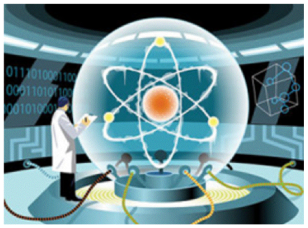
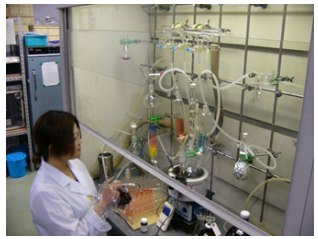
Design and Synthesis of Molecular Systems for Scalable Molecular-spin QC

Yasushi Morita, Osaka Univ.





Tools: { organic chemistry / coordination chemistry / supramolecular chemistry

Targets:

- Stable organic open-shell molecules for electron spin qubits
- Triple-stranded helical metal complexes for Lloyd's electron spin qubits
- Closed-shell molecules with periodical structure for Lloyd's nuclear spin qubits
- Regioselectively isotope-labeled molecules for scalable spin amplification

nature chemistry

PERSPECTIVE

PUBLISHED ONLINE: 21 FEBRUARY 2011 | DOI: 10.1038/NCHEM.985

1

Synthetic organic spin chemistry for structurally well-defined open-shell graphene fragments

2

Yasushi Morita[1]*, Shuichi Suzuki[2], Kazunobu Sato[2] and Takeji Takui[2]*

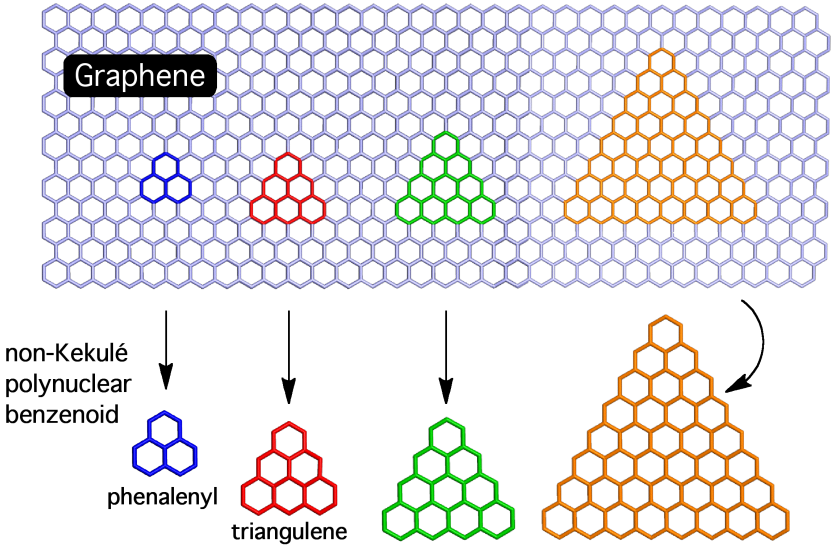
Graphene, a two-dimensional layer of sp^2-hybridized carbon atoms, can be viewed as a sheet of benzene rings fused together. Three benzene rings can be combined in three different ways, to yield linear anthracene and angular phenanthrene, where the rings share two C–C bonds, and the phenalenyl structure where three C–C bonds are shared between the rings. This third structure contains an uneven number of carbon atoms and, hence, in its neutral state, an uneven number of electrons — that is, it is a radical. All three structures may be viewed as being sections of graphene. Extension of this concept leads to an entire family of phenalenyl derivatives — 'open-shell graphene fragments' — that are of substantial interest from the standpoint of fundamental science as well as in view of their potential applications in materials chemistry, in particular quantum electronic devices. Here we discuss current trends and challenges in this field.

Synthetic organic spin chemistry:

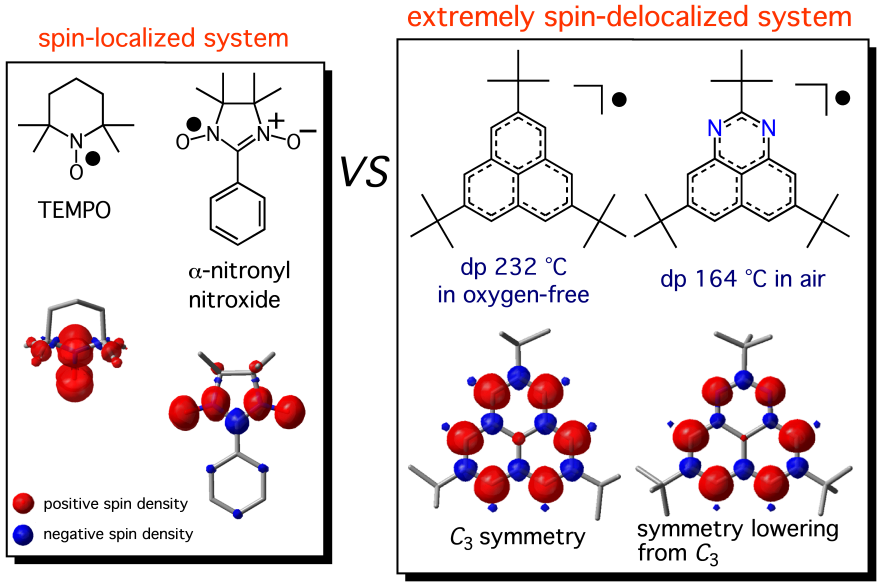
molecular design, bottom-up synthesis, and creation of intriguing physical properties of structually well-defined open-shell organic molecule

Nature Chemistry 2011

Open-shell Graphene Fragment: Designed by Triangular Zigzag-type Clipping from Graphene



Stabilities and Spin–Delocalized Nature

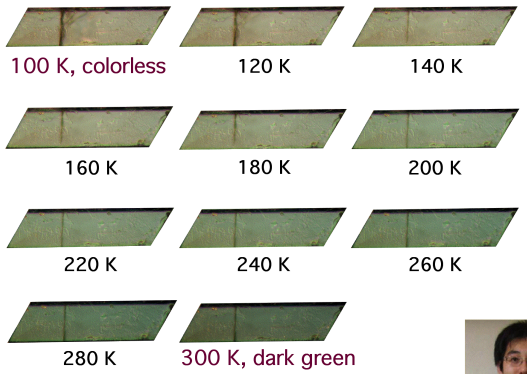


LETTERS

Nature Materials 2008

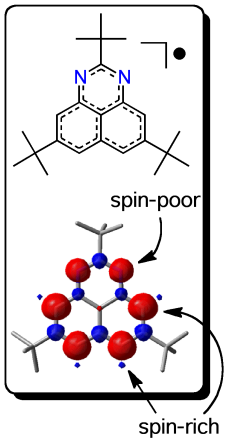
Thermochromism in an organic crystal based on the coexistence of σ- and π-dimers

特開2009-126954

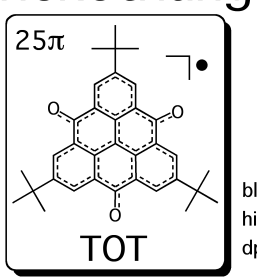


reversible continuous color-change in single-crystal

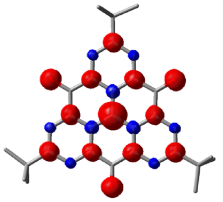
Dr. Shuichi Suzuki



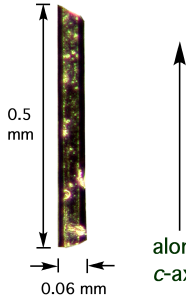
Trioxotriangulene Neutral Radical

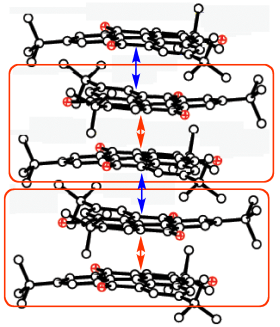


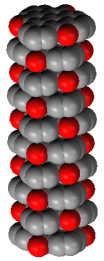
black hexagonal prism
high air-stability
dp > 300 °C in air !!



spin density distribution



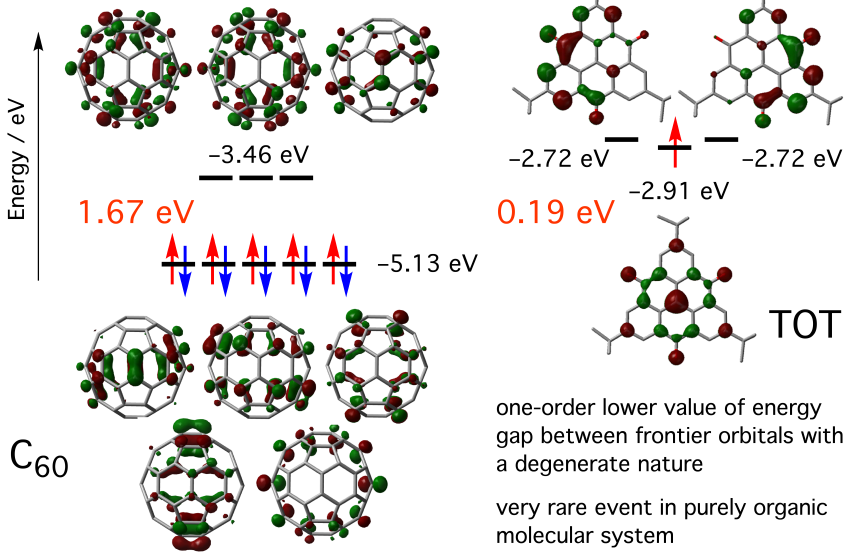




tert-butyl groups are omitted

C_{60} *vs* TOT

ROBLYP/6-31G(d, p)//UBLYP/6-31G(d, p)



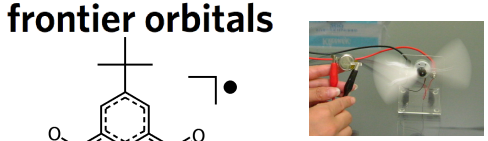
one-order lower value of energy gap between frontier orbitals with a degenerate nature

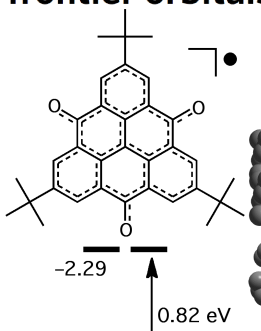
very rare event in purely organic molecular system

nature materials
LETTERS
PUBLISHED ONLINE: 16 OCTOBER 2011 | DOI: 10.1038/NMAT3142
2011年10月

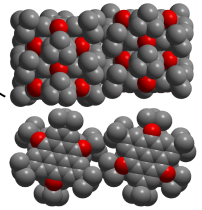
Organic tailored batteries materials using stable open-shell molecules with degenerate frontier orbitals

分子スピン電池



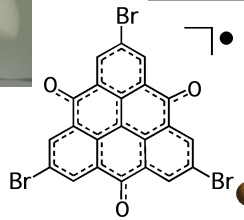


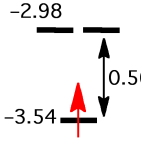
ROB3LYP/6-31G(d, p)//
UB3LYP/6-31G(d, p)

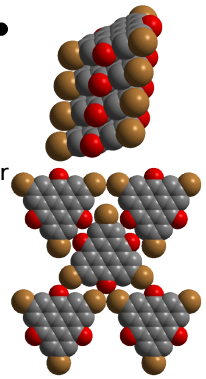


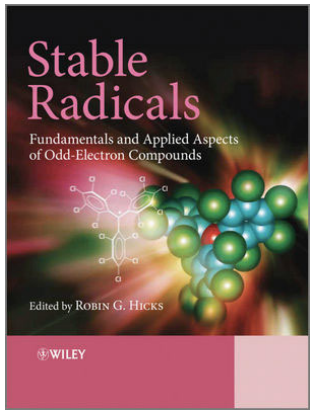
degenerate MO induced by topological symmetry

very narrow SOMO–LUMO gap









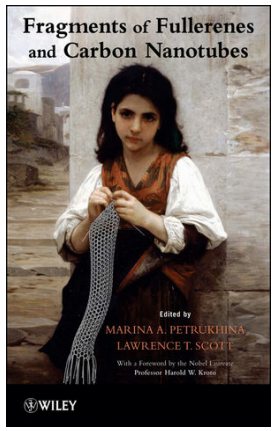
July 2010
US $195

chapter 3

"Phenalenyls, Cyclopentadienyls, and Other Carbon-Centered Radicals"

Morita, Y.; Nishida, S.

reference: 259; Figure: 66; Scheme: 13
60 page / total 608



November
2011
US $135

chapter 4

"Curved π-Conjugated Stable Open-shell Systems Possessing Three-dimensional Molecular/Electronic-spin Structures"

Morita, Y.; Ueda, A.

reference: 69; Figure: 15; Scheme: 2
34 page / total 376

Molecular Design of Molecular-spin QC Model Compounds

Electron-nucleus qubit system

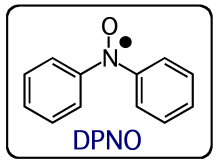
- Air-stable monoradical
- Various discriminable nuclear-spins coupled with electronic spin of radical

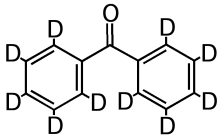
Electron-electron qubit system

- Air-stable oligo-radical
- Weak exchange interaction between spins
- *g*-engineering for discrimination of spins

DPNO Derivatives for Electron-Nucleus Qubit Systems

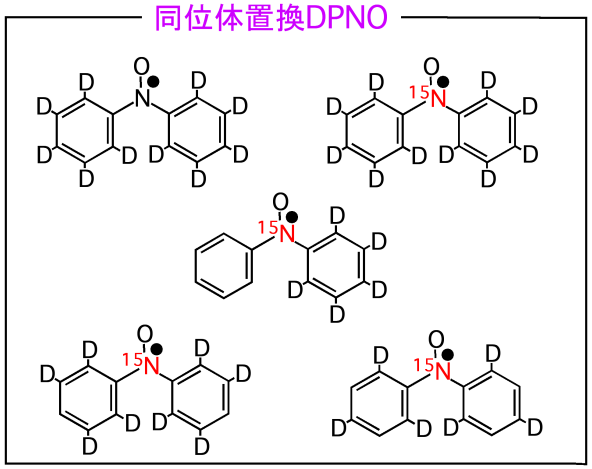
designed for narrowing ESR linewidth and/or discriminating nuclear-spins



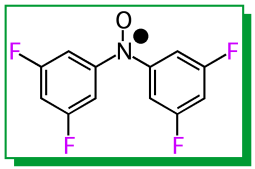


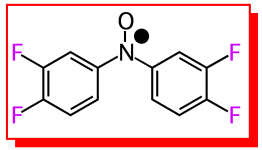
希釈単結晶用
ホスト分子

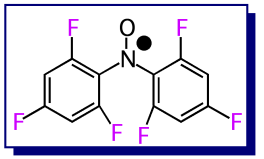
同位体置換DPNO

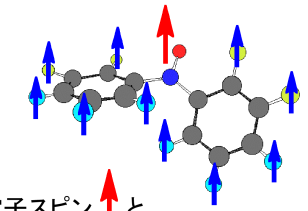


Fluorinated DPNOs as Synthetic Bus Spin-Qubit Radicals



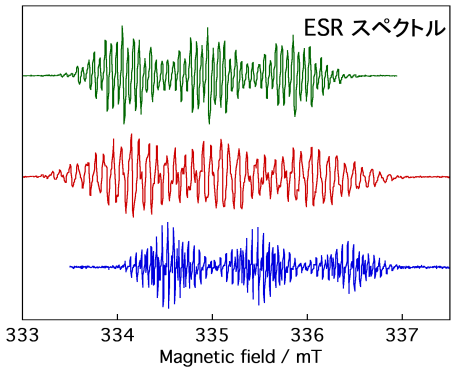




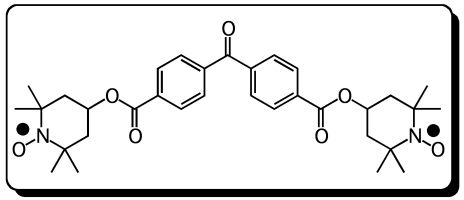


電子スピン ↑ と
水素およびフッ素の核スピン ↑ を
量子演算に利用する

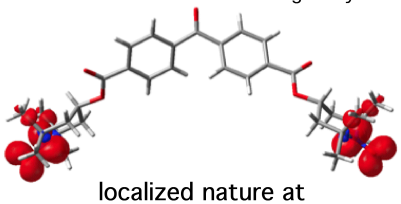
J. Phys. Chem. Lett. 2011



Crystal Structure and Spin Desnity Distribution of DPNO Biradical

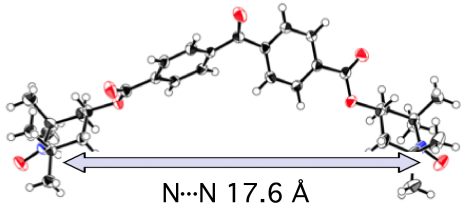


UB3LYP/6-31G*
using X-ray data



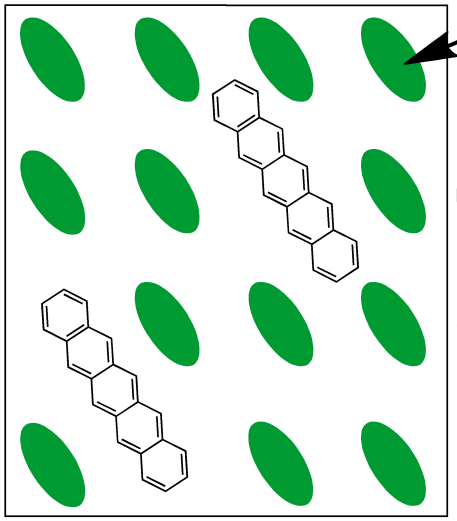
localized nature at each N-O moiety

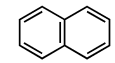
weak exchange interaction



orthorhombic, Z = 8, *Fdd2*,
a =22.480(7)Å, *b* = 46.46(1)Å
c = 6.025(2)Å, *V* = 6292(3) Å^3
R_1 = 0.039, R_w = 0.068

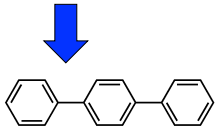
Pentacene-doped Single Crystal for Triplet DNP





naphthalene

- high polarization
- low concentration
- long spin-lattice relaxation time

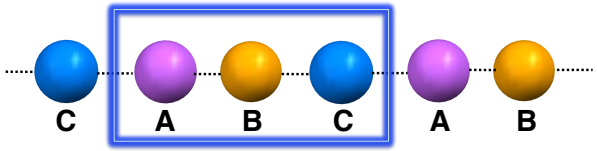


p-terphenyl

- fast polarization
- high concentration
- short spin-lattice relaxation time

Lloyd の $(ABC)_n$ 一次元周期モデル

「scalable qubit 化」を実現するための手段



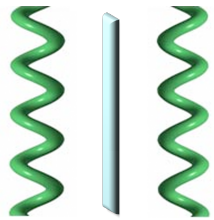
化学シフトの異なる **qubit A, B, C** を繰り返し単位とする一次元周期構造が、無限大の **qubit** を整列させた場合と同等のシステムとなる

Science **1993**; *Scientific American* **1995**

Prof. Seth Lloyd, MIT

具体的な物質系の報告例は皆無

Helical Structure



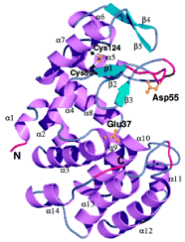
widely seen in nature

helical chirality

➡ left- and right-handed helix

DNA:
right-handed double helix

(MAKE: Japan © O'Reilly Media, Inc.)

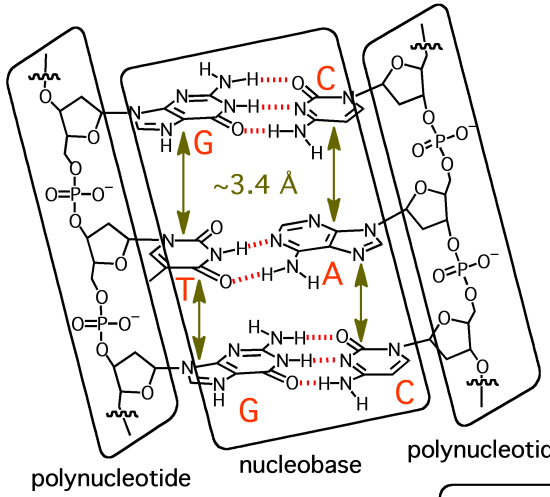


(© Laboratory of Molecular Biology, Chiba University)

α-helix:
left-handed helix

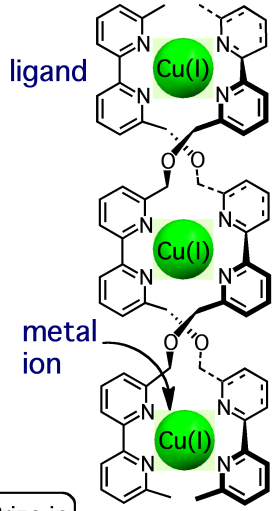
close and important relationship with life phenomena

DNA Duplex and Double-Stranded Helicate



polynucleotide nucleobase polynucleotide

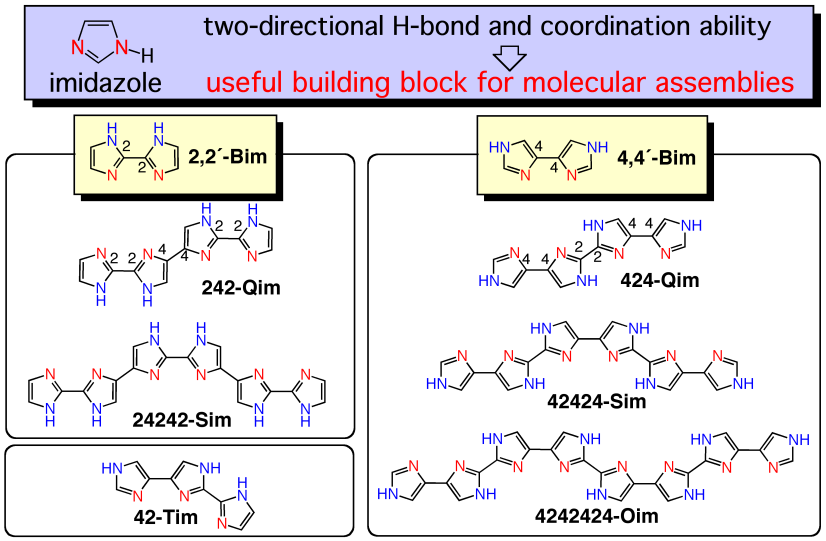
complementary hydrogen bond
π–π interaction



The Nobel Prize in Chemistry 1987

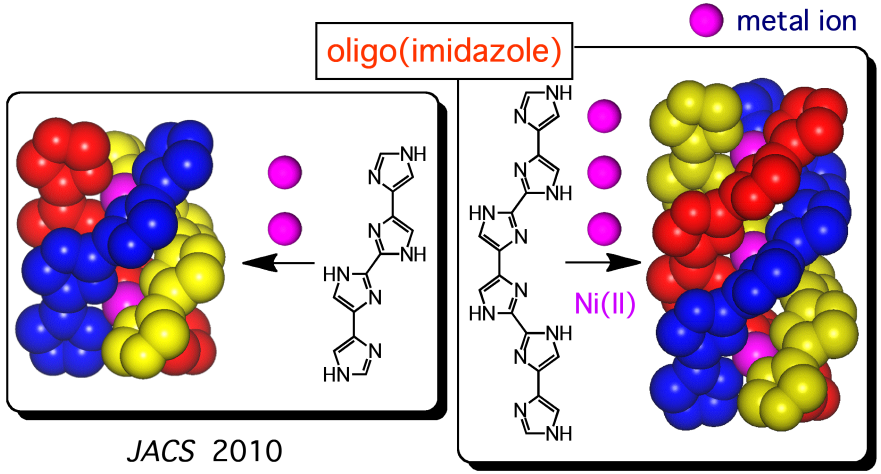
coordination bond
Lehn, J.-M. 1987

Oligo(imidazole)s



J. Chem. Soc., Perkin Trans. 1 2002; *Chem. Lett.* 2004; *J. Org. Chem.* 2005; *Cryst. Growth Des.* 2006; *Cryst. Growth Des.* 2008; *Cryst. Growth Des.* 2010

Triple-Stranded Helicate



JACS 2010

unpublished

universal building blocks
outward-directed H-bonds of amine functional groups

Magnetically Diluted Single Crystal

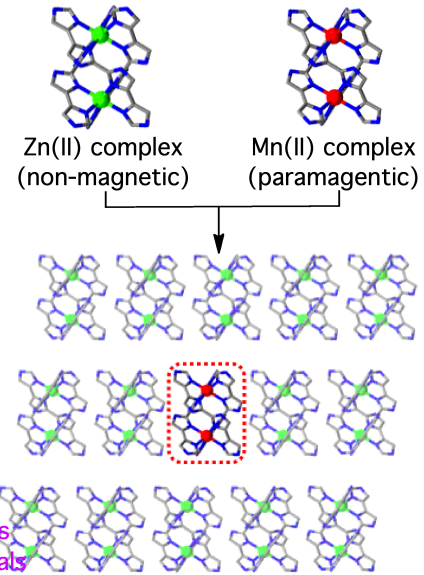
single-crystal
ESR spectroscopy:

strong inter-helicate magnetic interactions give a broad signal

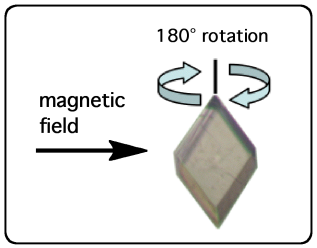
weaken inter-helicate magnetic interaction

manganese-centered helicates are isostructurally replaced and diluted in the zinc helicate lattices at a desired concentration

H-bond-driven replacement method gives a new approach to prepare diluted crystals

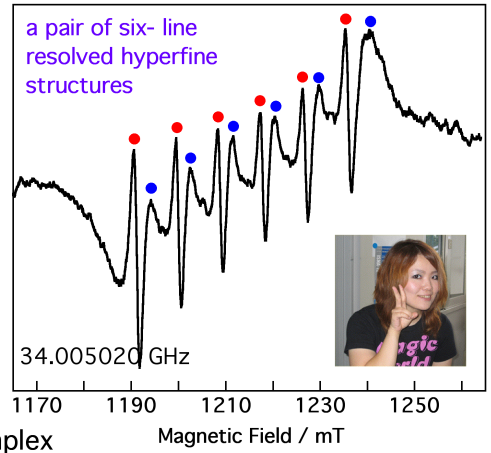


Occurrence of Targeted *g*-Engineering



angular-dependent Q-band ESR spectrum of magnetically diluted crystal

Obs. 15 K, rotation degree of 70°

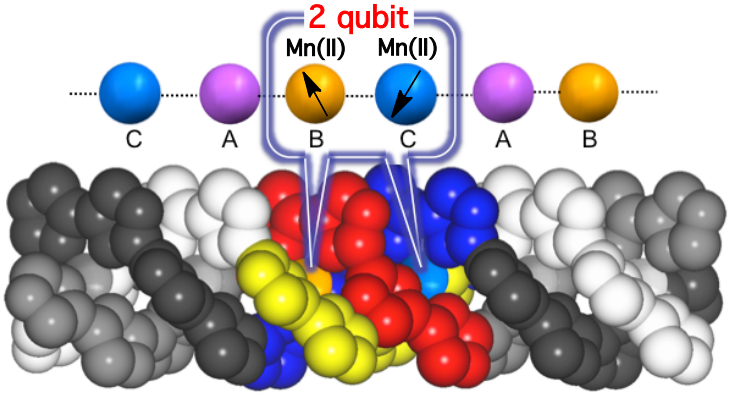


Each six-line hyperfine structure with a different *g*-value is attributed to the Mn(II) nuclear hyperfine in the sextet state ($S = 5/2$) of pseudo-octahedral symmetry

⇩

Each Mn(II) ion in Mn(II) complex is magnetically distinguishable

Addressable Electronic-spin in Metal Ion as Lloyd's Electronic-spin Qubits



novel metal complex system

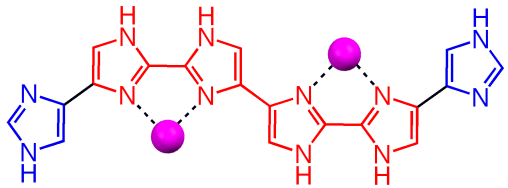
JACS 2010

pulse-based electron magnetic resonance spin technology is expected to act as the first scalable qubit

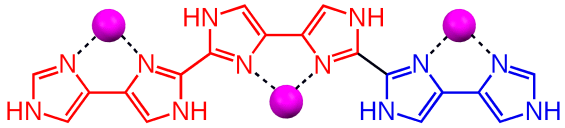
Scalability ?

challenge for (ABC)*n* type

Sim: imidazole hexamer



Dinuclear?



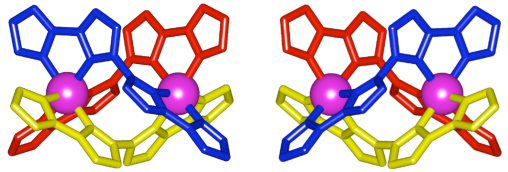
Trinuclear?

Electronic-spin Qubits and Chirality

optical-activation

⇩

extraction of electronic-spin information by optical method



right-handed left-handed

photon:

strong preservation of information and widely studied methodology

electronic-spin:

weaker preservation of information but high controllability

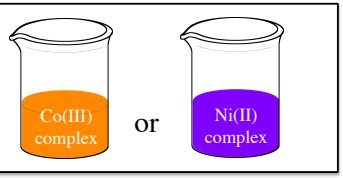
combination of electronic-spin qubits and photon qubits: challenging issue in quantum information technology

Method for Chiral Separation

sample preparation

MeOH solution of racemic complex

Metal: **Co(III)**, **Ni(II)**



separation

JAI: LC908
Recycling Preparative HPLC

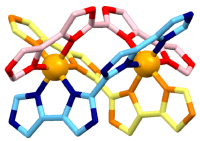
eluant: Hex–EtOH–MeOH–TFA
(no chiral component)

left-handed helicate right-handed helicate

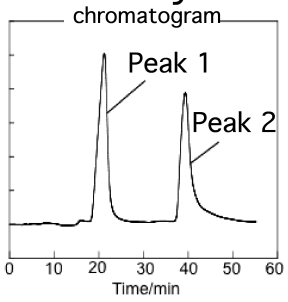
each enantiomer in a preparative scale

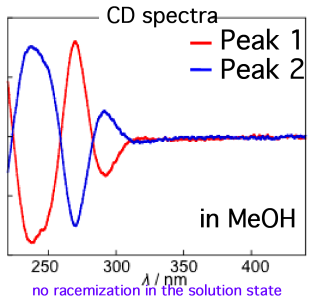
Optical Resolution by Chiral HPLC Column

Co(III) complex



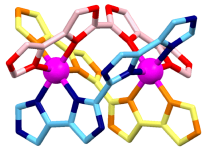
SUMICHIRAL OA
Hexane:EtOH:MeOH:TFA
= 70:20:10:0.05
1 mg/100 μL, 10 μL charge
Wavelength: 254 nm
Flow rate: 1 mL/min





no racemization in the solution state
at room temperature over 3 months

Ni(II) complex



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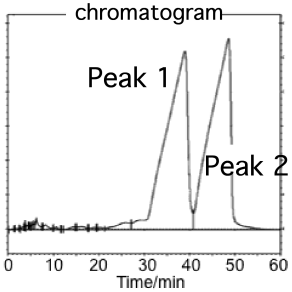
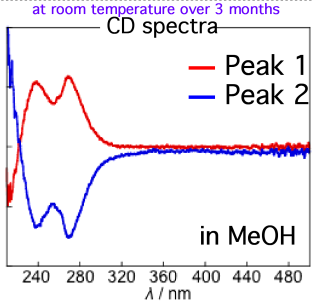
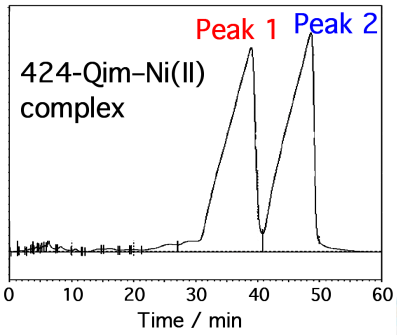
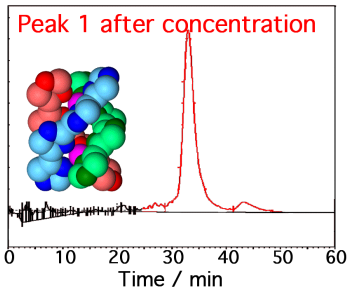


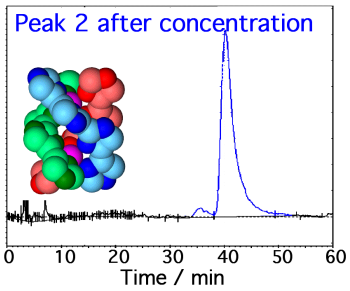


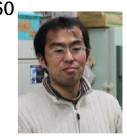
Isolation of Chiral Helicates

neutralization with Et_3N
before concentration



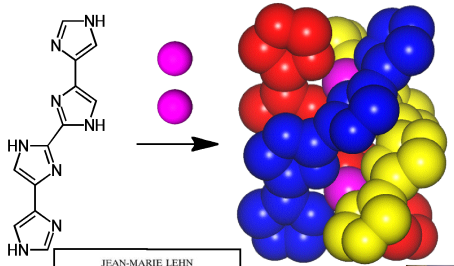


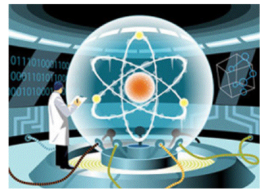




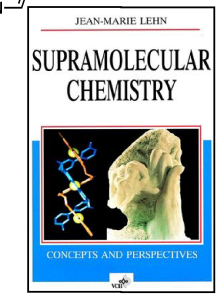
Eur. J. Inorg. Chem. 2011

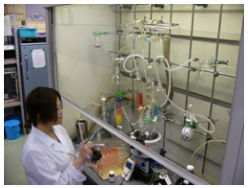
From Molecular/Supramolecular Chemistry to Quantum Electronics





Quantum computer/
information science





Lehn, J.-M.
1995

1 From Molecular to Supramolecular Chemistry