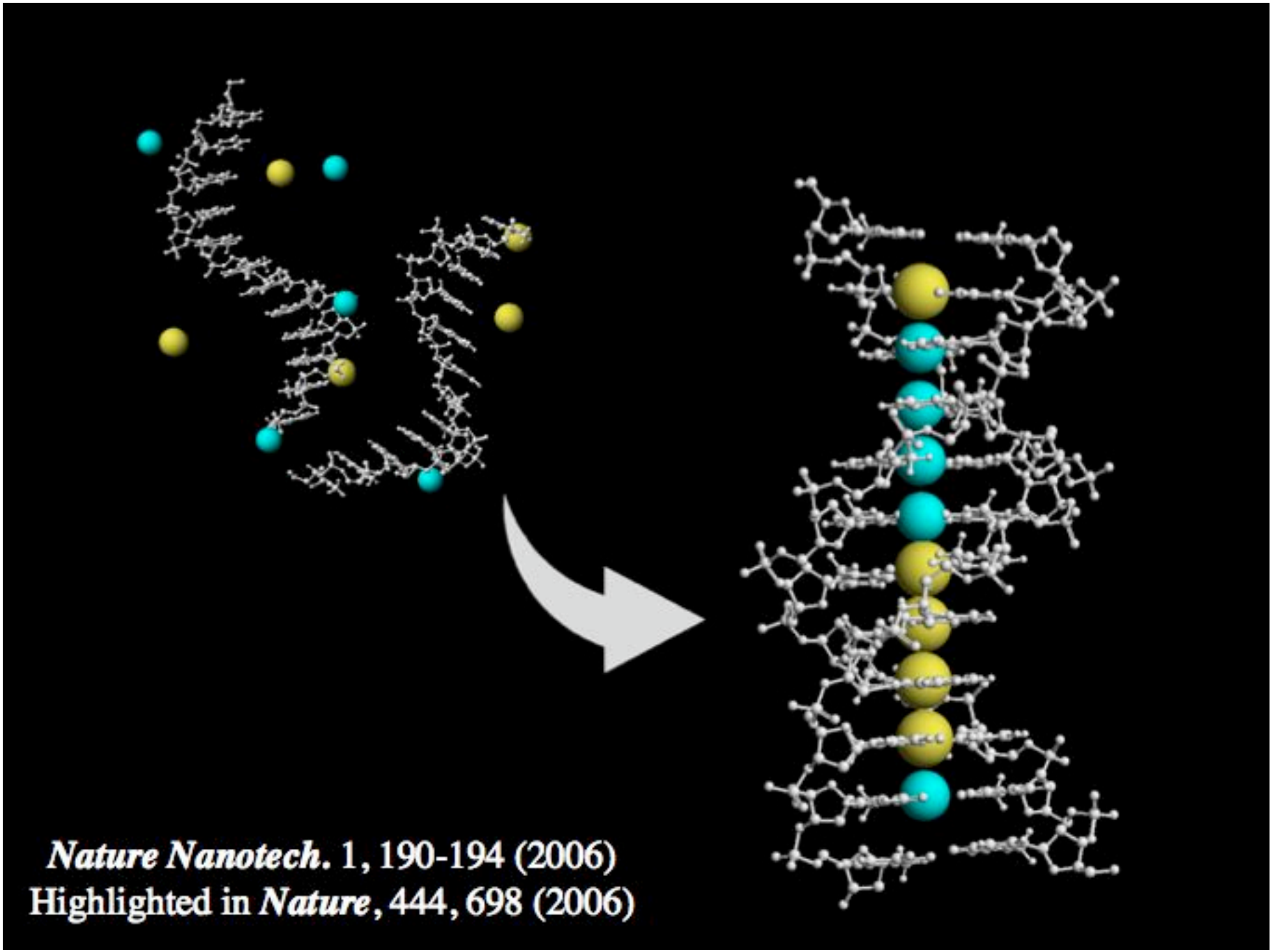


Heterogeneous Metal Array

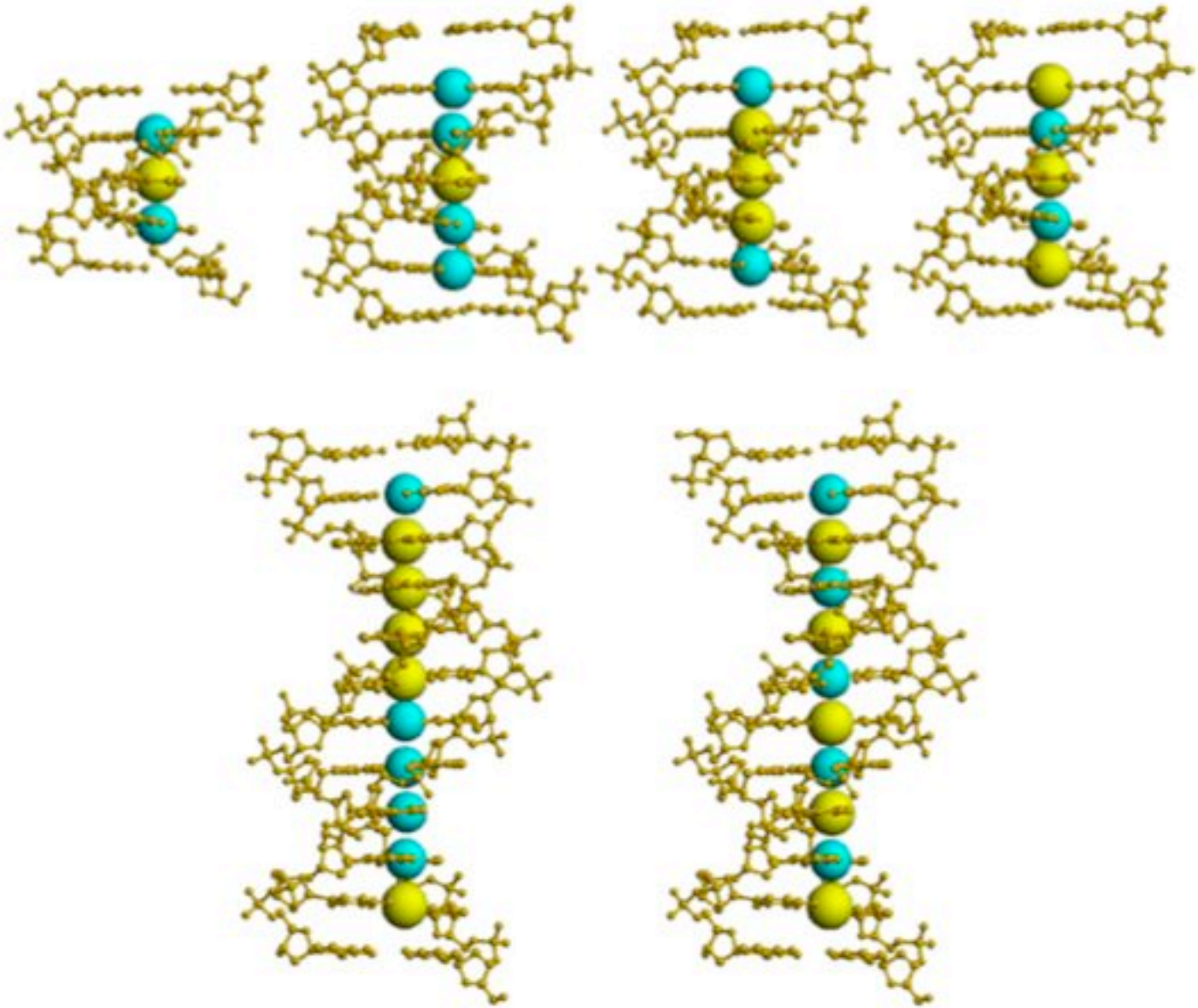




Clever and Carell

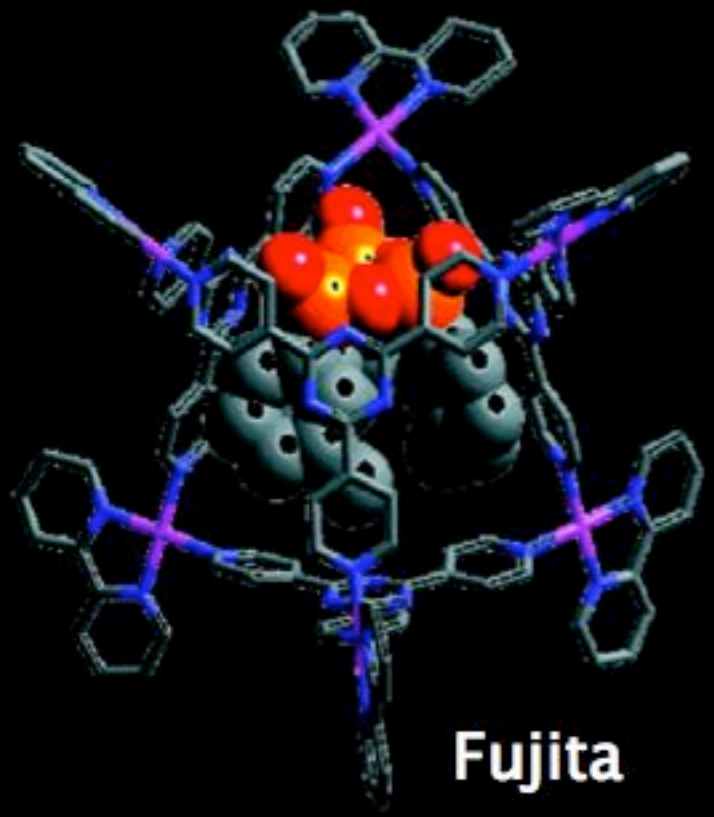

Nature Nanotech. 1, 190-194 (2006)
Highlighted in *Nature*, 444, 698 (2006)

Programmable Metal Arrays in Artificial DNAs

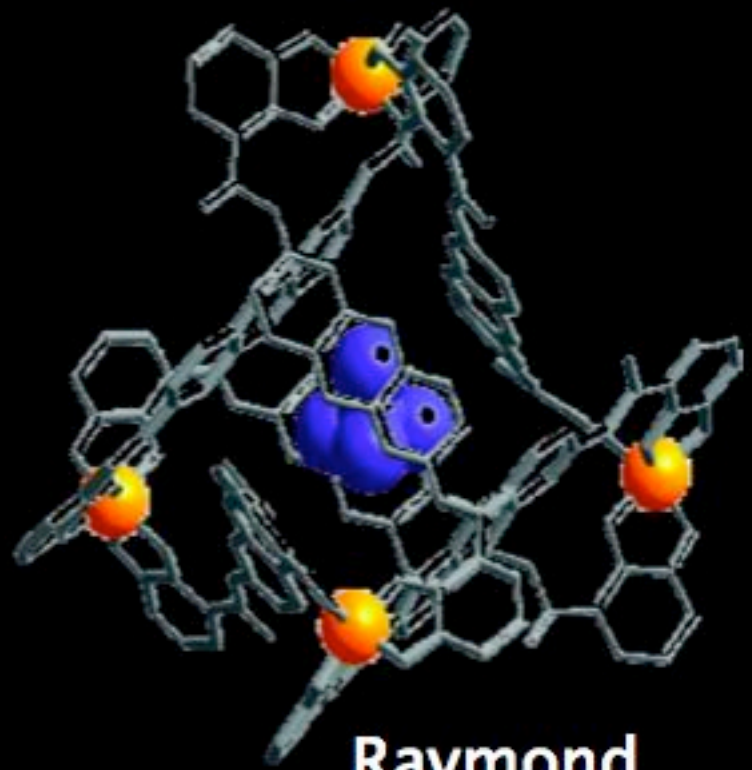


Space

Metal-assembled Molecular Capsules

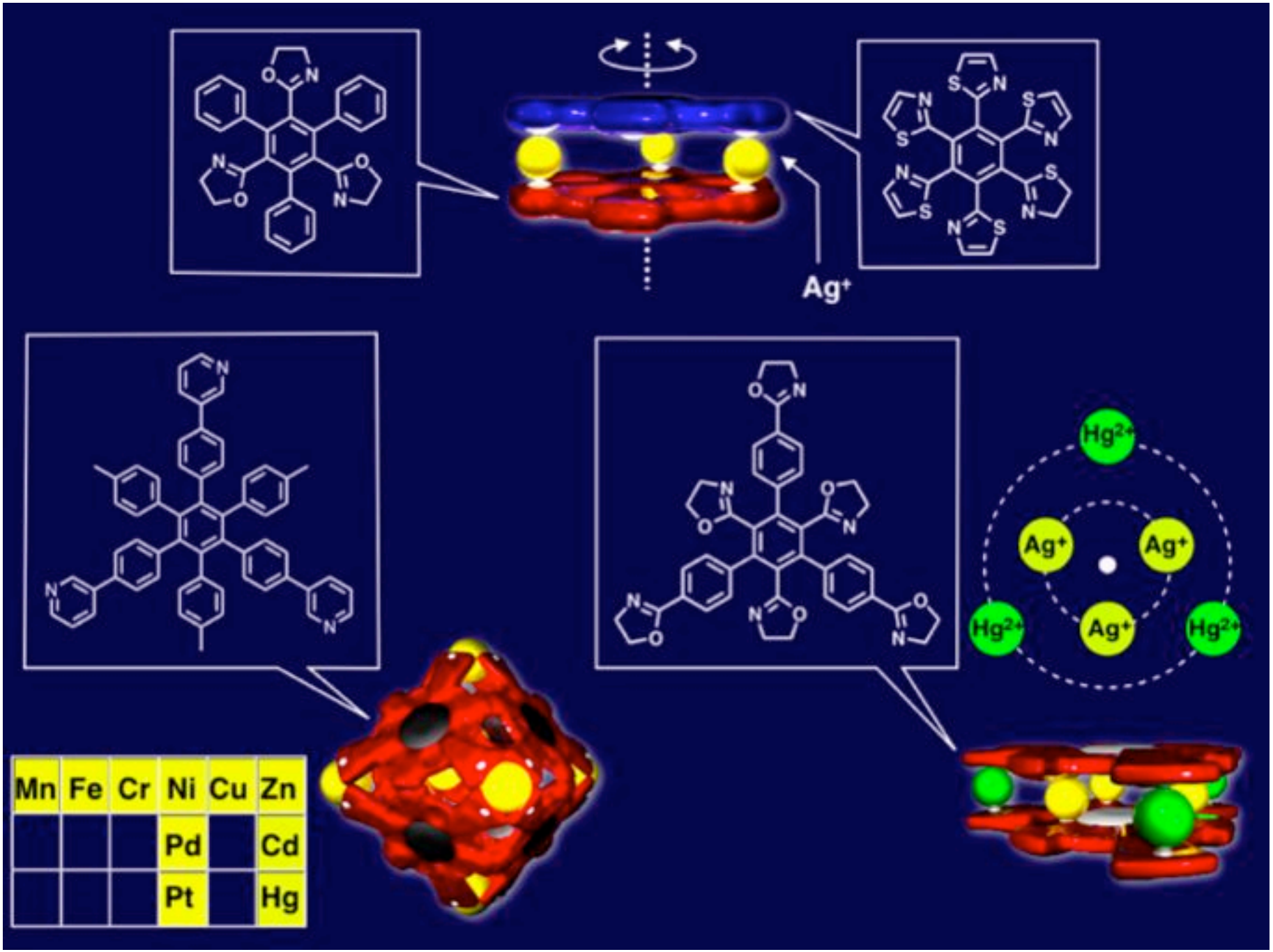


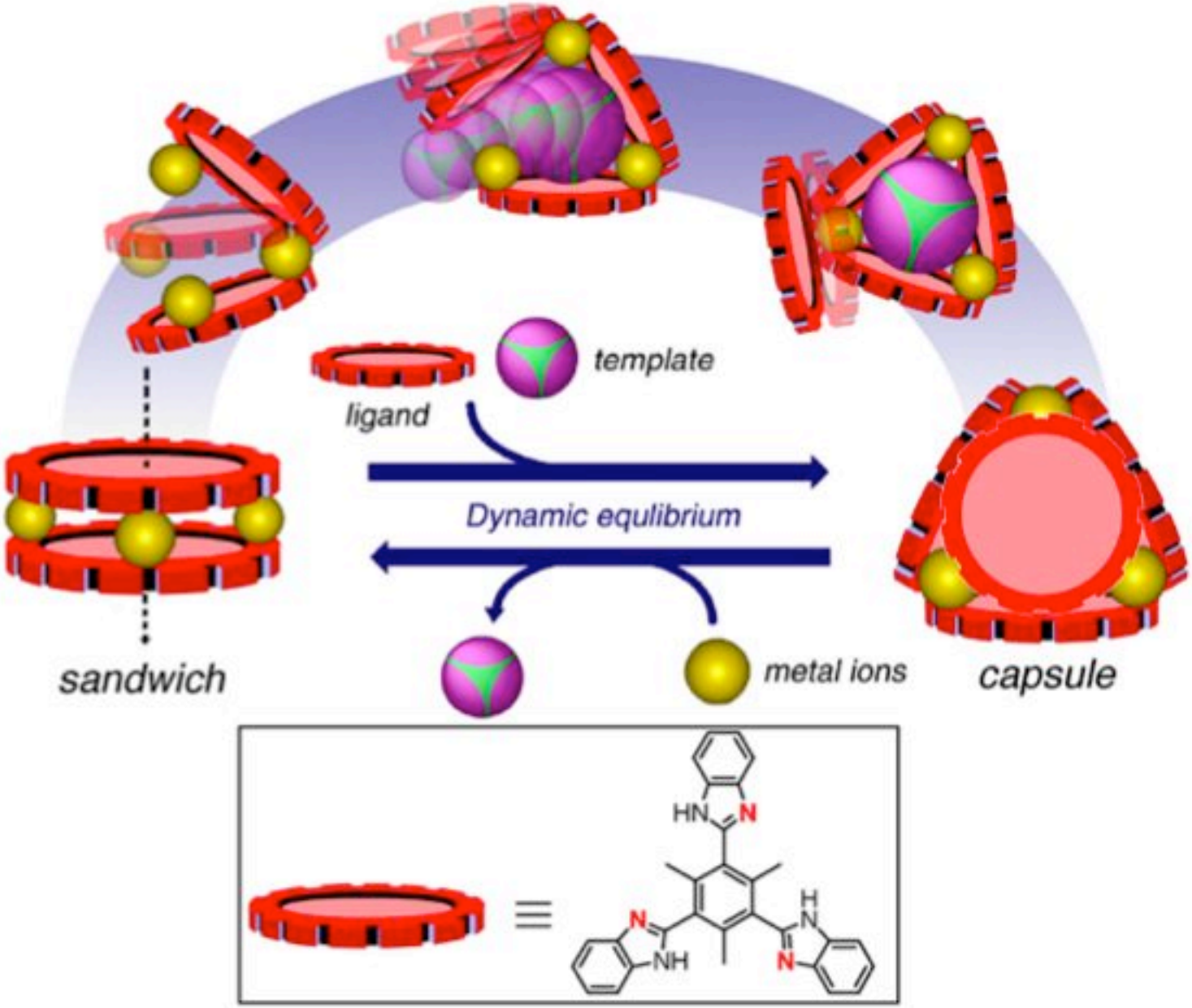
Fujita



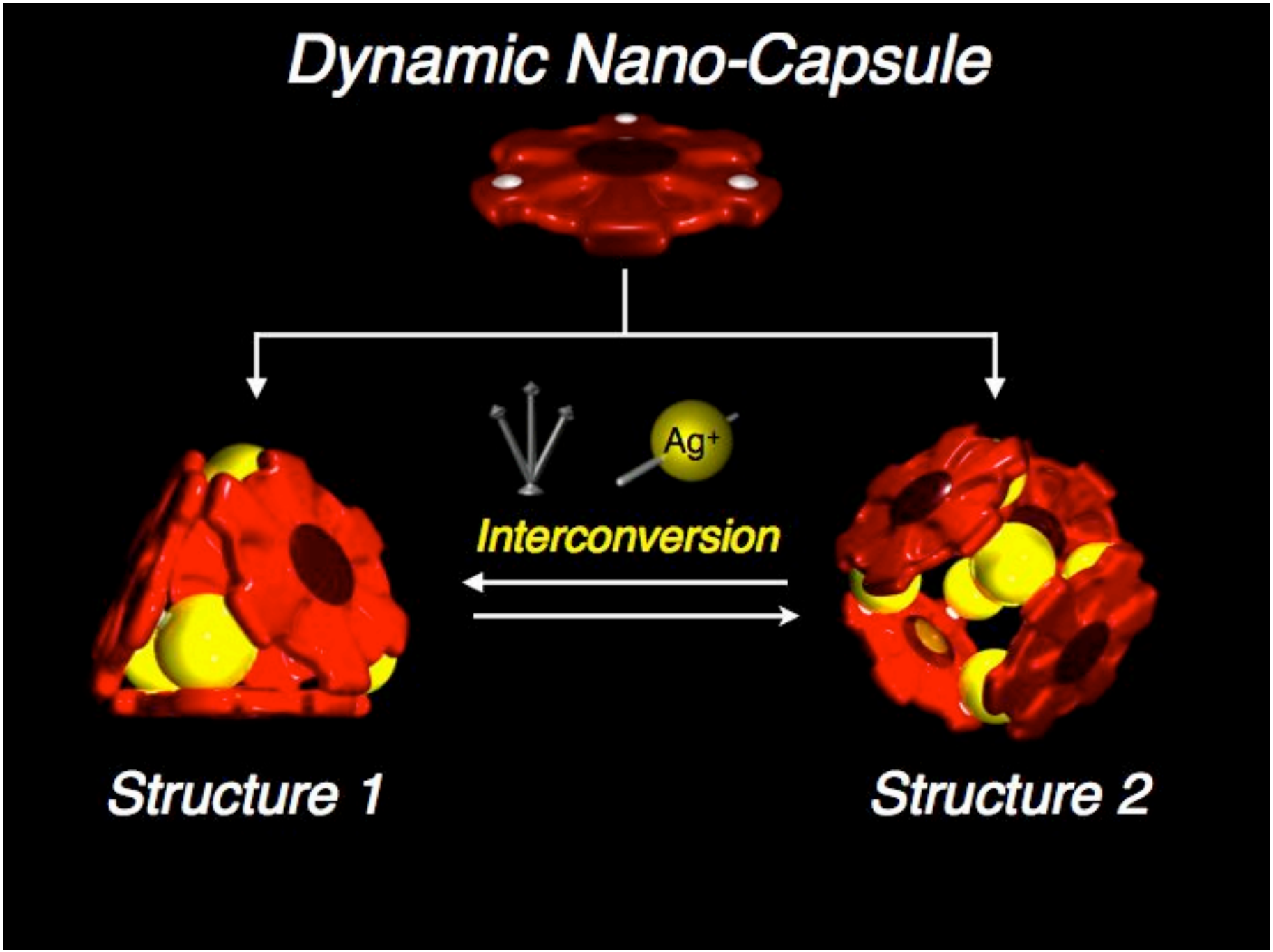
Raymond

- Moleculra recognition
- Chemical transformation

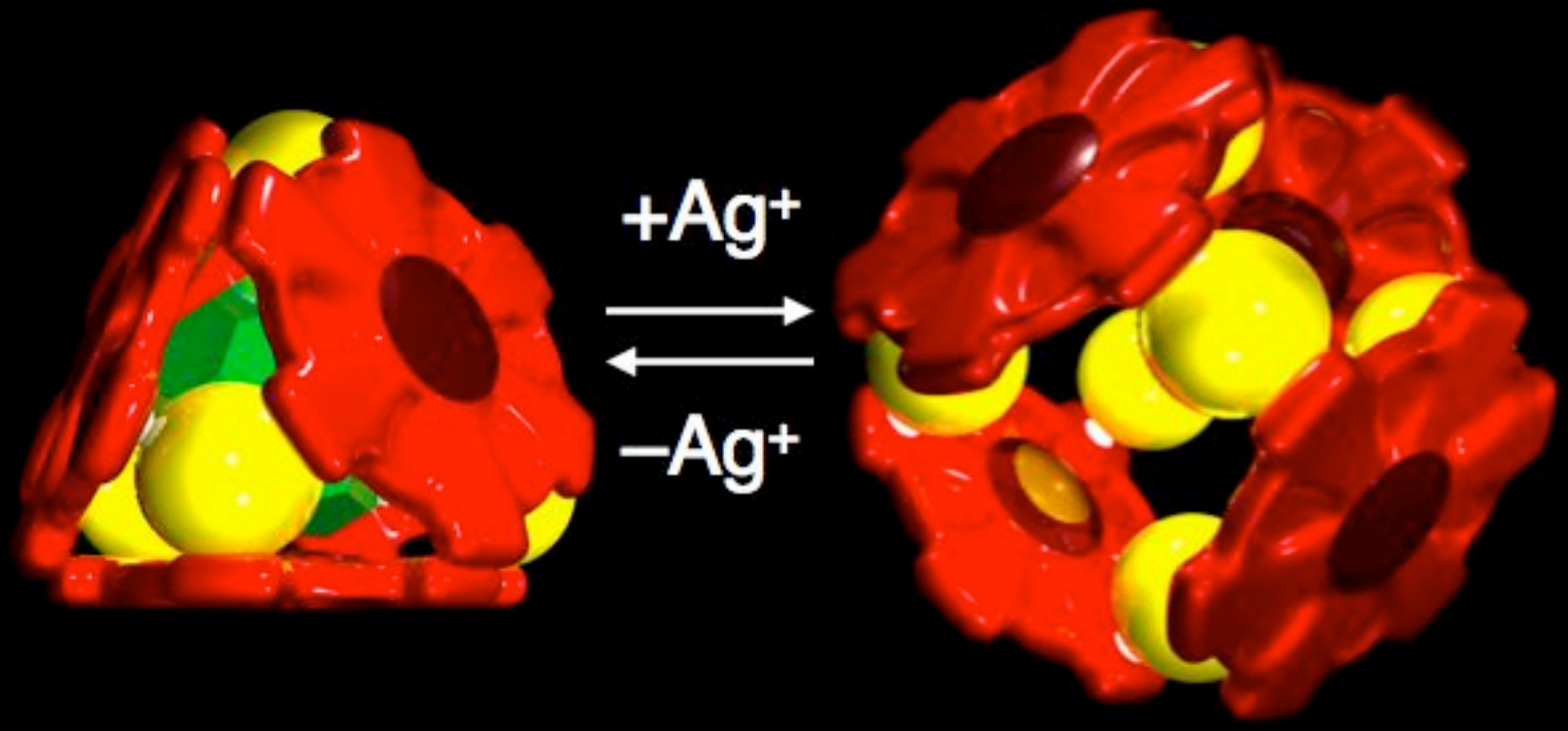

Ag+
Hg2+
Ag+
Ag+
Hg2+
Ag+
Hg2+
Mn Fe Cr Ni Cu Zn
Pd Cd
Pt Hg



J. Am. Chem. Soc. **2002**, *124*, 14510.


Dynamic Nano-Capsule
Ag+
Interconversion
Structure 1
Structure 2

Dynamic Nano-Capsule



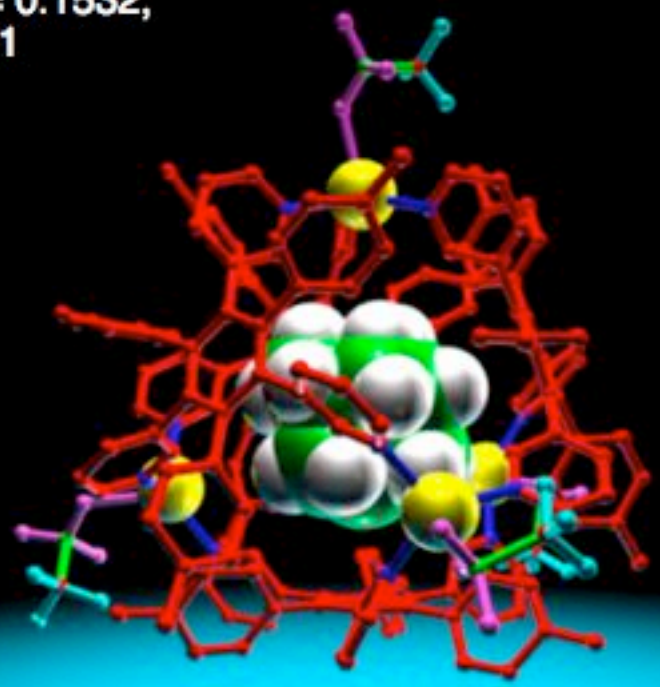
$G \subset Ag_4L_4$ Ag_6L_4

Angew. Chem. Int. Ed. **2005**, *44*, 2727.

Crystal Structure

Crystal Structure of Ag_4L_4 Capsule

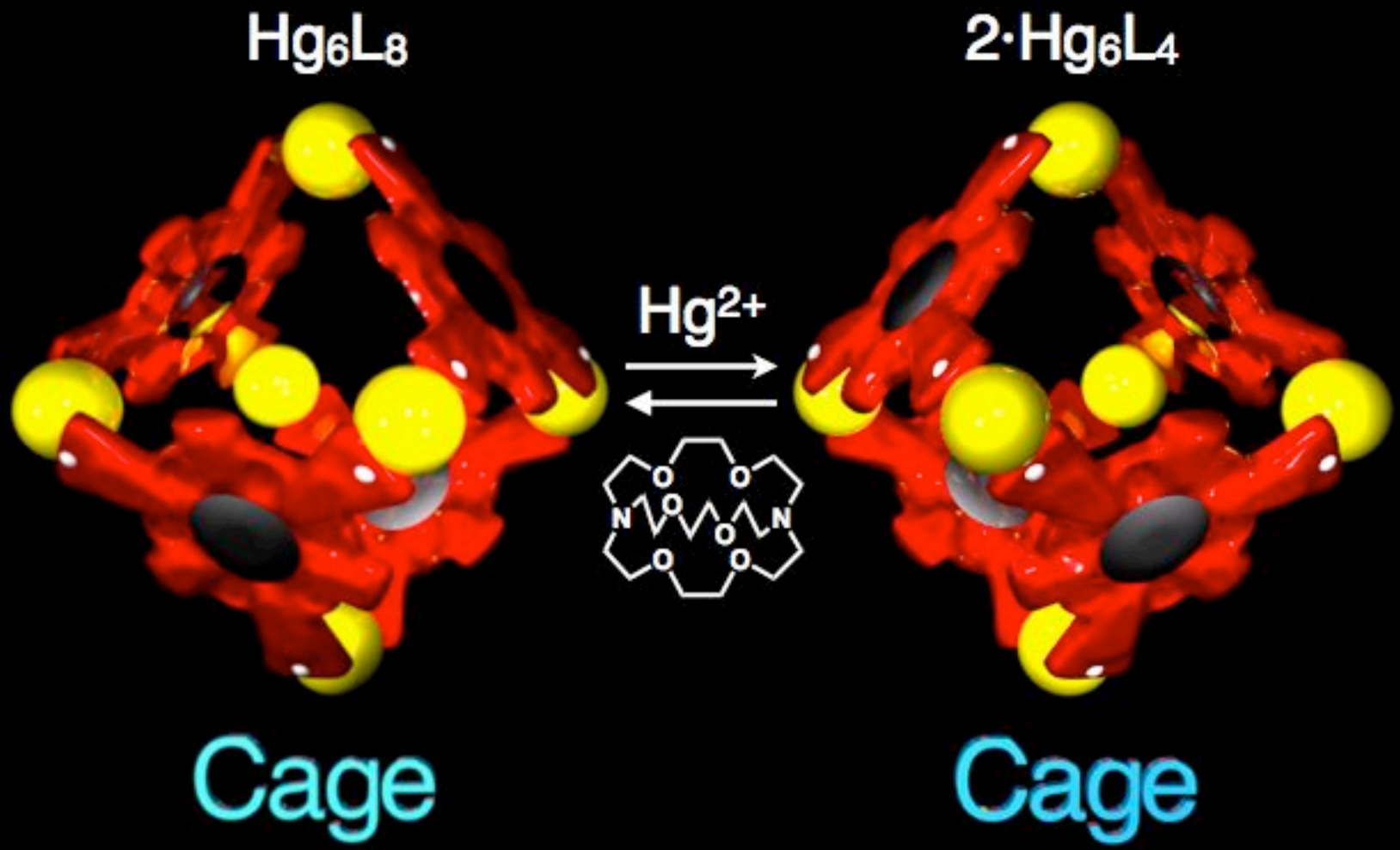
Crystal Data ($C_{185}H_{173}Ag_4F_{12}N_{15}O_{26}S_4$):
M = 3810.18, colorless, 0.20 x0.12x0.07 mm^3
orthorhombic, *Pccn*
a = 16.414(11), b = 32.34(2), c = 37.30(2)
V = 19800(21) $Å^3$, Z = 4, R_1 = 0.1532,
$wR(F_0^2)$ = 0.482, GOF = 1.091



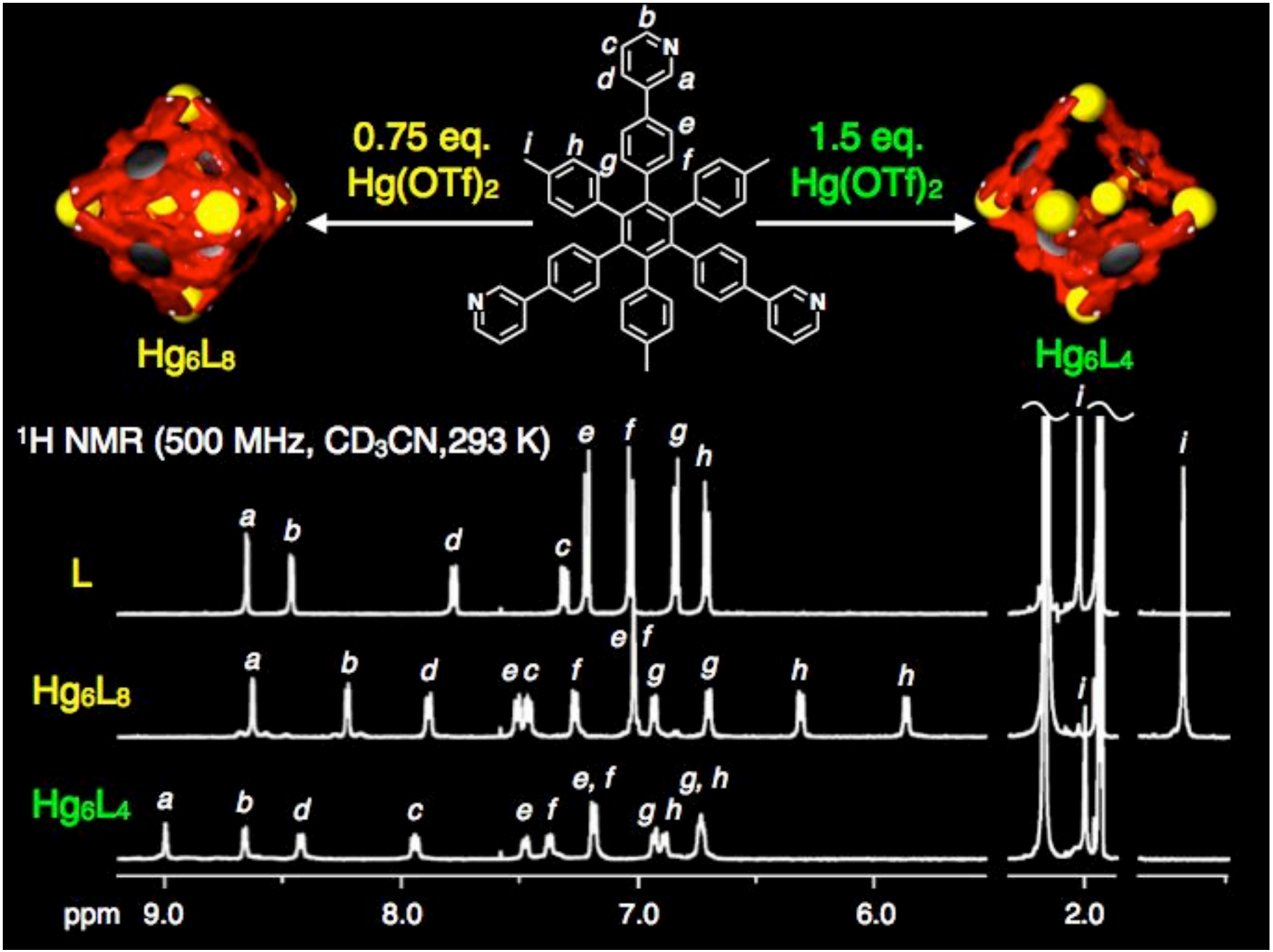
crystal structure of Ag(I) capsule

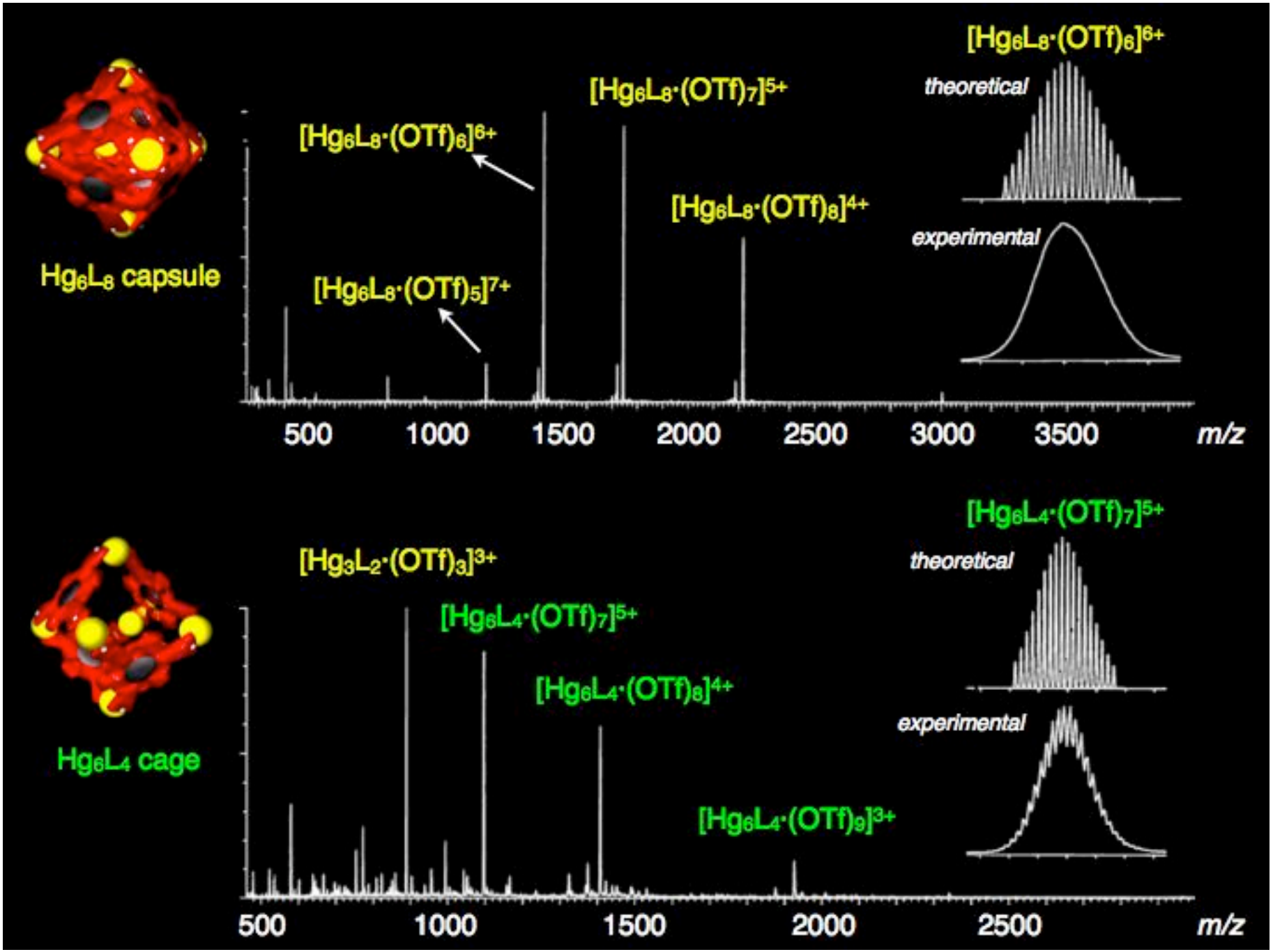
One more example

Interconversion

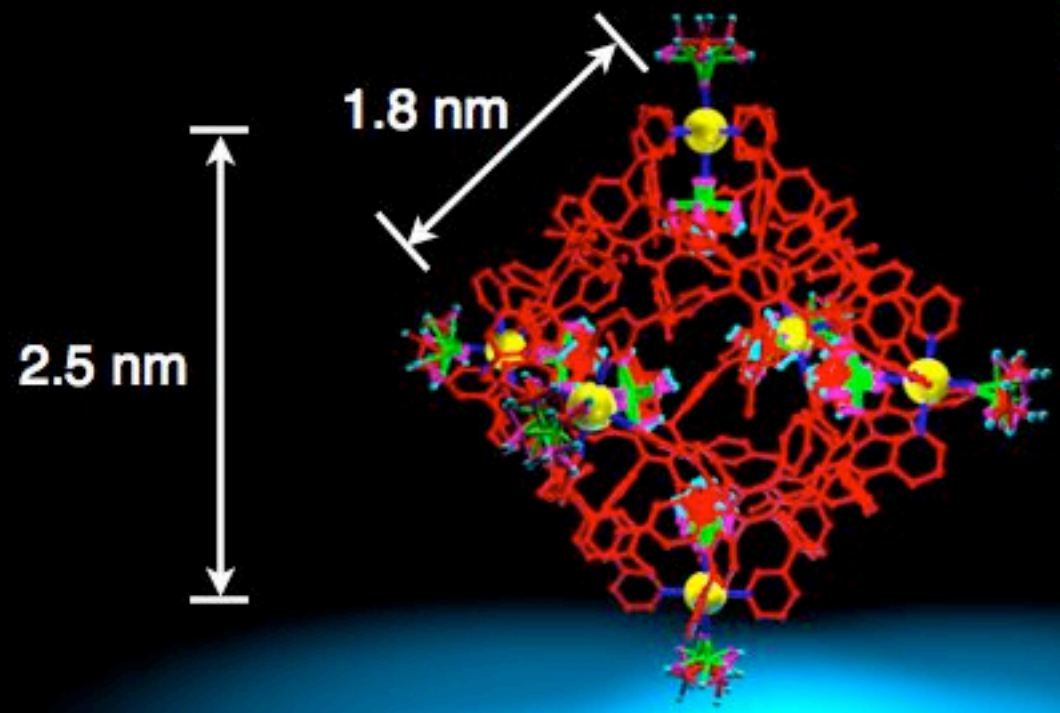


J. Am. Chem. Soc. in press


0.75 eq.
Hg(OTf)2
1.5 eq.
Hg(OTf)2
Hg6L8
Hg6L4
1H NMR (500 MHz, CD3CN,293 K)
L
Hg6L8
Hg6L4
ppm 9.0
8.0
7.0
6.0
2.0


Hg6L8 capsule
[Hg6L8·(OTf)6]6+
[Hg6L8·(OTf)7]5+
[Hg6L8·(OTf)5]7+
[Hg6L8·(OTf)8]4+
theoretical
experimental
500
1000
1500
2000
2500
3000
3500
m/z
Hg6L4 cage
[Hg3L2·(OTf)3]3+
[Hg6L4·(OTf)7]5+
[Hg6L4·(OTf)8]4+
[Hg6L4·(OTf)9]3+
theoretical
experimental
500
1000
1500
2000
2500
m/z

Crystal Structure of Hg_6L_8

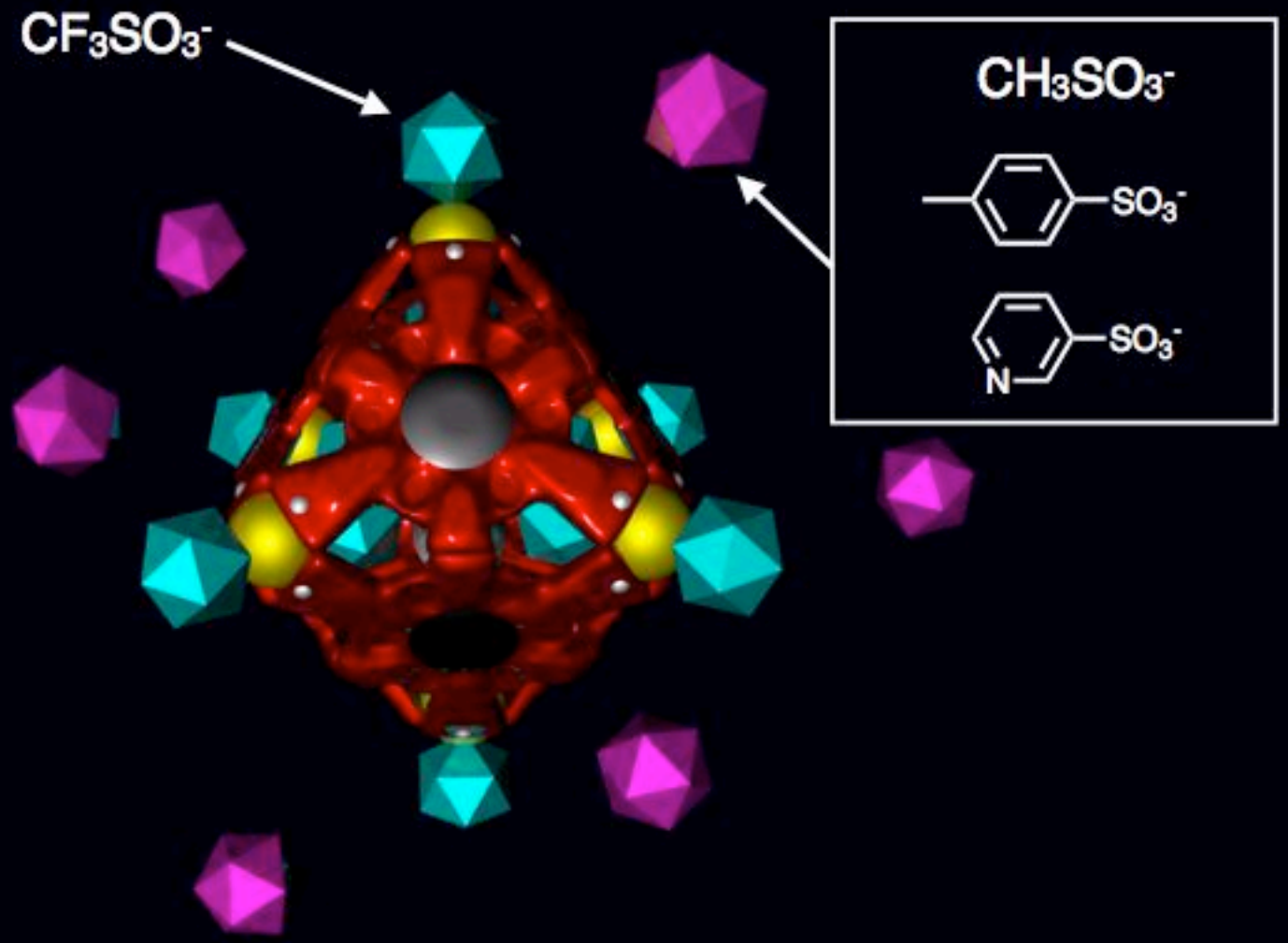


Crystal Data

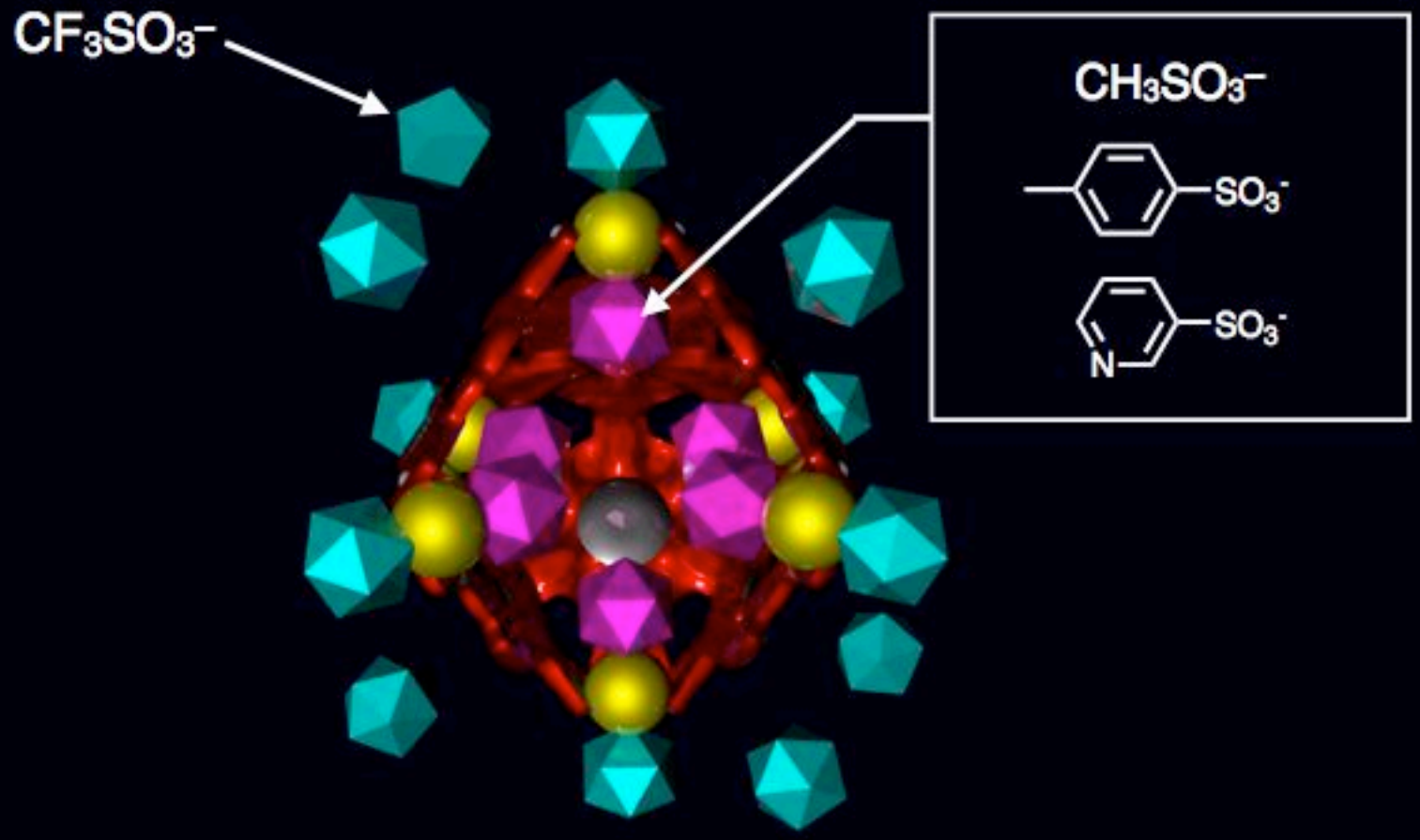
Cubic, Space Group: *F*432
$a = b = c = 48.0818(13)$ Å
$V = 111158(5)$ Å^3 , $Z = 4$
$R_1 = 0.0901$, $wR(F_o^2) = 0.2868$
GOF = 0.968

Crystal structure of Hg(II)-capsule

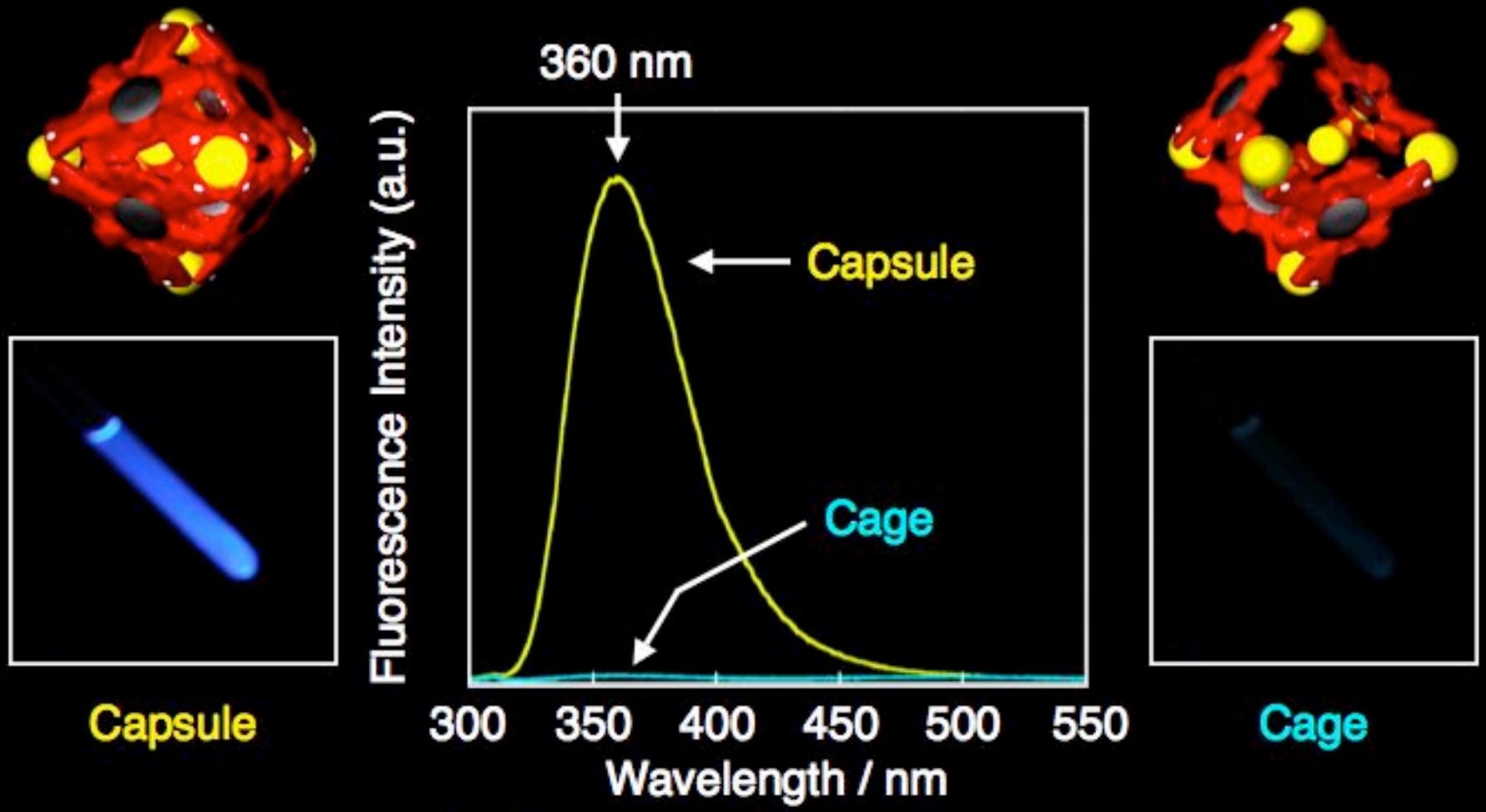
Selective Exchange



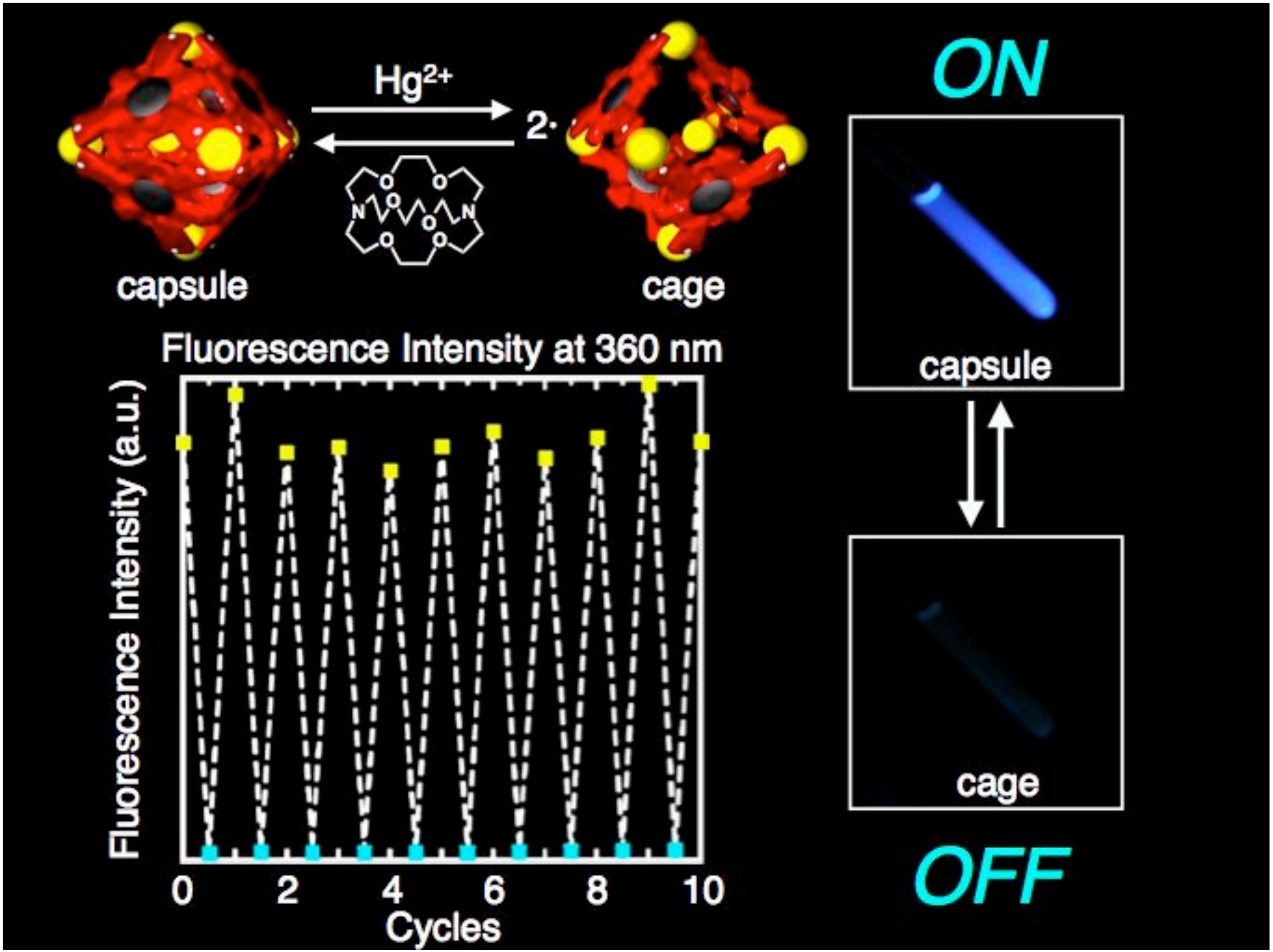
Selective Exchange



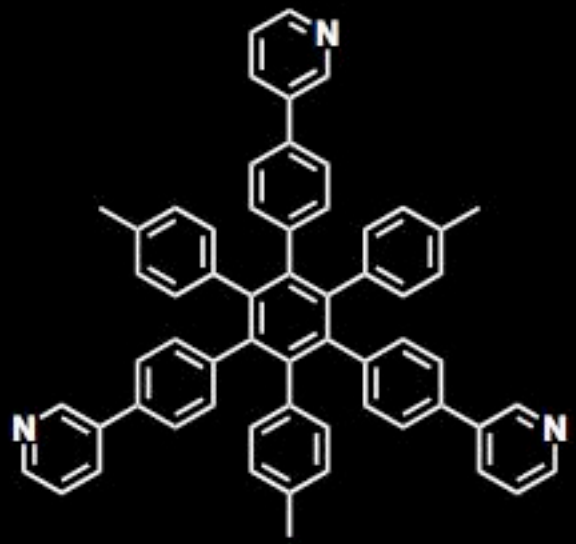
Emission Spectra



(excitation: 284 nm, CH_3CN, 293 K, [L] = 10 μM)


Hg2+
2·
capsule
cage
ON
capsule
cage
OFF
Fluorescence Intensity at 360 nm
Fluorescence Intensity (a.u.)
0
2
4
6
8
10
Cycles

Coordination Molecular Capsules

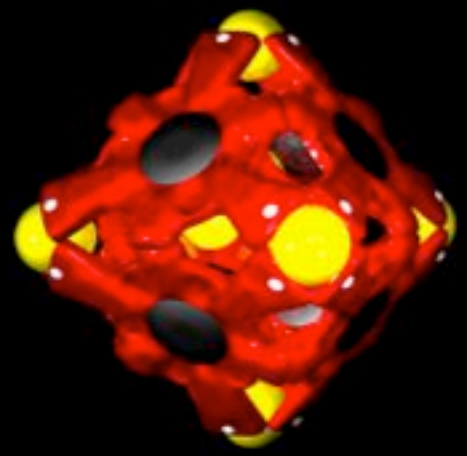


Ten Kinds of Metal Ions

Mn	Fe	Co	Ni	Cu	Zn
Tc	Ru	Rh	Pd	Ag	Cd
Re	Os	Ir	Pt	Au	Hg

Disk-Shaped Ligand (L)

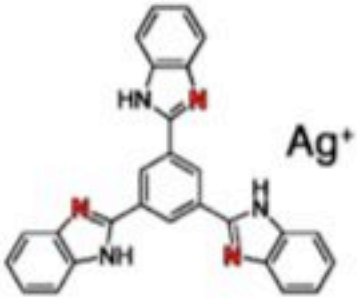
M^{2+} →

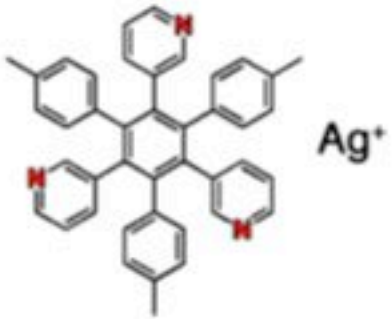


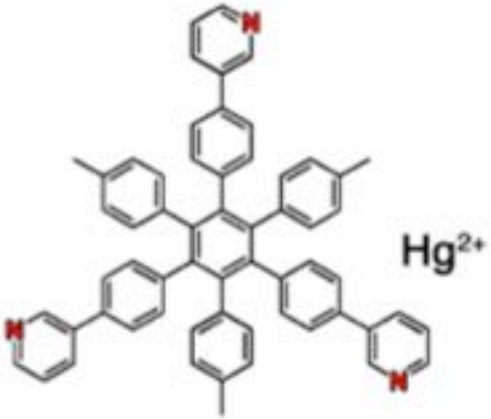
M_6L_8

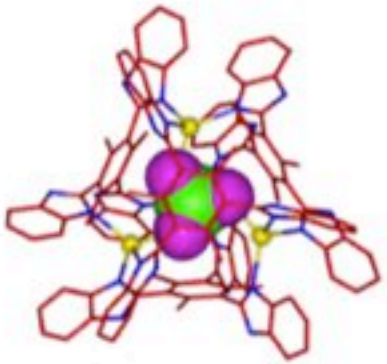
Octahedron-shaped
Nanocapsules

VIP paper & cover picture
Angew. Chem. Int. Ed. 45, 6488 (2006)

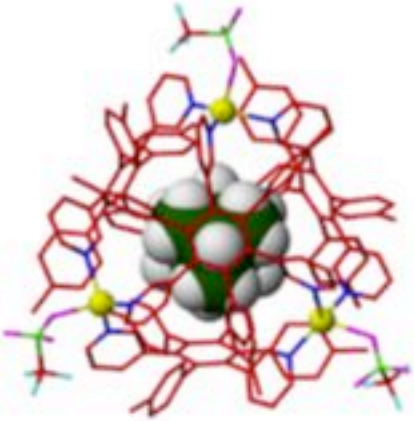




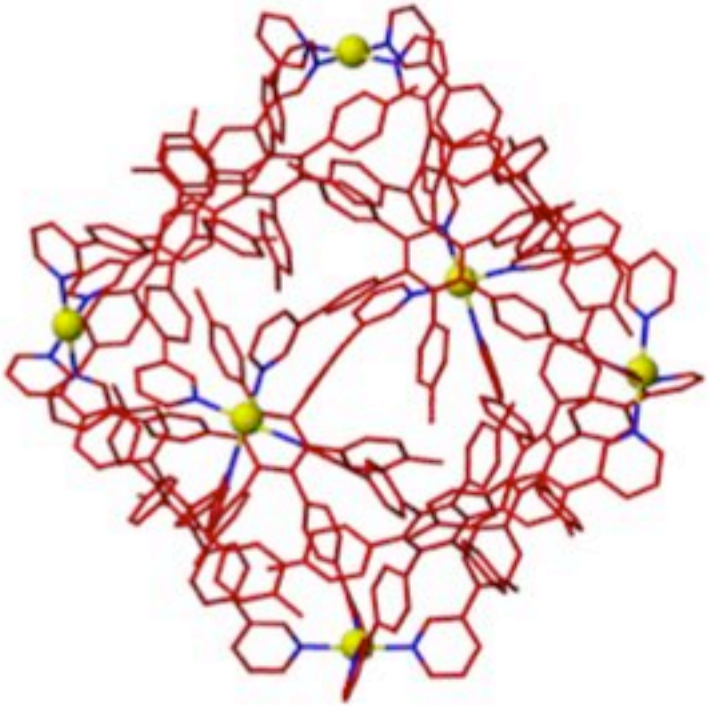




M-M = 0.6 nm
V = 40 Å^3



M-M = 1.0 nm
V = 200 Å^3



M-M = 1.8 nm
V = 2700 Å^3

Motion

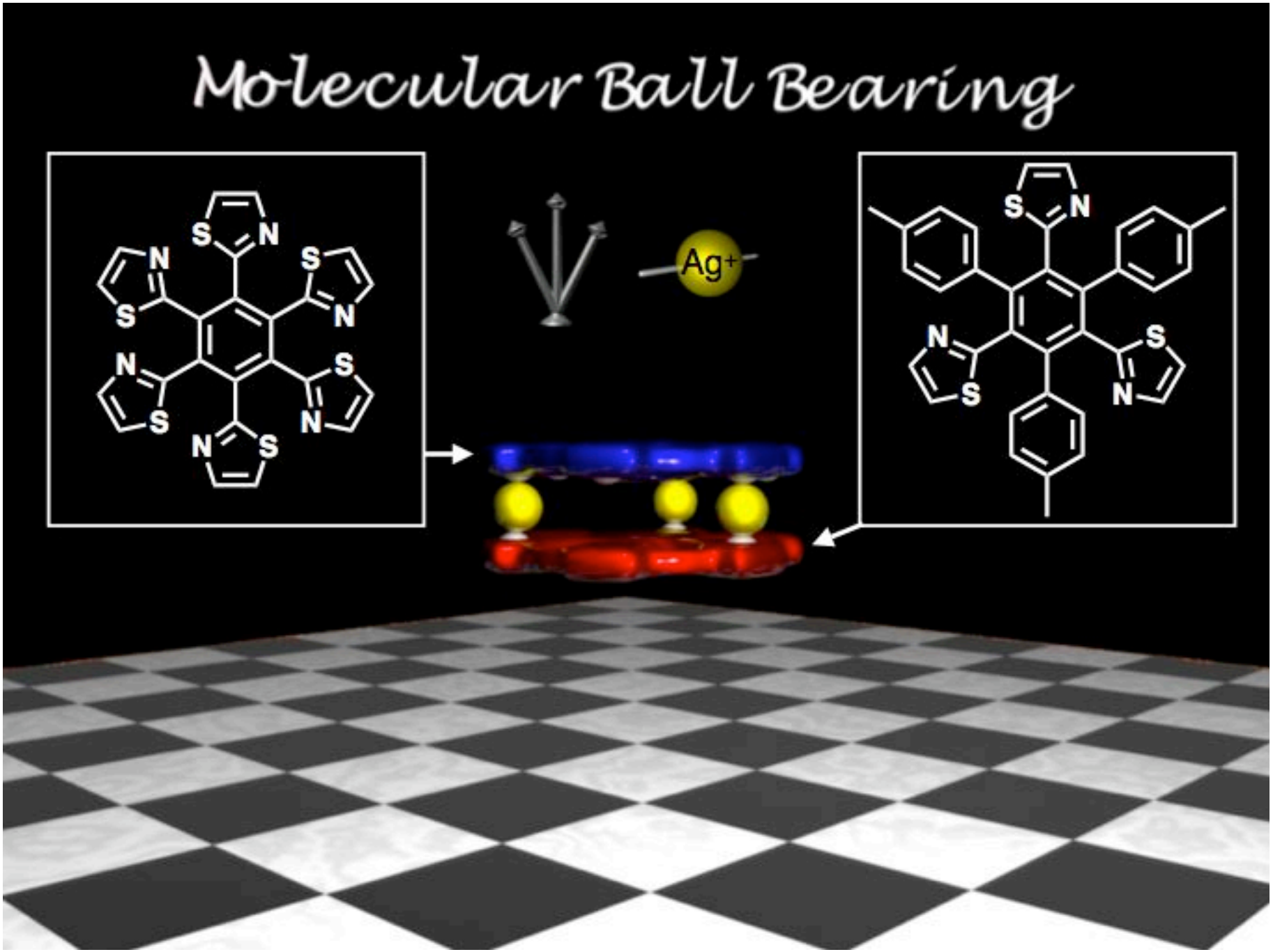
Molecular Ball Bearing

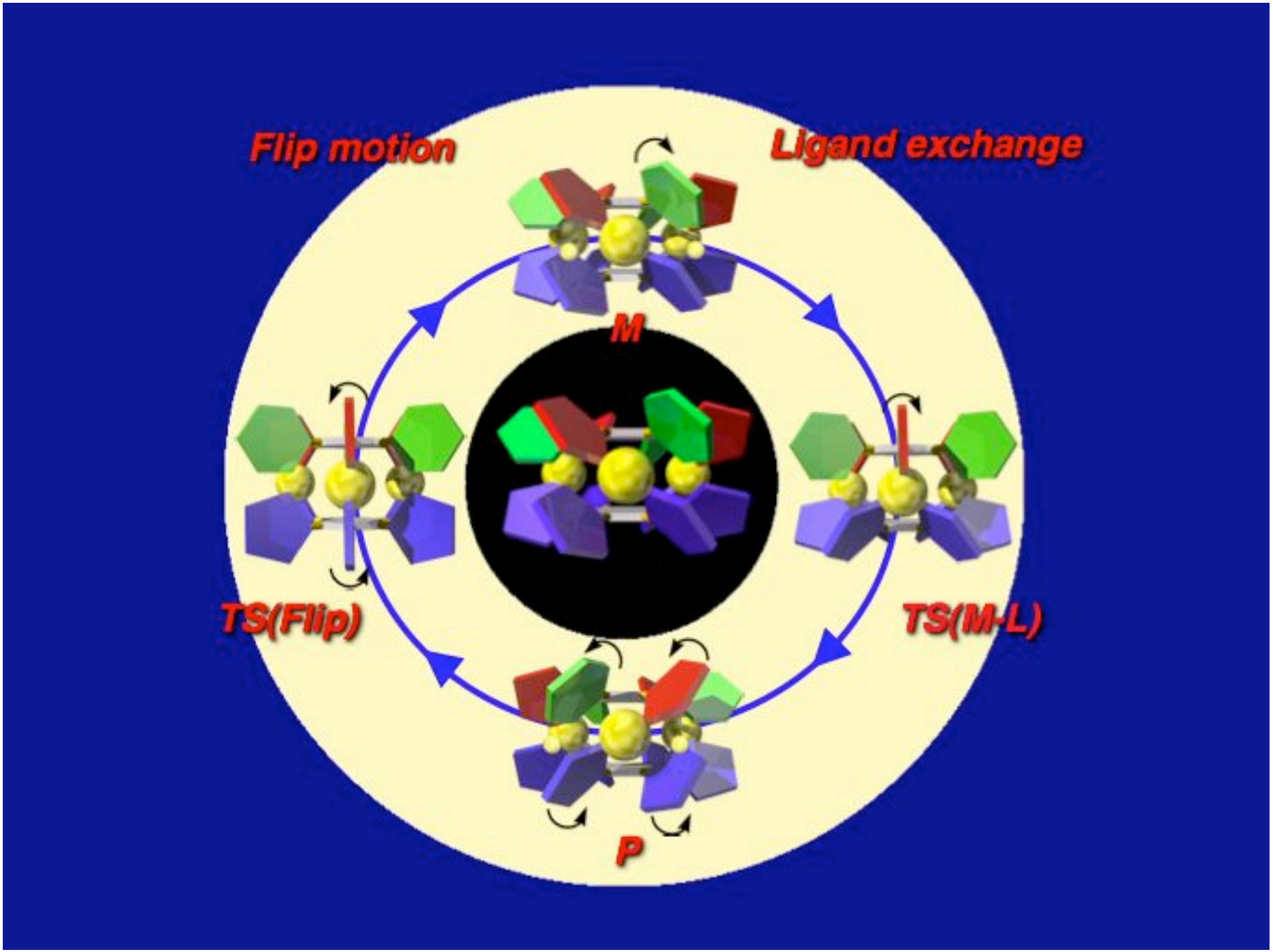
Thrust Ball Bearings

Highlighted in *Nature*, **2004**, *427*, 597

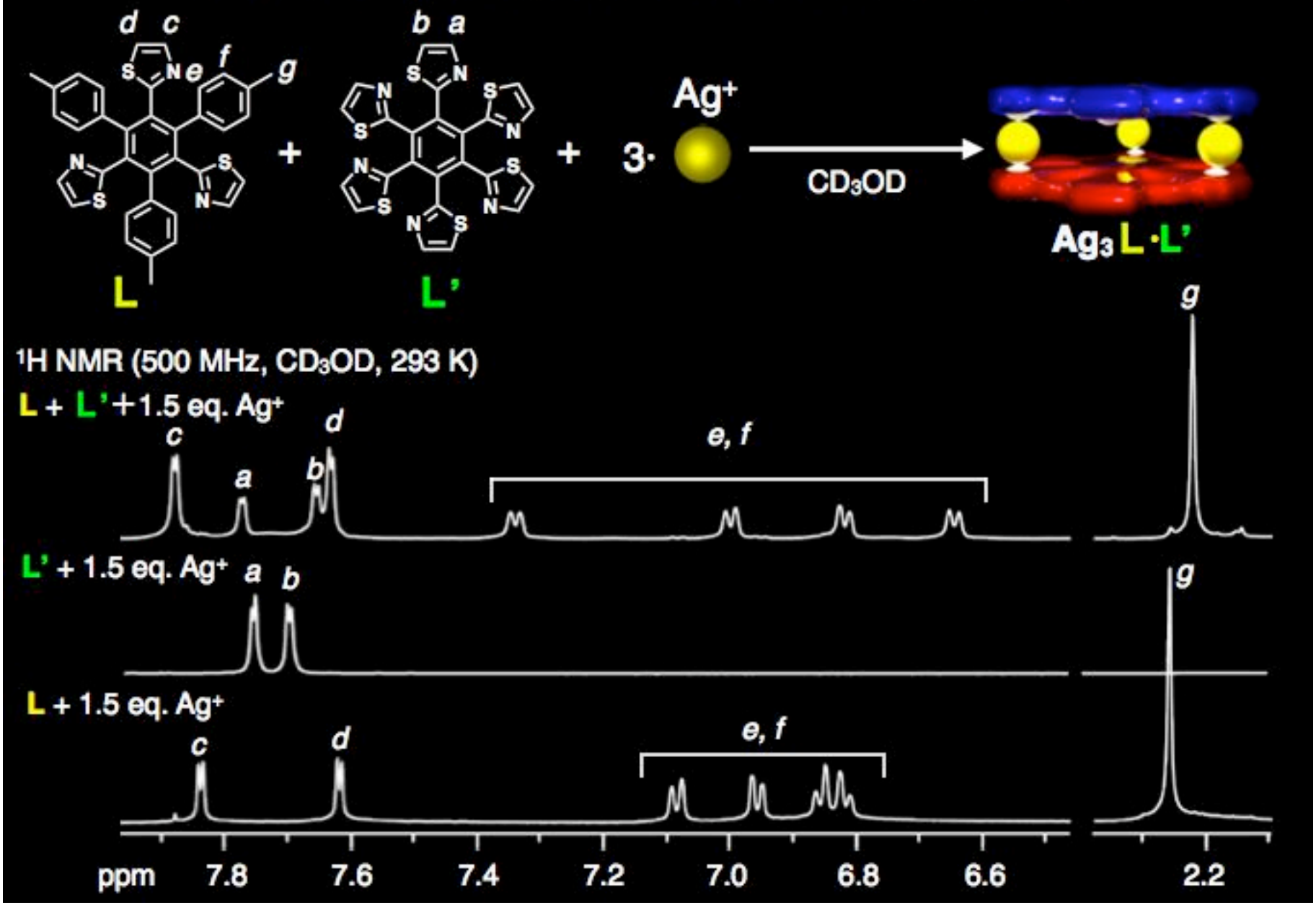
J. Am. Chem. Soc., **2002**, *124*, 14510
Angew. Chem. Int. Ed., **2003**, *42*, 5182
J. Am. Chem. Soc., **2004**, *126*, 1214.
Angew. Chem. Int. Ed., **2004**, *43*, 3814.

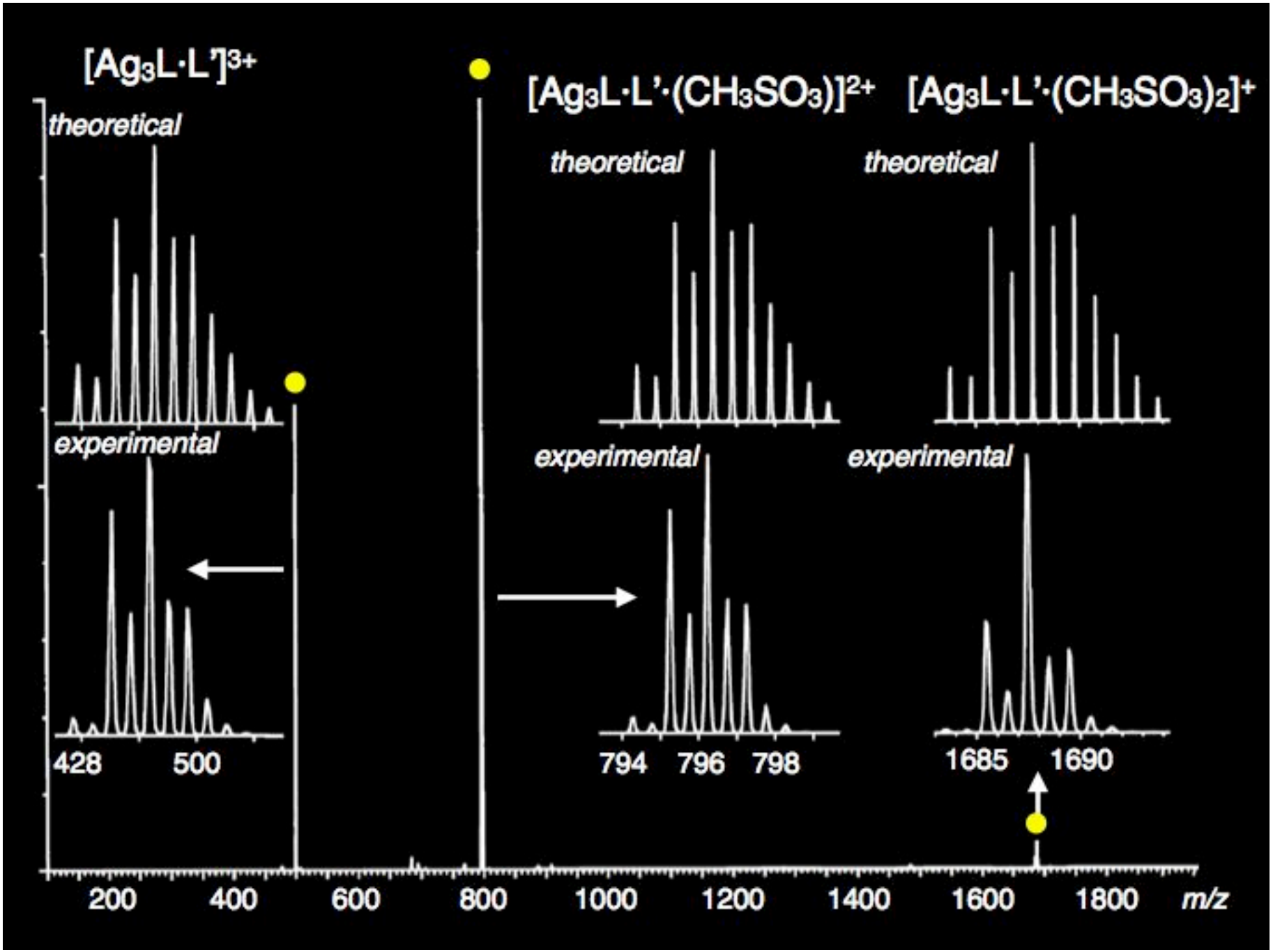
Molecular Ball Bearing



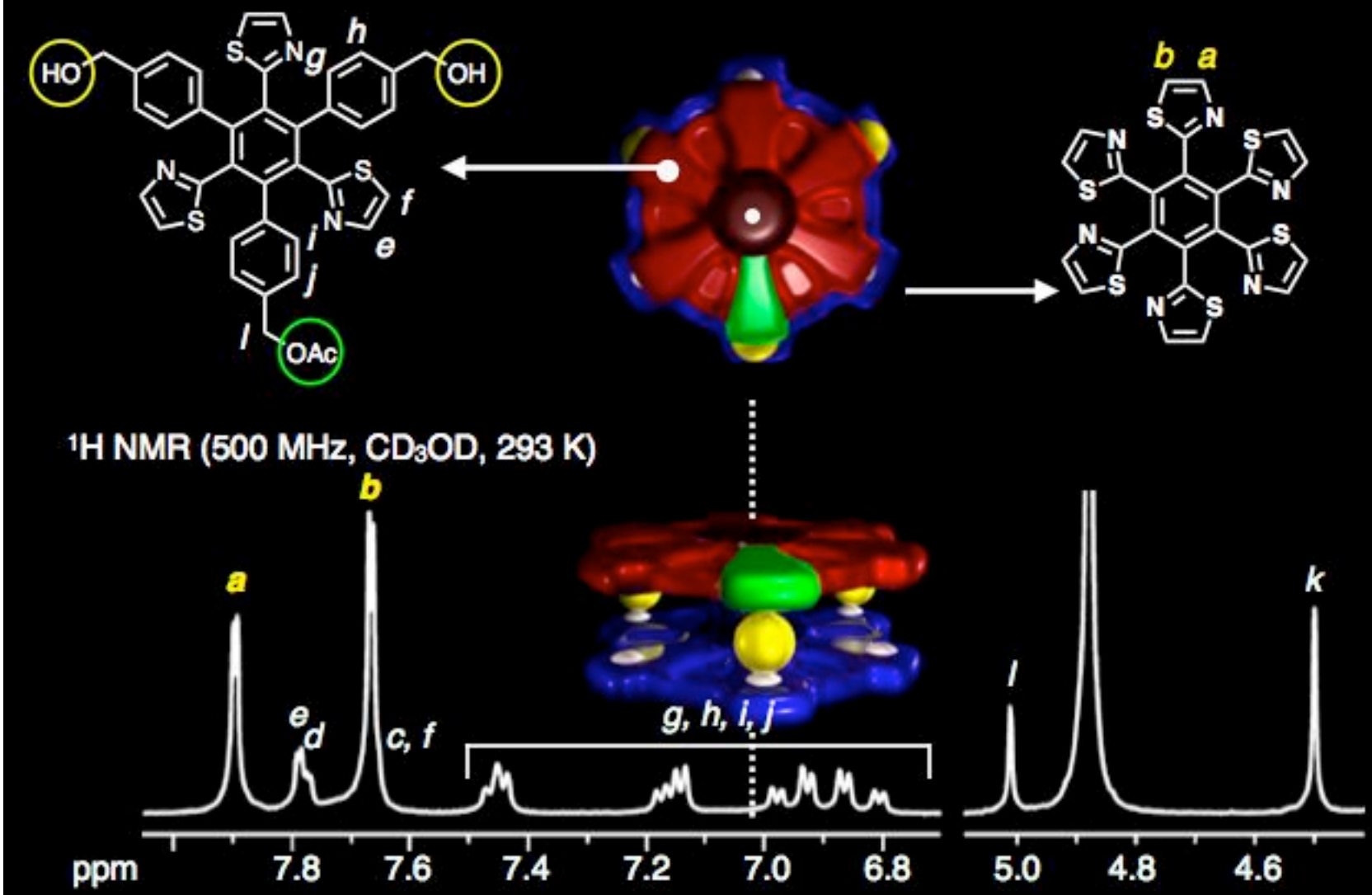

Flip motion
Ligand exchange
M
TS(Flip)
TS(M-L)
P

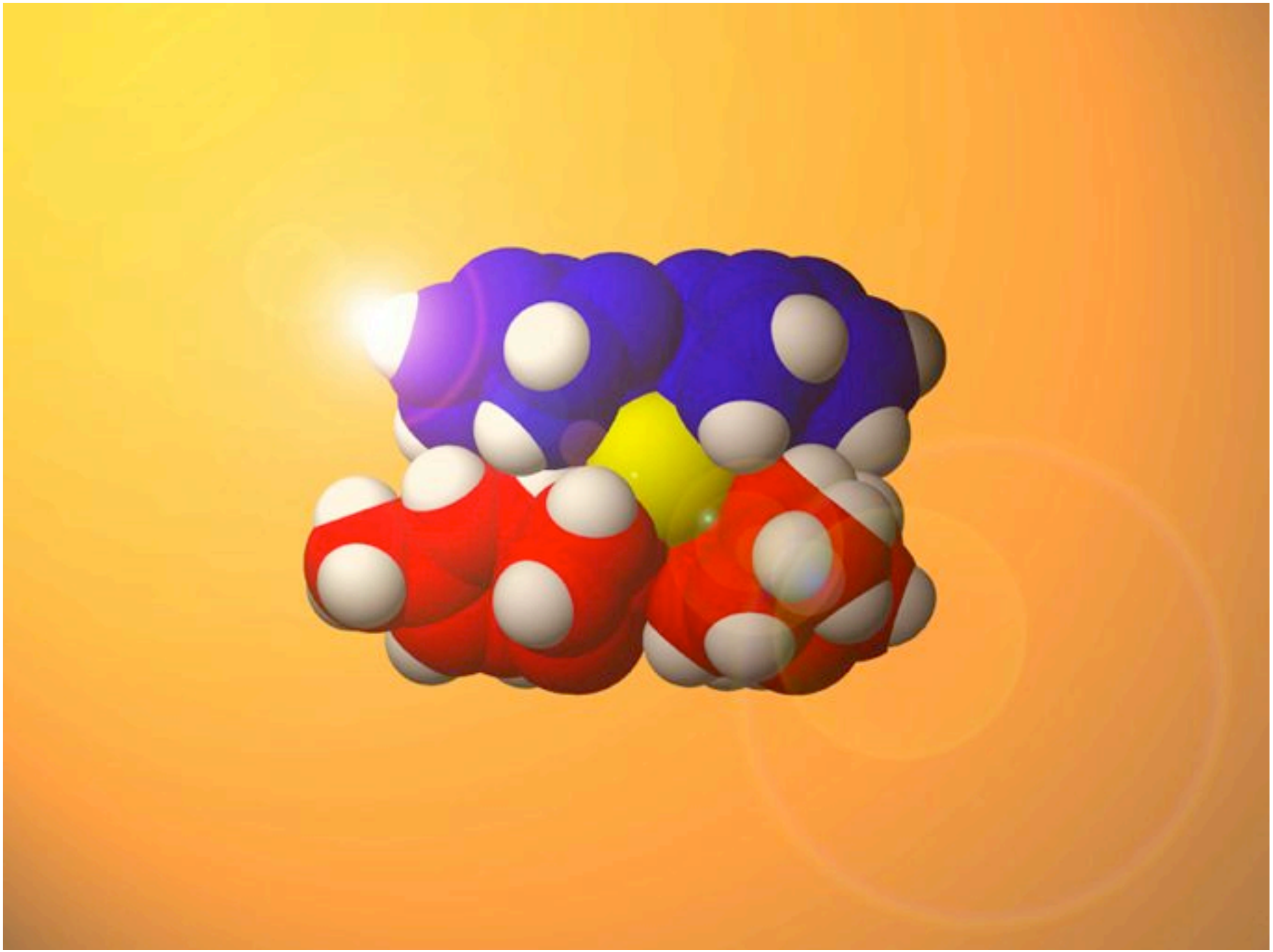
Formation of Molecular BB

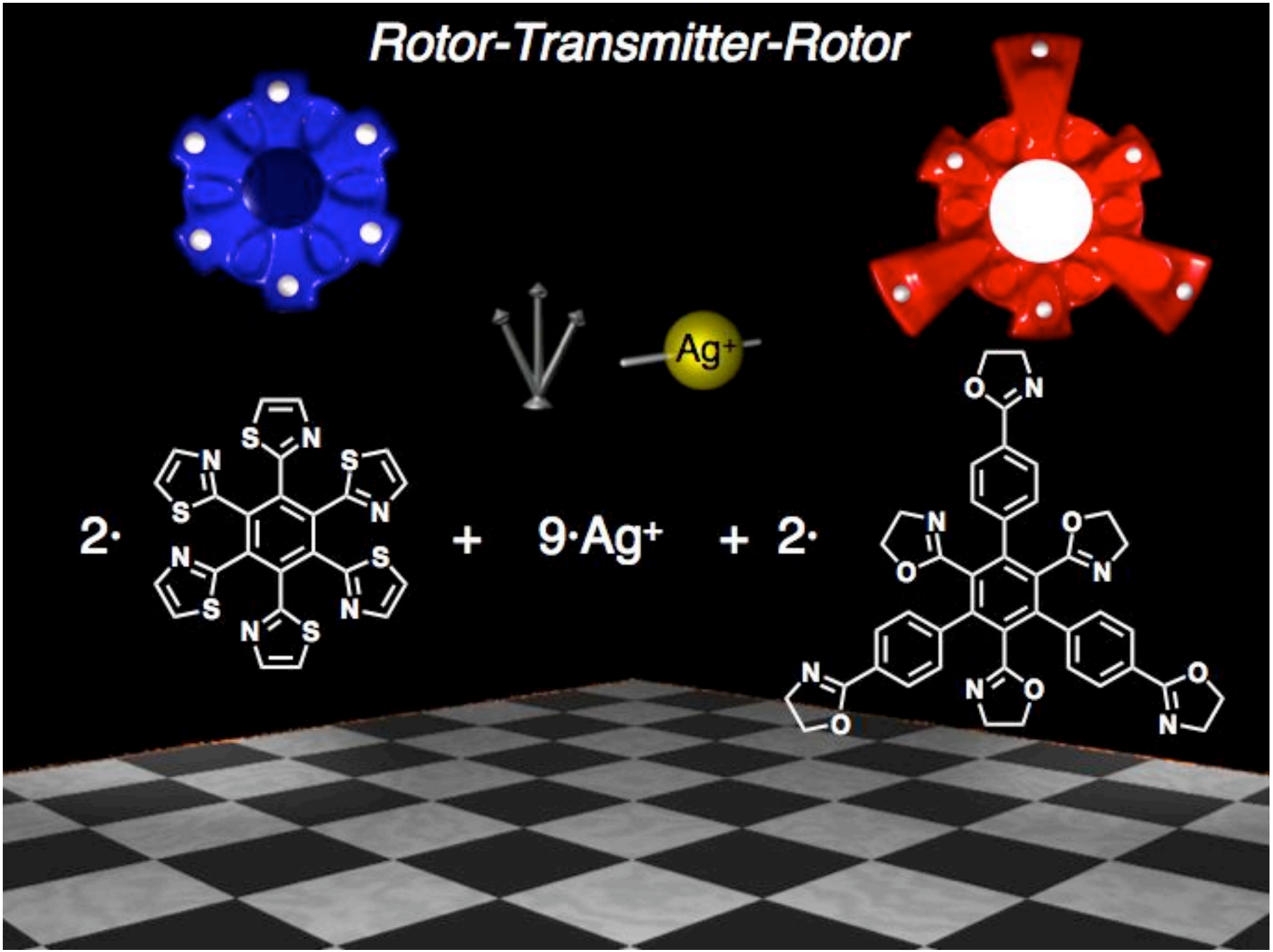


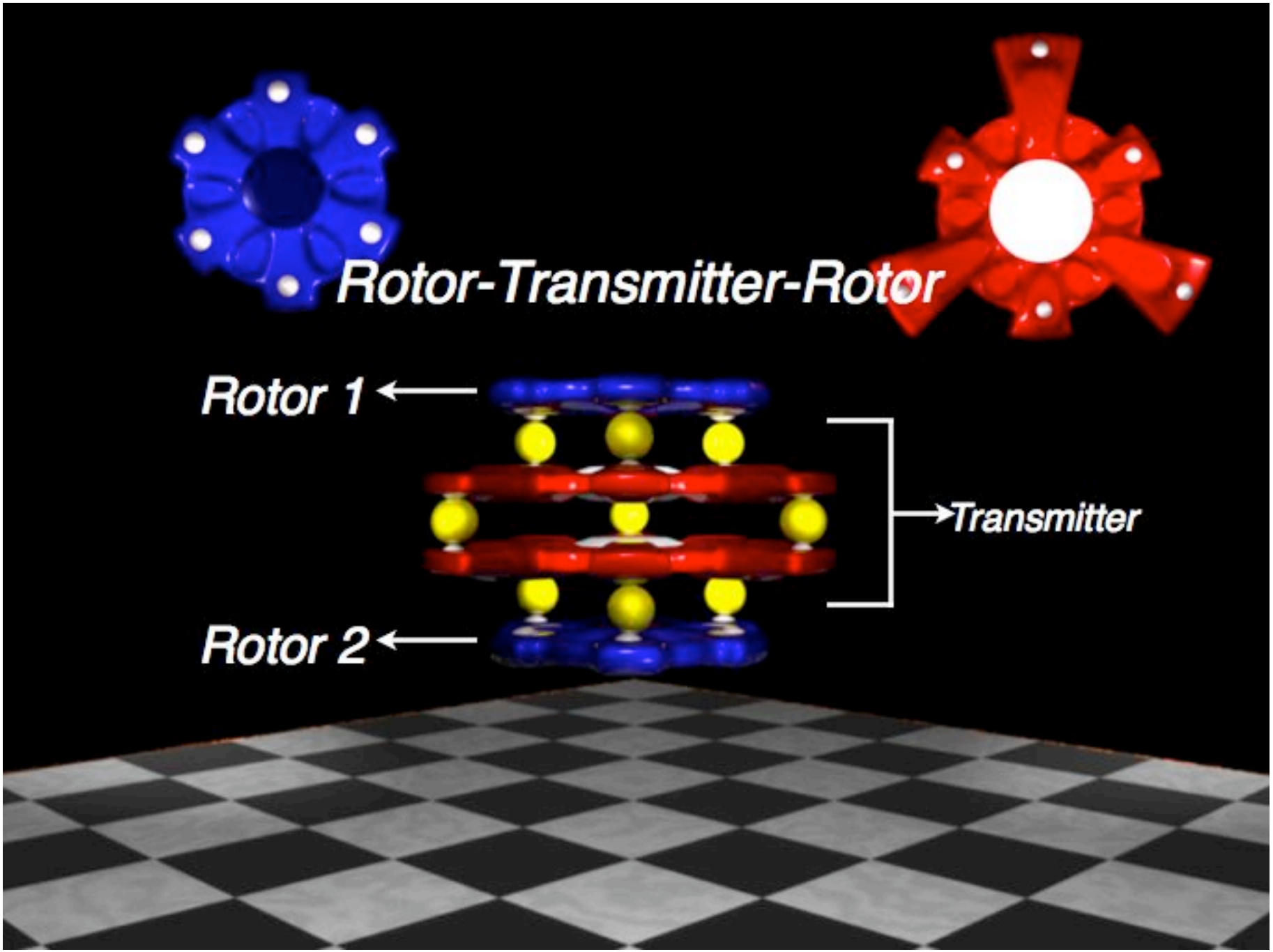

[Ag3L·L']3+
theoretical
experimental
428
500
[Ag3L·L'·(CH3SO3)]2+
theoretical
experimental
794
796
798
[Ag3L·L'·(CH3SO3)2]+
theoretical
experimental
1685
1690
200
400
600
800
1000
1200
1400
1600
1800
m/z

Full Rotation



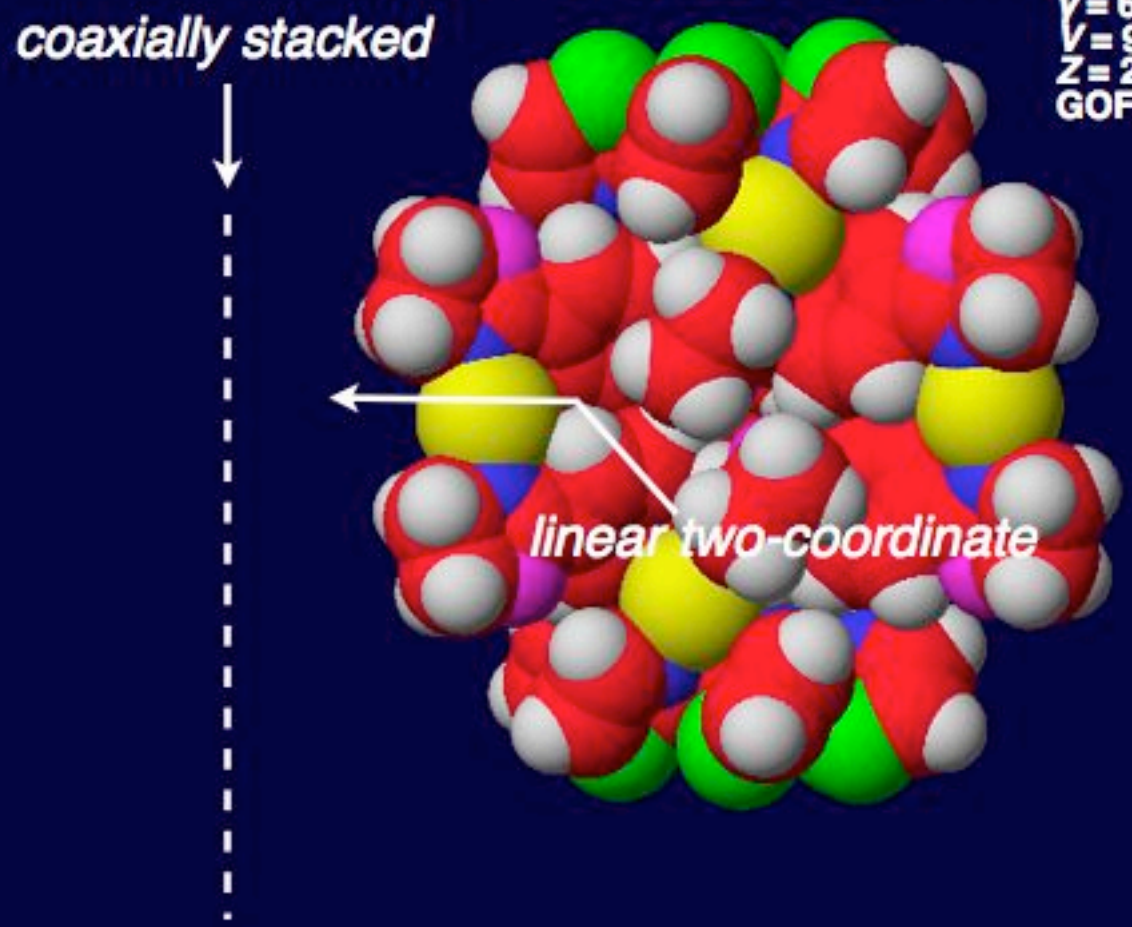



Rotor-Transmitter-Rotor
Ag+
2·
+ 9·Ag+ + 2·


Rotor-Transmitter-Rotor
Rotor 1
Transmitter
Rotor 2

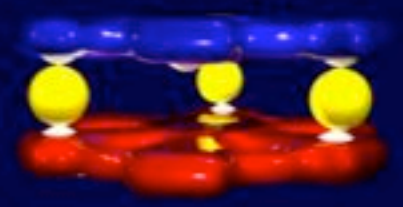
Rotor-Transmitter-Rotor

crystal data:
Formula: $C_{132}H_{72}Ag_9N_{24}O_{12}S_{12}$
$9\cdot(CF_3SO_3)\ 7\cdot(CH_4O)$
triclinic, P1,
a = 21.2194(9) Å, b = 21.3055(8) Å
c = 24.4632(10) Å
α = 79.325(3)°, β = 79.310(3)°
γ = 63.263(3)°
V = 9673.3(7) Å^3
Z = 2, R = 0.1345, wR = 0.3908
GOF = 1.055



Rate of Ligand Exchange

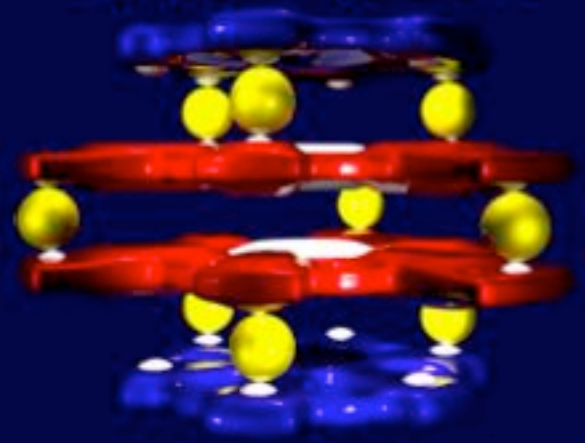
k_{298} = 250,000 s^{-1}



$Ag_3 1 \cdot 3$

$\Delta G^{\ddagger}_{298}$ = 54.4 kJ mol^{-1}

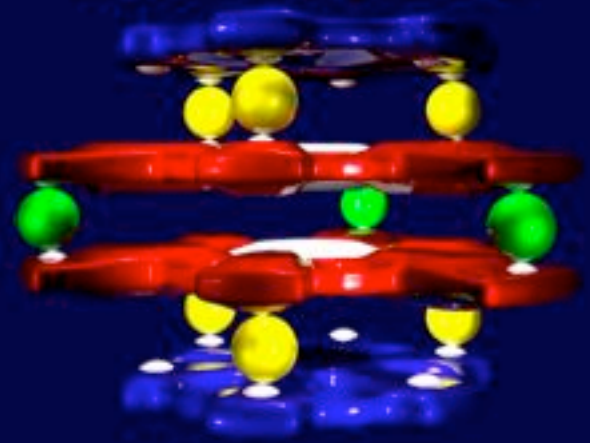
k_{298} = 4,500 s^{-1}



$Ag_9 \cdot 2_2 \cdot 3_2$

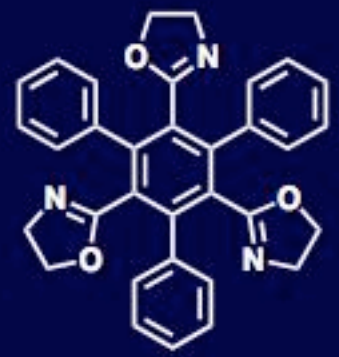
$\Delta G^{\ddagger}_{298}$ = 64.8 kJ mol^{-1}

k_{298} = 2,500 s^{-1}

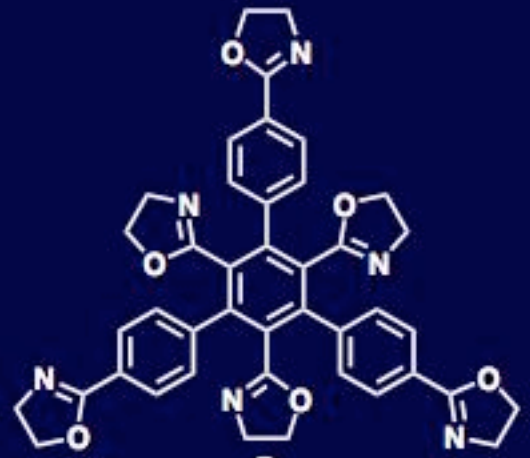


$Ag_6Hg_3 \cdot 2_2 \cdot 3_2$

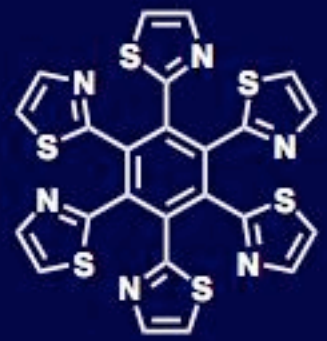
$\Delta G^{\ddagger}_{298}$ = 66.3 kJ mol^{-1}



1

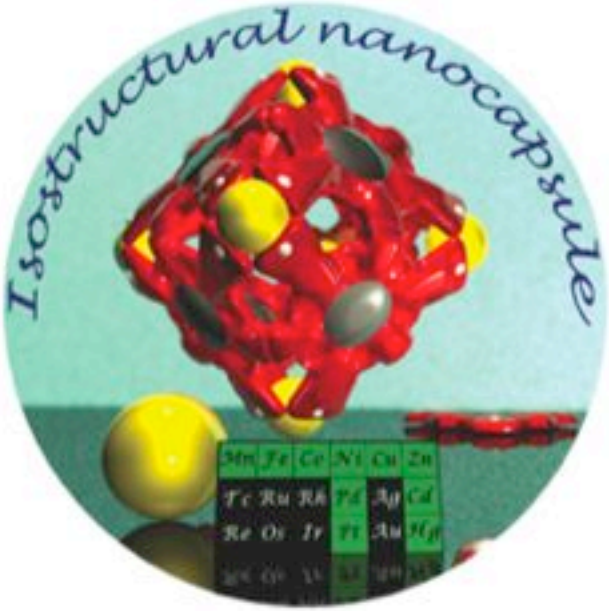


2



3

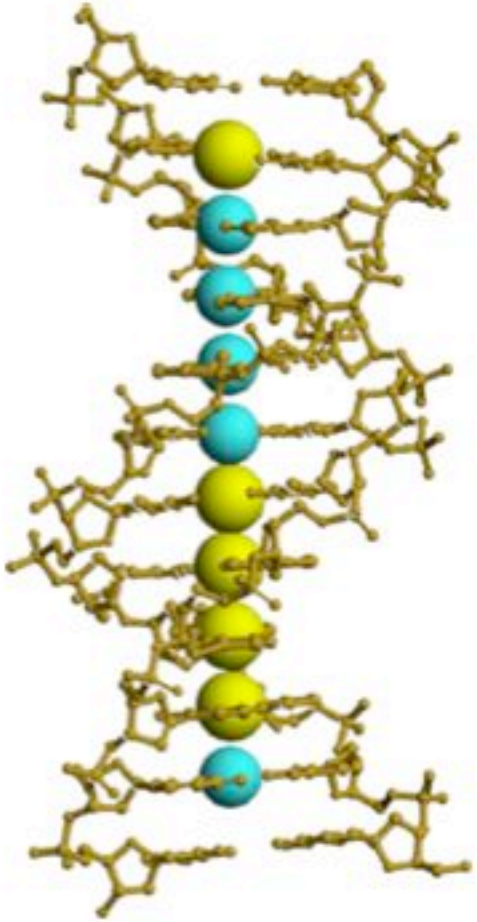
Space



Nanocapsules

J. Am. Chem. Soc.
2002, 2006, 2007
Angew. Chem. 2005, 2006

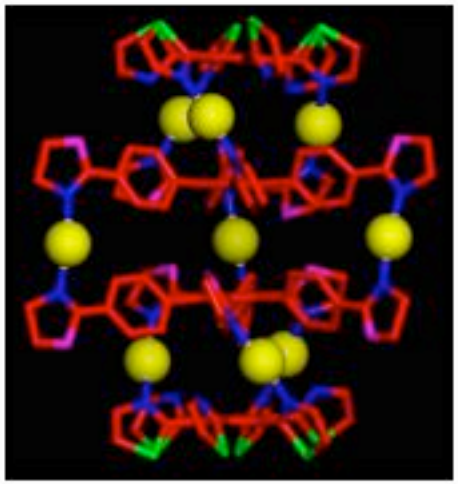
Array



Metallo-DNA

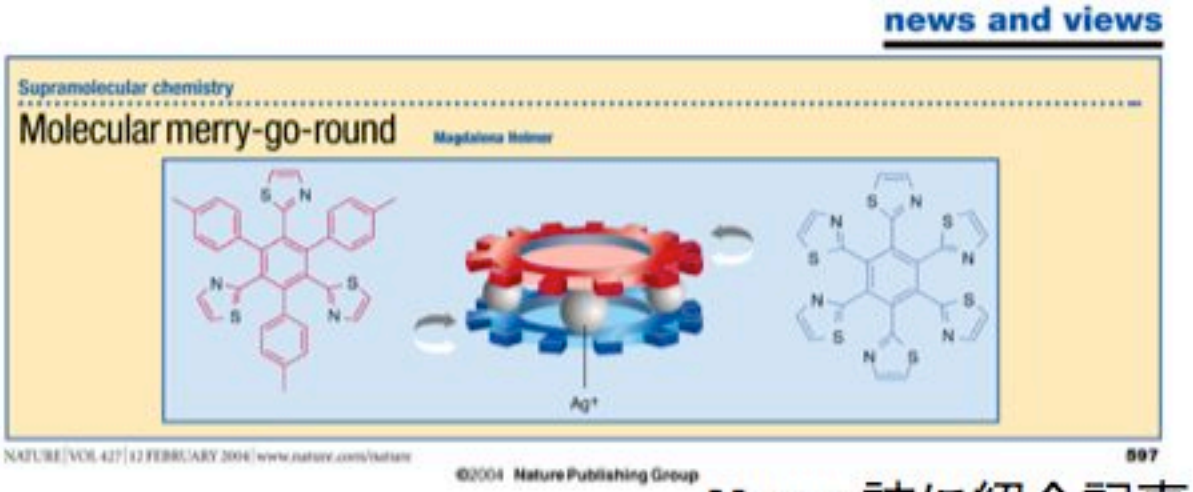
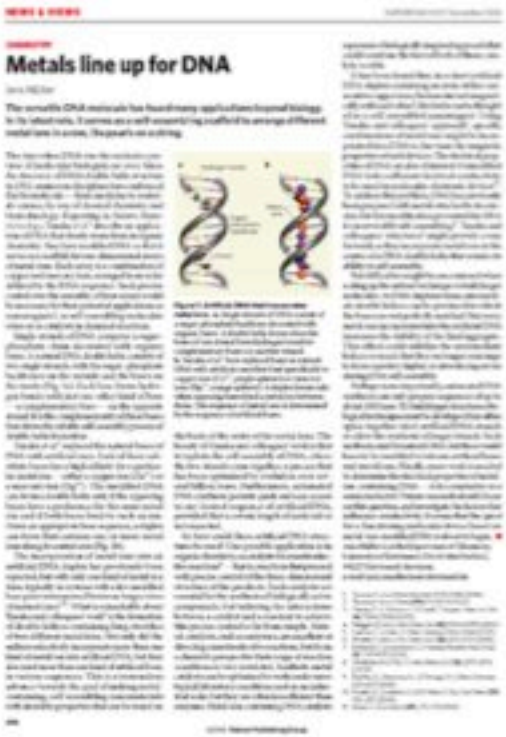
J. Org. Chem. 1999
J. Am. Chem. Soc. 2002, 2003
Science 2003
Nature Nanotech. 2006

Motion



Molecular Machines

(Rotor-Transmitter-Rotor)
J. Am. Chem. Soc. 2004, 2006
Angew. Chem. 2003, 2004
Submitted for publication



*Nature*誌に紹介記事