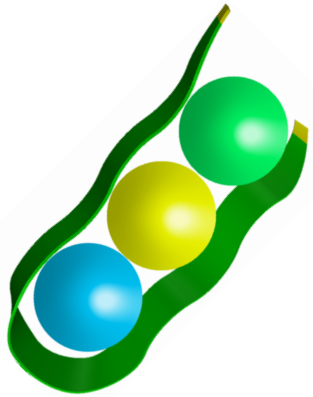
International Workshop on DNA-based nanotechnology:
Construction, mechanics, and electronics
May 11-15, 2009
Max-Planck Institut für Physik komplexer Systeme, Dresden, Germany

Metal Strings in Artificial DNA

(The Univ. of Tokyo) Mitsuhiko Shionoya

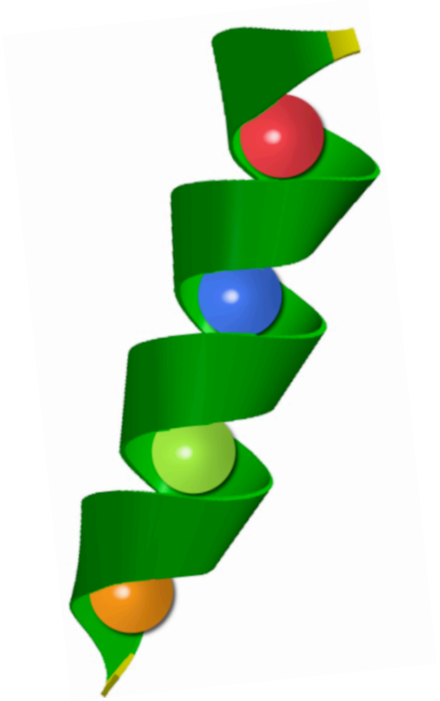
Bio-inspired Novel Structural Motifs with Metals



Hair-pin

β-Sheet

ds-Helix



α-Helix

Chemical Bonding in Molecular Architectures

Atoms ——bonding——> Molecules ——bonding——> Assemblies

Covalent

Stronger & Rigid
Irreversible
Rotation
X—Y, **X=Y**, *etc*

Noncovalent

Weaker but Flexible
Reversible
Exchange / Motion
X—Metal, **XH---Y**, *etc*

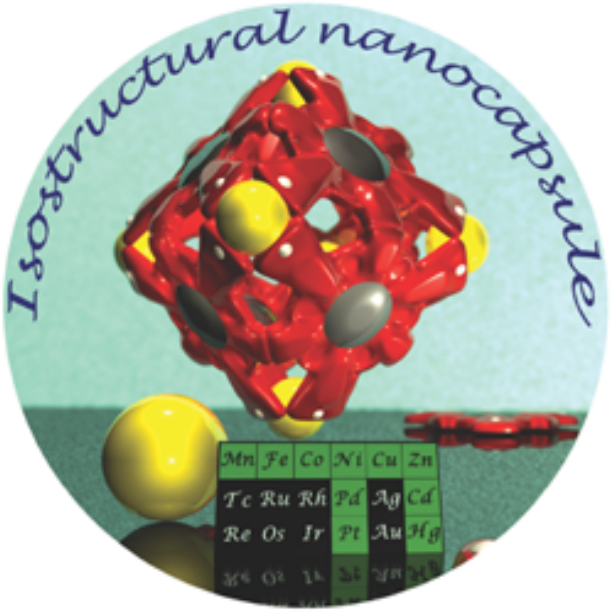
Quantitative Design of "*Elements*"
Dynamic Control of "*Bonding*"

New Molecular Functions

Molecular Machine (Device)
Functional Materials

Advanced Molecular Systems

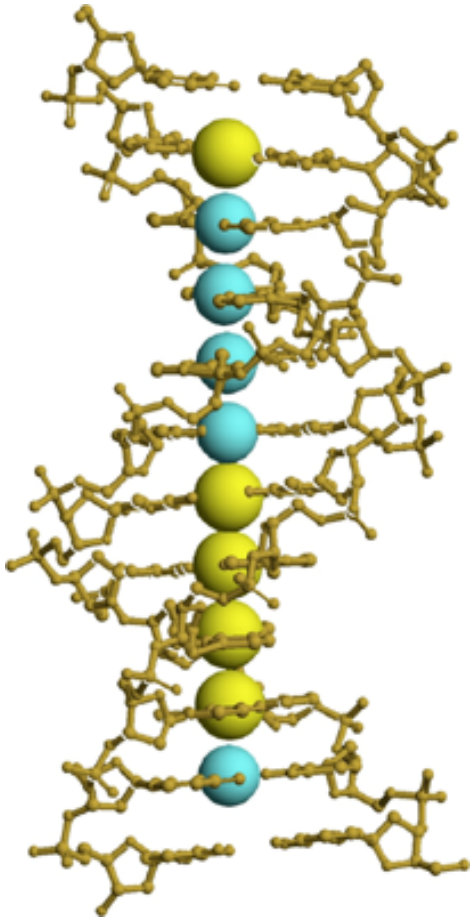
Space



Dynamic Nanocapsules

J. Am. Chem. Soc.
2002, 2006, 2007, 2008, 2008
Angew. Chem. Int. Ed.
2005, 2006

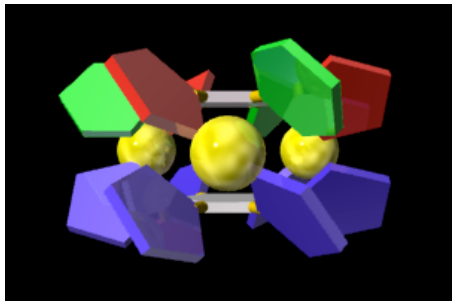
Array



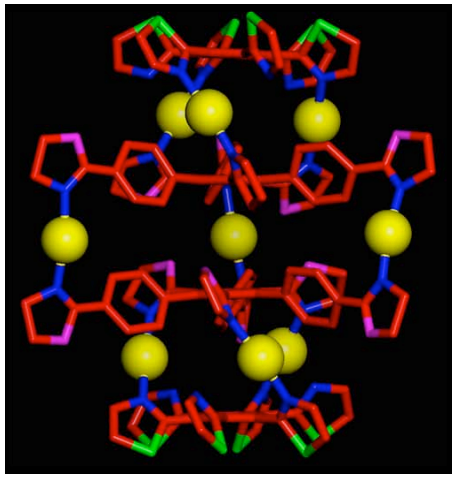
Metallo-DNA (& Peptides)

J. Org. Chem. 1999, 2008
J. Am. Chem. Soc. 2002, 2002, 2008
Science 2003
Nature Nanotech. 2006
Angew. Chem. Int. Ed. 2009

Motion



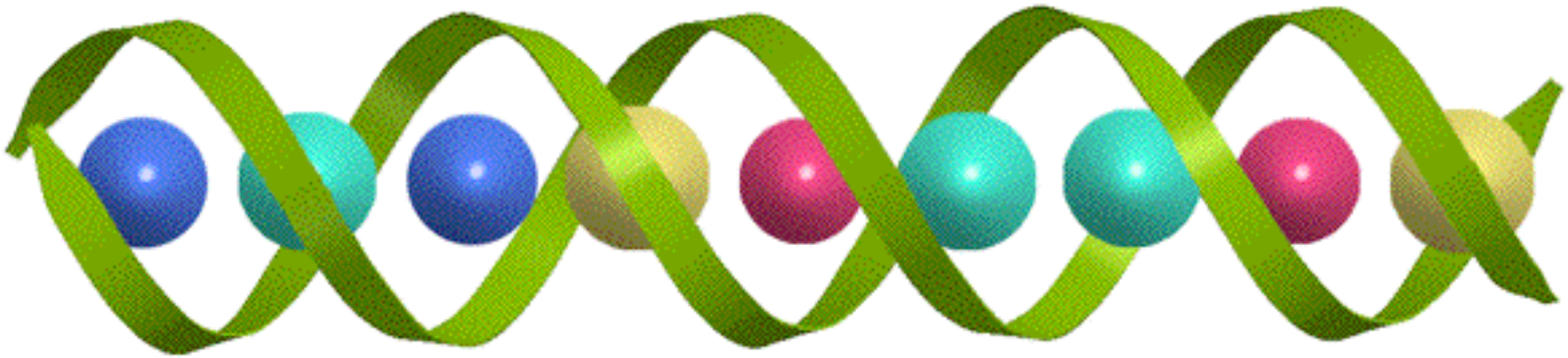
(Molecular Ball Bearing)

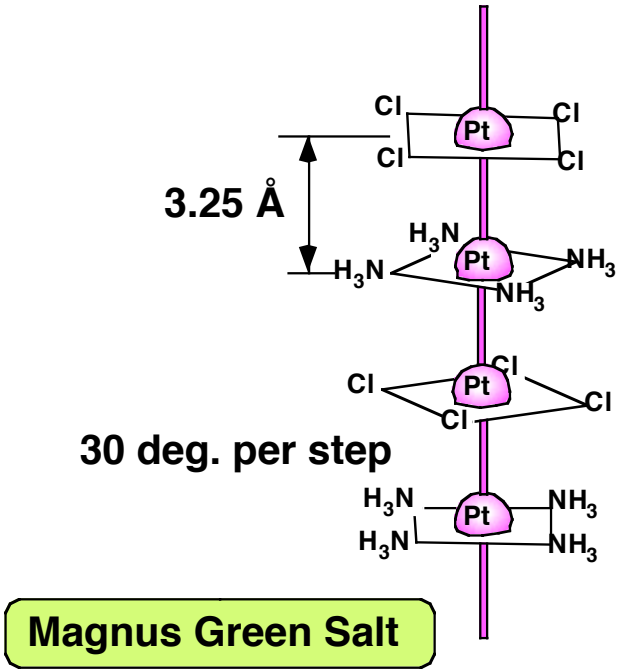


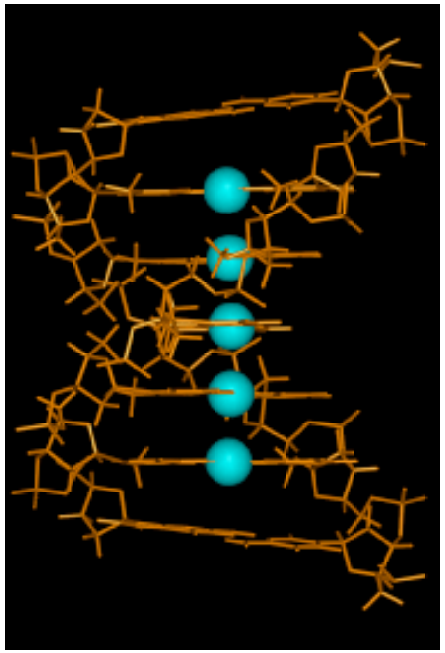
(Rotor-Transmitter-Rotor)

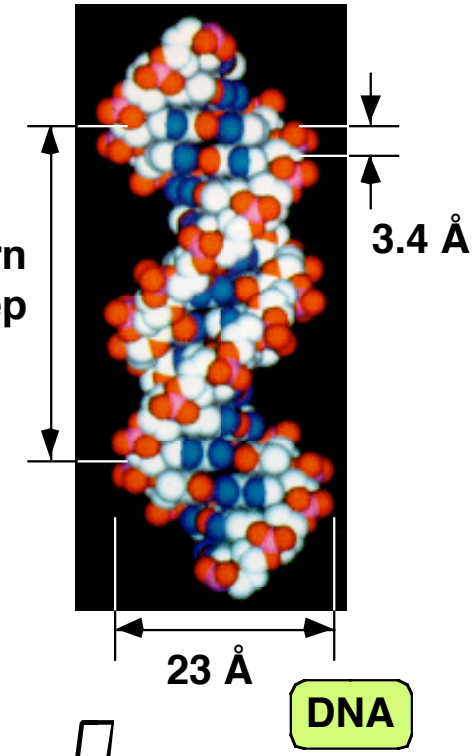
Motional Devices

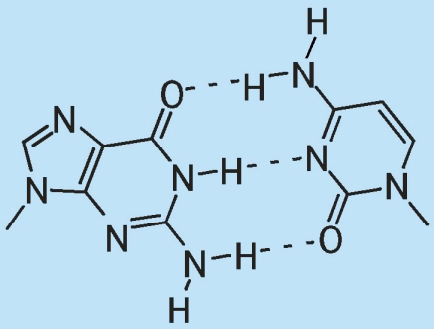
J. Am. Chem. Soc.
2004, 2006, 2008, 2009
Angew. Chem. Int. Ed.
2003, 2004

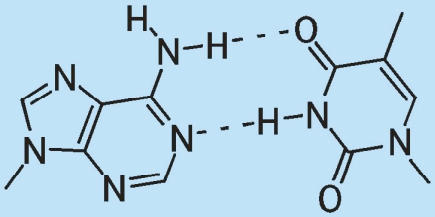



Cl
Pt
Cl
Cl
Cl
3.25 Å
H_3N
Pt
NH_3
H_3N
NH_3
Cl
Cl
Pt
Cl
Cl
30 deg. per step
H_3N
Pt
NH_3
H_3N
NH_3
Magnus Green Salt

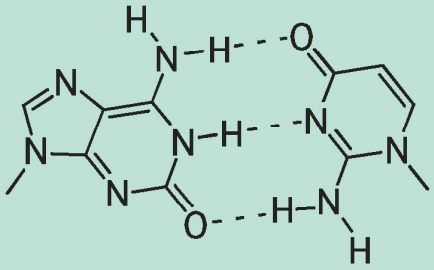



10 bp / turn
36 deg. per step
3.4 Å
23 Å
DNA

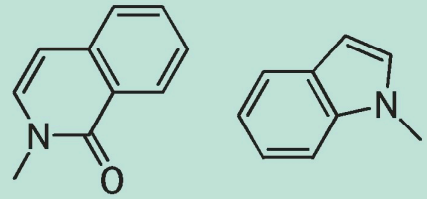




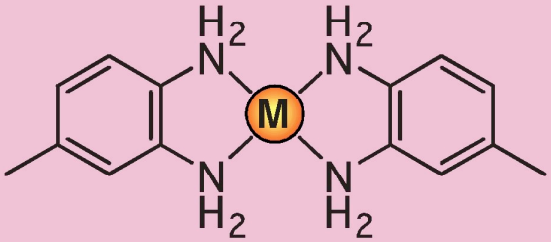
Watson-Crick Hydrogen Bonding



Alternative Hydrogen Bonding

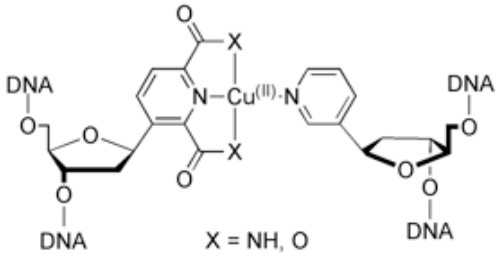


Hydrophobic Packing

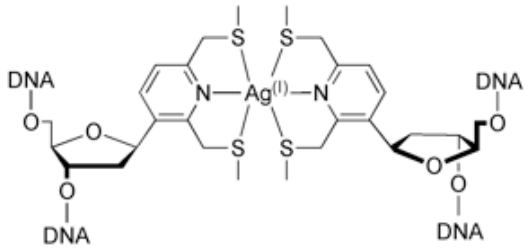


Metal Coordination (1999)

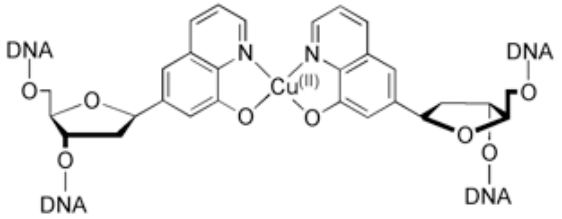
Natural and Modified DNA Base Pairs



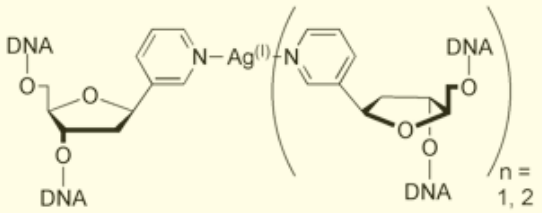
Schultz, *J. Am. Chem. Soc.* **2000**



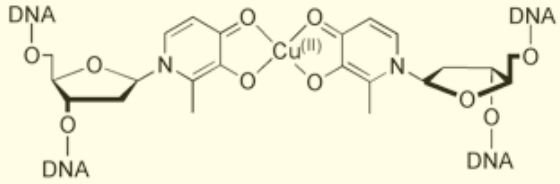
Schultz, *J. Am. Chem. Soc.* **2002**



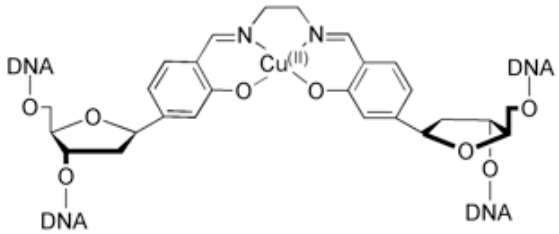
Meggers, *JACS* **2005**



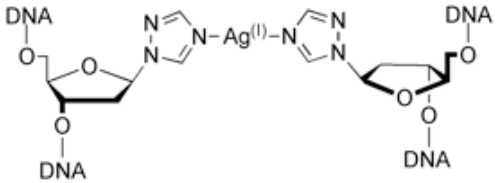
Shionoya, *J. Am. Chem. Soc.* **2002**



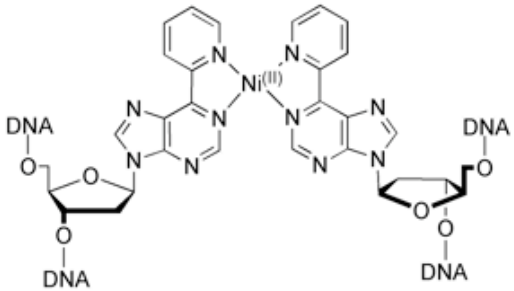
Shionoya, *Science* **2003**



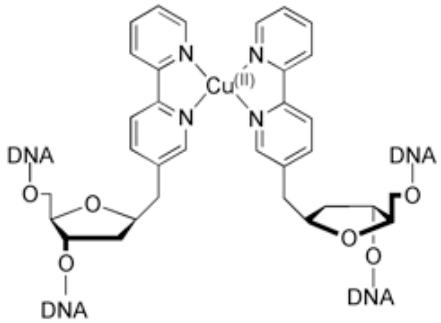
Carell, *Angew. Chem.* **2005**



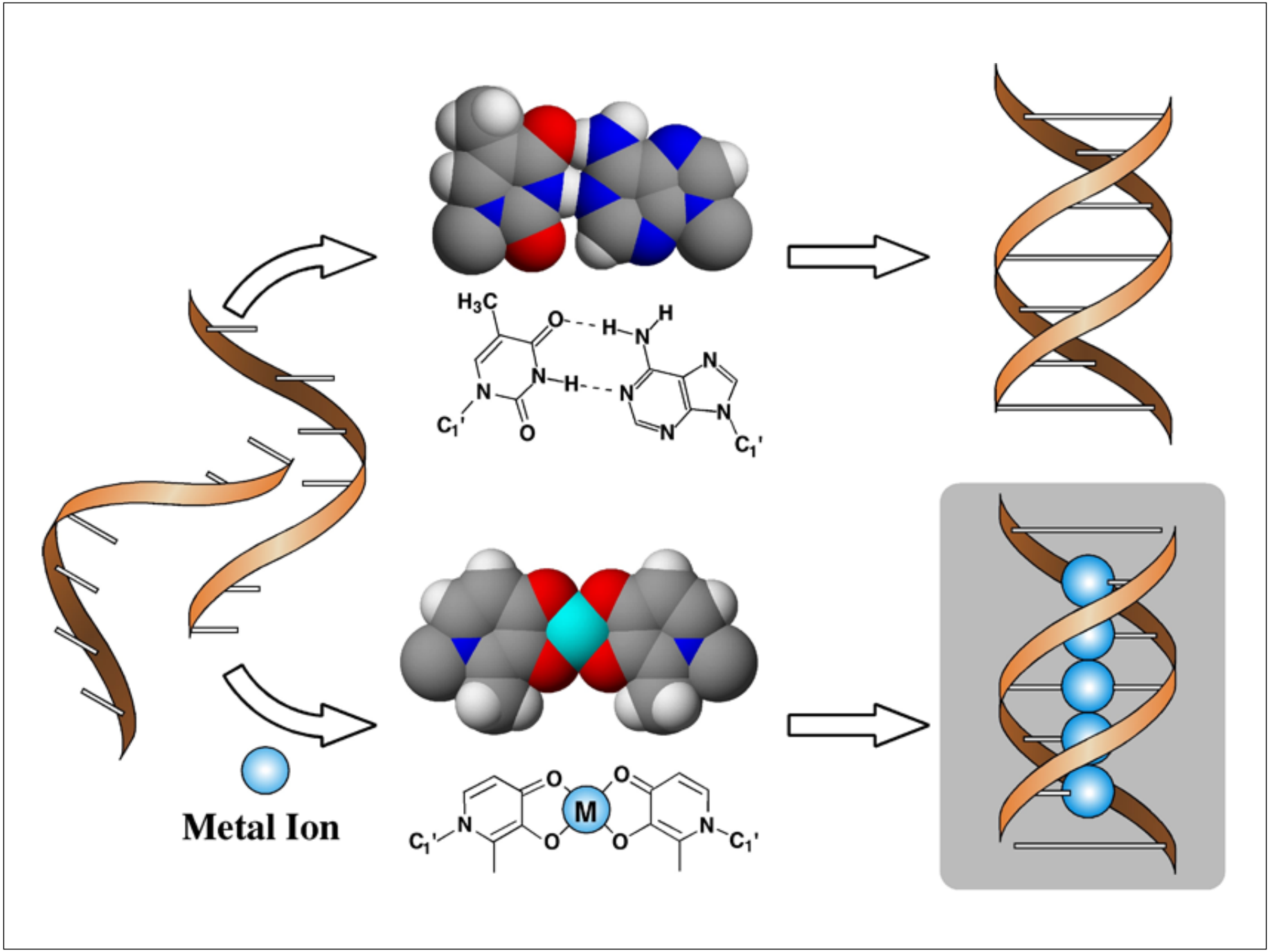
Müller, *Chem. Eu. J.* **2005**



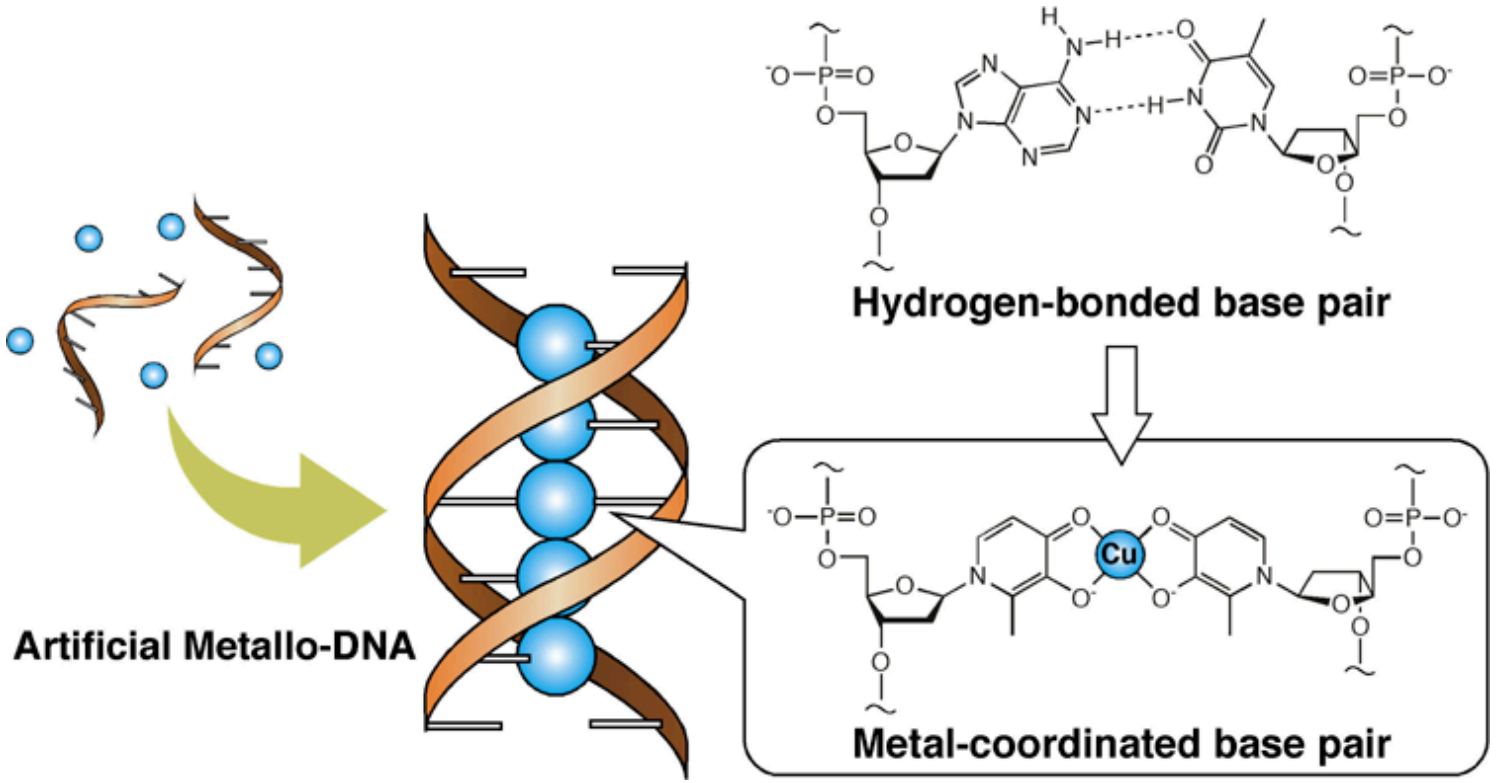
Switzer, *Angew. Chem.* **2005**



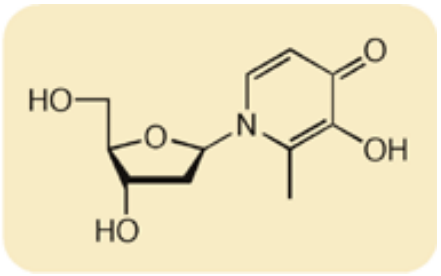
Weizmann, *J. Am. Chem. Soc.* **2001**


Metal Ion
M

A Discrete Self-Assembled Metal Array in Artificial DNA



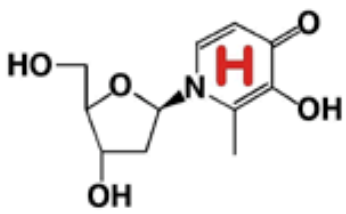
H =

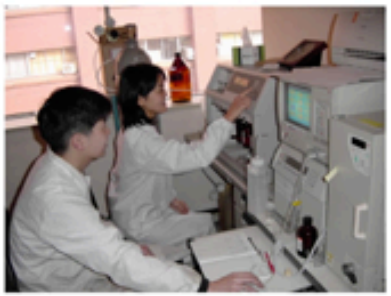


d(5'-G**HHHHHH**C-3') d(5'-G**HHHH**C-3')
d(3'-C**HHHHHH**G-5') d(3'-C**HHHH**G-5')

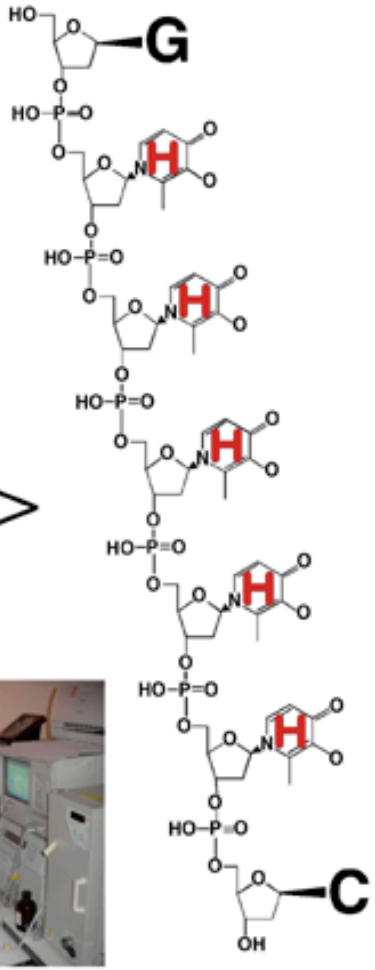
d(5'-G**HHH**C-3') d(5'-G**HH**C-3') d(5'-G**H**C-3')
d(3'-C**HHH**G-5') d(3'-C**HH**G-5') d(3'-C**H**G-5')

Design &
Synthesis





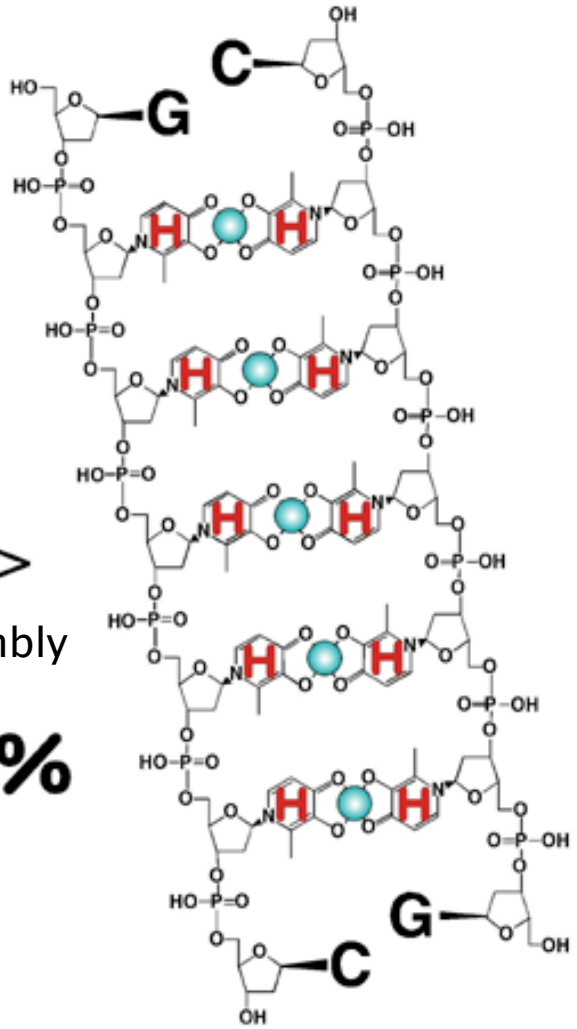
DNA synthesizer



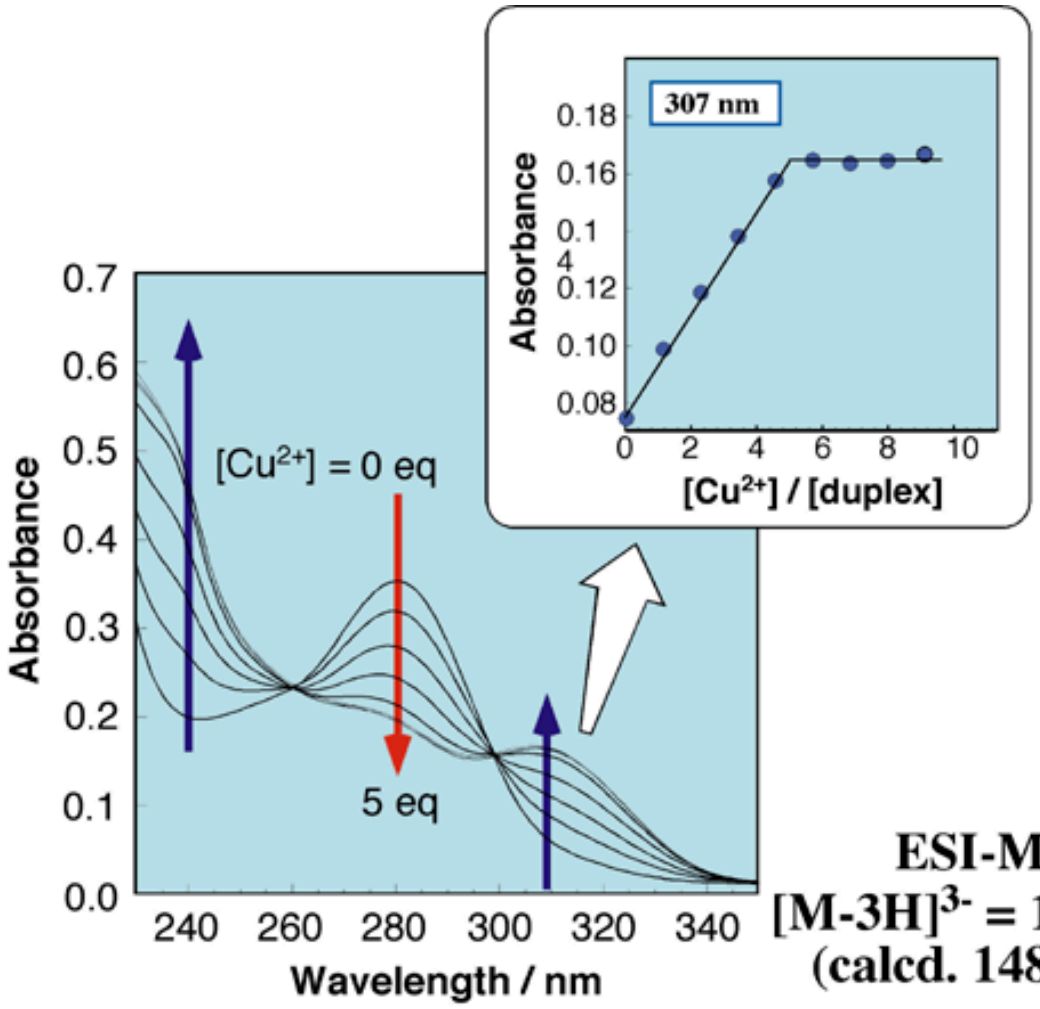
Cu

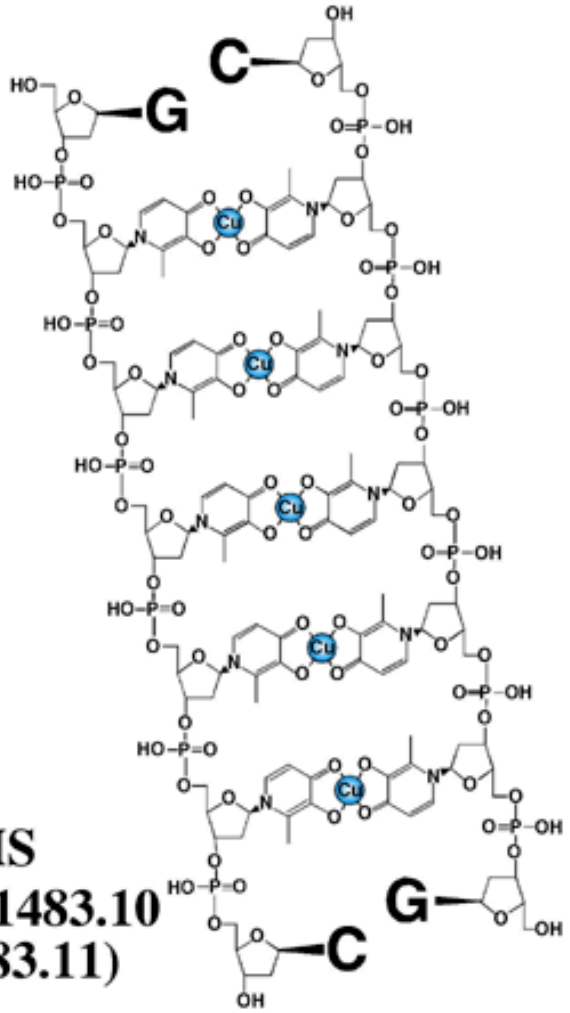
Self-assembly

100%



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

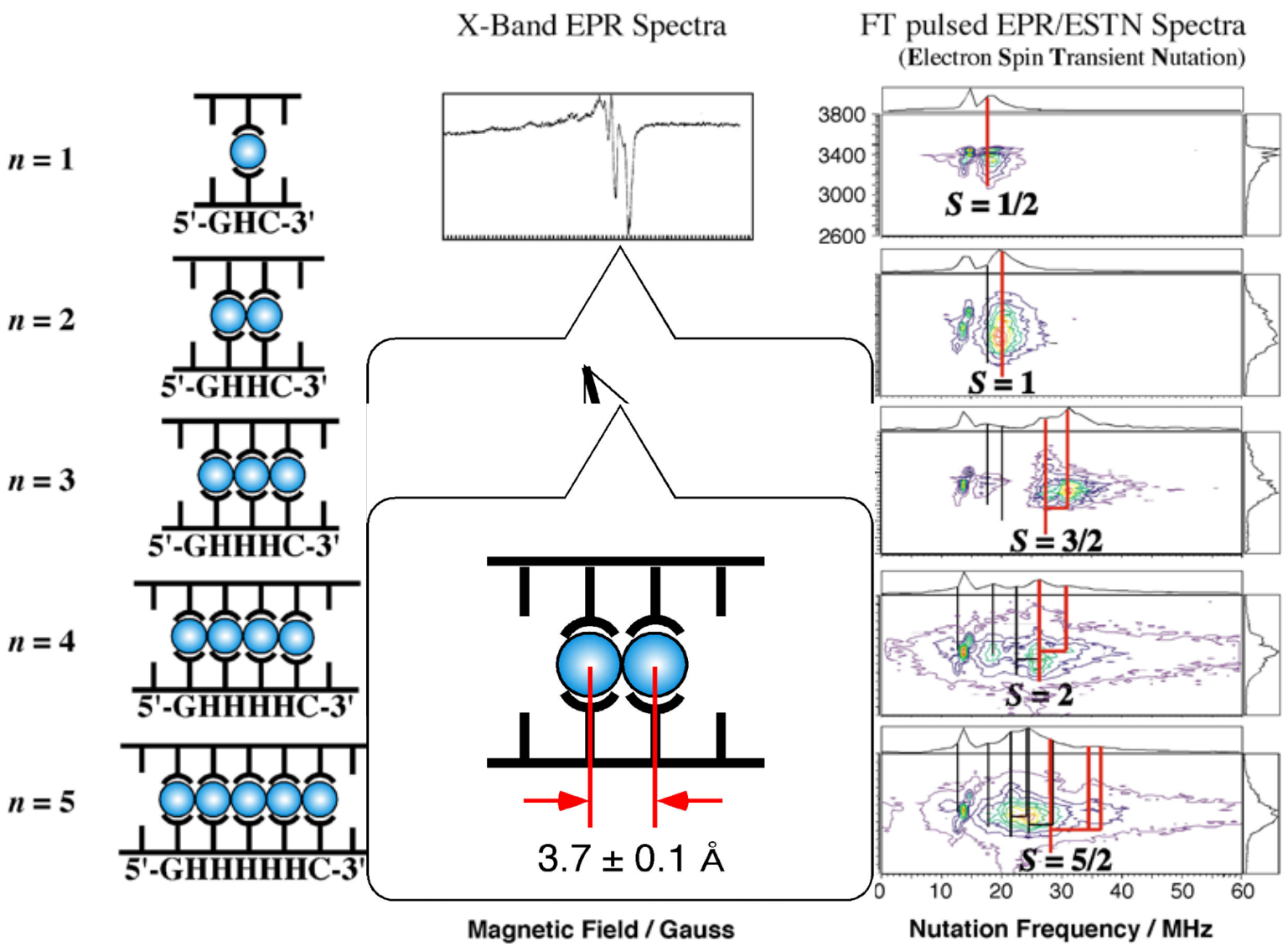




ESI-MS
$[M-3H]^{3-}$ = 1483.10
(calcd. 1483.11)

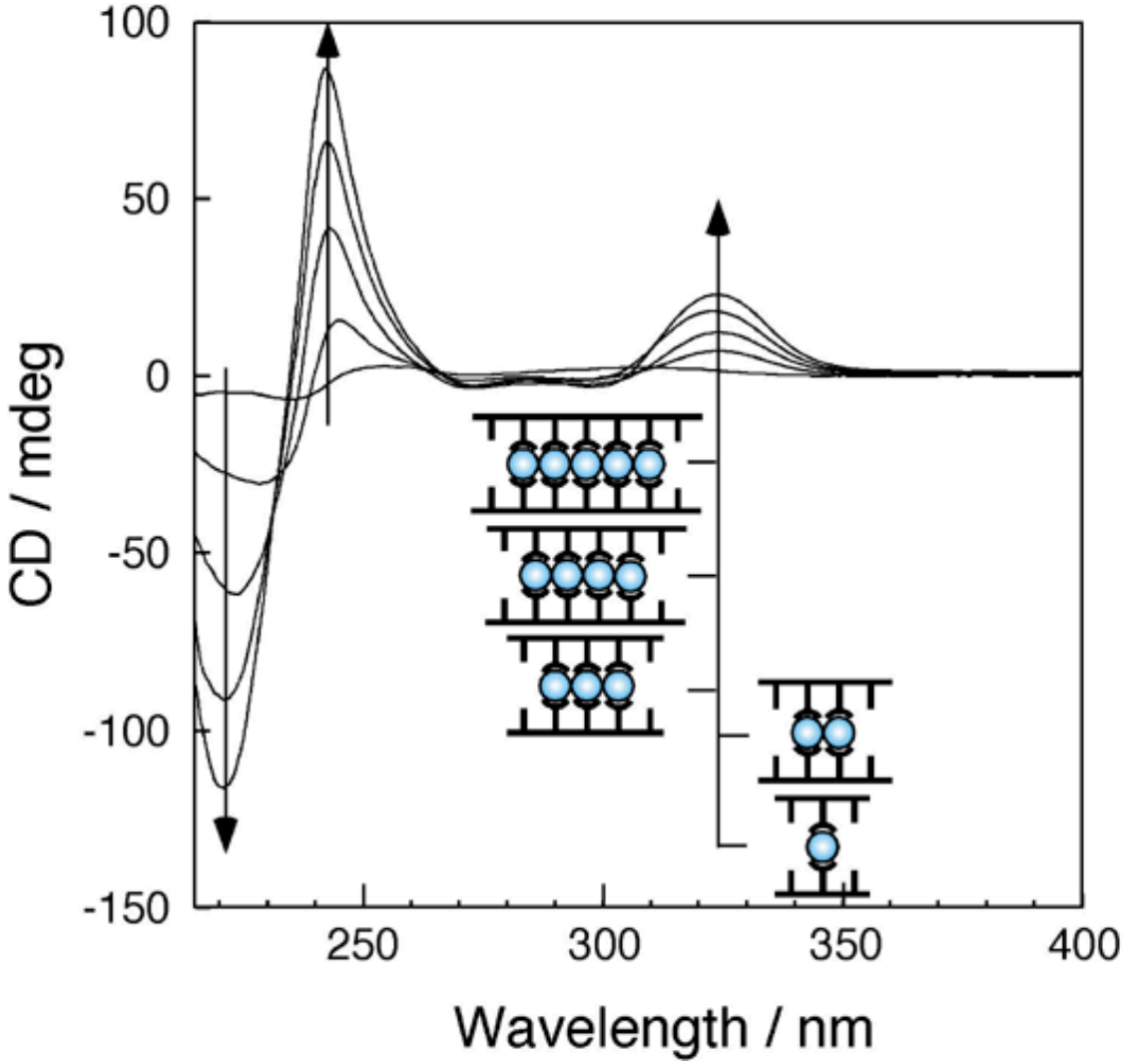
[DNA duplex] = 2.0 μM in 10 mM HEPES (pH 7.0). 50 mM NaCl. 25 °C

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



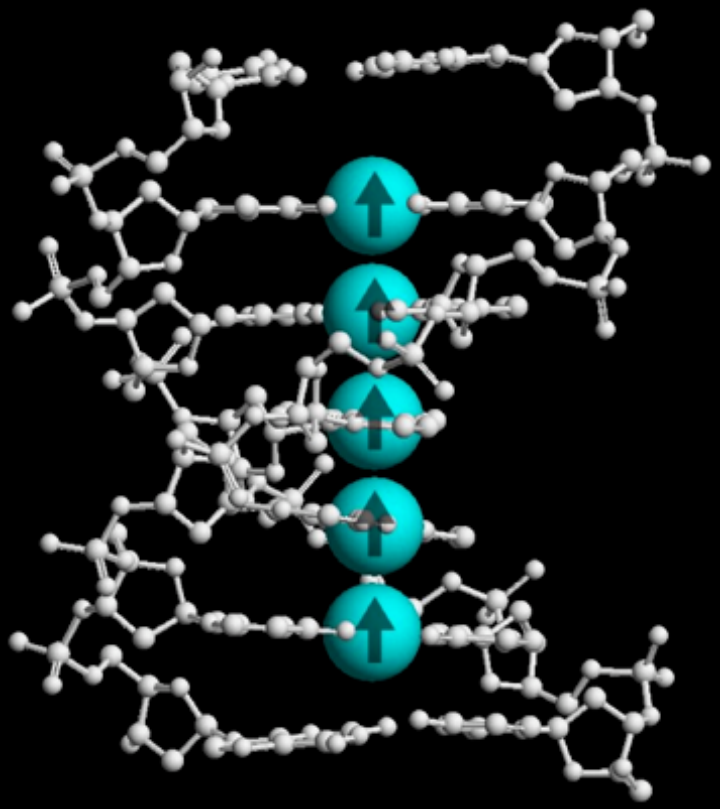
[DNA duplexes] = 100 μM with *n* eq. $CuSO_4$ in 10 mM HEPES (pH 7.0), 50 mM NaCl, at 1.5 K.

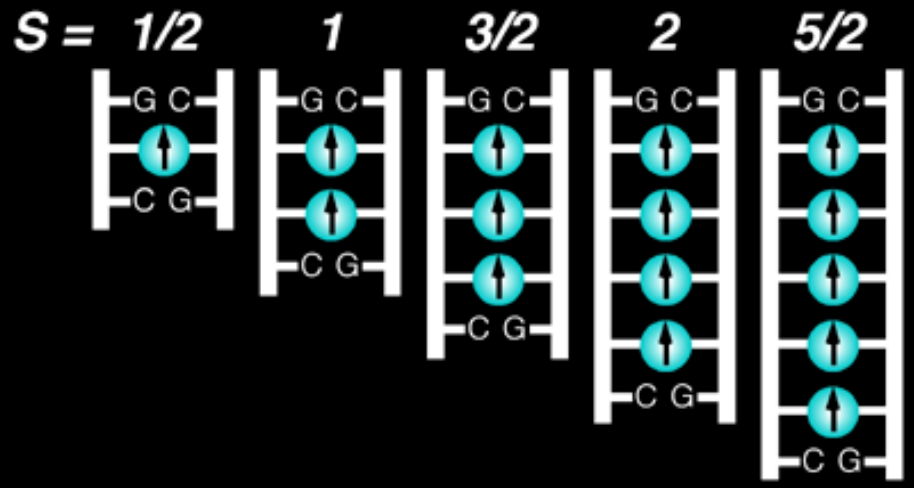
CD Spectra of Cu^{2+}_n·d(5'-GH_nC-3')$_2$



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

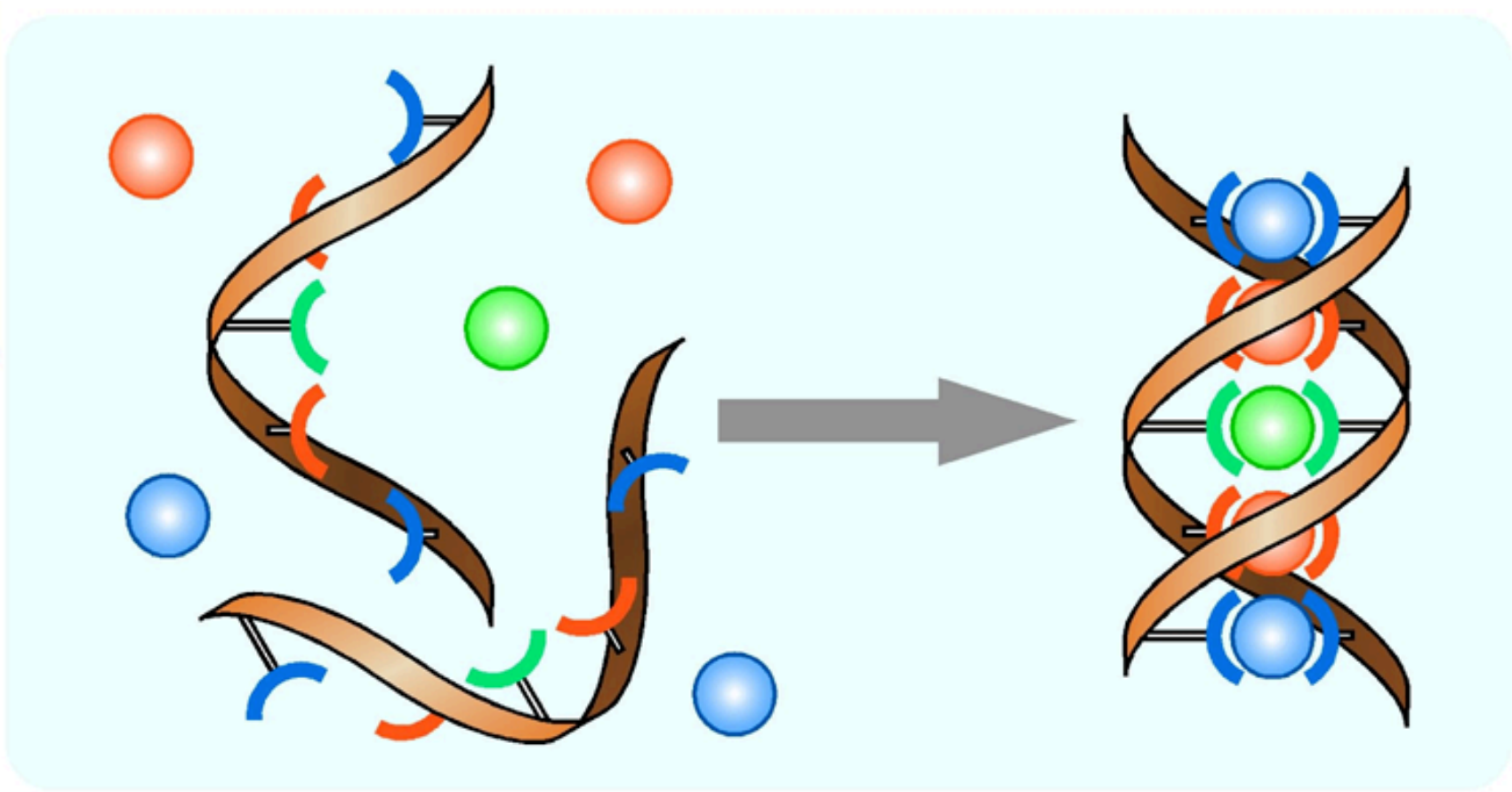
Discrete Metal Arrays in Artificial DNA



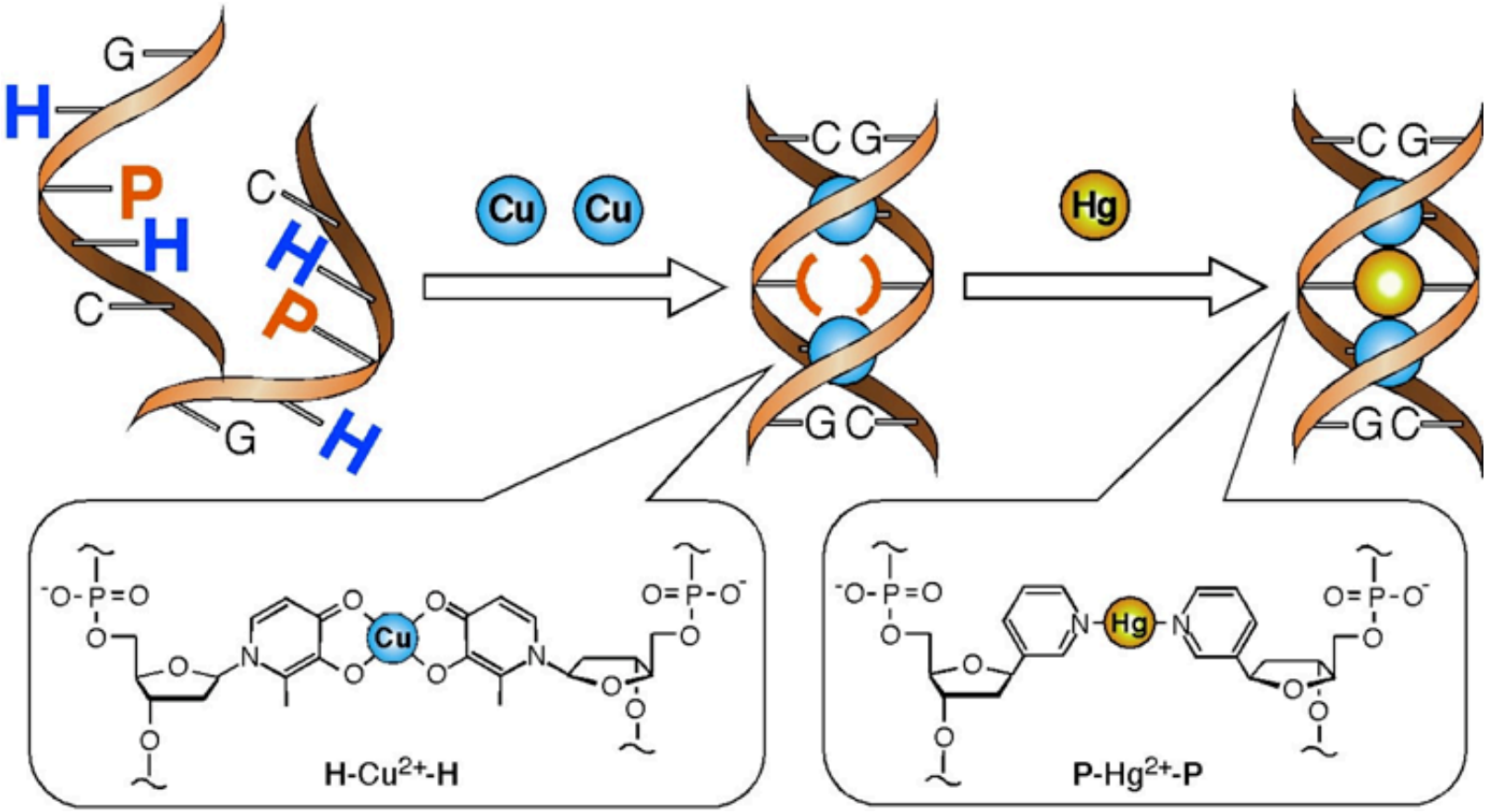


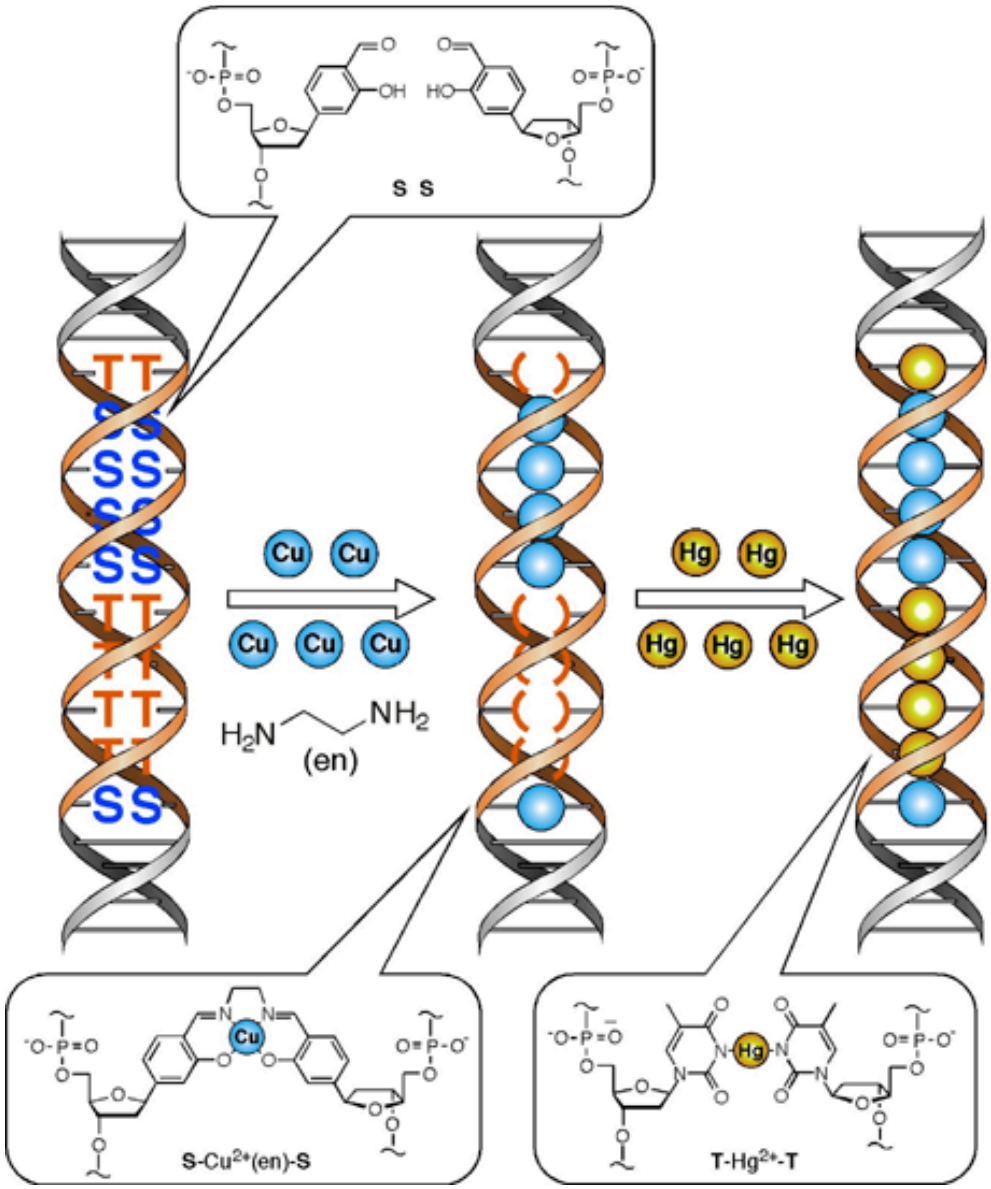
Science, *299*, 1212 (2003)

Programmable Heterogeneous Metal Arrays

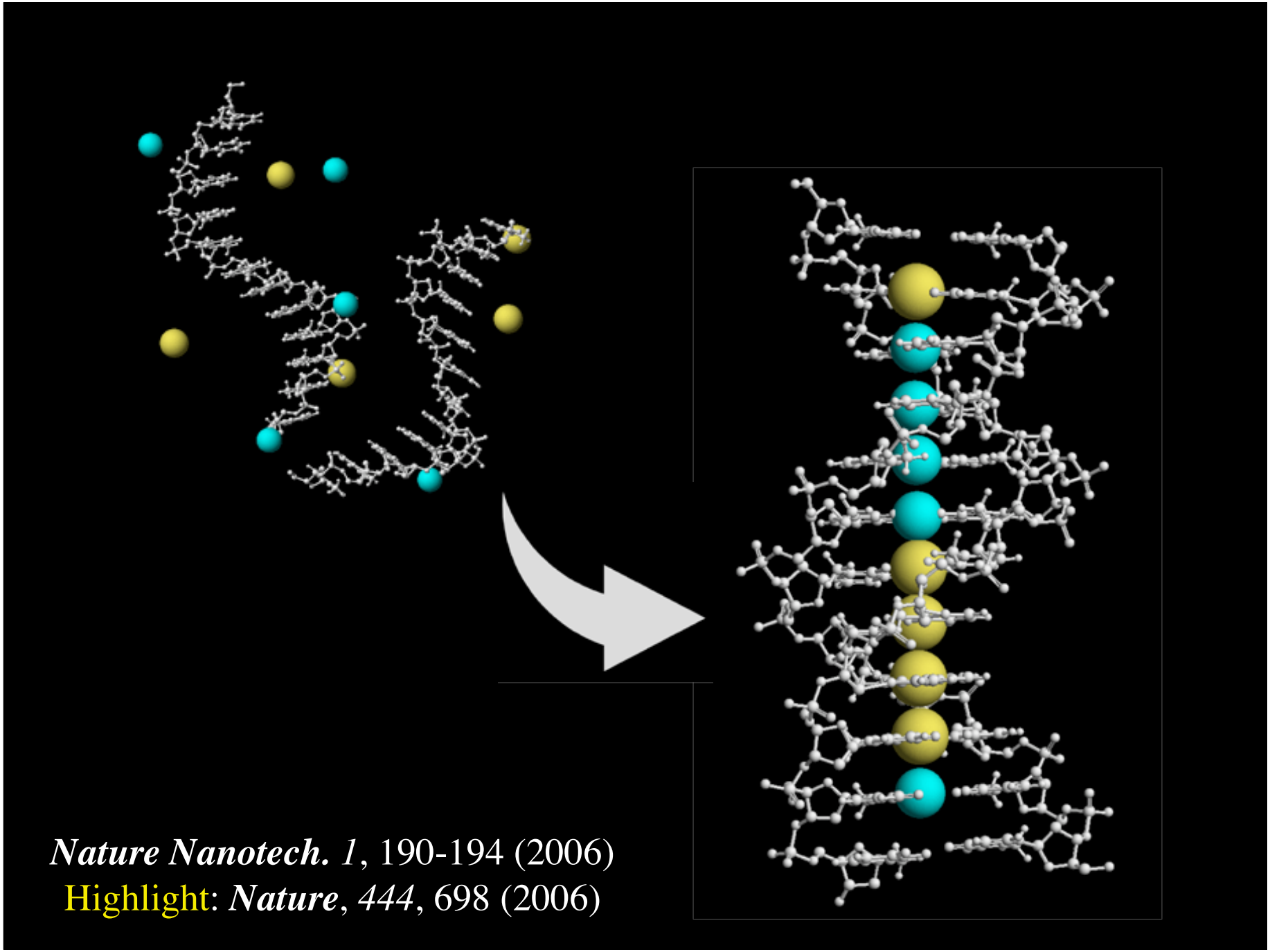


Heterogeneous Metal Array

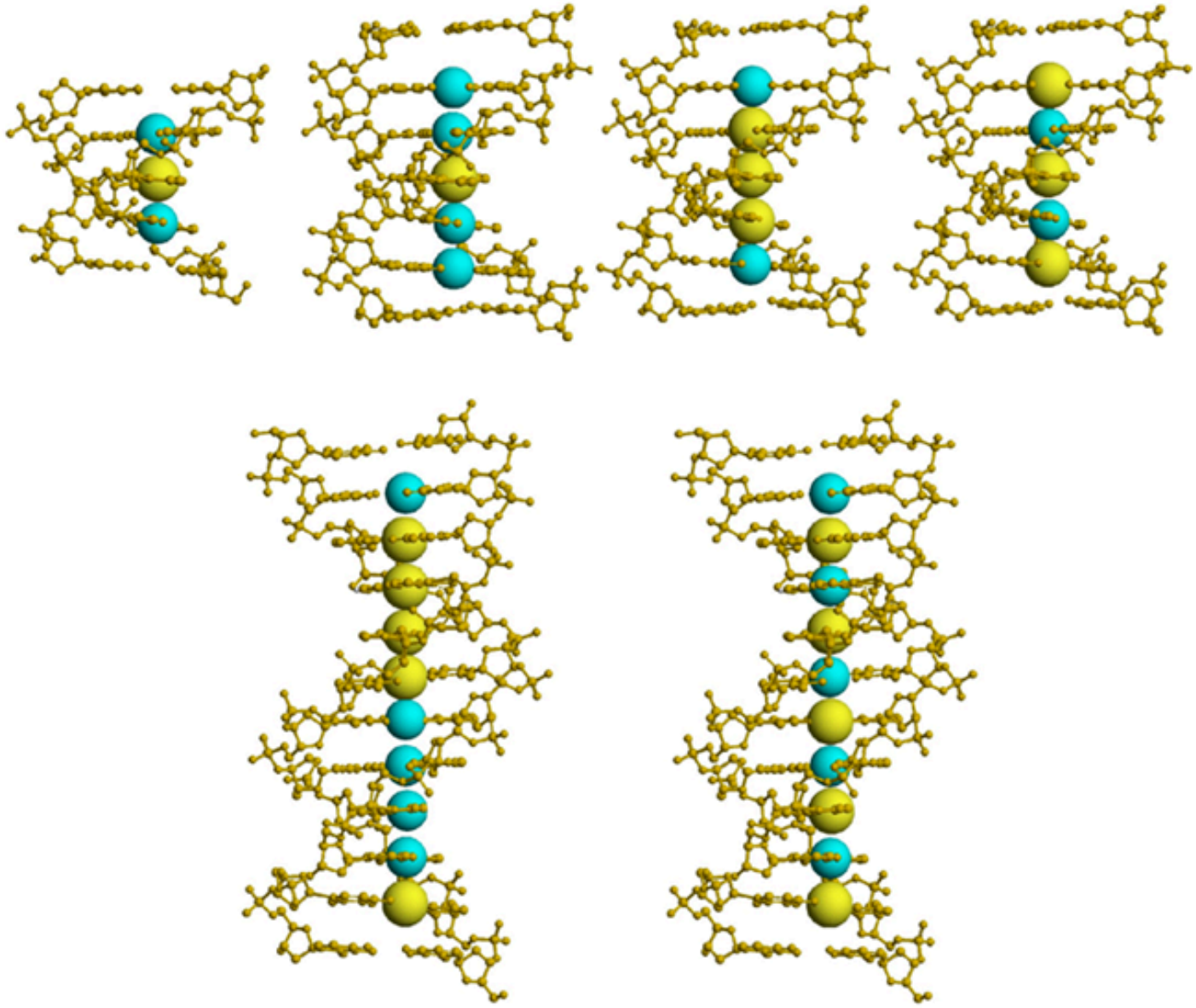




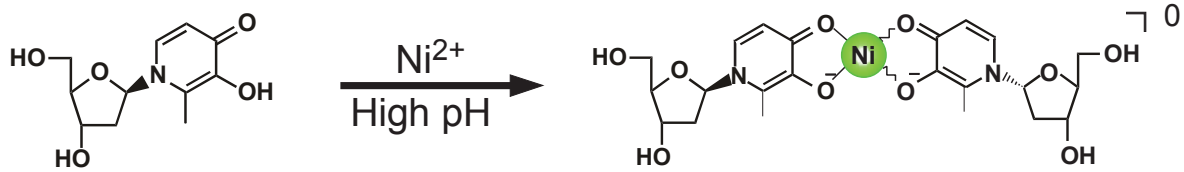
Clever and Carell


Nature Nanotech. *1*, 190-194 (2006)
Highlight: *Nature*, *444*, 698 (2006)

Programmable Metal Arrays in Artificial DNAs

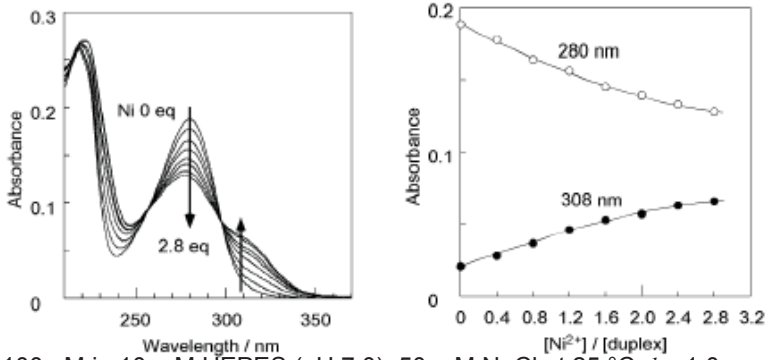


pH-dependent Coordination of Nickel(II)



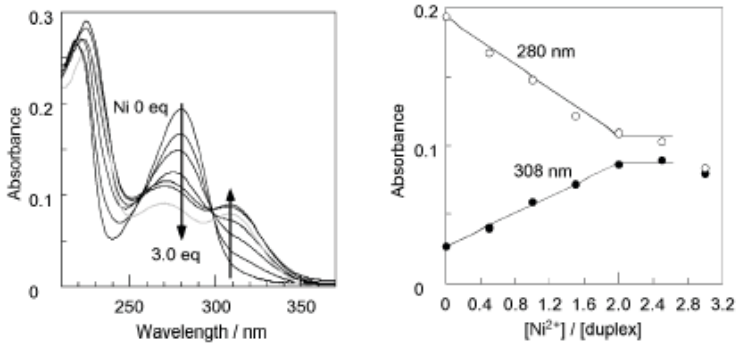
The formation of the nickel-hydroxypyridone base pair requires a higher pH

pH = 7.0
Not Quantitative

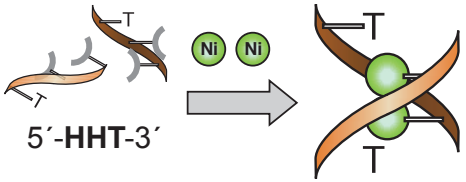


[H] = 100 μM in 10 mM HEPES (pH 7.0), 50 mM NaCl at 25 °C, *l* = 1.0 cm

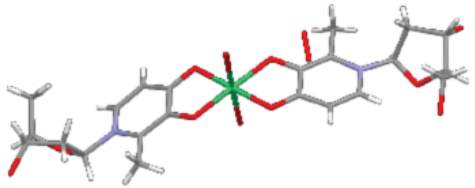
pH = 8.0
Quantitative



[H] = 100 μM in 10 mM HEPES (pH 8.0), 50 mM NaCl at 25 °C, *l* = 1.0 cm

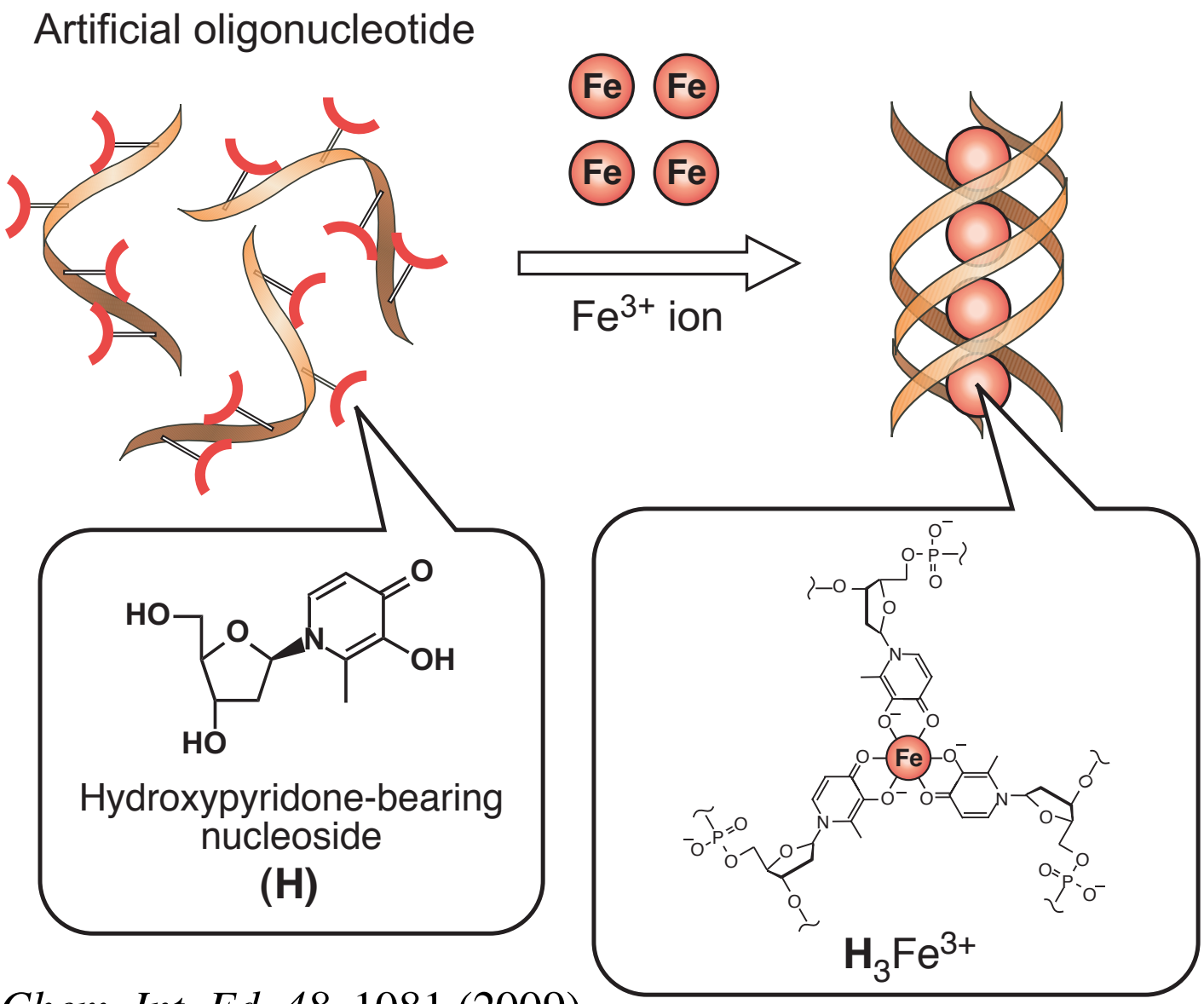


The formation of longer helices seems to be hampered by hairpin formation



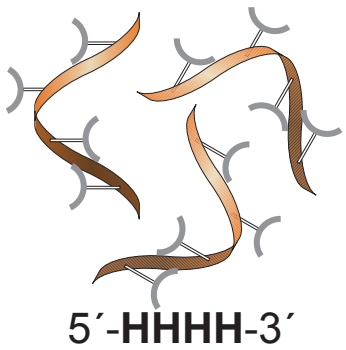
X-ray structure of the monomeric Ni-hydroxypyridone metal base pair

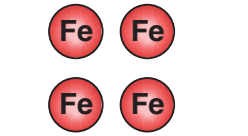
Triple Helicate



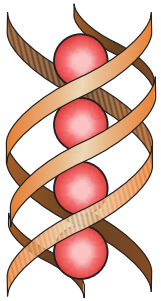
Angew. Chem. Int. Ed. **48**, 1081 (2009)

Triple Helix Formation using Fe(III)

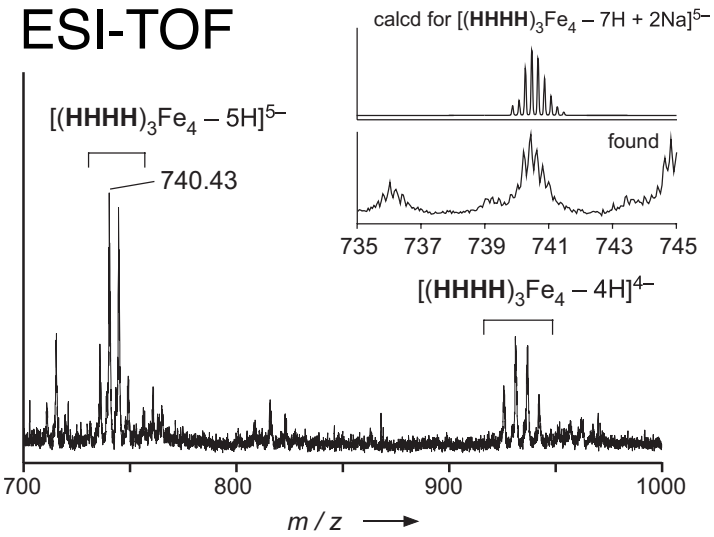




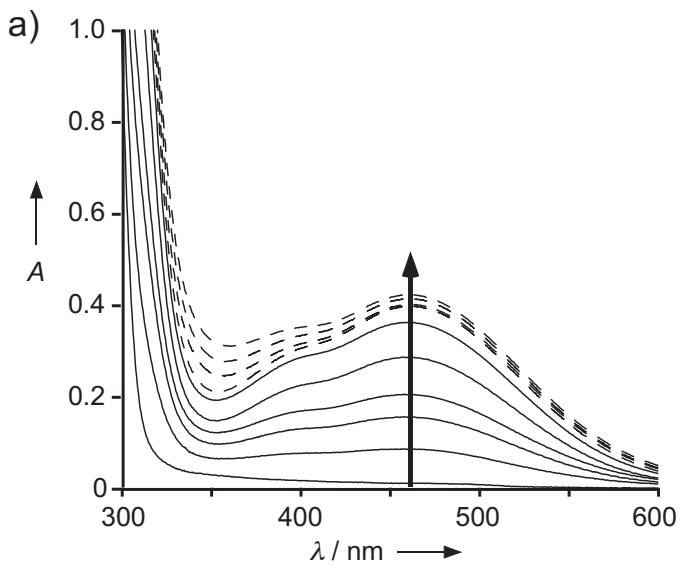
85 °C
2 days

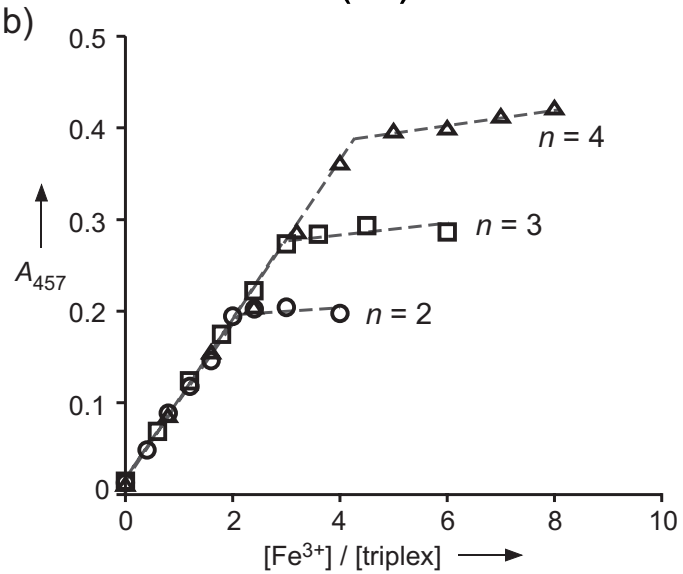


ESI-TOF

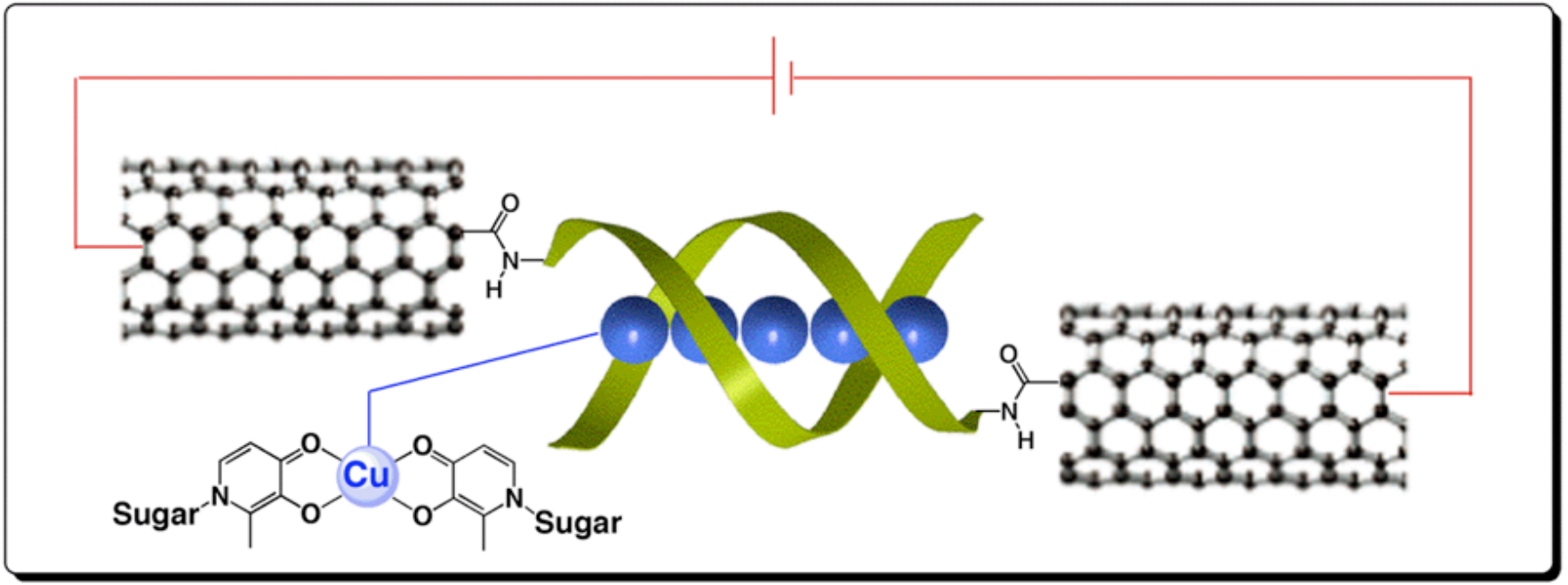


UV-vis-monitored titration of Fe(III)





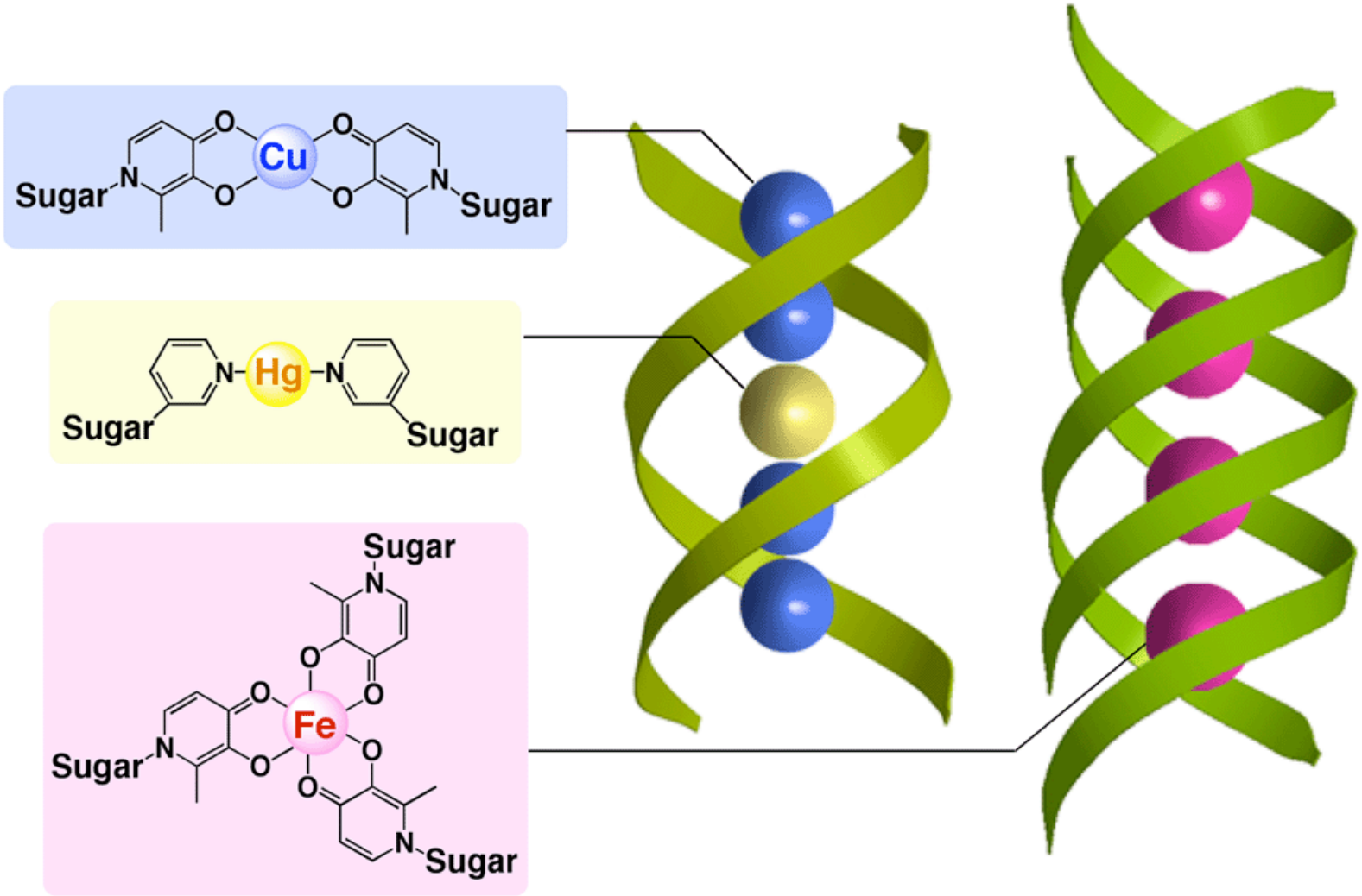
Conductivity of a single metallo-DNA duplex



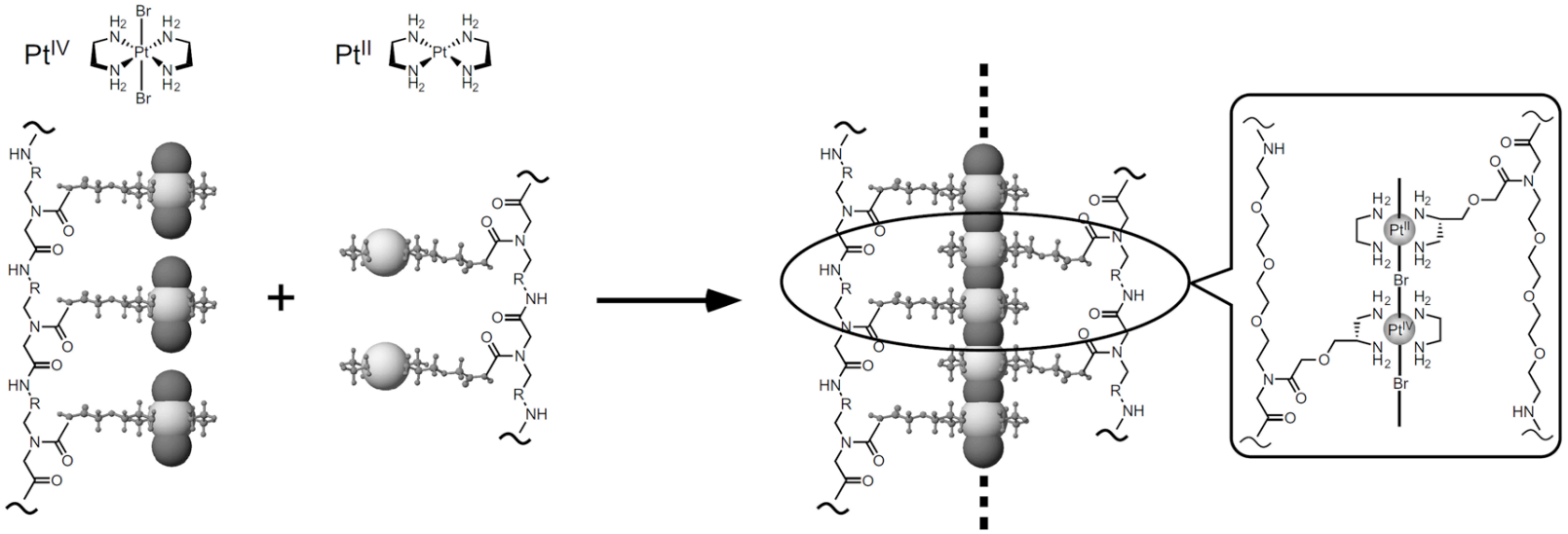
SWNT—C(=O)—N(H)—$(CH_2)_3$-NHOCO-5'-AGT ACA GTC ATC GCG-3'

3'-TCA TGT CAG TAG CGC-5'-OCONH-$(CH_2)_3$—N(H)—C(=O)—SWNT

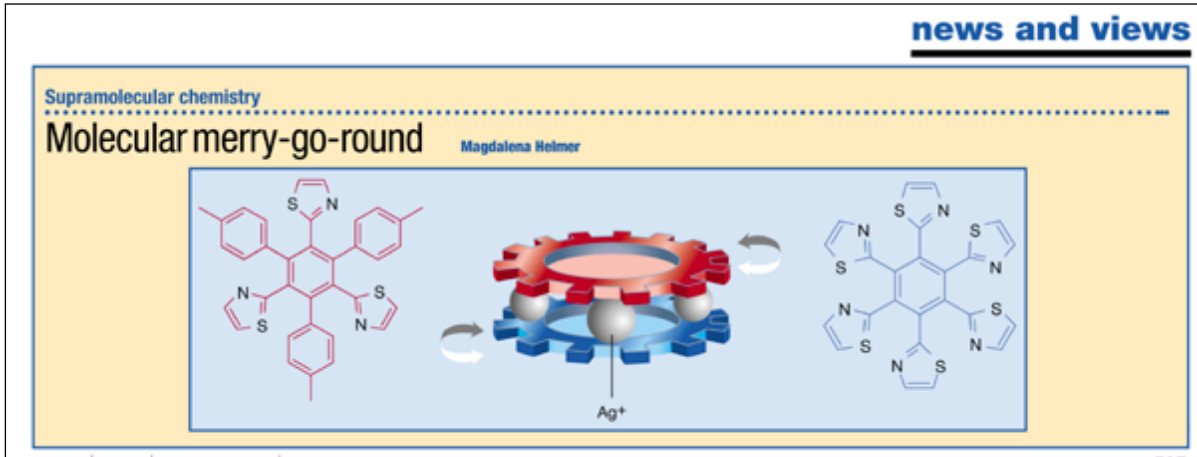
X. Guo, A. A. Gorodetsky, J. Hone, J. K. Barton, and C. Nuckolls, *Nature nanotech.* **2008**, *3*, 163


Sugar
N
O
Cu
O
O
O
N
Sugar
N
Hg
N
Sugar
Sugar
Sugar
N
O
O
Fe
O
O
O
Sugar
N
O
N
Sugar

Halogen-bridged Mixed-valence Pt Complexes on Artificial Peptides

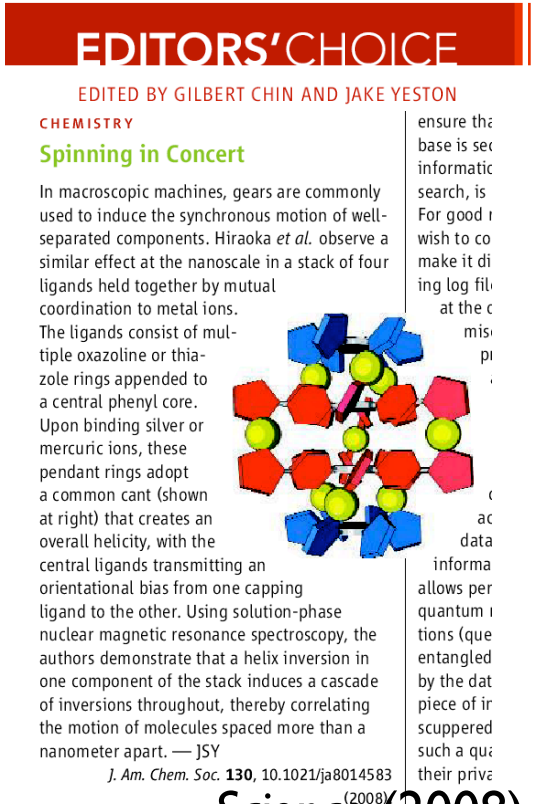


Dalton Trans., **2007**, 5369



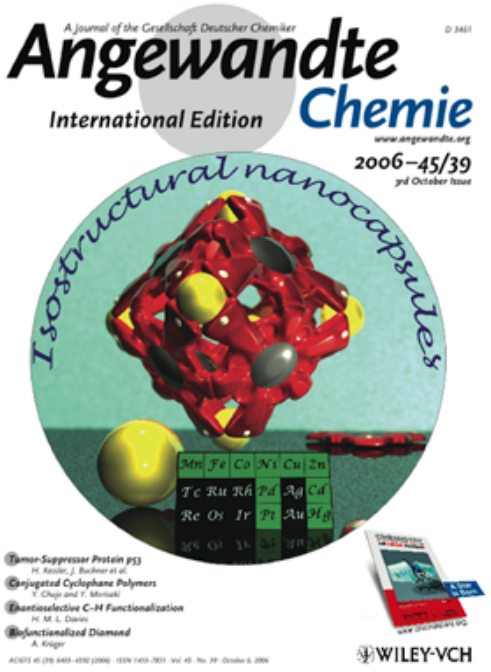
Nature (2004)

Nature (2006)



Science (2008)

(2007)



(2006)