

International Workshop on DNA-based nanotechnology:
Construction, mechanics, and electronics

May 11-15, 2009

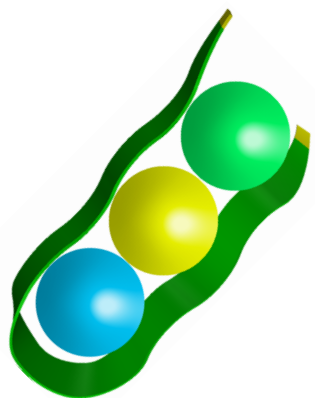
Max-Planck Institut für Physik komplexer Systeme, Dresden, Germany

Metal Strings in Artificial DNA

(The Univ. of Tokyo) Mitsuhiro Shionoya



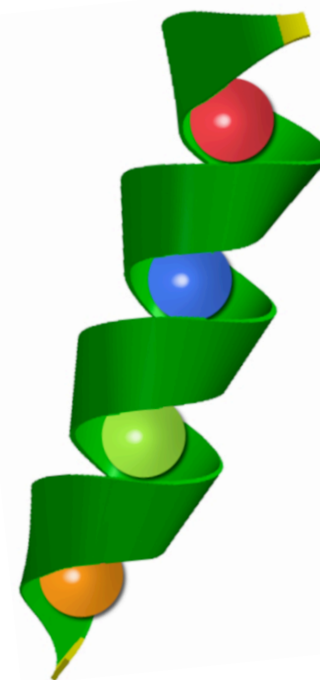
Bio-inspired Novel Structural Motifs with Metals



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

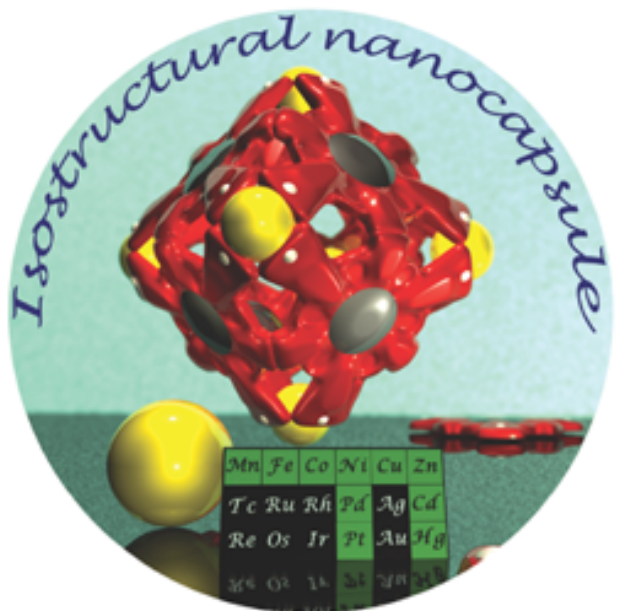


Molecular Machine (Device)
Functional Materials



Advanced Molecular Systems

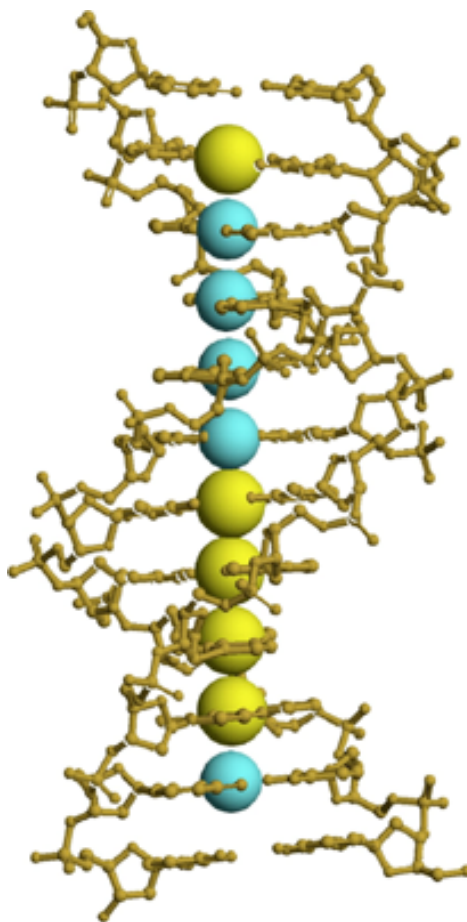
Space



Dynamic Nanocapsules

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

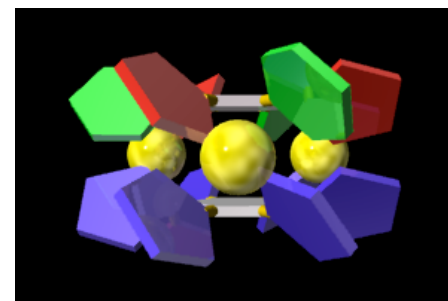
Array



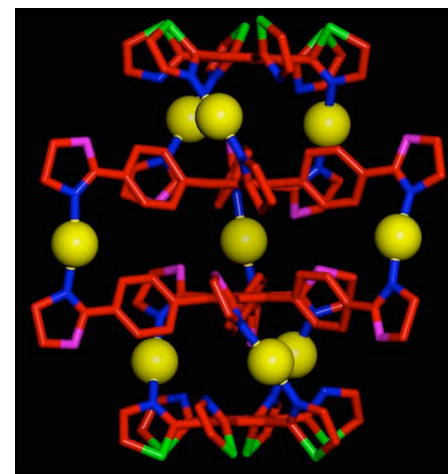
Metallo-DNA (& Peptides)

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

Motion



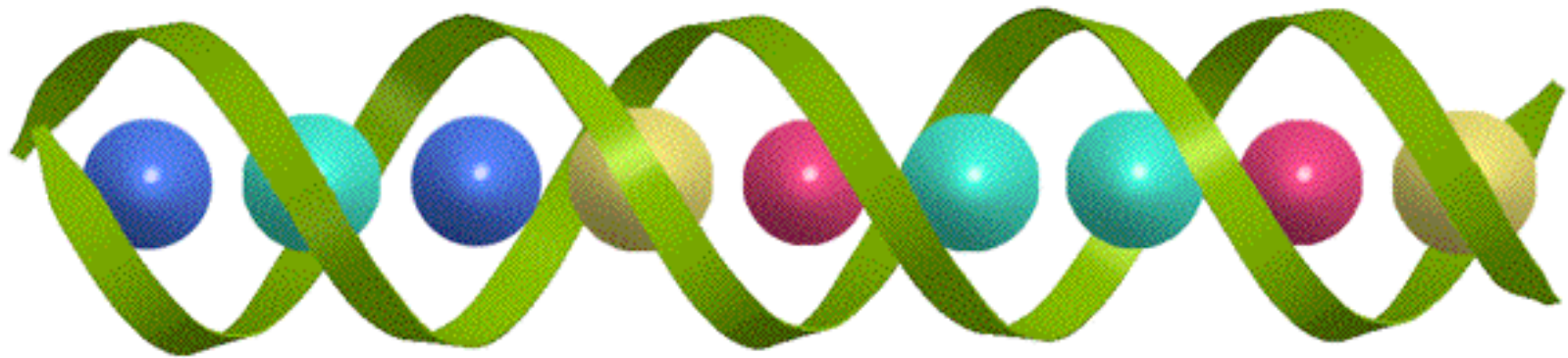
(Molecular Ball Bearing)

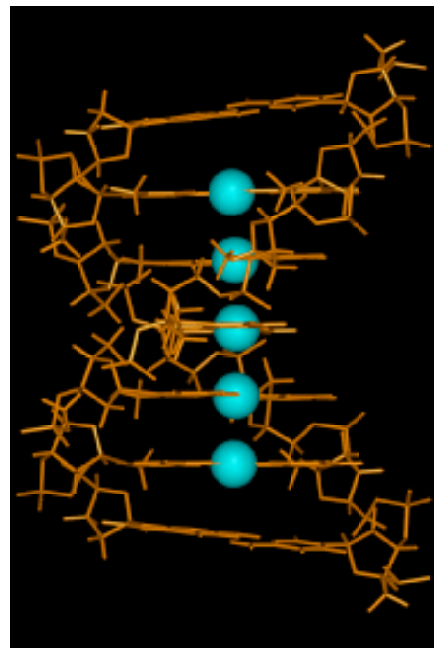
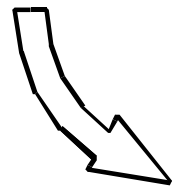
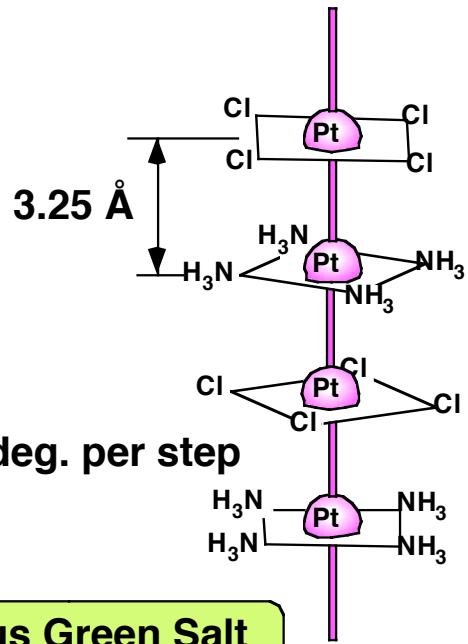


(Rotor-Transmitter-Rotor)

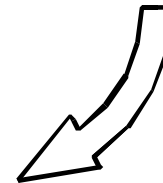
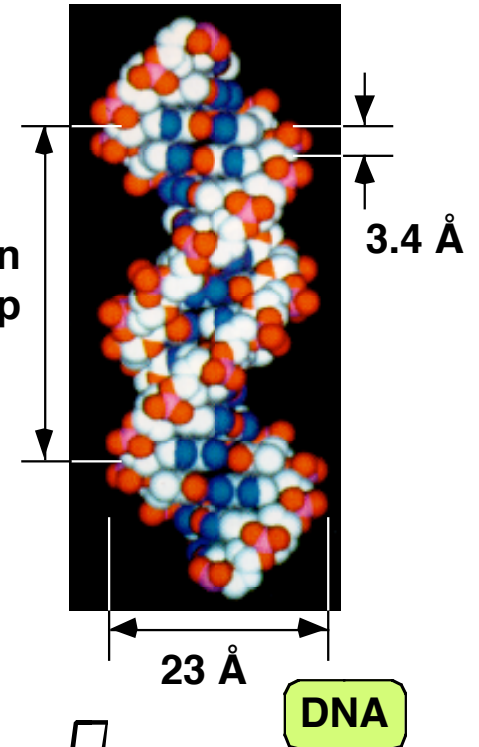
Motional Devices

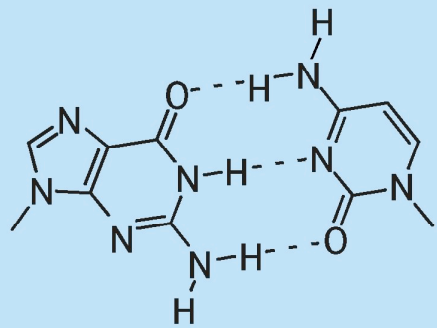
J. Am. Chem. Soc.
2004, 2006, 2008, 2009
Angew. Chem. Int. Ed.
2003, 2004



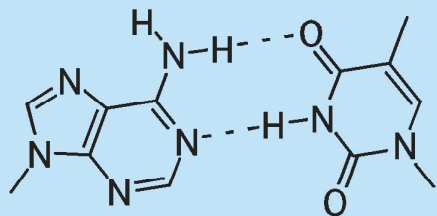


10 bp / turn
36 deg. per step



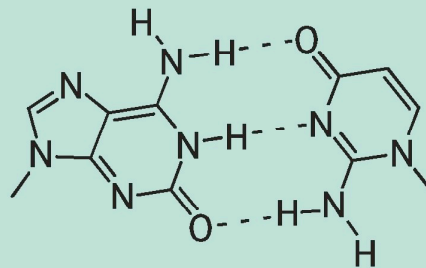


G C

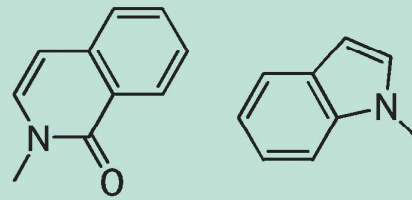


A T

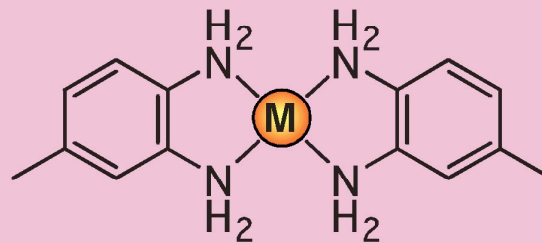
**Watson-Crick
Hydrogen Bonding**



**Alternative
Hydrogen Bonding**

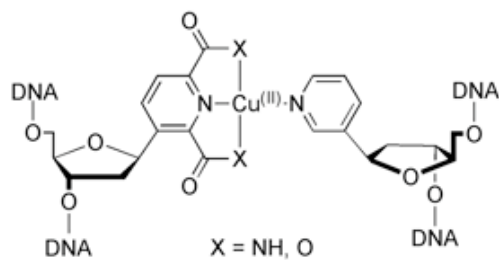


**Hydrophobic
Packing**

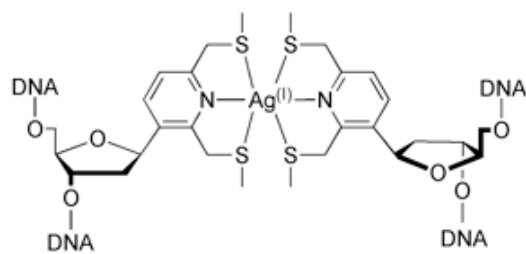


**Metal
Coordination
(1999)**

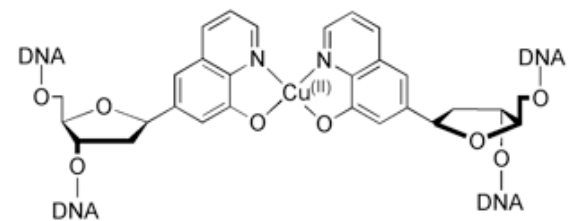
Natural and Modified DNA Base Pairs



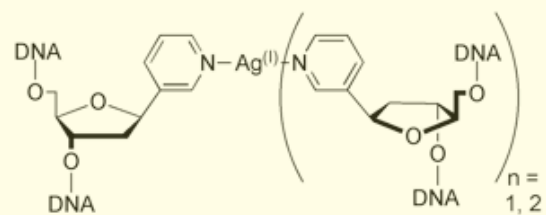
Schultz, *J. Am. Chem. Soc.* **2000**



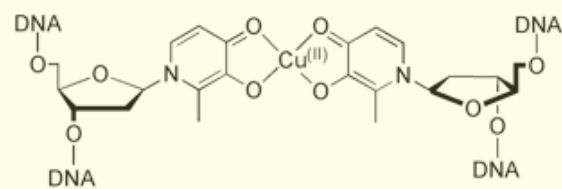
Schultz, *J. Am. Chem. Soc.* **2002**



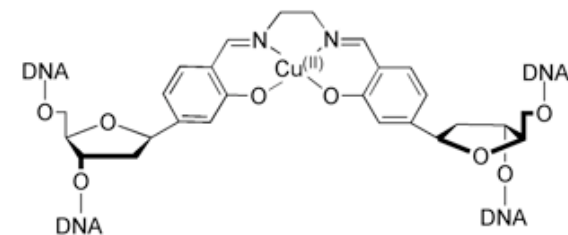
Meggers, *JACS* **2005**



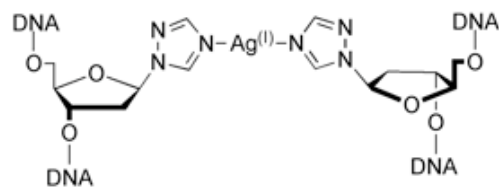
Shionoya, *J. Am. Chem. Soc.* **2002**



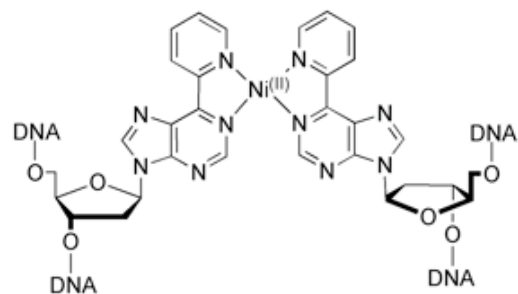
Shionoya, *Science* **2003**



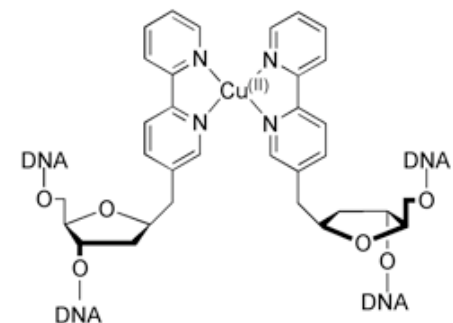
Carell, *Angew. Chem.* **2005**



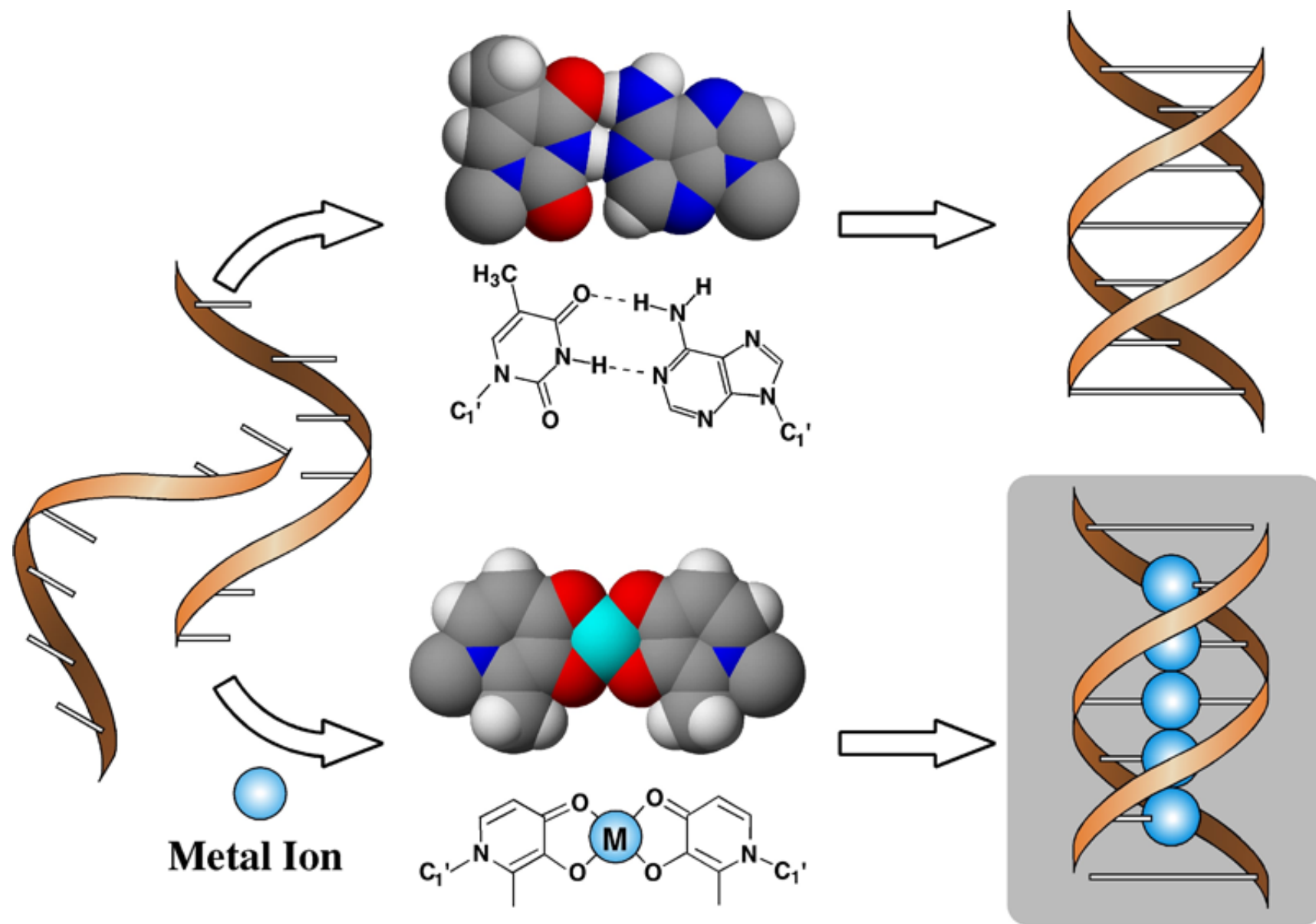
Müller, *Chem. Eu. J.* **2005**



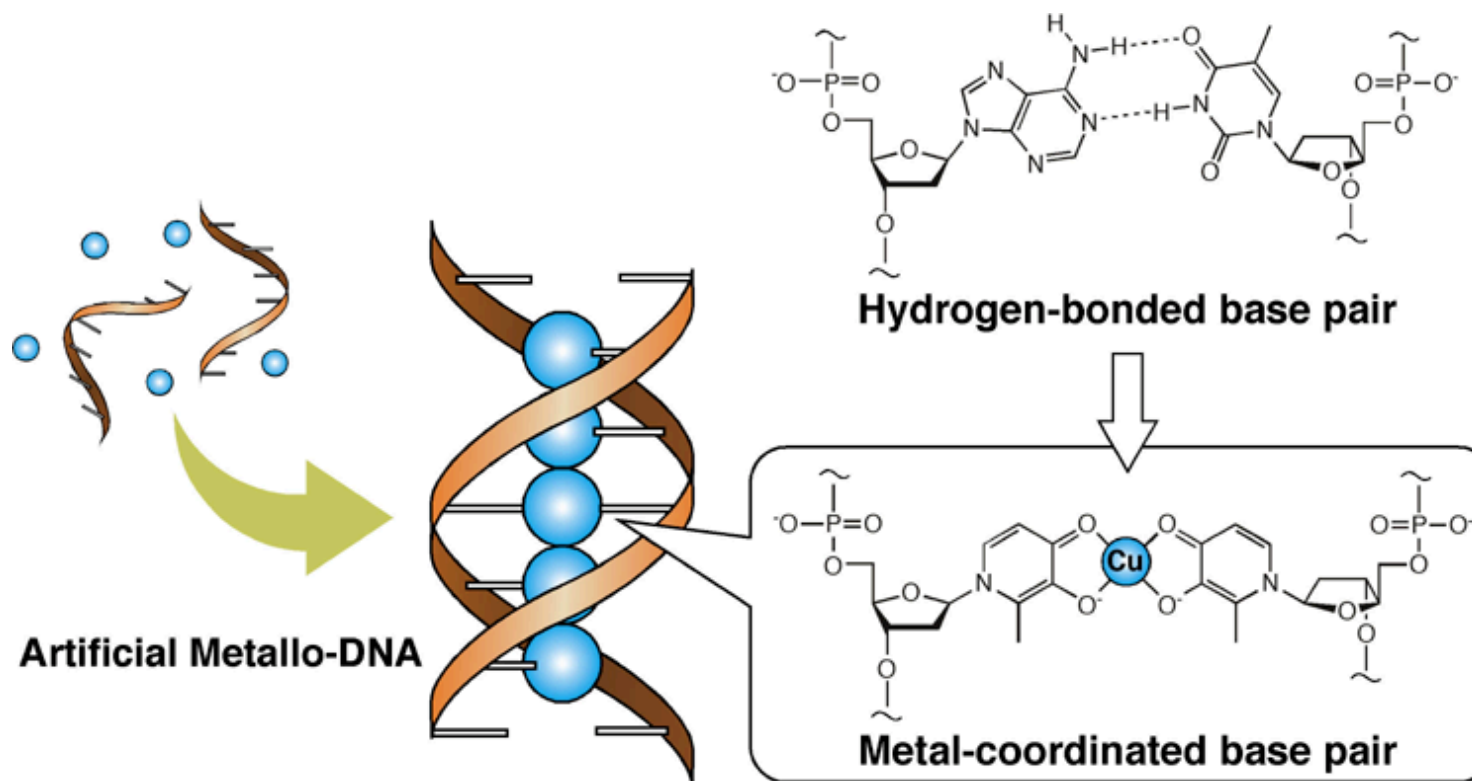
Switzer, *Angew. Chem.* **2005**



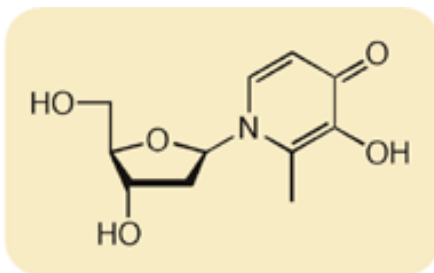
Weizmann, *J. Am. Chem. Soc.* **2001**



A Discrete Self-Assembled Metal Array in Artificial DNA



H =



d(5'-GHHHHHC-3')

d(5'-GHHHHHC-3')

d(3'-CHHHHHG-5')

d(3'-CHHHHHG-5')

d(5'-GHHHC-3')

d(5'-GHHC-3')

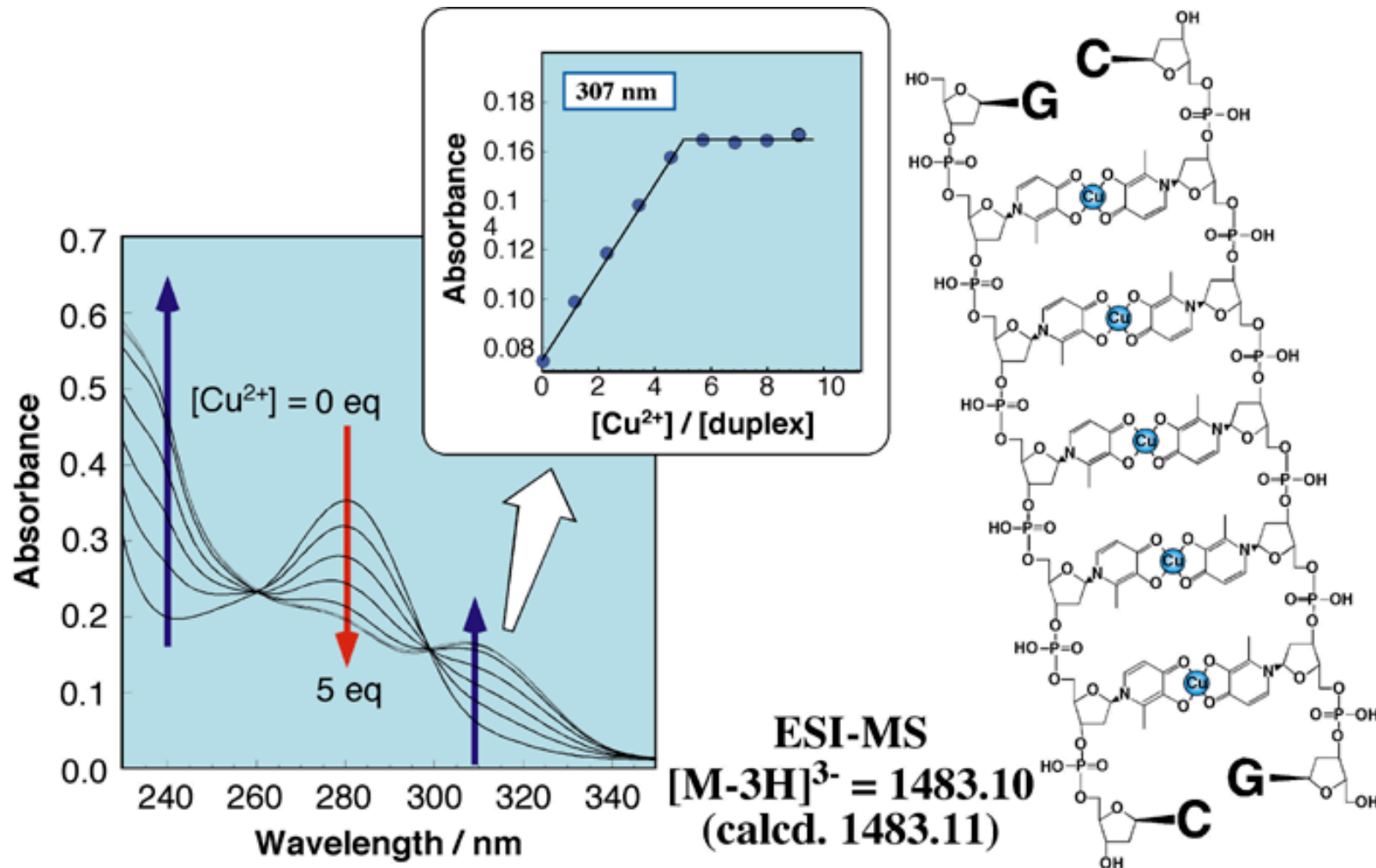
d(5'-GHC-3')

d(3'-CHHHG-5')

d(3'-CHHG-5')

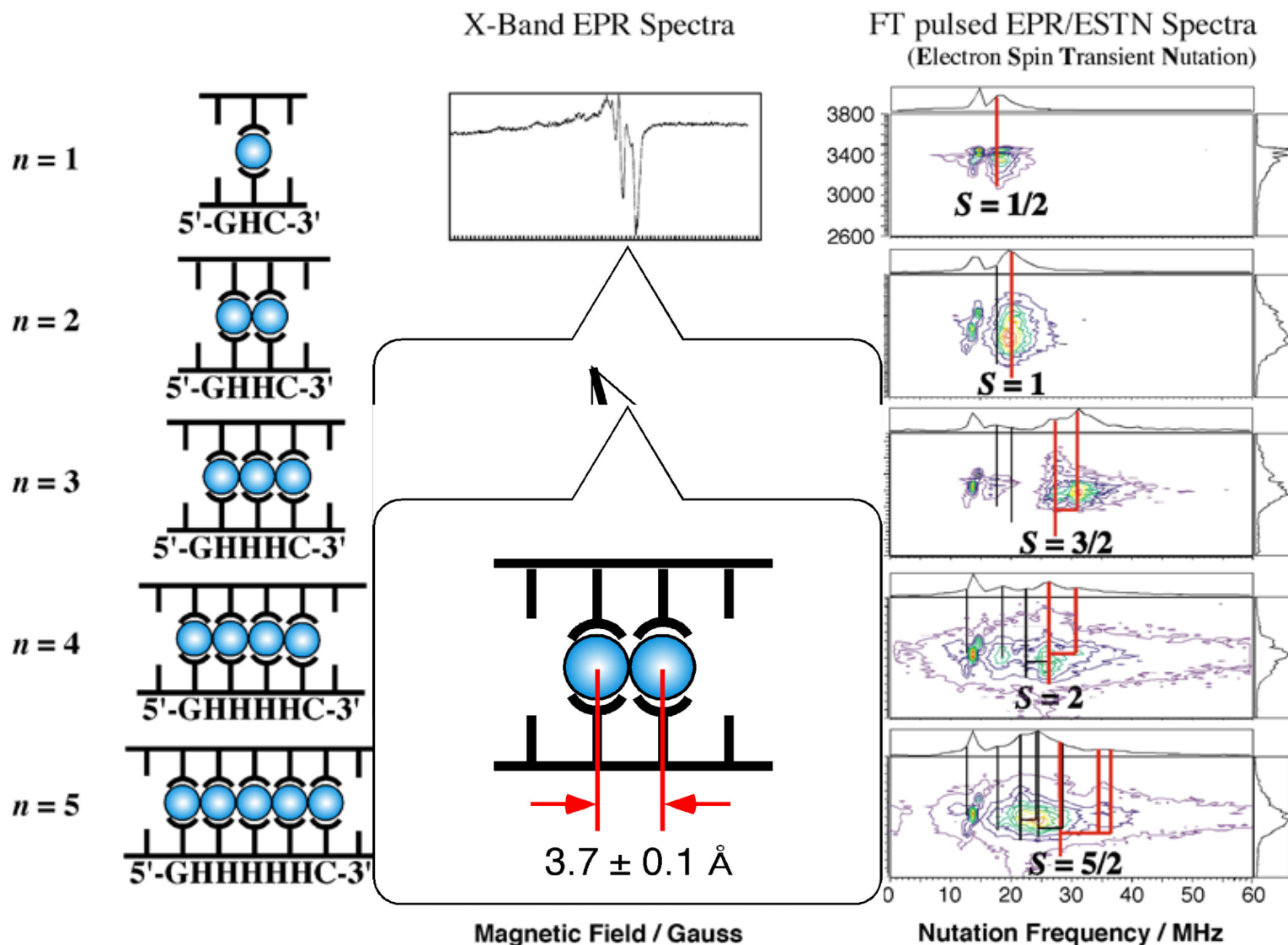
d(3'-CHG-5')

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



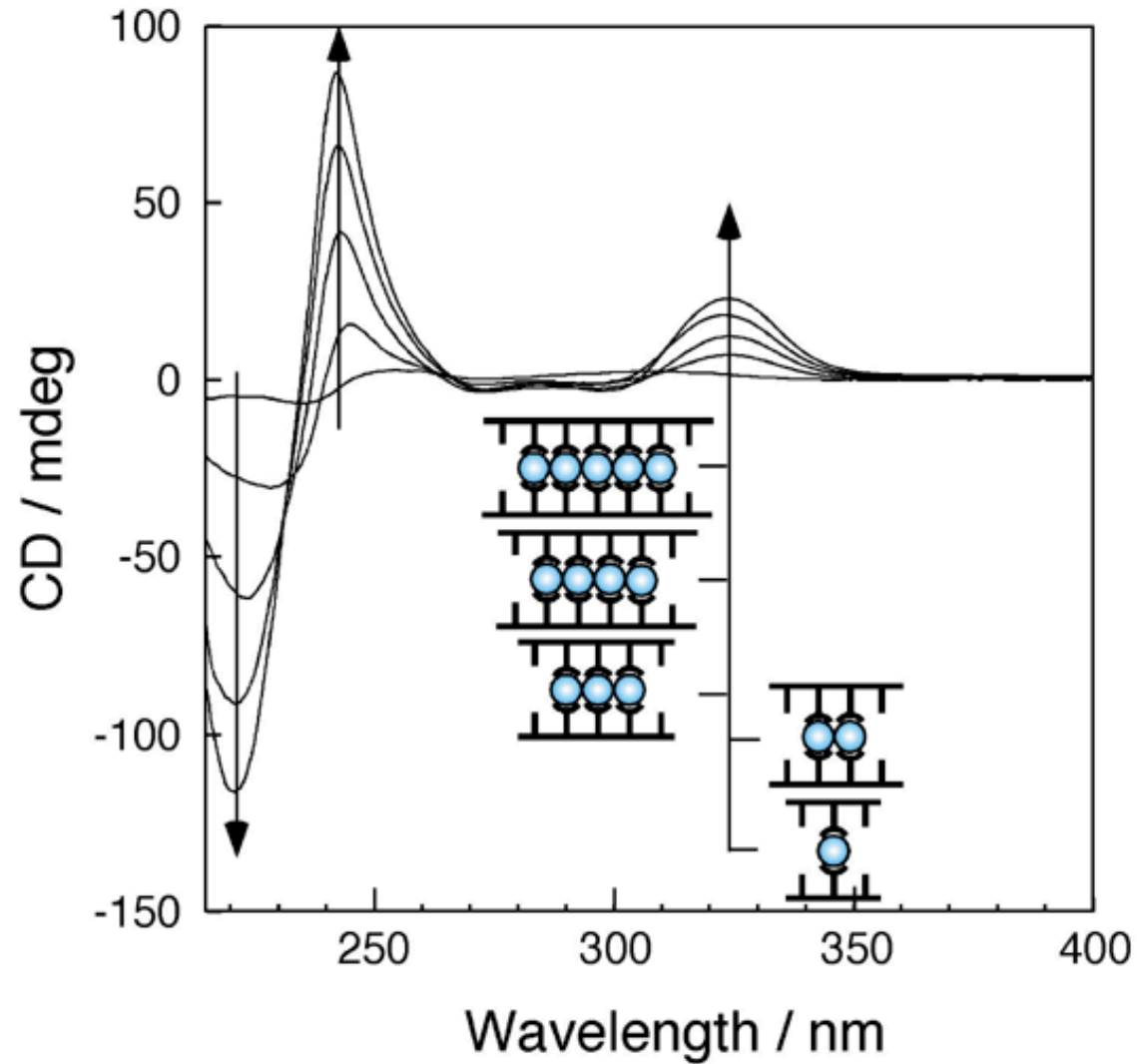
[DNA duplex] = 2.0 μM in 10 mM HEPES (pH 7.0). 50 mM NaCl. 25 $^{\circ}\text{C}$

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



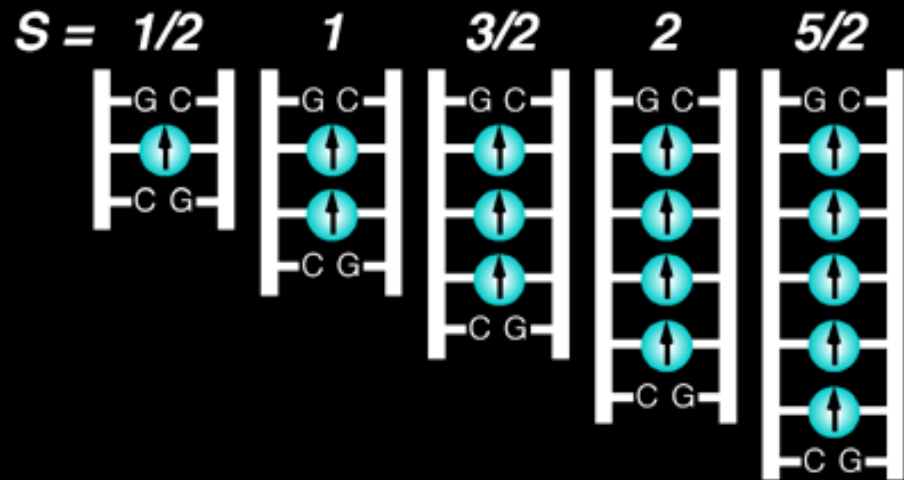
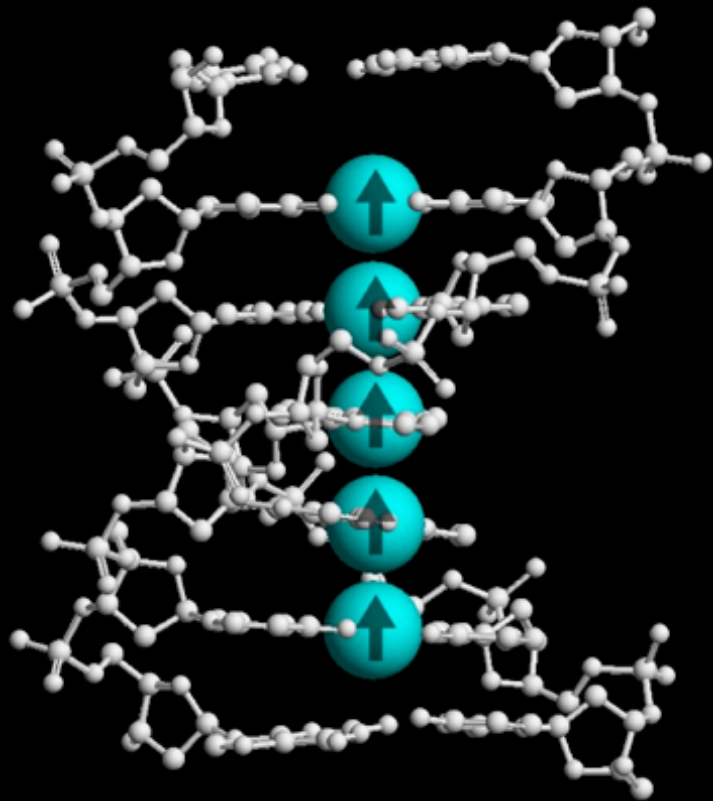
[DNA duplexes] = 100 μM with n eq. CuSO_4 in 10 mM HEPES (pH 7.0), 50 mM NaCl, at 1.5 K.

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



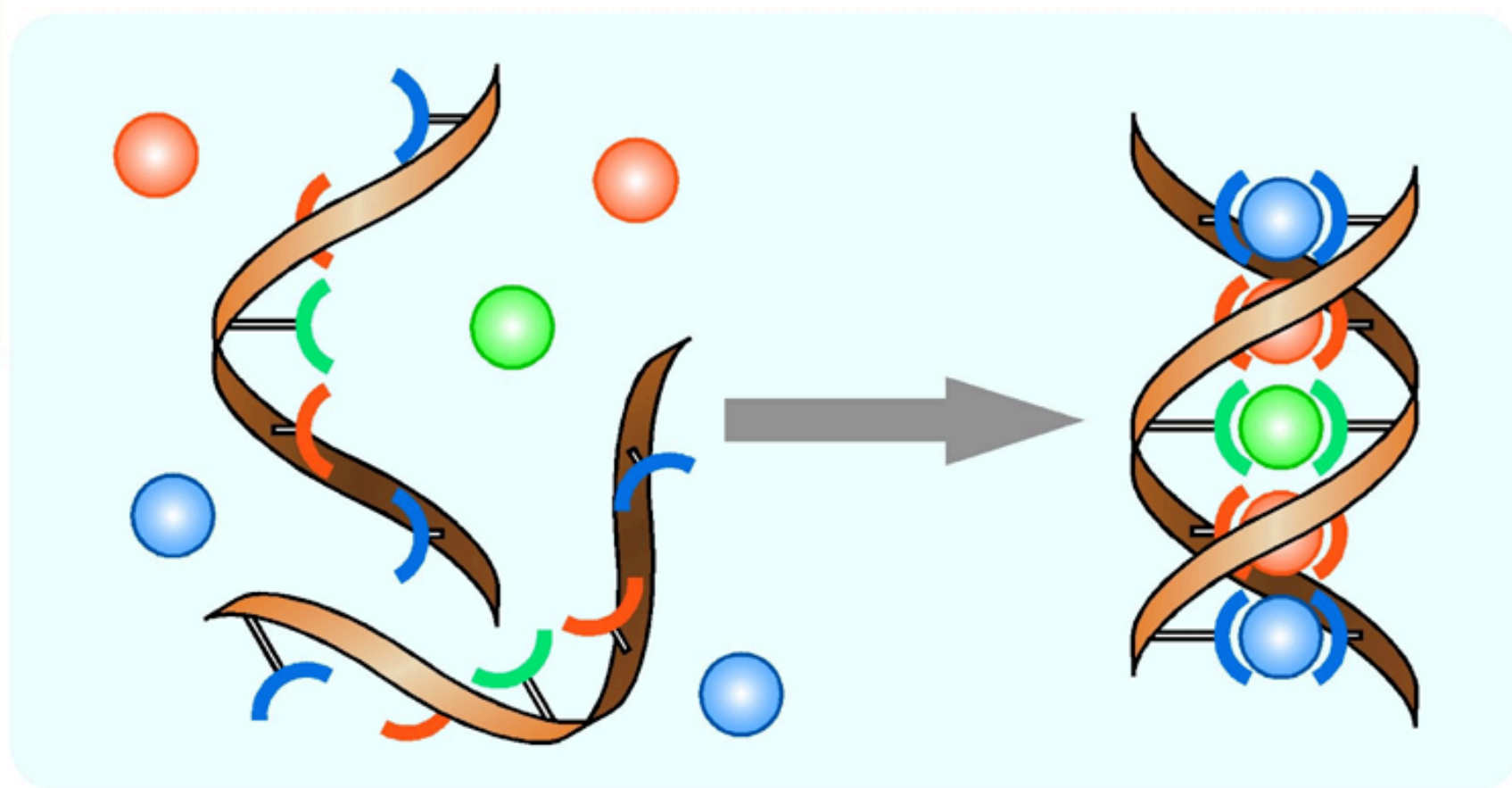
[DNA duplex] = 8.0 μM in 10 mM HEPES (pH 7.0). 50 mM NaCl. l = 1 cm. 25 $^\circ\text{C}$

Discrete Metal Arrays in Artificial DNA

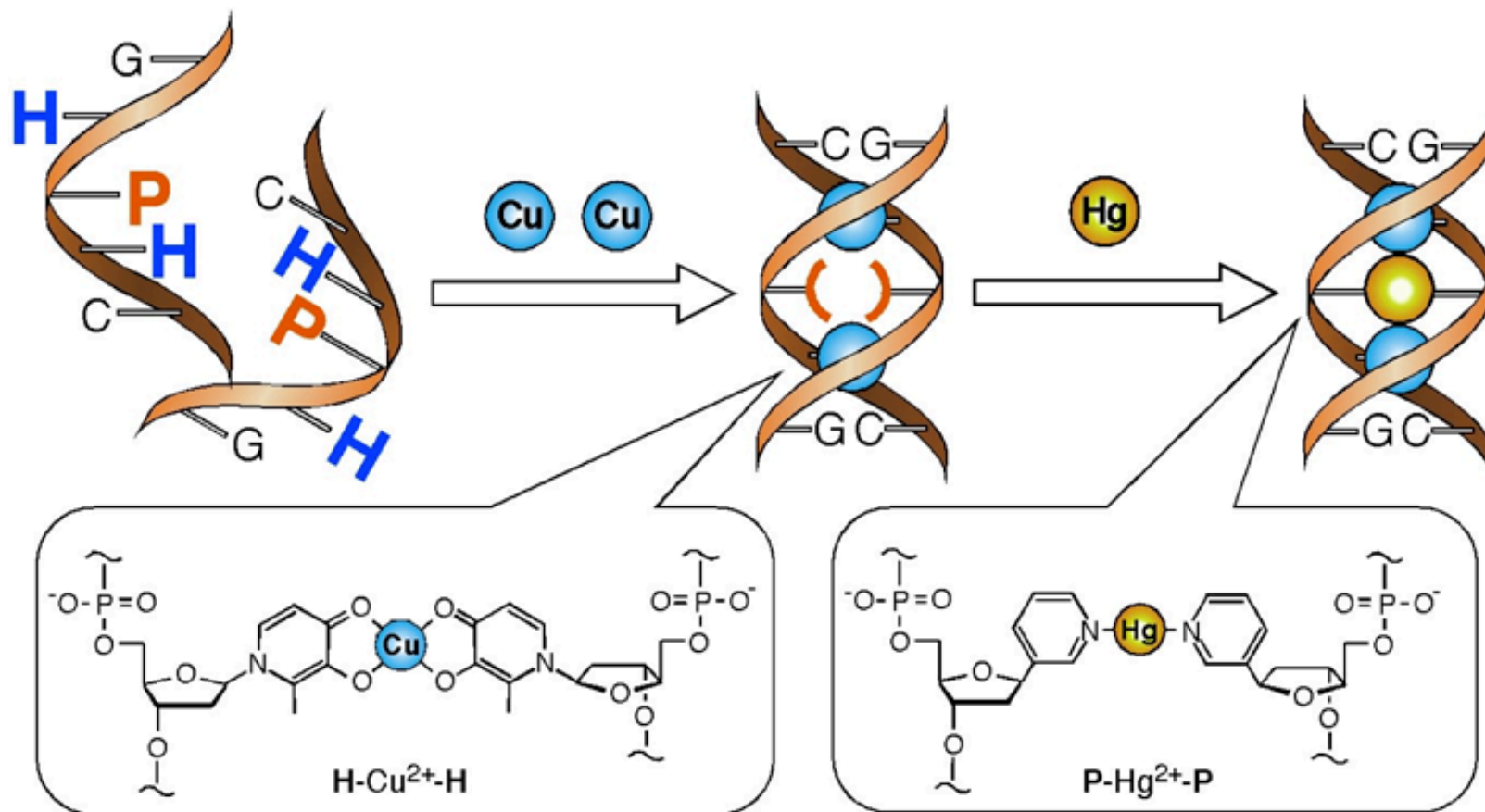


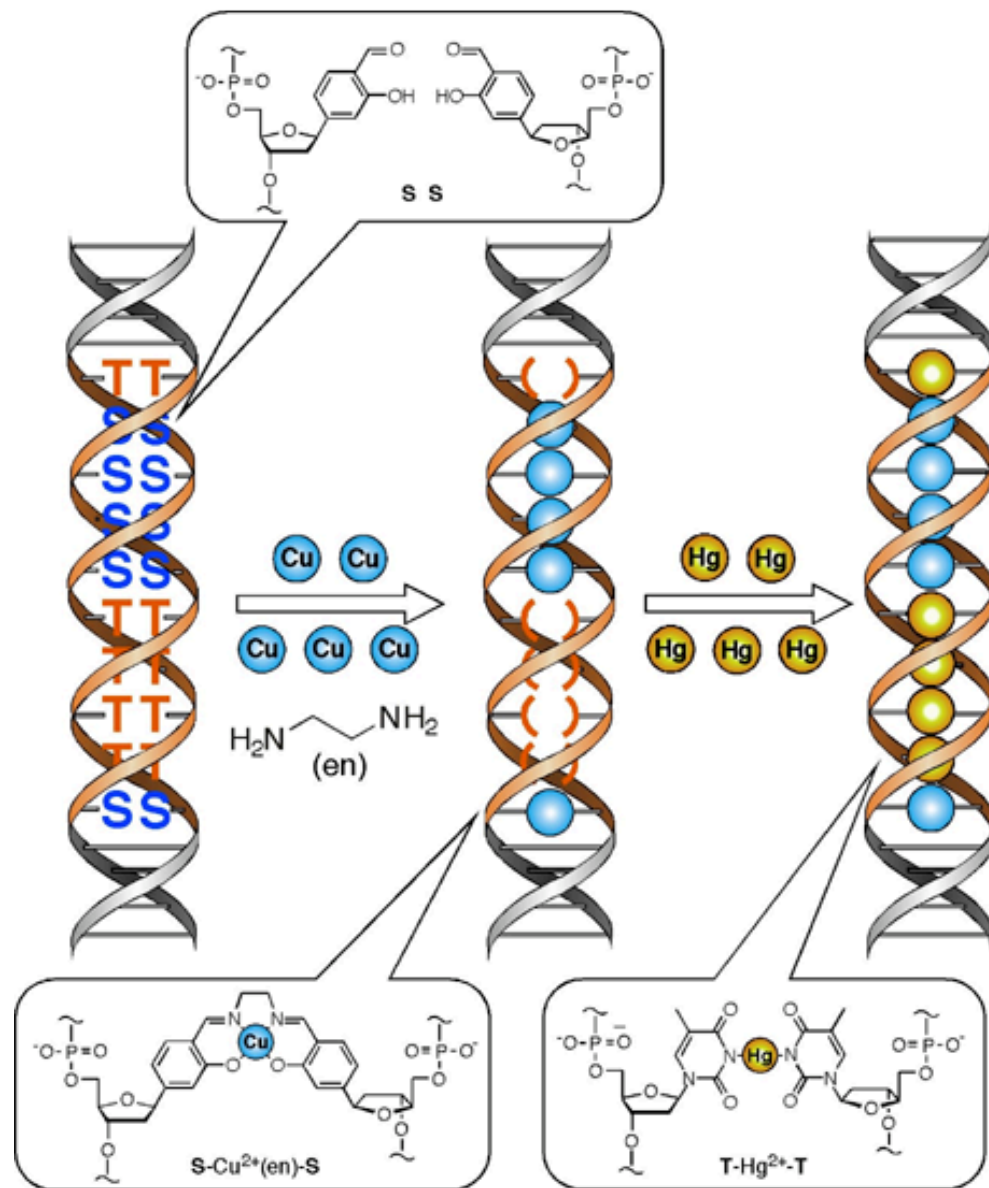
Science, 299, 1212 (2003)

Programmable Heterogeneous Metal Arrays

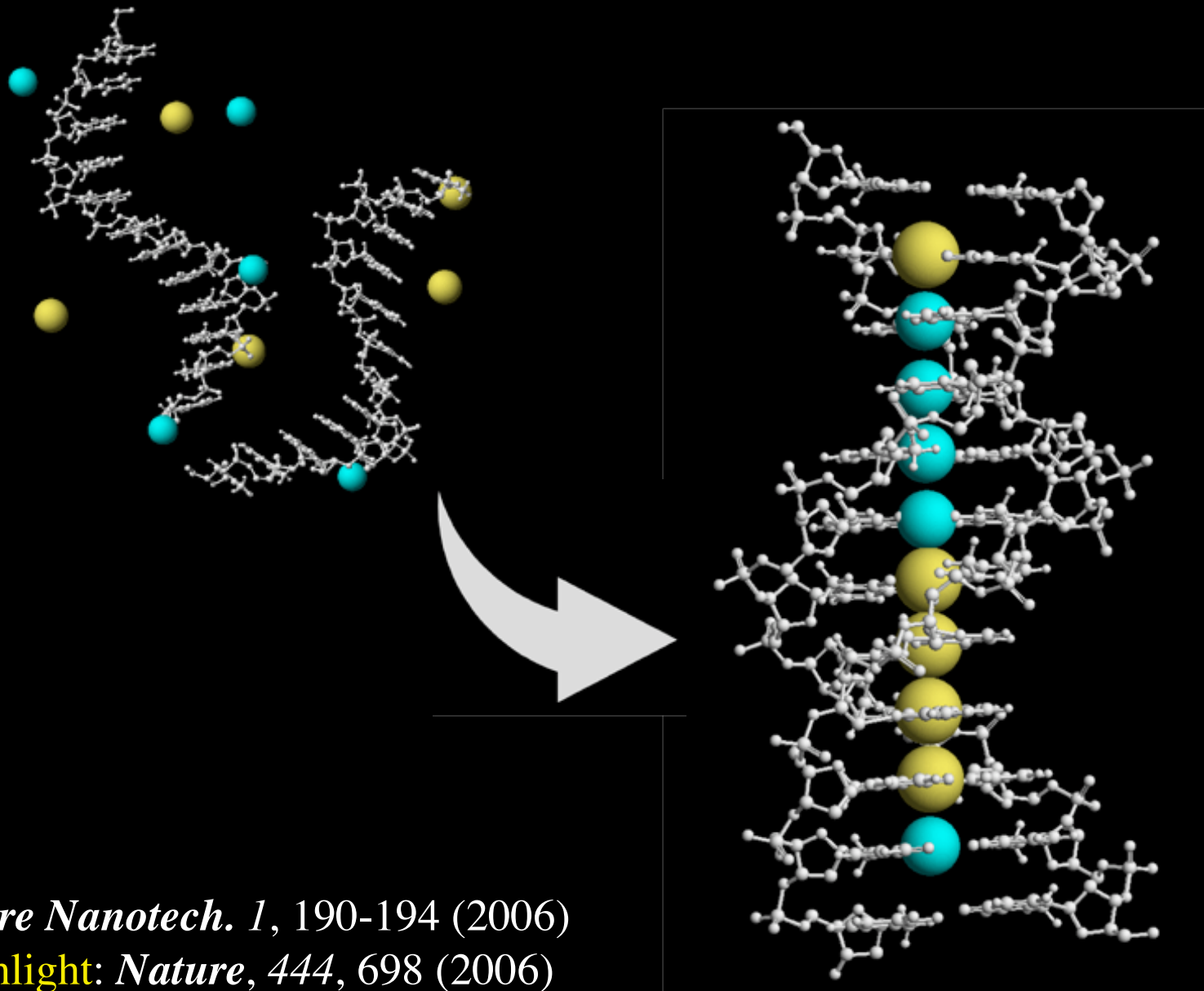


Heterogeneous Metal Array





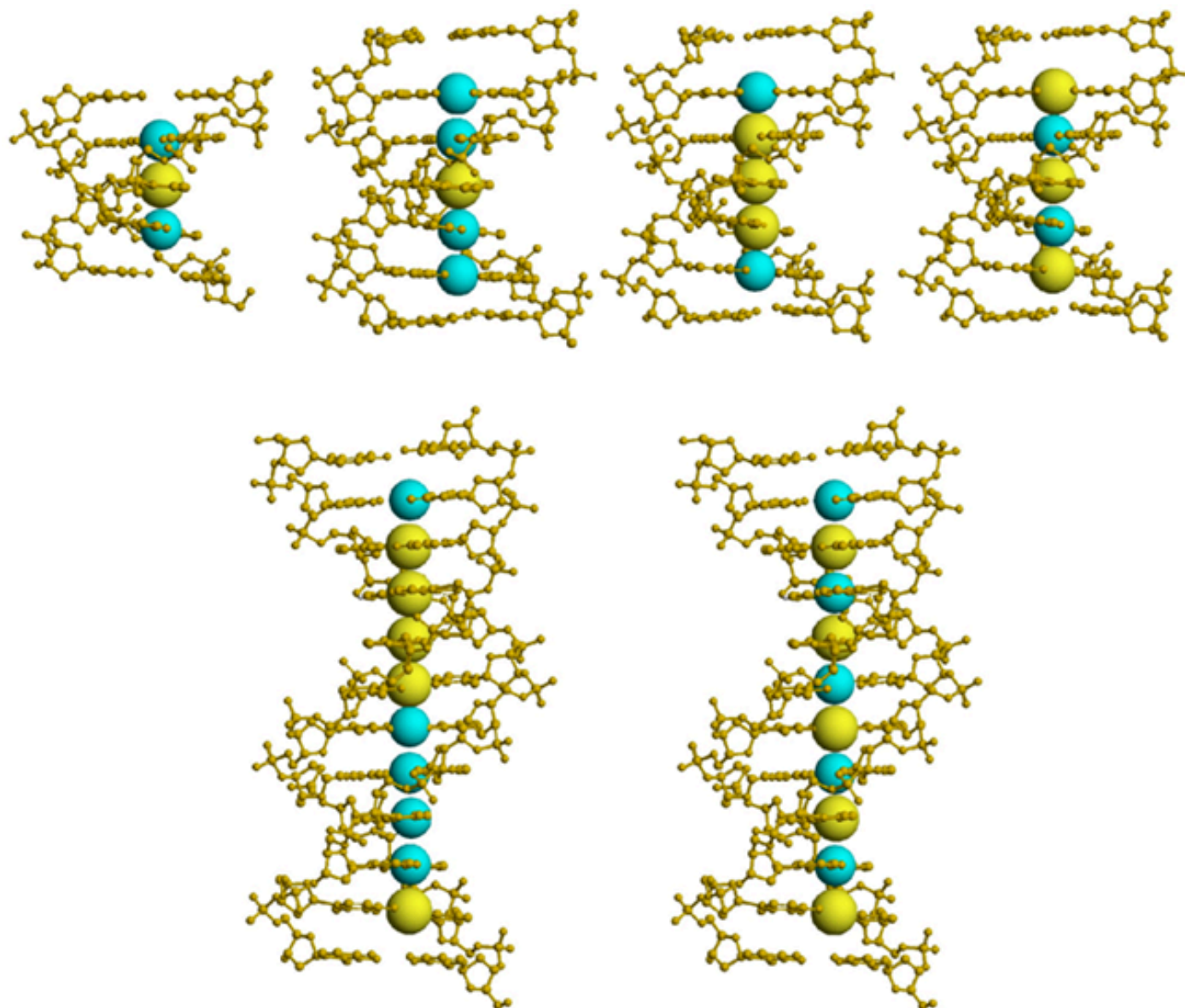
Clever and Carell



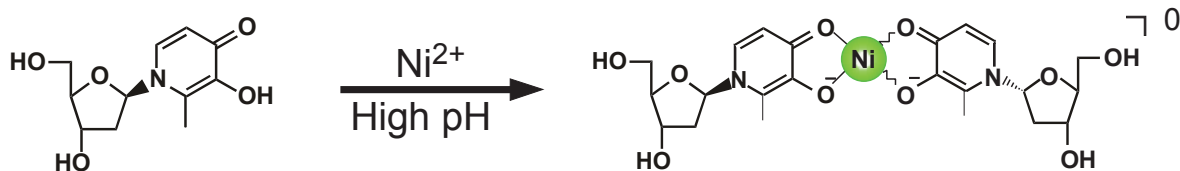
Nature Nanotech. 1, 190-194 (2006)

Highlight: *Nature*, 444, 698 (2006)

Programmable Metal Arrays in Artificial DNAs

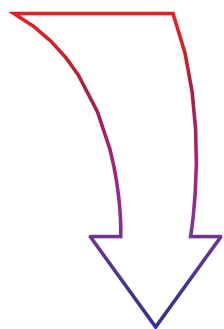


pH-dependent Coordination of Nickel(II)

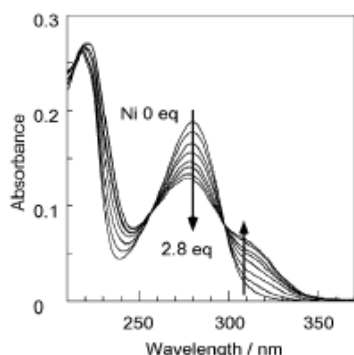


The formation of the nickel-hydroxypyridone base pair requires a higher pH

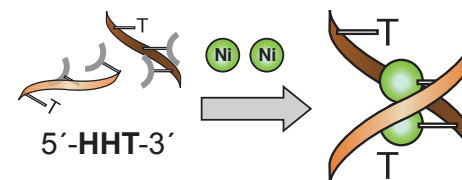
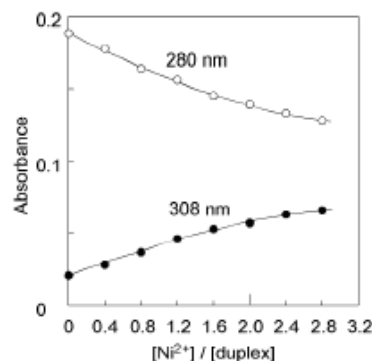
pH = 7.0
Not Quantitative



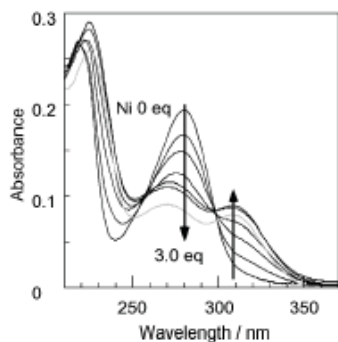
pH = 8.0
Quantitative



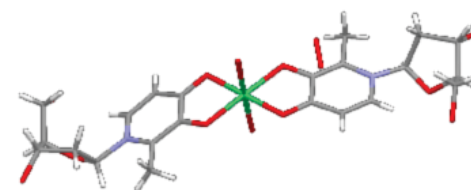
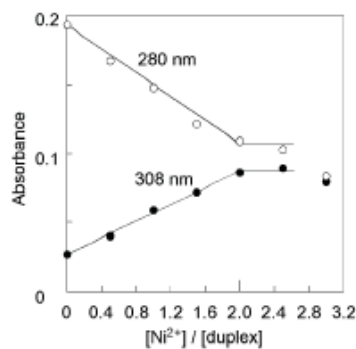
[H] = 100 μM in 10 mM HEPES (pH 7.0), 50 mM NaCl at 25 $^{\circ}\text{C}$, $l = 1.0$ cm



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



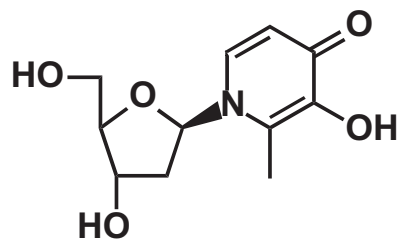
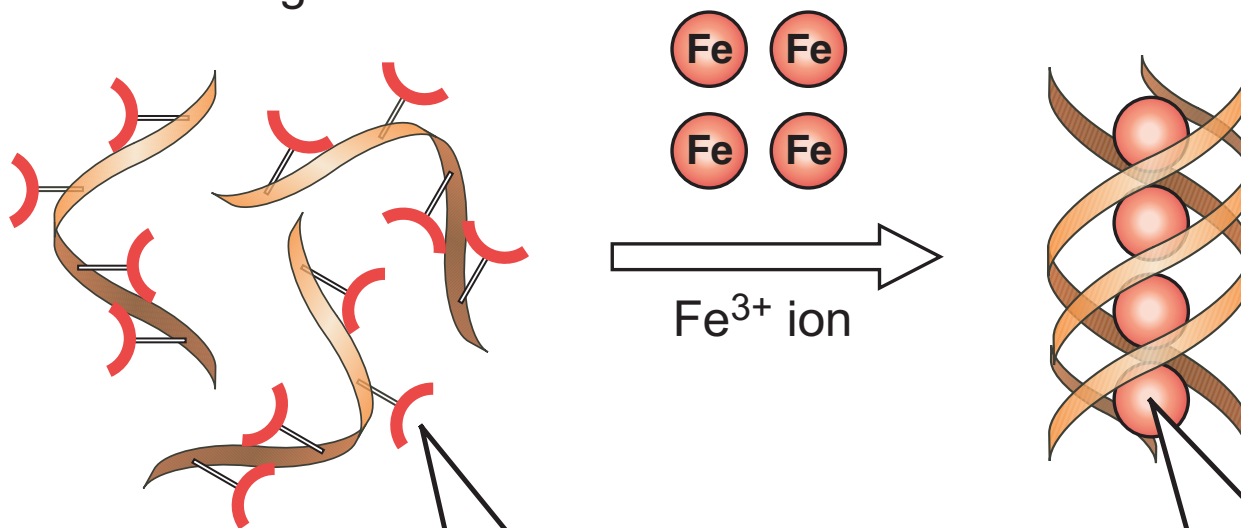
[H] = 100 μM in 10 mM HEPES (pH 8.0), 50 mM NaCl at 25 $^{\circ}\text{C}$, $l = 1.0$ cm



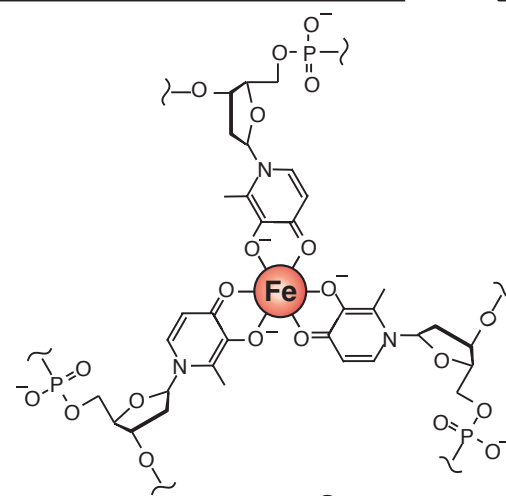
X-ray structure of the monomeric Ni-hydroxypyridone metal base pair

Triple Helicate

Artificial oligonucleotide



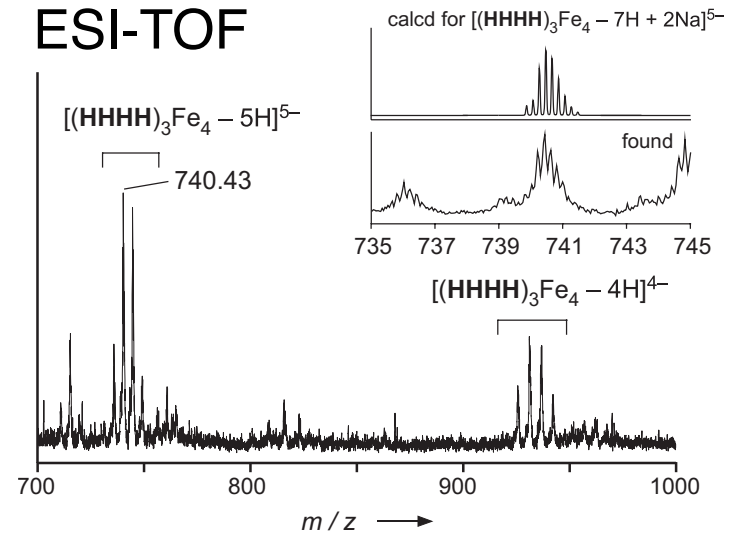
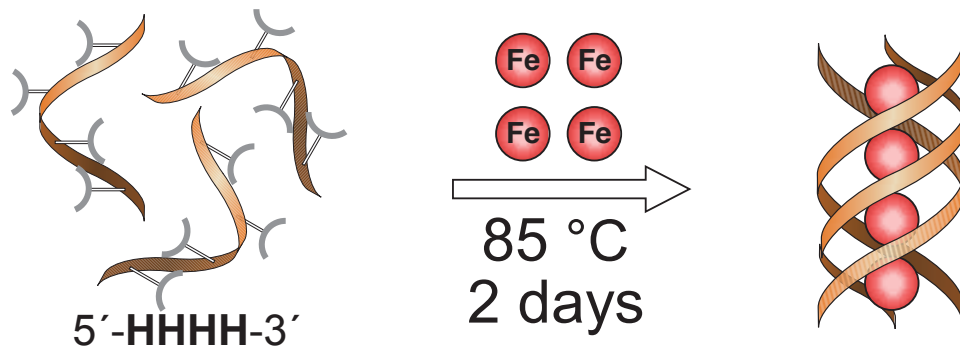
Hydroxypyridone-bearing
nucleoside
(H)



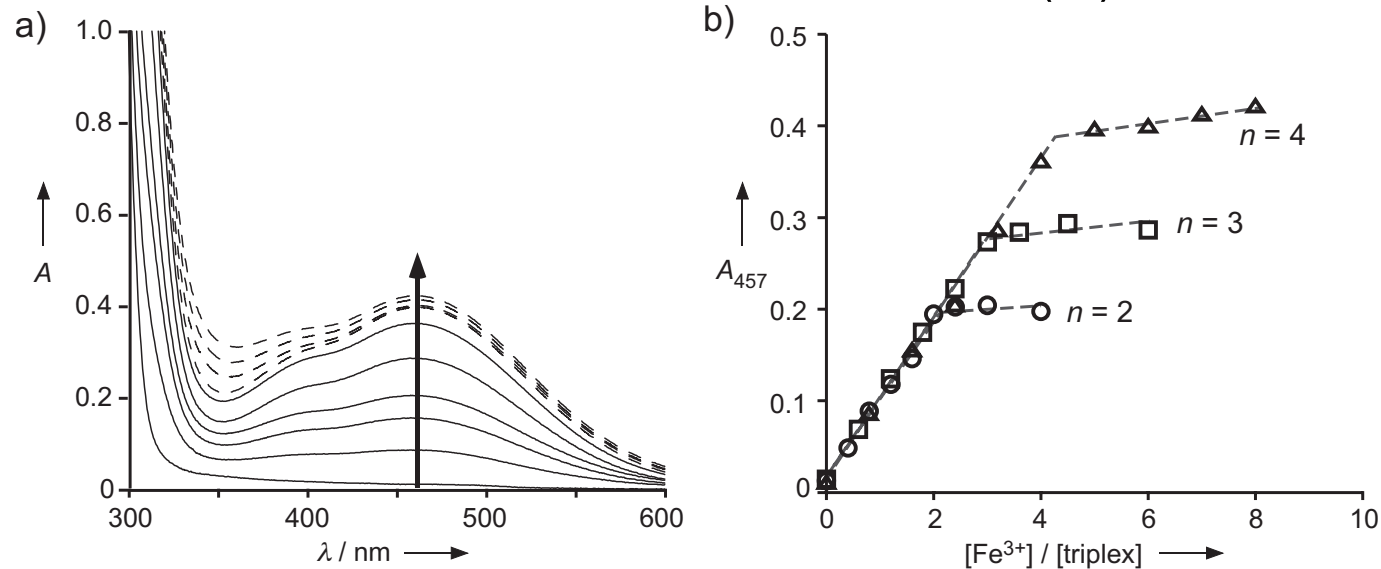
H_3Fe^{3+}

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

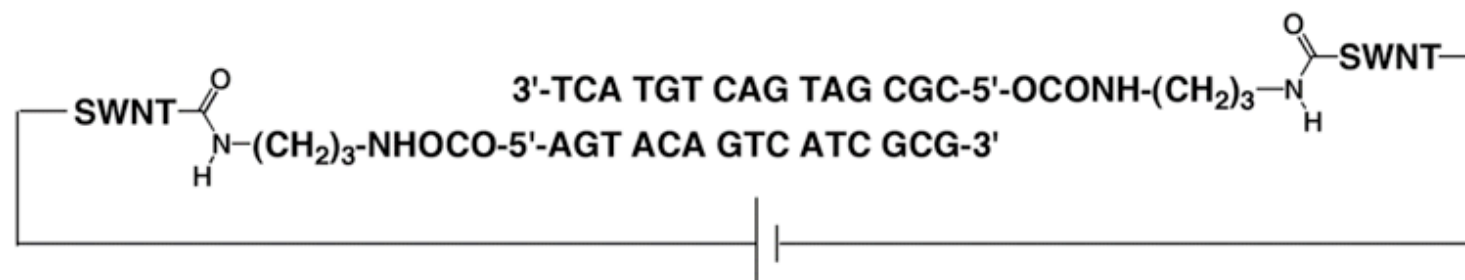
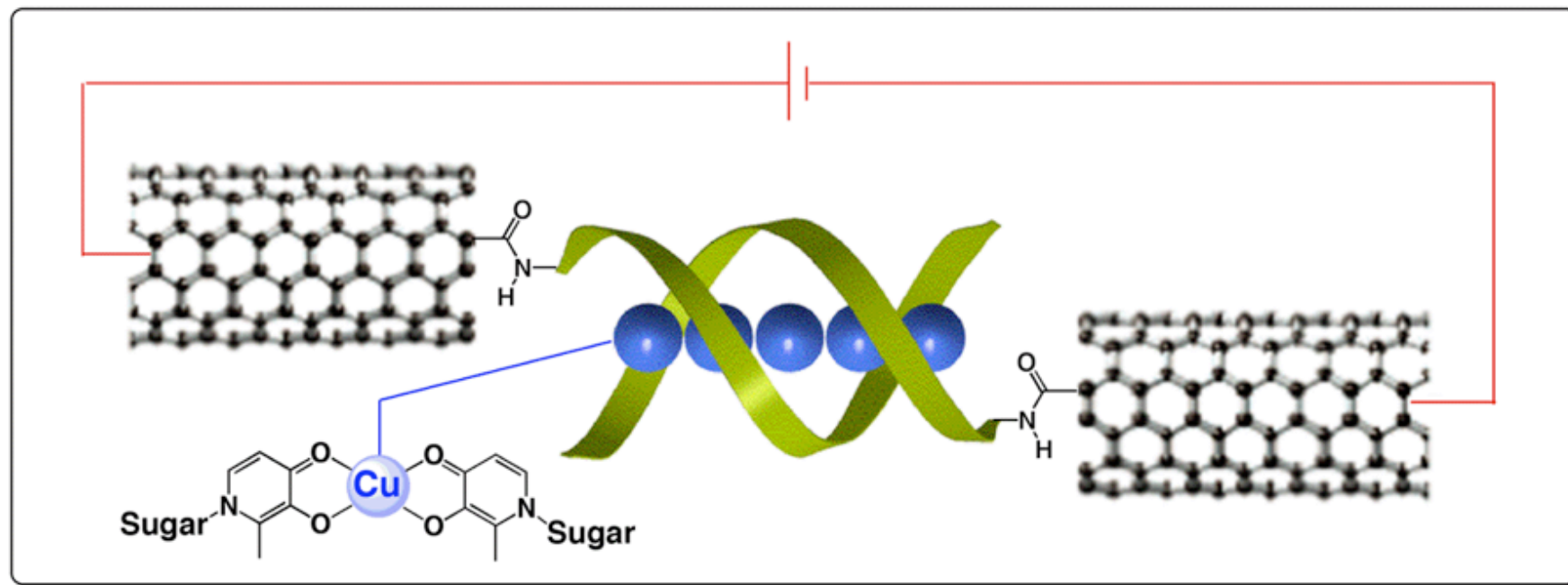
Triple Helix Formation using Fe(III)



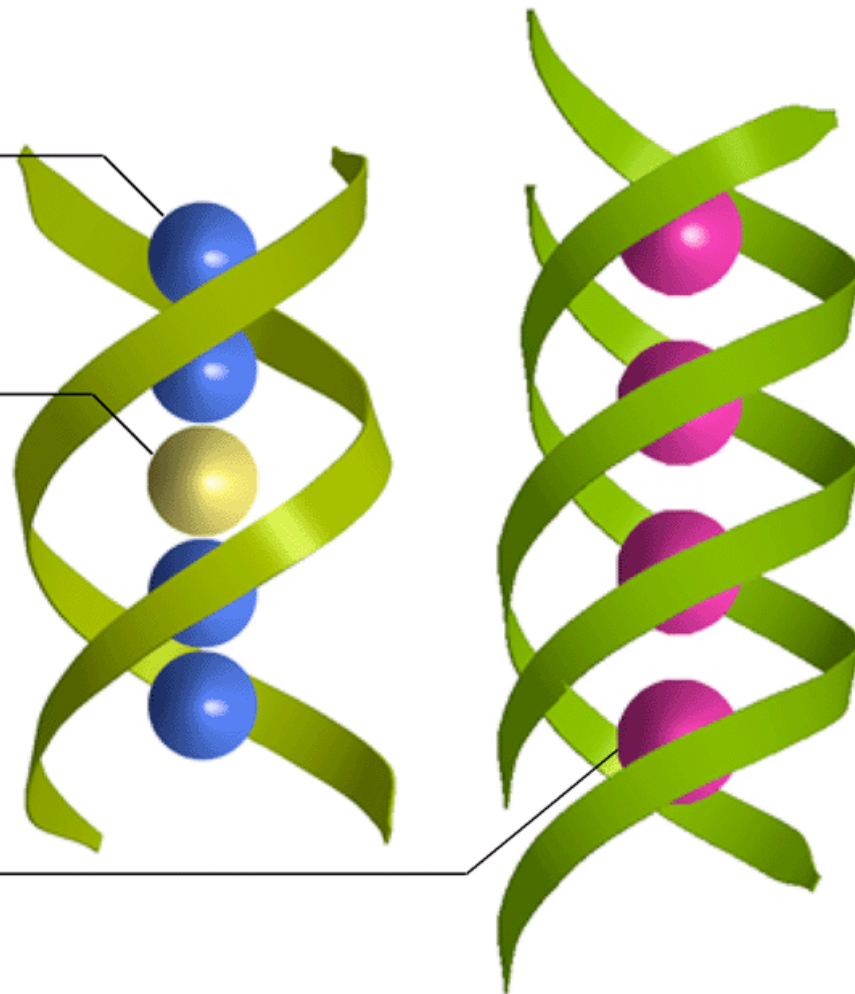
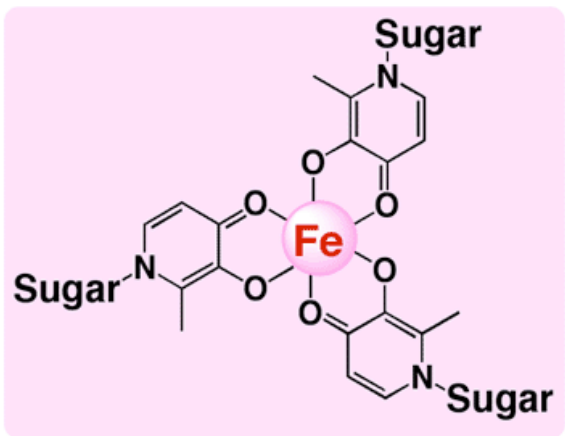
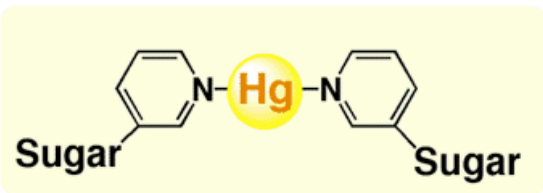
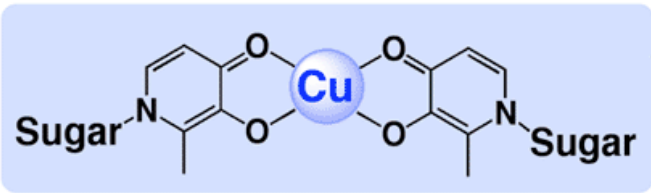
UV-vis-monitored titration of Fe(III)



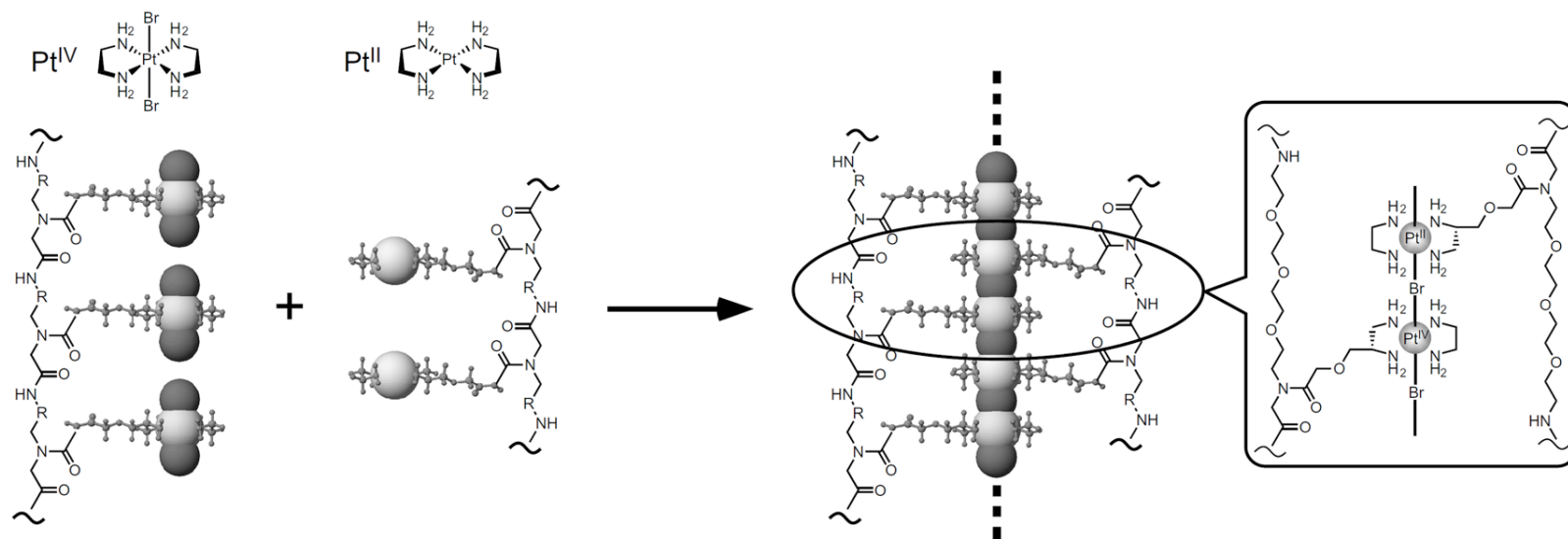
Conductivity of a single metallo-DNA duplex



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



Halogen-bridged Mixed-valence Pt Complexes on Artificial Peptides



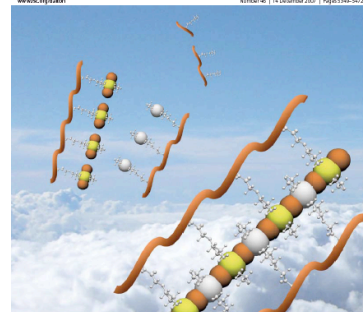
Dalton Trans., 2007, 5369

**Dalton
Transactions**

An International Journal of inorganic chemistry

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Number 46 | 14 December 2007 | Pages 5368-5422



0951-8036

RSC Publishing

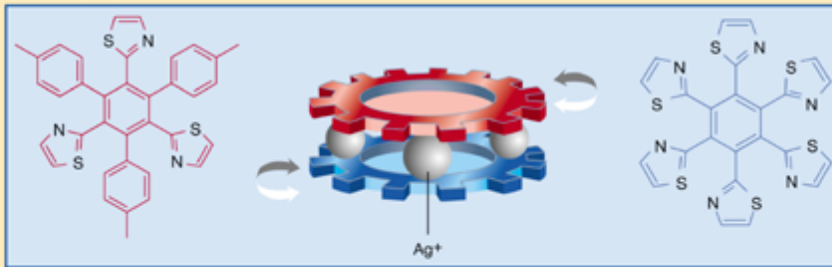
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1000-0001

Supramolecular chemistry
Molecular merry-go-round

Magdalena Helmer



NATURE | VOL 427 | 12 FEBRUARY 2004 | www.nature.com/nature

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Nature (2004)

597

NEWS & VIEWS

CHEMISTRY
Metals line up for DNA

Jens Müller

The versatile DNA molecule has found many applications beyond biology. In its latest role, it serves as a self-assembling scaffold to arrange different metal ions in a row, like pearls on a string.

The idea when DNA was the exclusive province of molecular biologists are over. Since the discovery of DNA double-helix structure in 1953, numerous disciplines have embraced the molecule — from medicine to materials science, by way of chemical chemistry and biotechnology. Reporting in *Nature Nanotechnology*, Tanaka *et al.* describe an application of DNA that clearly stems from inorganic chemistry: they have modified DNA to form a narrow scale scaffold for one-dimensional arrays of metal ions. Each array is a combination of copper and mercury ions, arranged in an order dictated by the DNA sequence. Such precise control over the assembly of these arrays would be necessary for their potential applications as nanocomposites, as well as controlling molecular wires or as catalysts in chemical reactions. Single strands of DNA comprise a negatively charged phosphate chain decorated with organic bases. A natural DNA double helix consists of two single strands, with the major phosphate backbone on the outside and the bases on the inside (Fig. 1a). Each base forms hydrogen bonds with just one other kind of base — a complementary base — on the opposite strand in the complementary of these bases that describe the helix will assembly precisely of double helix formation.

Tanaka *et al.* exploit the natural bases of DNA with artificial ones. Each of these substituents has a high affinity for a particular metal ion — either a copper ion (Cu²⁺) or a mercury ion (Hg²⁺). The modified DNA can form a double helix only if the opposing bases have a preference for the same metal ion and if both bases bind to such an ion. Given an appropriate base sequence, a single can form that contains one or more metal ions along its entire length (Fig. 1b).

The incorporation of metal ions into an artificial DNA duplex has previously been reported, but with only a small number of metal ions, typically in contact with a few modified base pairs interspersed between longer runs of natural ones^{1,2}. What is remarkable about Tanaka and colleagues' work is the formation of stable helices containing long stretches of two different metal ions. Not only did the authors selectively incorporate two different kinds of metal ions into artificial DNA, but they also used more than one kind of artificial base to enhance sequence. This is a tremendous advance since towards the goal of making metal-containing, self-assembling nanomaterials with desirable properties that can be used in

represent a biologically inspired approach that could combine the best of both of these catalytic worlds.

It has been found that, in a short artificial DNA duplex containing an array of five consecutive copper ions, the distance is significantly with each other (the helix axis) thought of as a well-ordered nanowire³. Using Tanaka and colleagues' approach¹, specific combinations of metal ions might be incorporated into DNA to determine the magnetic properties of nanowires. The choice of properties of DNA are also of interest. Unmodified DNA lacks sufficient electrical conductivity to be used in molecular electronic devices⁴. To address this problem, DNA has previously been equipped with metal-olefinic helices⁵, but their reversibility self-assembly⁶. Tanaka and colleagues' structures¹ might provide a way forward, as they incorporate metal ions in the center of a DNA double helix that retains its ability to self-assemble.

That difficulty might be circumvented when scaling up the authors' technique to build longer molecules. An DNA duplex forms, intermediate double helices can be produced in which the bases are not perfectly matched. But every metal ion incorporated into the artificial DNA increases the stability of the final aggregate. This effect could stabilize the intermediate helices so much that they no longer manage to form a perfect duplex, or introducing ions along DNA will assemble.

Perhaps more important, extension of DNA synthesis can only proceed sequentially up to about 300 bases. To build longer structures, hybridization techniques for developing that other splice together short artificial DNA strands or allow the synthesis of longer strands. Such methods are not natural DNA, but they would have to be modified to tolerate artificial bases and metal ions. Finally, more work is needed to determine the electrical properties of metal ion-containing DNA — is a conductor or a semiconductor? Future research should focus on these questions, and investigate the factors that influence conductivity. It seems that the quest for a functioning molecular device based on metal ion-modified DNA is about to begin.

More info in the Department of Chemistry, University of Darmstadt, Otto-Str. 26/27a, 64287 Darmstadt, Germany.
e-mail: jens.mueller@chemie.uni-darmstadt.de

1. Tanaka, T. *et al.* *Nature Nanotechnol.* **5**, 204 (2010).
2. Tanaka, T. *et al.* *Nature Nanotechnol.* **5**, 204 (2010).
3. Tanaka, T. *et al.* *Nature Nanotechnol.* **5**, 204 (2010).
4. Tanaka, T. *et al.* *Nature Nanotechnol.* **5**, 204 (2010).
5. Tanaka, T. *et al.* *Nature Nanotechnol.* **5**, 204 (2010).
6. Tanaka, T. *et al.* *Nature Nanotechnol.* **5**, 204 (2010).

Nature (2006)

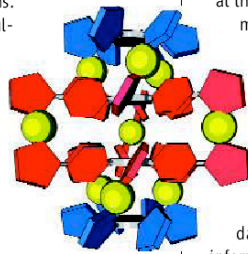
EDITORS' CHOICE

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CHEMISTRY
Spinning in Concert

In macroscopic machines, gears are commonly used to induce the synchronous motion of well-separated components. Hiraoka *et al.* observe a similar effect at the nanoscale in a stack of four ligands held together by mutual coordination to metal ions.

The ligands consist of multiple oxazoline or thiazole rings appended to a central phenyl core. Upon binding silver or mercury ions, these pendant rings adopt a common cant (shown at right) that creates an overall helicity, with the central ligands transmitting an orientational bias from one capping ligand to the other. Using solution-phase nuclear magnetic resonance spectroscopy, the authors demonstrate that a helix inversion in one component of the stack induces a cascade of inversions throughout, thereby correlating the motion of molecules spaced more than a nanometer apart. — JSY



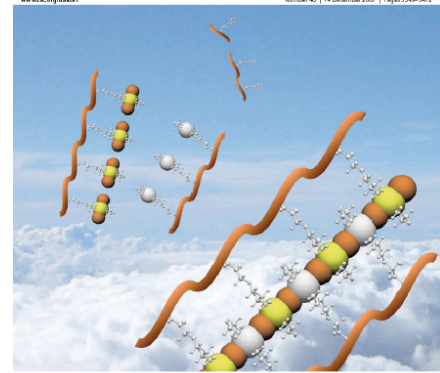
J. Am. Chem. Soc. **130**, 10.1021/ja8014583

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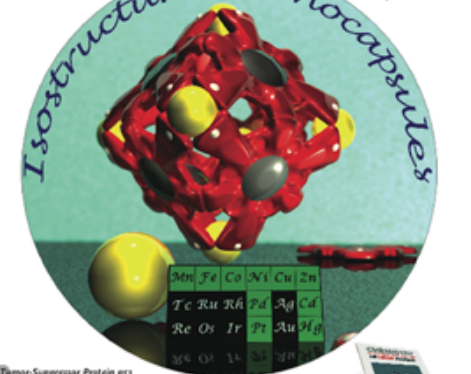


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