スピンクロスオーバー現象とその光･スピン･電荷による相乗効果

Outline

(1) History of spin crossover phenomena

(2) Light induced excited state trapping (LIESST) and its related phenomena

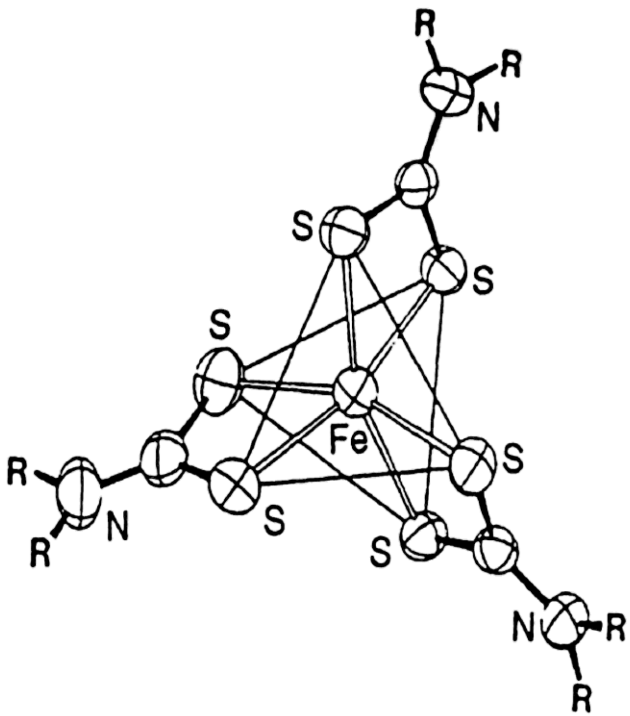
(3) Spin crossover transition at r.t. toward molecular devices

(4) Development of spin crossover complex film

(5) Development of assembled-metal complex exhibiting dynamical spin equilibrium

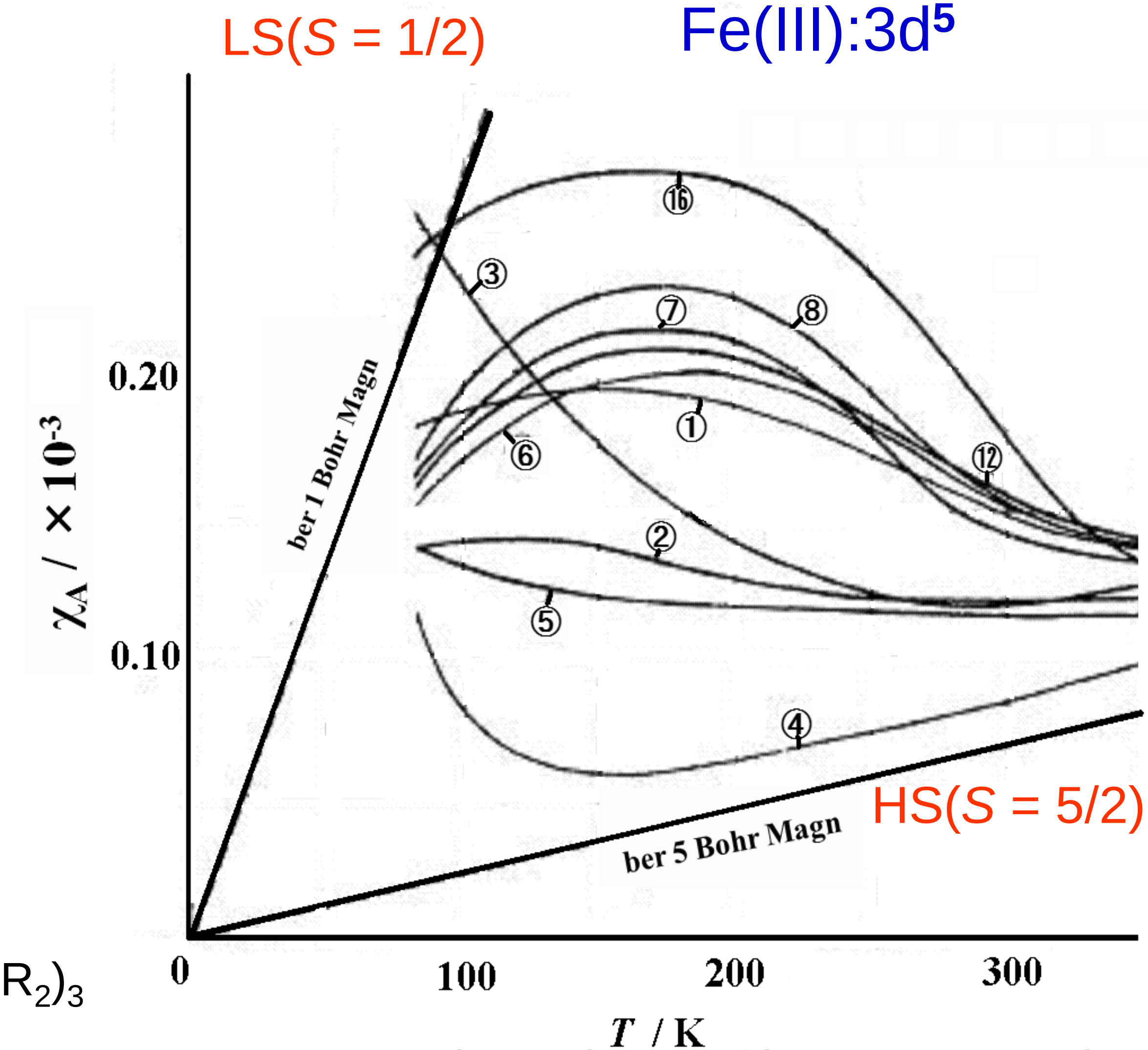
(6) Development of mixed-valence complex exhibiting charge transfer phase transition

First report of spin-crossover phenomenon



Molecular structure of $Fe(S_2CNR_2)_3$ (R = n-C_nH_{2n+1}, etc.).

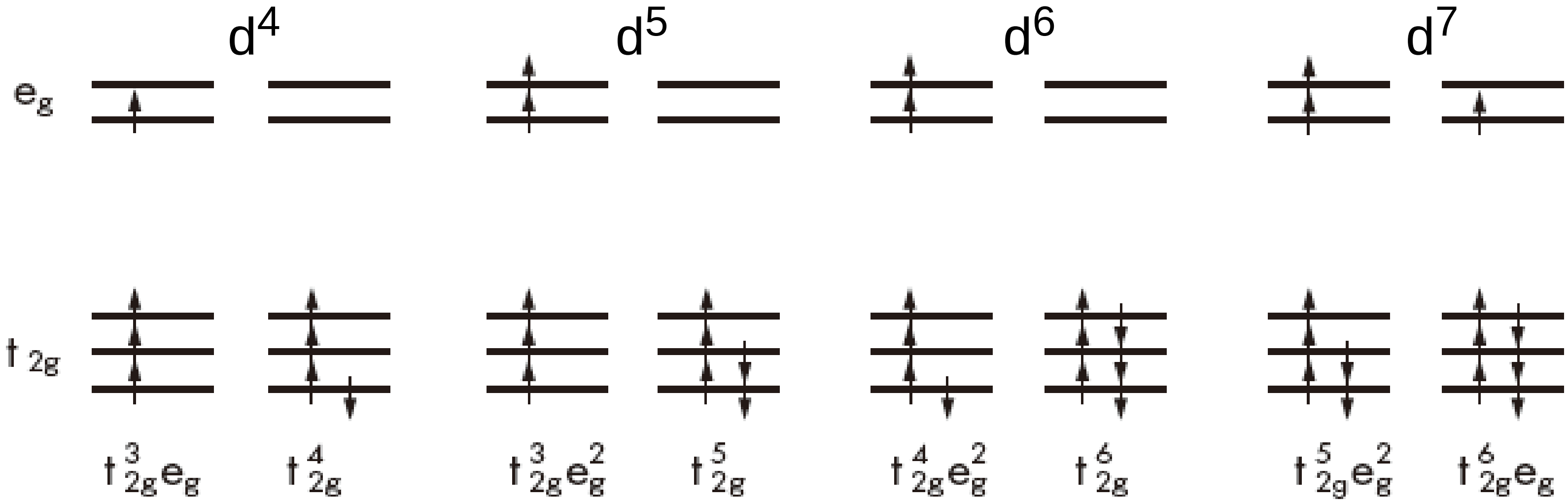
K. Stahl, i. Ymén, *Acta Chem. Scand., A* **1983**, *37*, 729



Temperature dependence of inverse magnetic susceptibility for $Fe(S_2CNR_2)_3$ (R = n-C_nH_{2n+1}).

L. Cambi, L. Szegö, *Ber. Deutsch. Chem. Ges*. **1933**, *66*, 656 (1933).
L. Cambi and A. Cagnasso, *Atti Accad. Naz. Lincei*. **1931,** *13*, 809

Spin configuration of d^4 – d^7: It is possible that the low-spin (LS) state and the high-spin (HS) state compete with each other in the ground state.

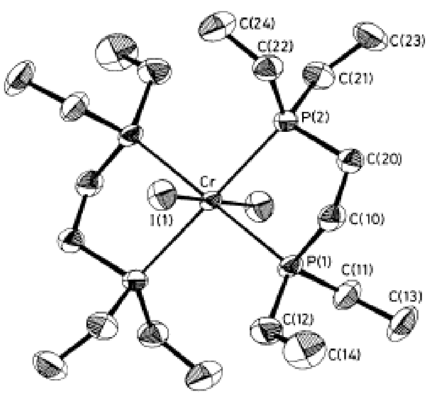


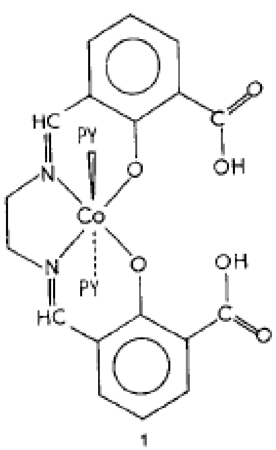
$[Cr(II)I_2(depe)_2]$

many Fe(III) complexes

many Fe(II) complexes

$[Co(II)(H_2fsa_2en)(py)_2]$



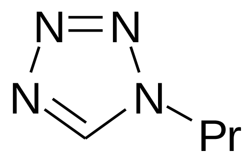


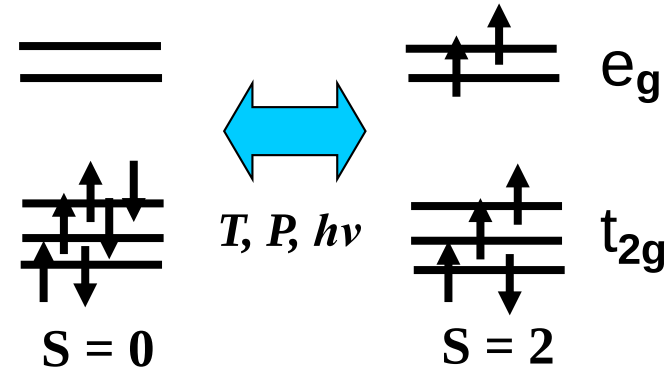
D.M. Halepoto, et al., *J. Chem. Soc., Chem. Commun*., **1989**, 1322.

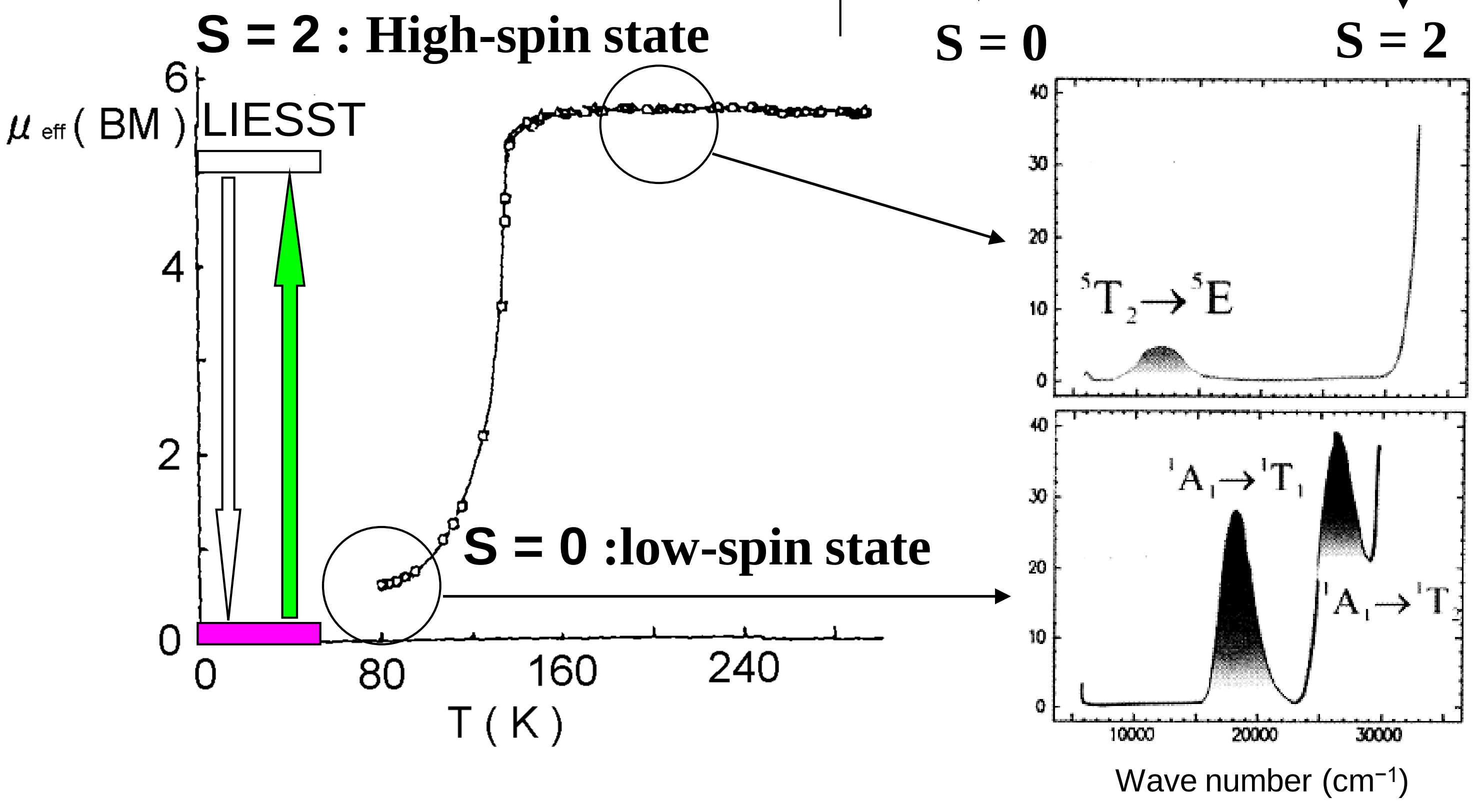
P. Charpin, et al., *J. Cryst. Spectrosc. Res*., **1988**, 18, 429.

Light Induced Excited Spin State Trapping (LIESST)

$[Fe^{II}(ptz)_6](BF_4)_2$ Ptz =

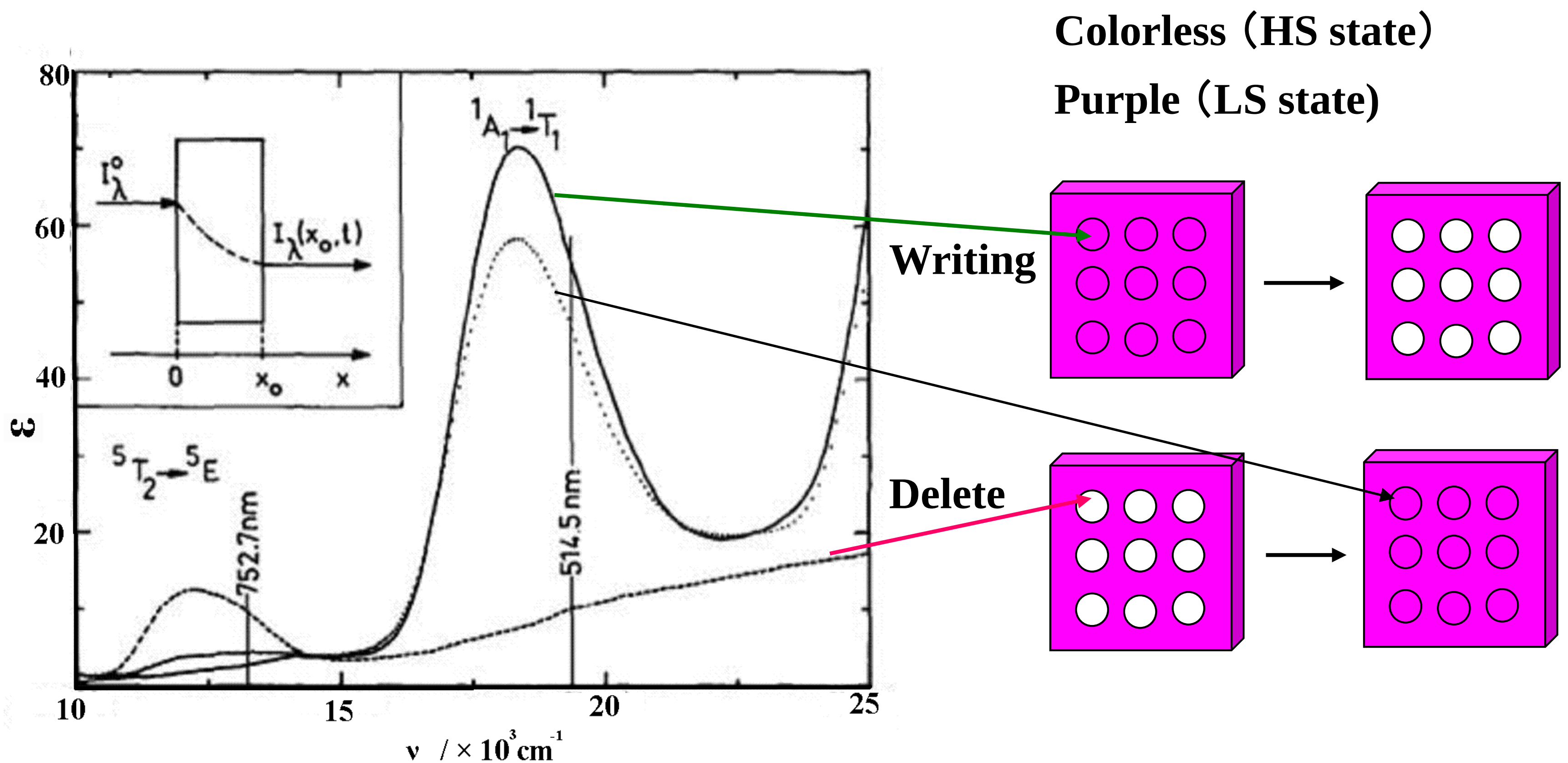






(1)P. L. Franke, et al. *Inorganica Chimica Acta*, **1982**, *59*, 5, **(2) S. Decurtins et al. *Chem. Phys. Lett.* 1984, *105*, 1.**

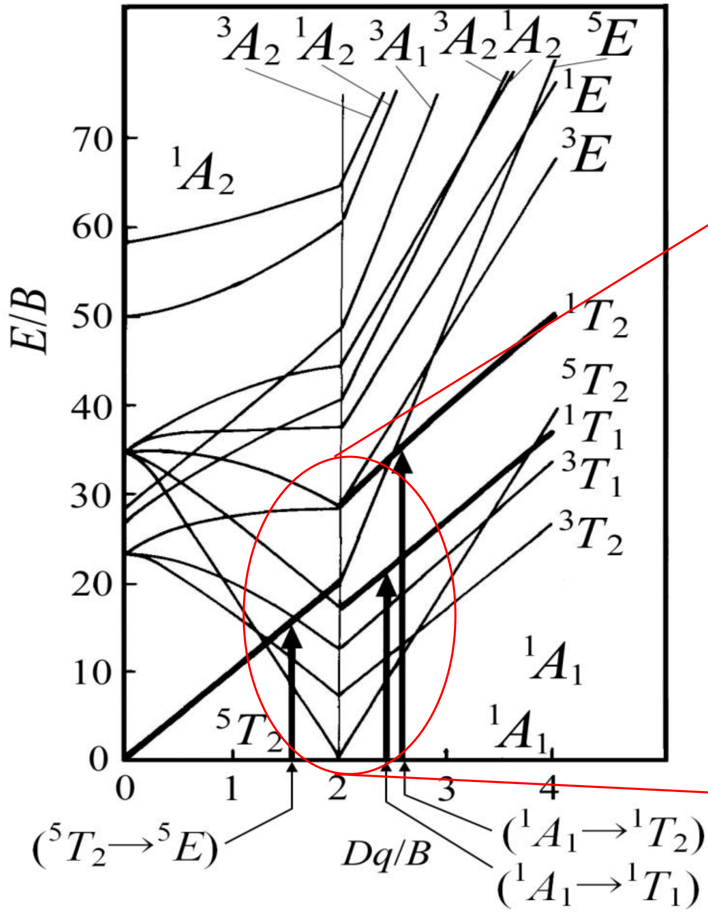
LIESST (Light Induced Excited Spin State Trapping)



Near-infrared and visible absorption spectra of $[Fe(ptz)_6](BF_4)_2$ at 10 K: (—) before light irradiation, (– – –) after irradiation with λ = 514.5 nm (300 mJ), (……) after subsequent irradiation with λ = 752.7 nm (≈3000 mJ).

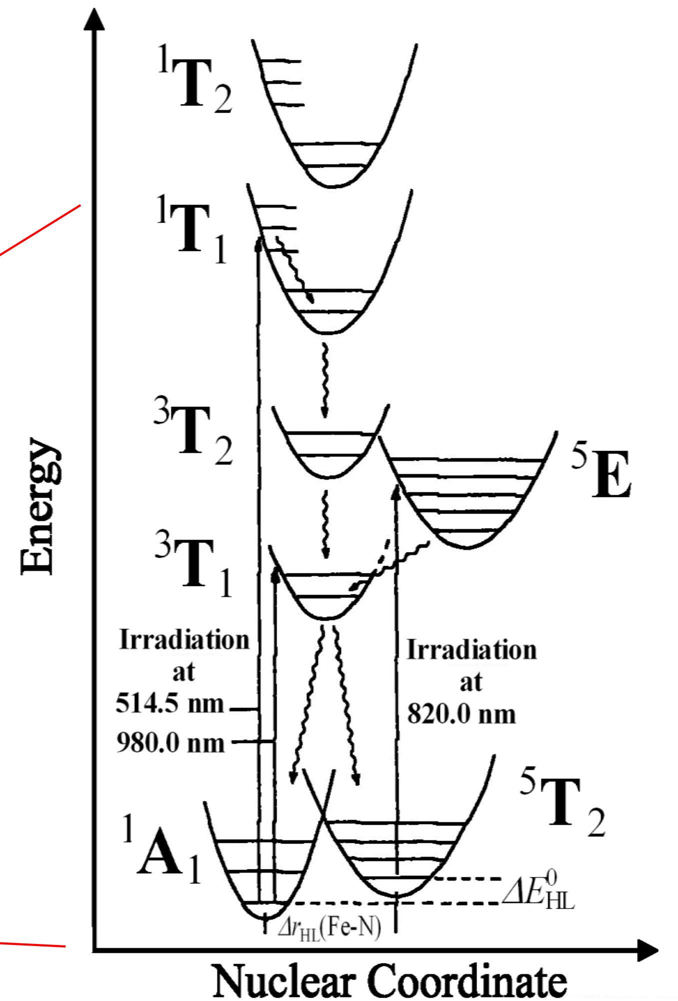
A. Hauser, *Chem. Phys. Lett*. **1986**, *124*, 543

Mechanism of LIESST and Reverse-LIESST



Tanabe-Sugano diagram

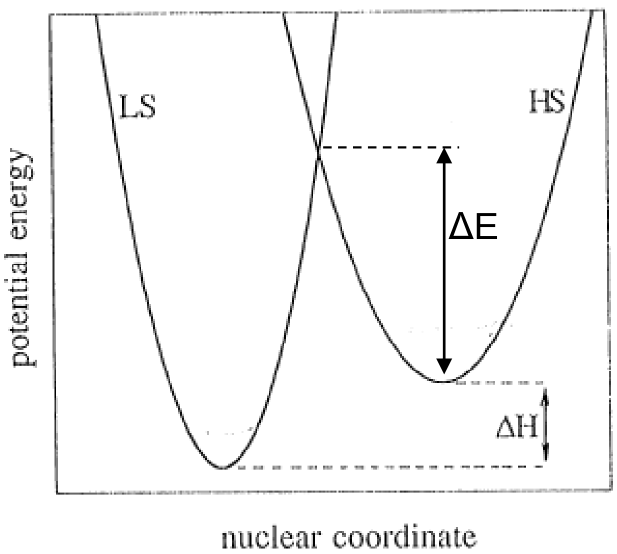
Y. Tanabe, S. Sugano, *J. Phys. Soc. Jpn*. **1954**, *9*, 766.

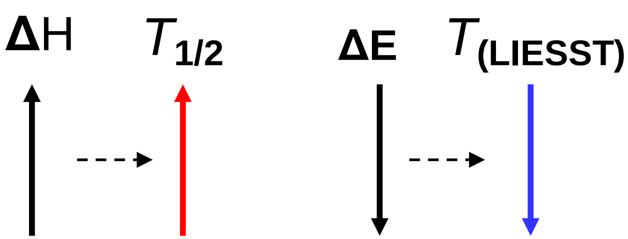


Mechanism of LIESST and Reverse-LIESST

A. Hauser, *Chem. Phys. Lett*. **1986**, *124*, 543

Upper limit of LIESST





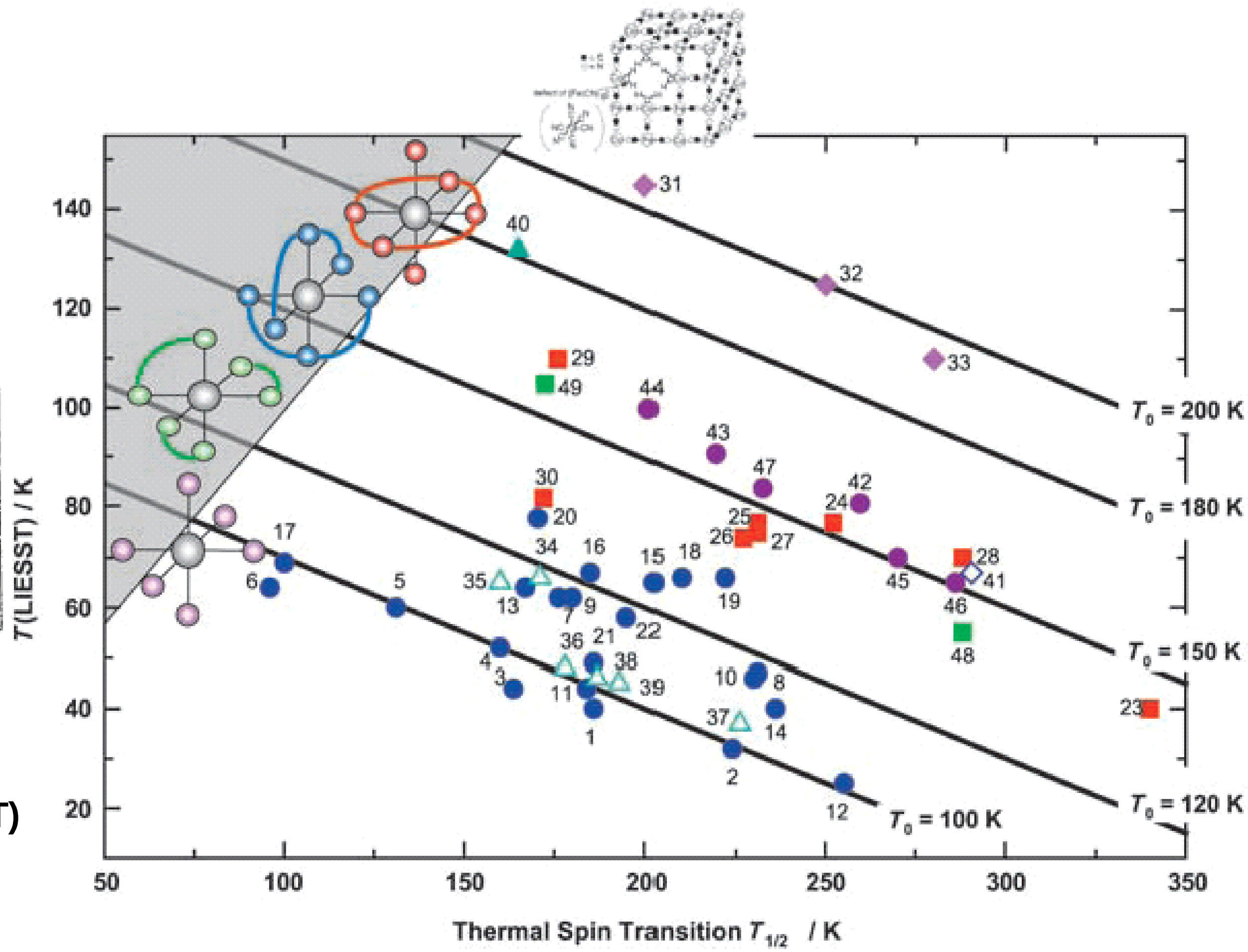
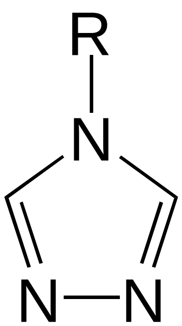


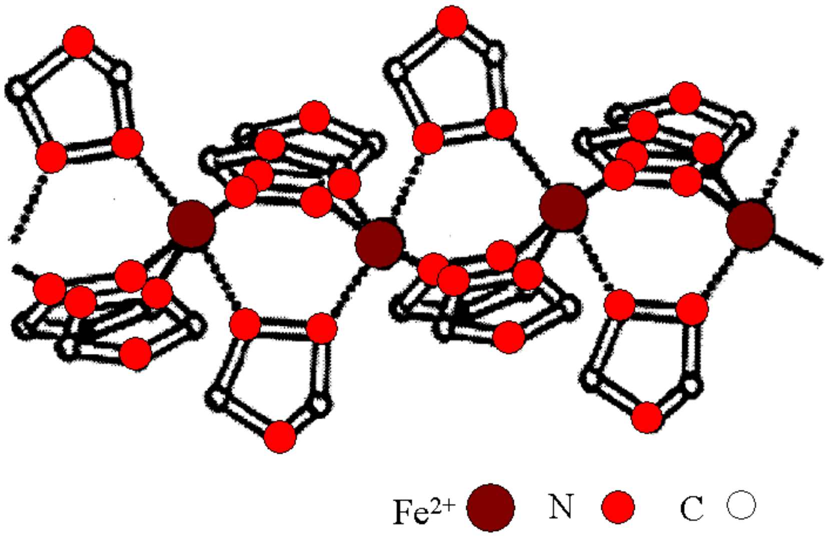
Figure 1. 7. Spin-crossover transition temperature vs LIESST temperature. The lines represent the correlation between the spin-crossover transition and LIESST temperatures; $T(\text{LIESST}) = T0 - 0.3T1/2$.

J. F. Létard *et al.*, *Chem. Phys. Lett.* **1999**, *313*, 115. .

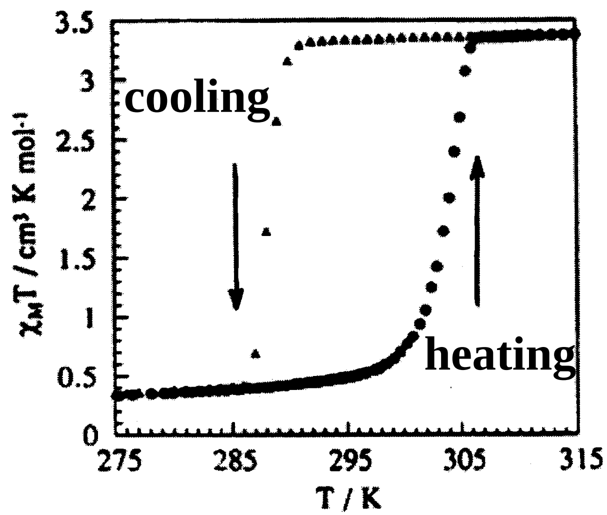
Spin crossover transition of $[Fe^{II}(R\text{-}trz)_3]A_2 \cdot nH_2O$



1,2,4-R-triazole
R = H, NH_2, C_nH_{2n+1},etc



$\chi_M T$ vs. T for $[Fe(H\text{-}trz)_{2.85}(NH_2\text{-}trz)_{0.15}](ClO_4)_2$

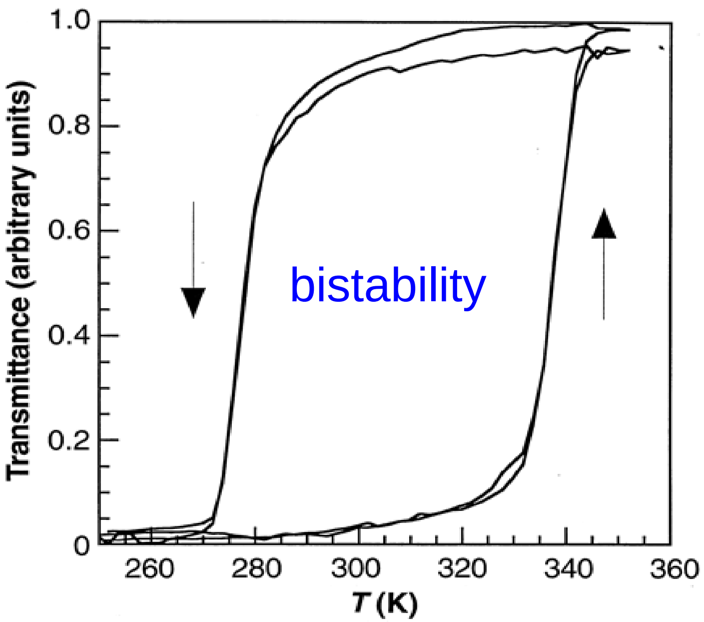


J. Kröber, E. Codjovi, O. Kahn, F. Grolière, C. Jay: *J. Am. Chem. Soc*. **1993**, *115*, 9810.

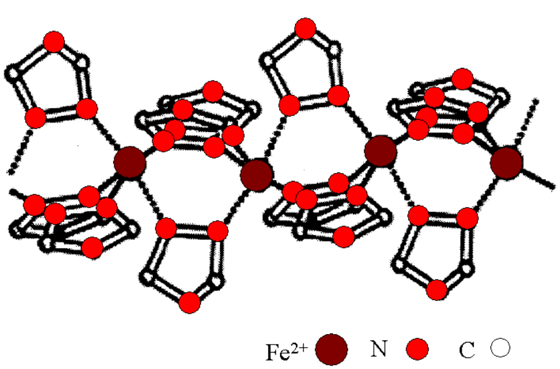
memory, display device

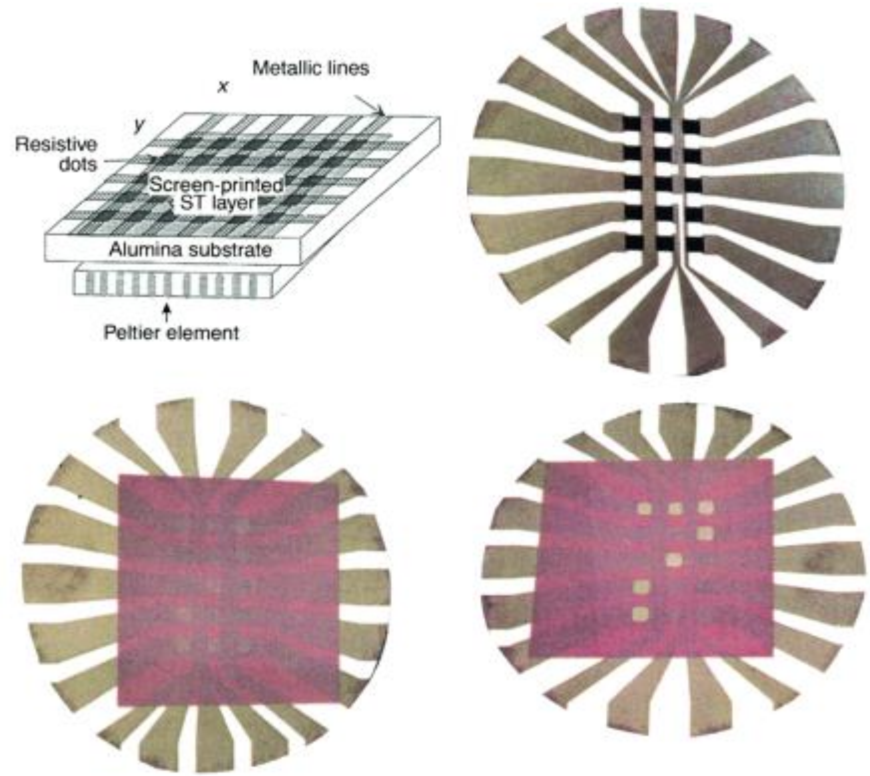
Spin-transition polymers: From molecular materials toward memory devices

O. Kahn, C. Jay Martinez, *Science*, **1998**, *279*, 44.



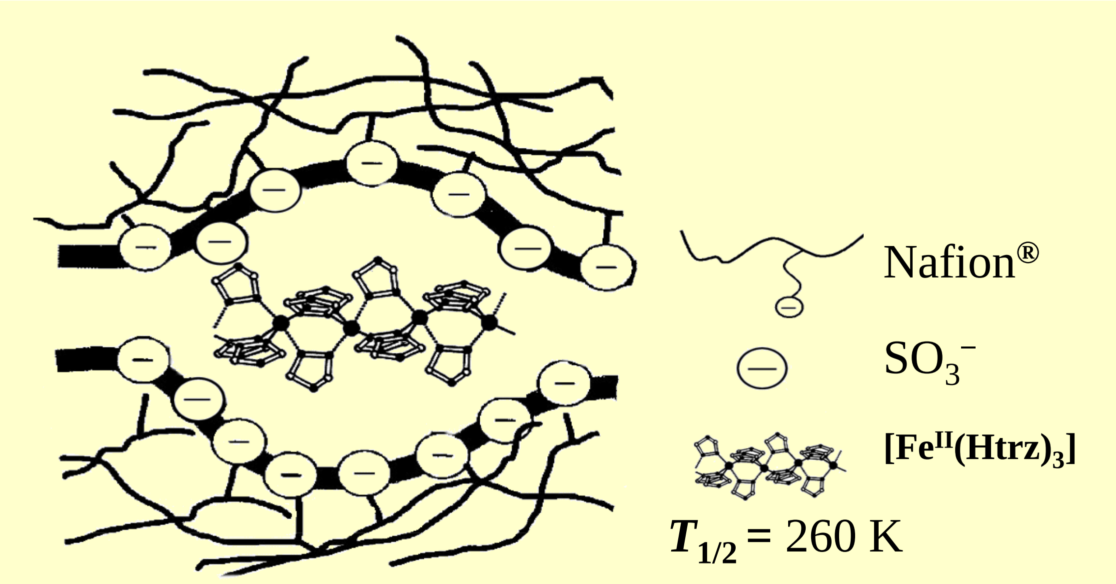
Spin crossover transition of $[Fe^{II}(NH_2trz)_3](NO_3)_{1.7}(BF_4)_{0.3}$

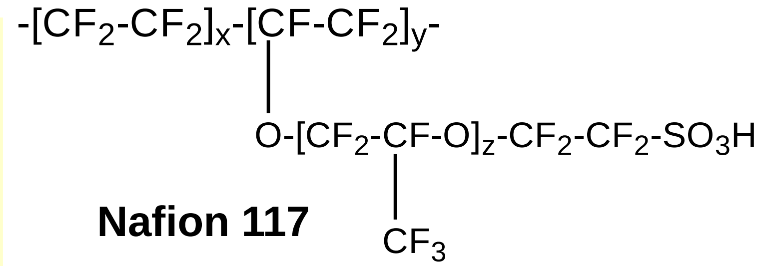




Principles of a display using a spin-transition polymer.

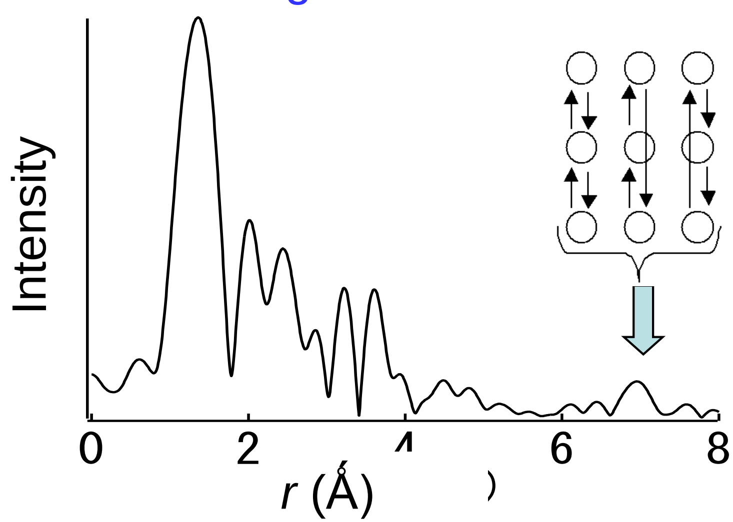
Development of Spin-crossover complex film

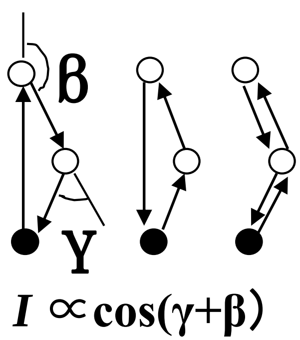




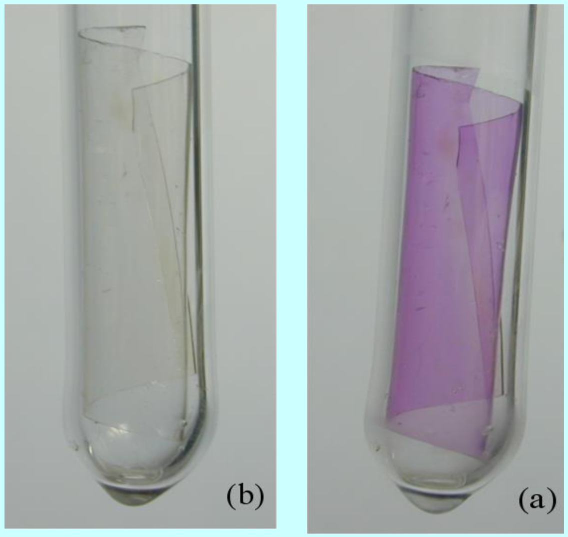
$Fe^{II}(NH_2\text{-}trz)_3$—Nafion

Fe-K edge EXAFS





$[Fe^{II}(Htrz)_3]$-Nafion®

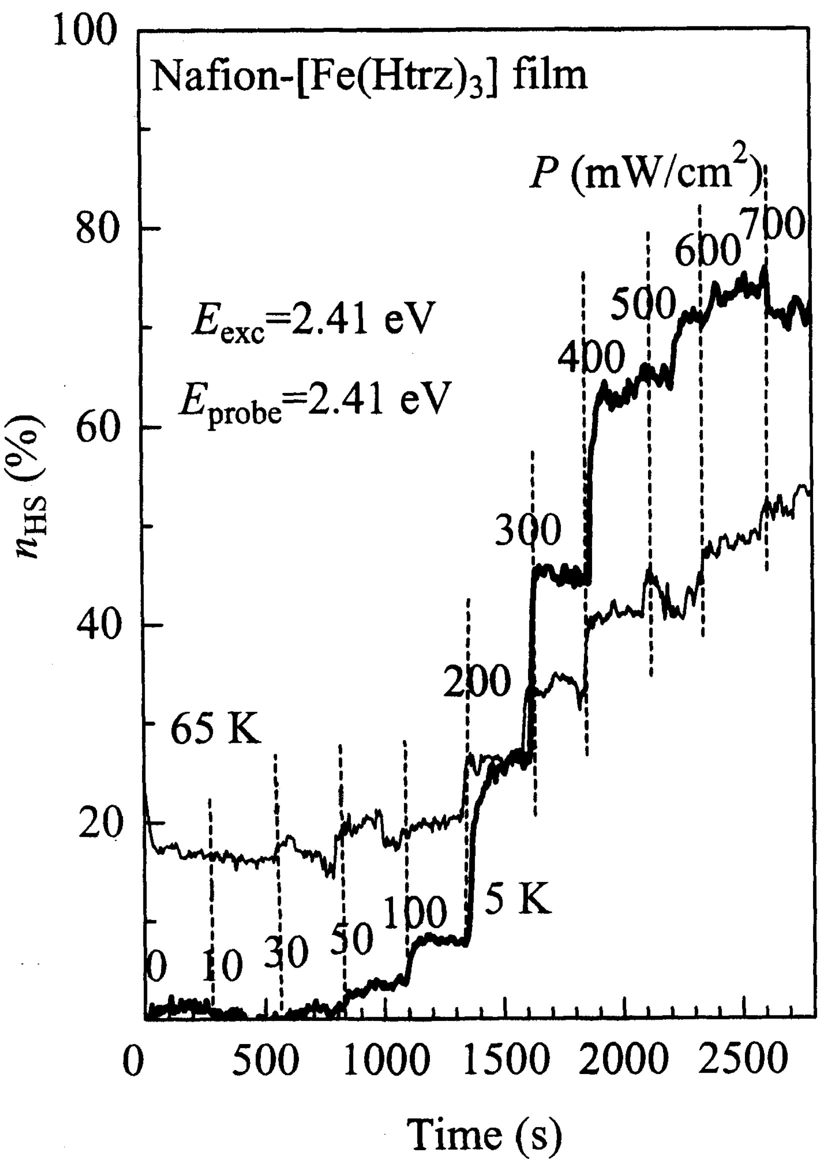


T = 300 K *T* = 77 K

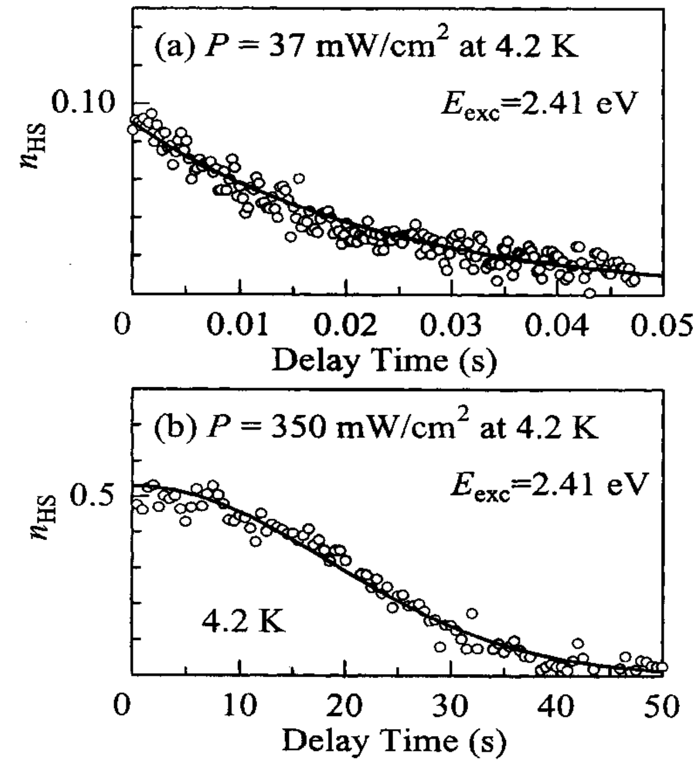
A. Nakamoto, N. Kojima, et al., *Chem. Lett*. **2003**, *32*, 336.

A. Nakamoto, N. Kojima et al., *Polyhedron*, **2005**, *24*, 2909.

Photo-generated HS state of Nafion-[Fe(Htrz)$_3$] film



Life time of photo-generated HS state

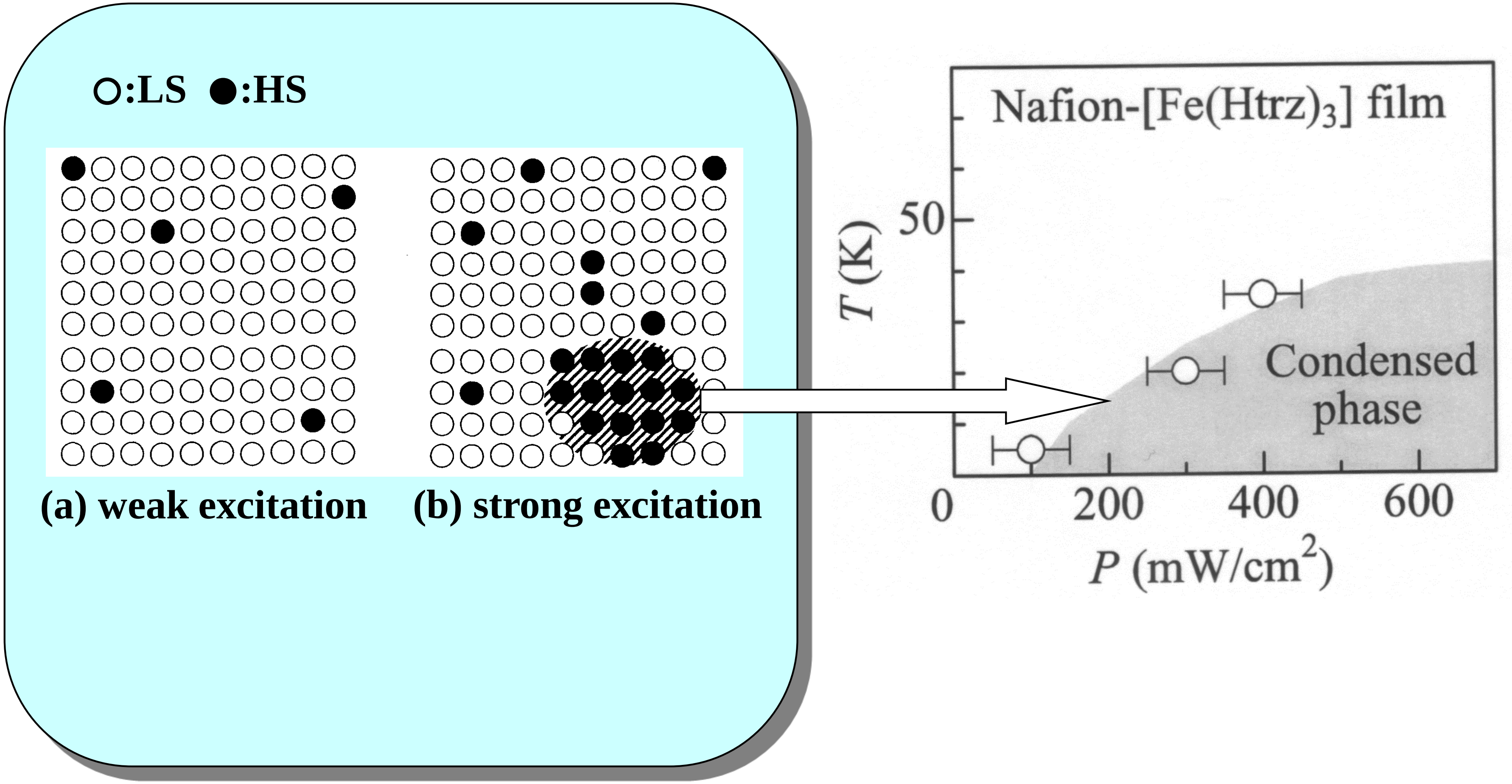


(a) $$n_{HS} \propto \exp\left({-t(s)}/{0.023} \right)$$

(b) $$n_{HS} \propto \exp\left\{ -\left({t(s)}/{25} \right)^2 \right\}$$

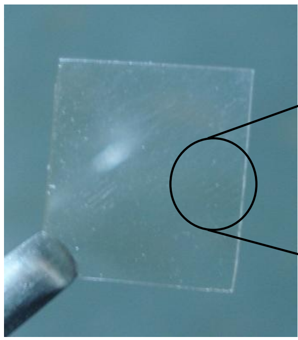
X.J. Liu, Y. Moritomo, N. Kojima, et al. Phys. Rev. *B*, **2013**, *67*, 012102-1

Condensed phase of photo-generated high-spin state

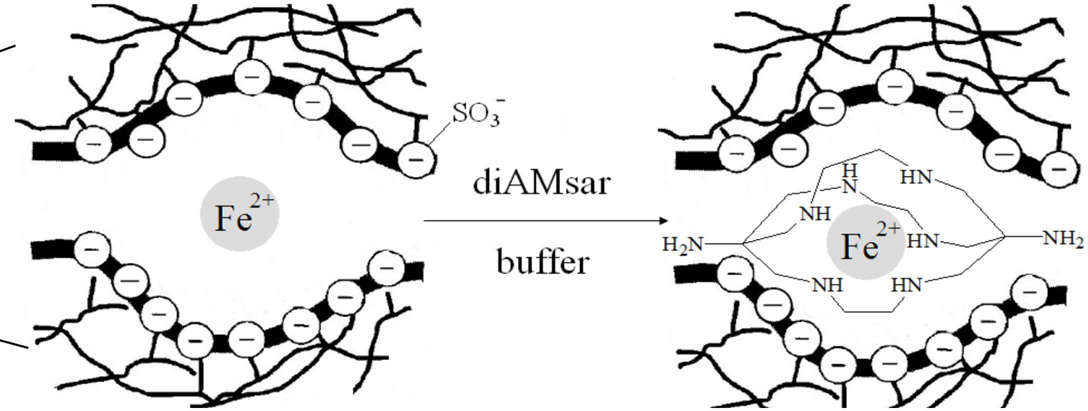


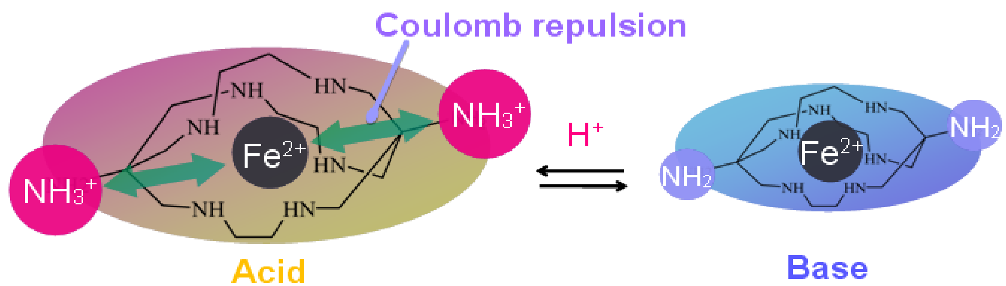
X.J. Liu, Y. Moritomo, N. Kojima, et al. *J. Phys. Soc. Jpn*. **2003**, *72*, 1615.

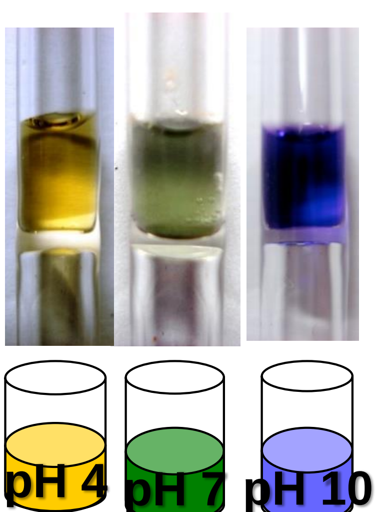
Preparation of pH-sensitive spin-crossover complex film, $[Fe^{II}(diAMsar)]$-Nafion



Nafion 117







Volume expansion due to the Coulomb repulsion between Fe^{2+} and NH_3^+

⬇

High-spin state
(S = 2; $^5T_2$)

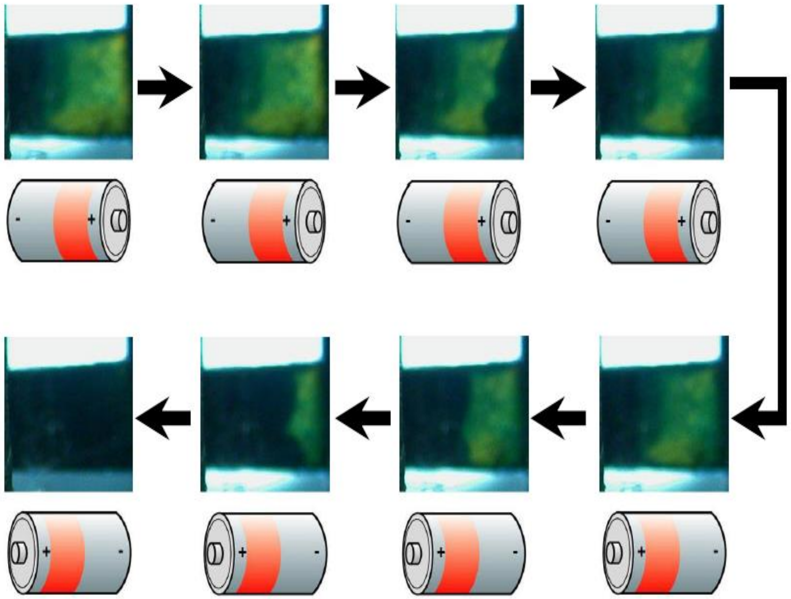
Absence of the volume expansion

⬇

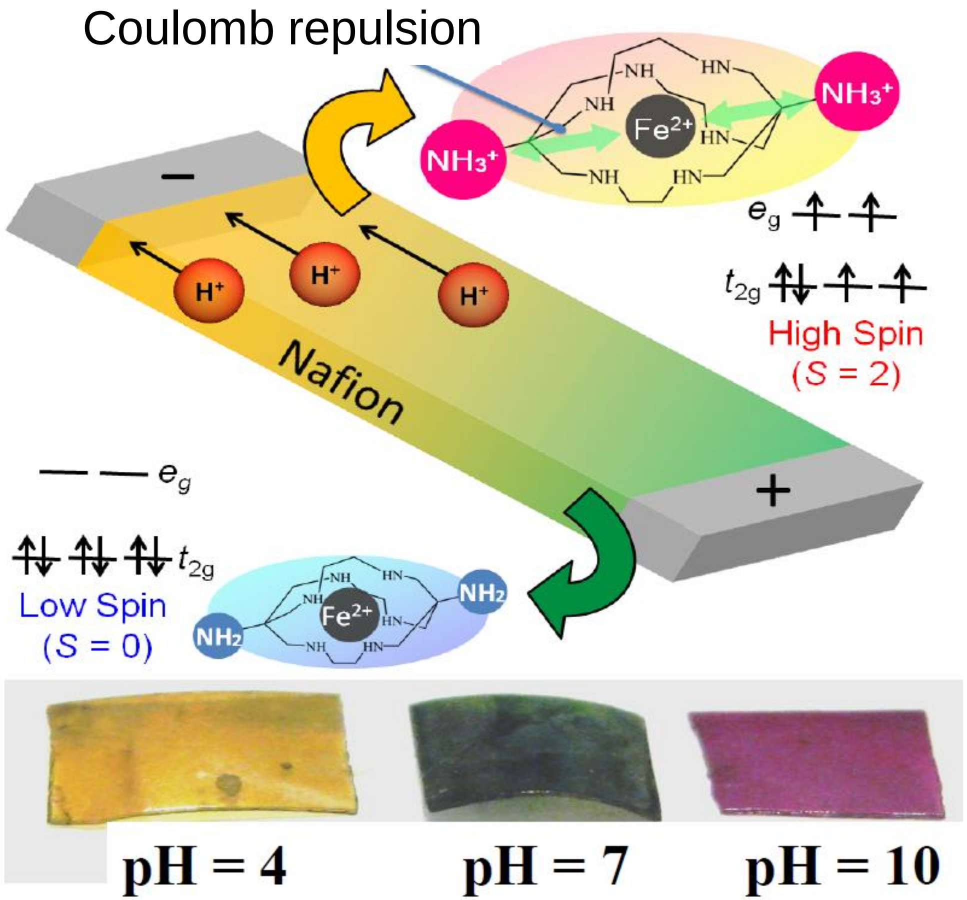
Low-spin state
(S = 0; $^1A_1$)

H. Kamebuchi, N. Kojima et al., *Chem. Lett.* **2011**, *40*, 888.

Manipulating the spin state by applied voltage

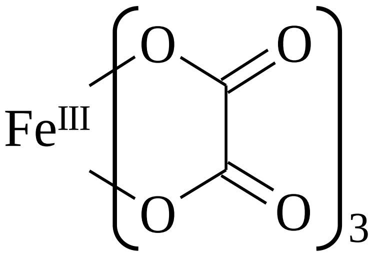


- Voltage: 20 V
- Current: ca.15 μA (average)
- Time: 60 min

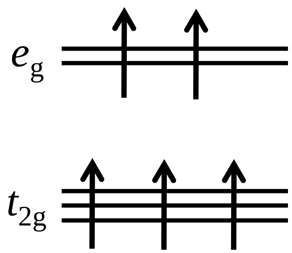


H. Kamebuchi: **XXIV ICCBC, June 6, 17:10-17:20**

Spin State of $Fe^{III}O_3S_3$

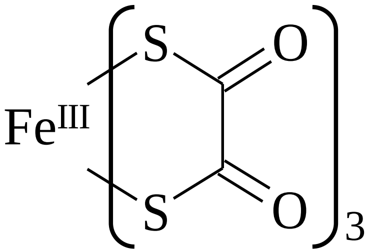


$Fe^{III}(ox)_3$

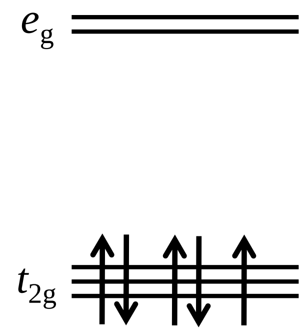


Weak ligand field

HS (S = 5/2)

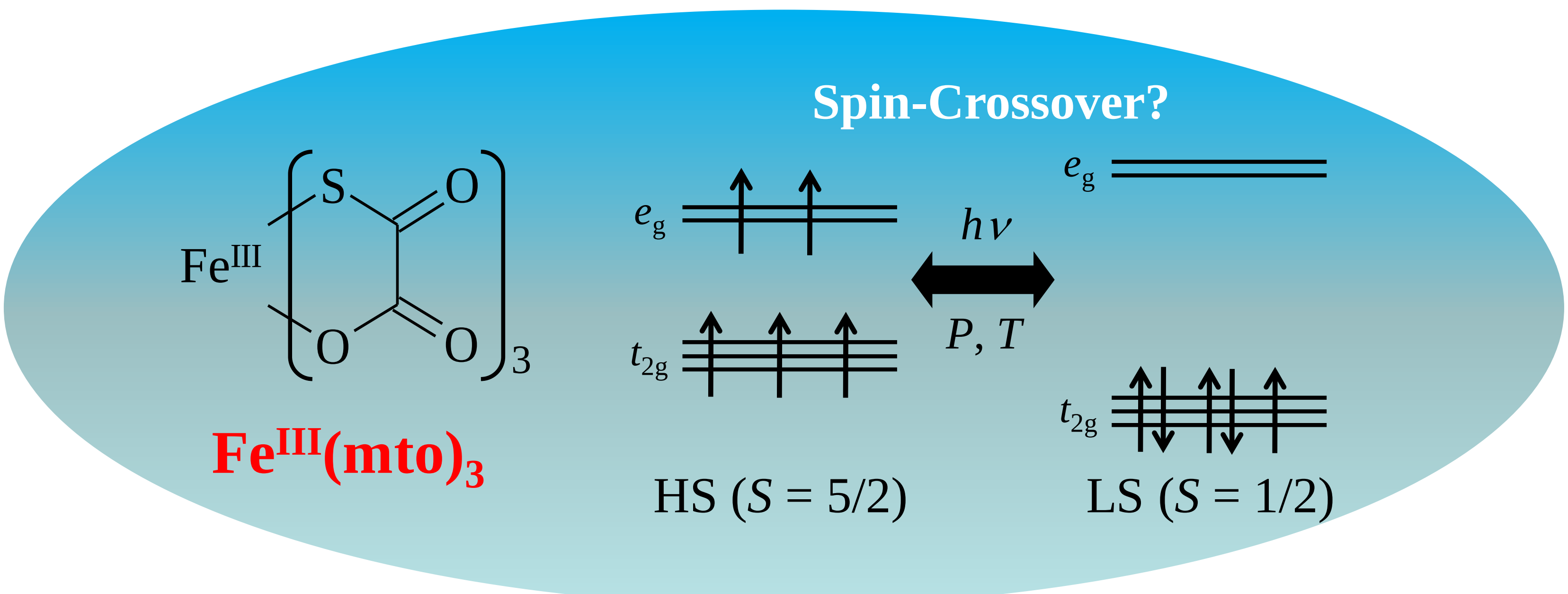


$Fe^{III}(dto)_3$



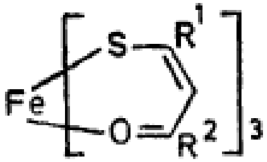
Strong ligand field

LS (S = 1/2)



Slow spin-equilibrium at $Fe^{III}S_3O_3$ ($\tau > 10^{-7}$ s)

Tris(monothio-β-diketonato)iron(III)



(I)

a; $R^1 = R^2 = Ph$
b; $R^1 = R^2 = Me$
c; $R^1 = Me$, $R^2 = Ph$
d; $R^1 = Ph$, $R^2 = Me$

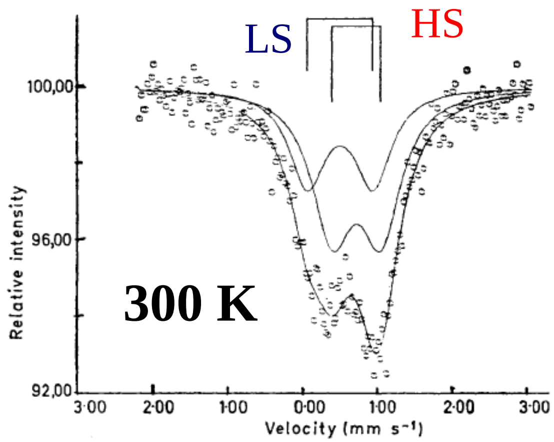


FIGURE 1 Spectrum of compound (Ia) at 300 K

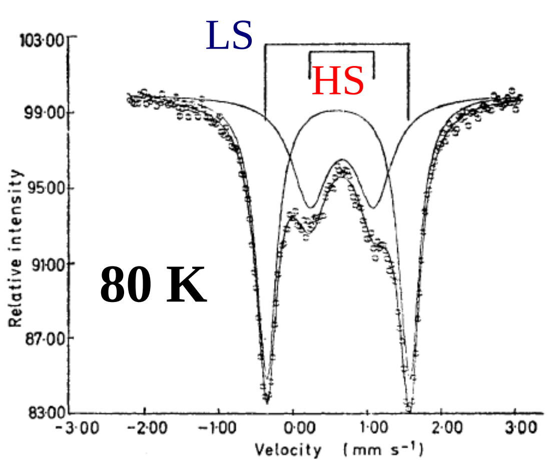
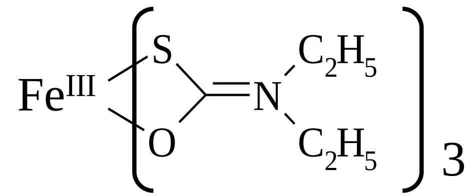


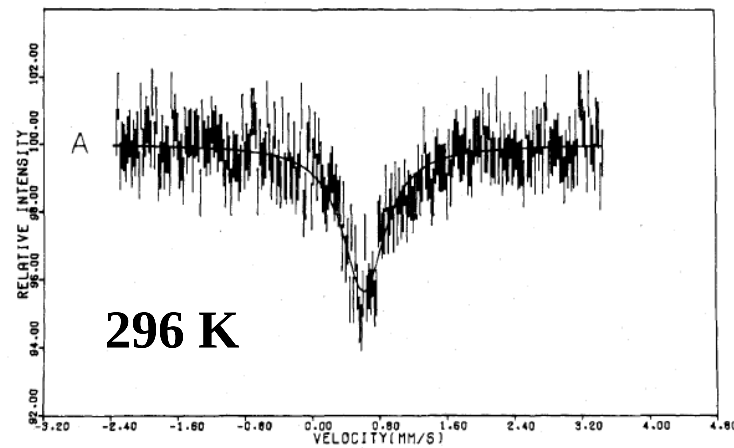
FIGURE 2 Spectrum of compound (Ia) at 80 K

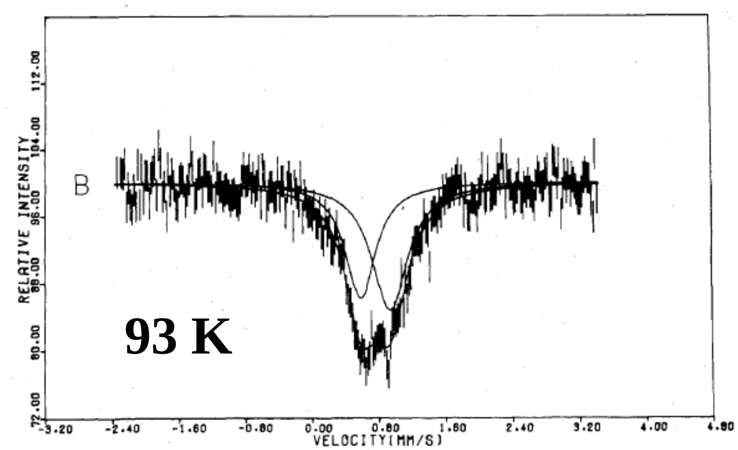
M. Cox, et al, *J. Chem. Soc. Dalton trans*, **1972**, 1192.

Rapid spin-equilibrium at $Fe^{III}S_3O_3$ ($\tau < 10^{-7}$ s)

Tris(monothiocarbamato)iron(III)





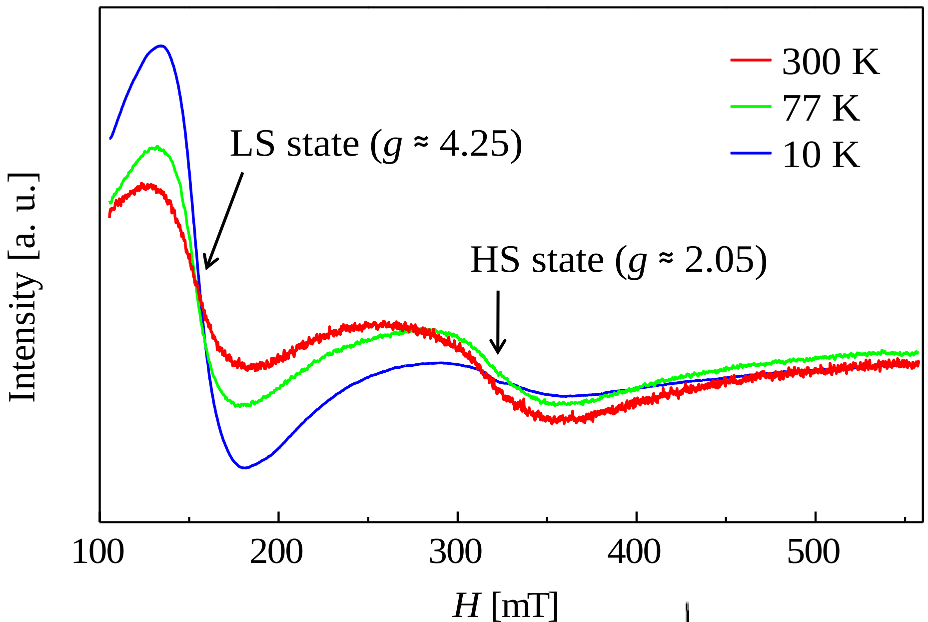


Mössbauer spectra of $Fe(Et_2mtc)_3$

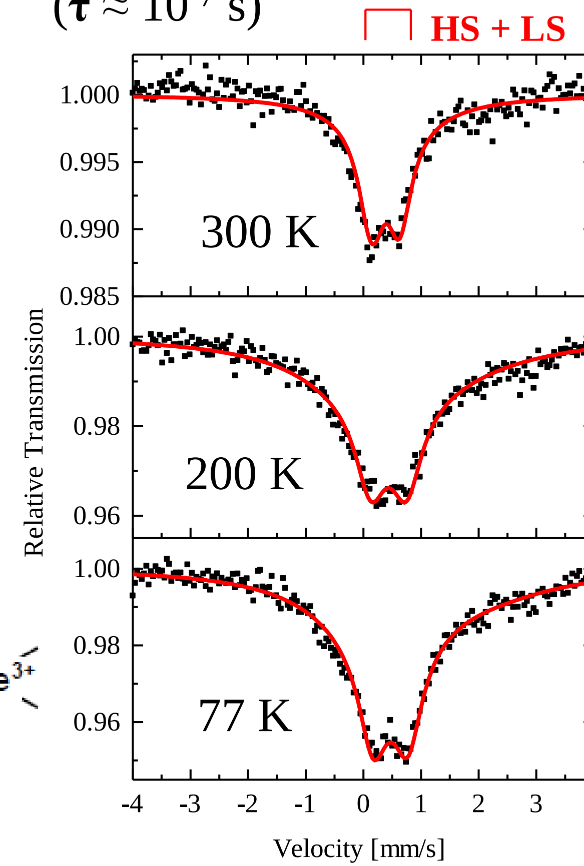
K. R. Kunze, et al, *Inorg. Chem*, **1977**, *16*, 594.

Rapid spin-equilibrium of Fe^{III} in $(C_6H_5)_4P[Zn^{II}Fe^{III}(mto)_3]$

X-band ESR ($\tau \approx 10^{-10}$ s)

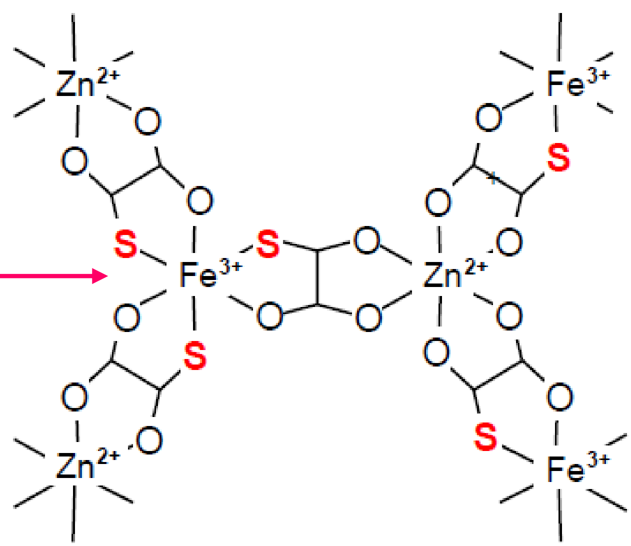


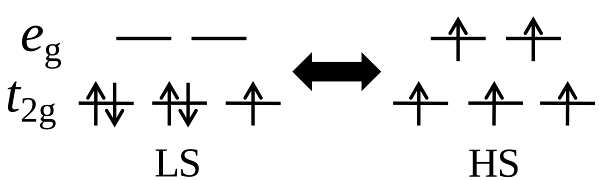
^{57}Fe Mössbauer spectra ($\tau \approx 10^{-7}$ s)



Rapid spin equilibrium

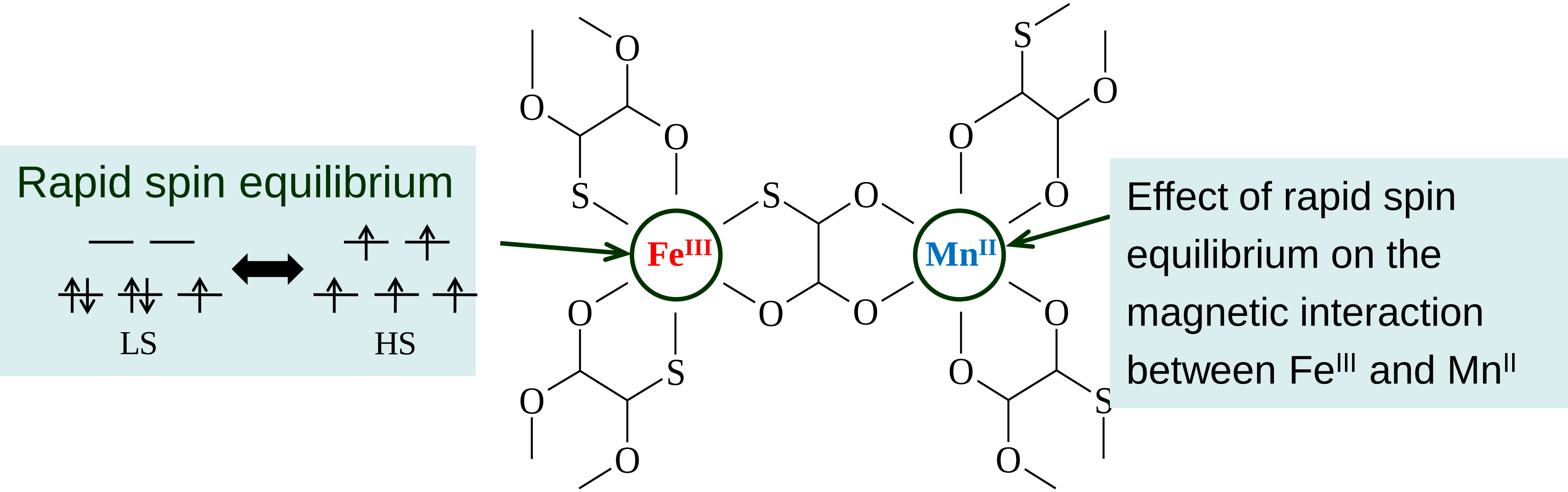
(10^{-10} s < τ < 10^{-7} s)





K. Kagesawa, N. Kojima, et al., *Chem. Lett.*, **2010**, *39*, 872.

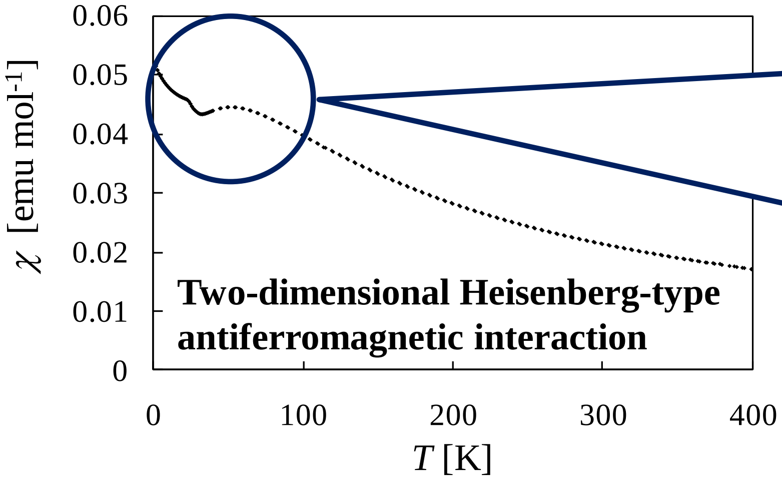
Spin state of $(C_6H_5)_4N[Mn^{II}Fe^{III}(mto)_3]$ (mto = C_2O_3S)

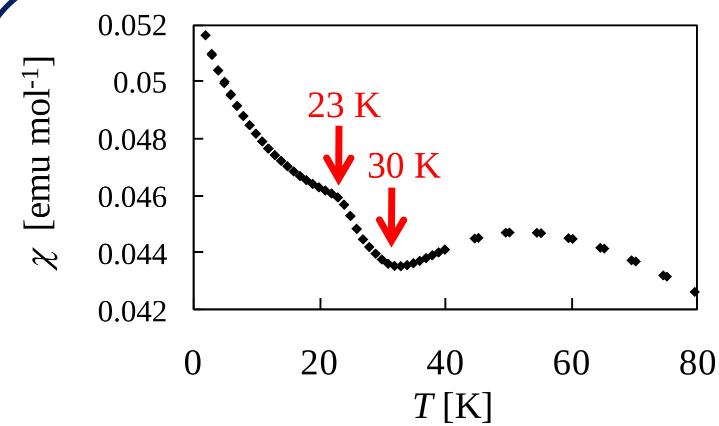


Concerted phenomenon between the rapid spin equilibrium and the succeeding magnetic phase transitions for $(Ph)_4N[Mn^{II}Fe^{III}(mto)_3]$.

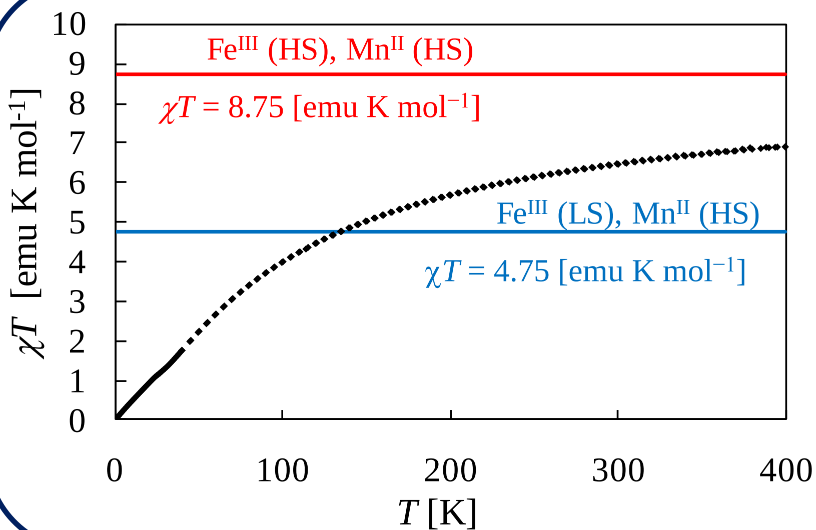
Magnetic properties of $(C_6H_5)_4P[Mn^{II}Fe^{III}(mto)_3]$

Temperature dependence of magnetic susceptibility





30 K
23 K } **magnetic ordering ?**



Theoretical value

Fe^{III} (HS), Mn^{II} (HS)→ χT = 8.75 [emu K mol^{-1}]

Fe^{III} (LS), Mn^{II} (HS)→ χT = 4.75 [emu K mol^{-1}]

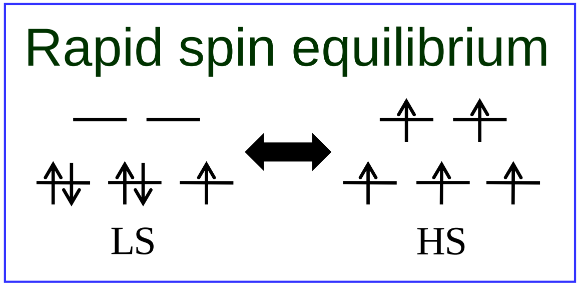
Experimental value

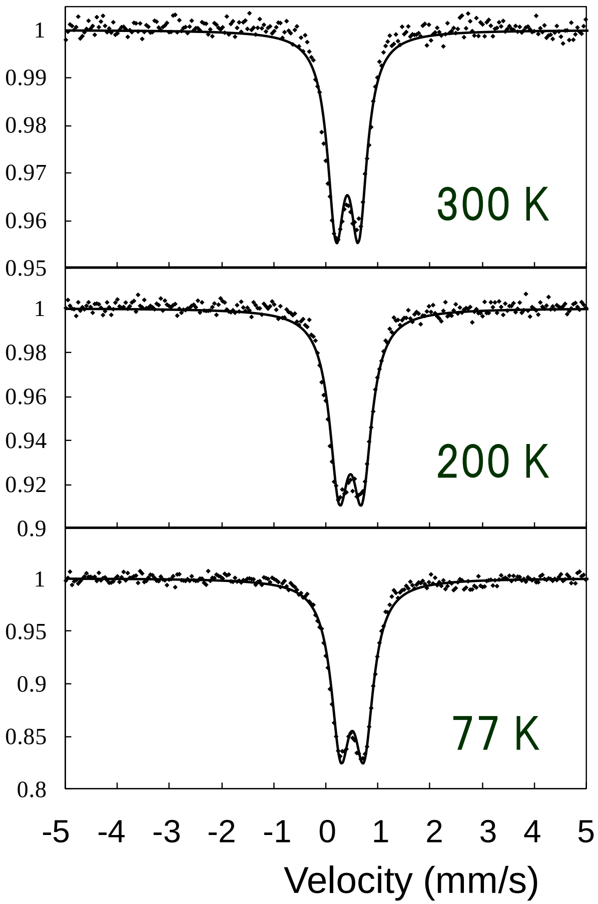
χT = 6.90 [emu K mol^{-1}] (@400K)

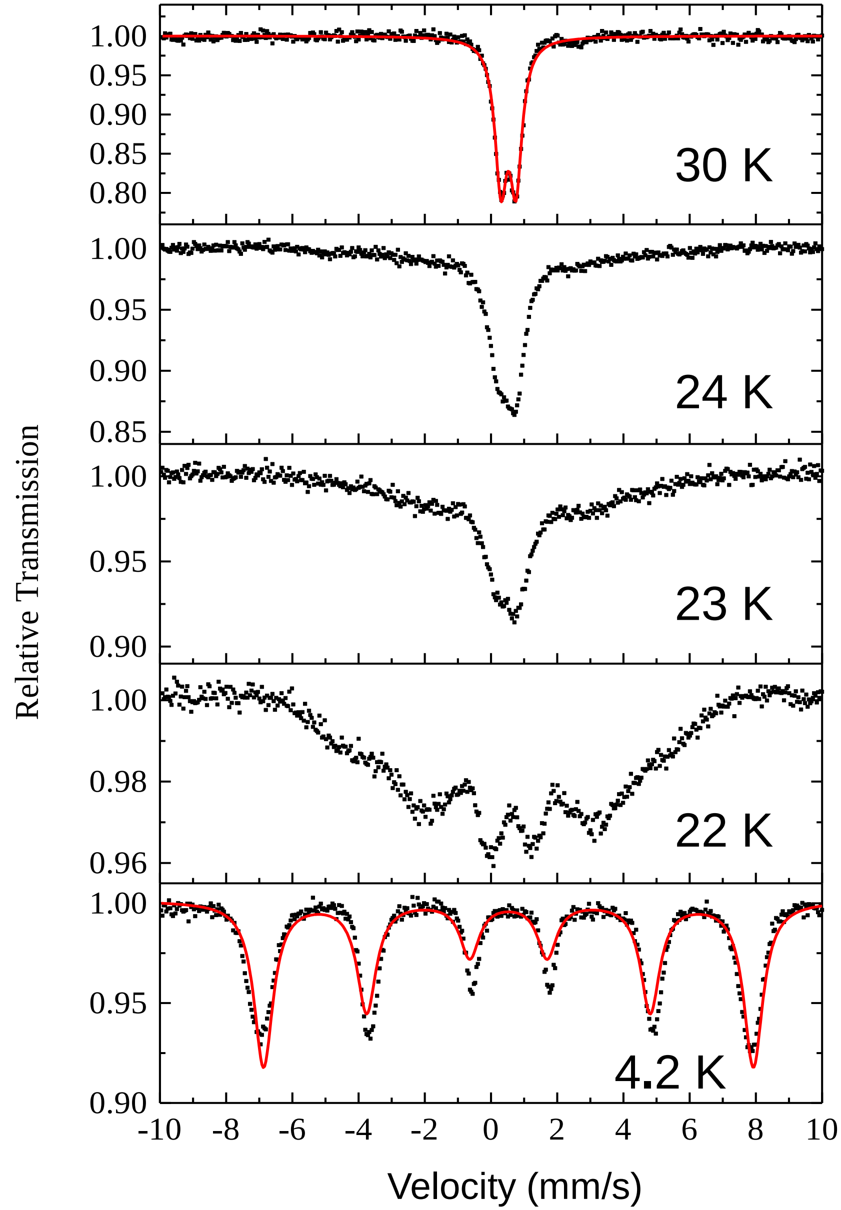
→spin equilibrium at $Fe^{III}O_3S_3$

K. Kagesawa, *Doctoral Thesis* (Univ. Tokyo, 2011)

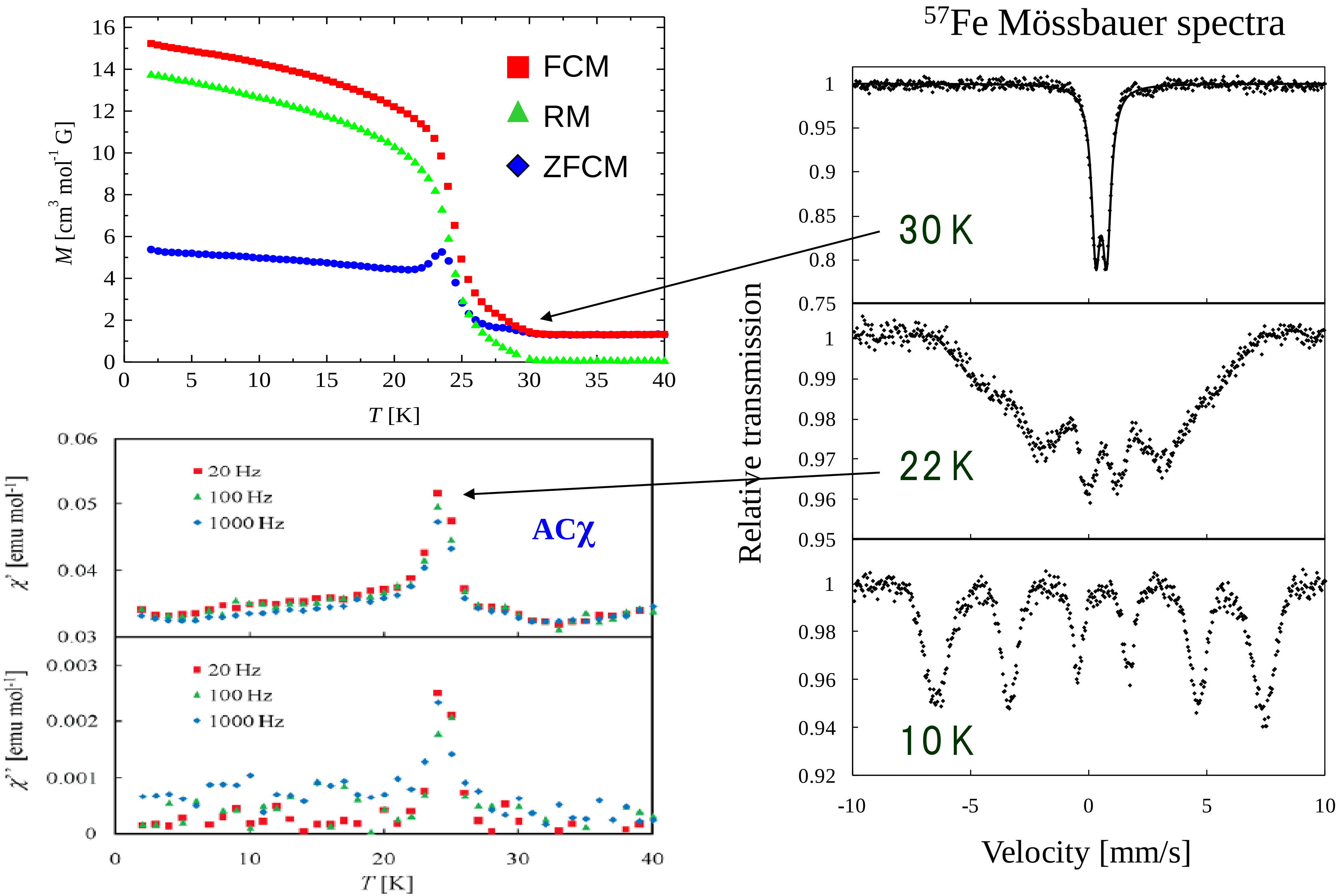
^{57}Fe Mössbauer spectra of $(C_6H_5)_4P[Mn^{II}Fe^{III}(mto)_3]$





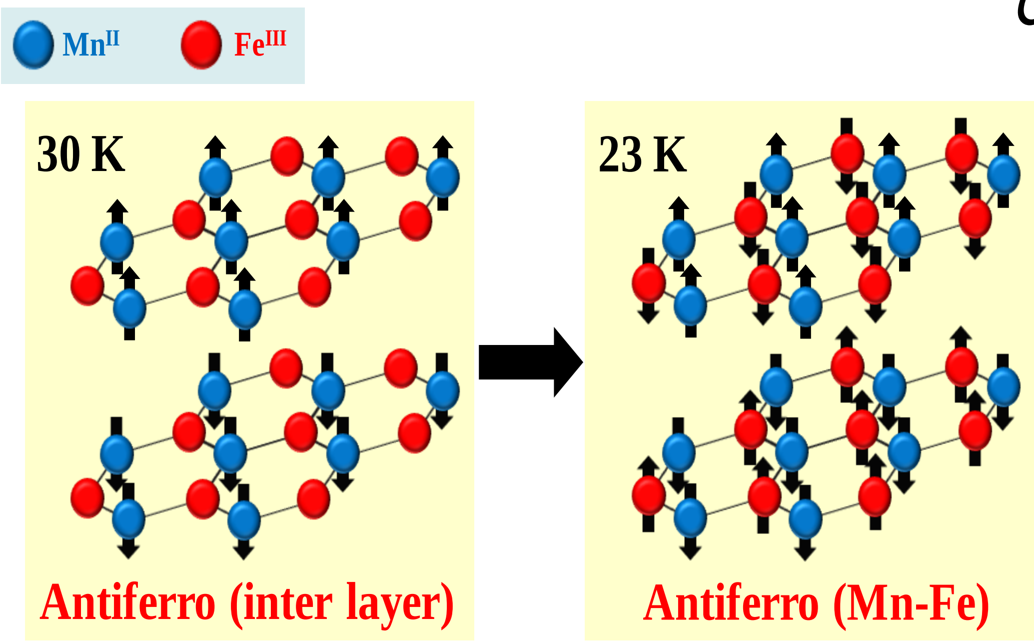


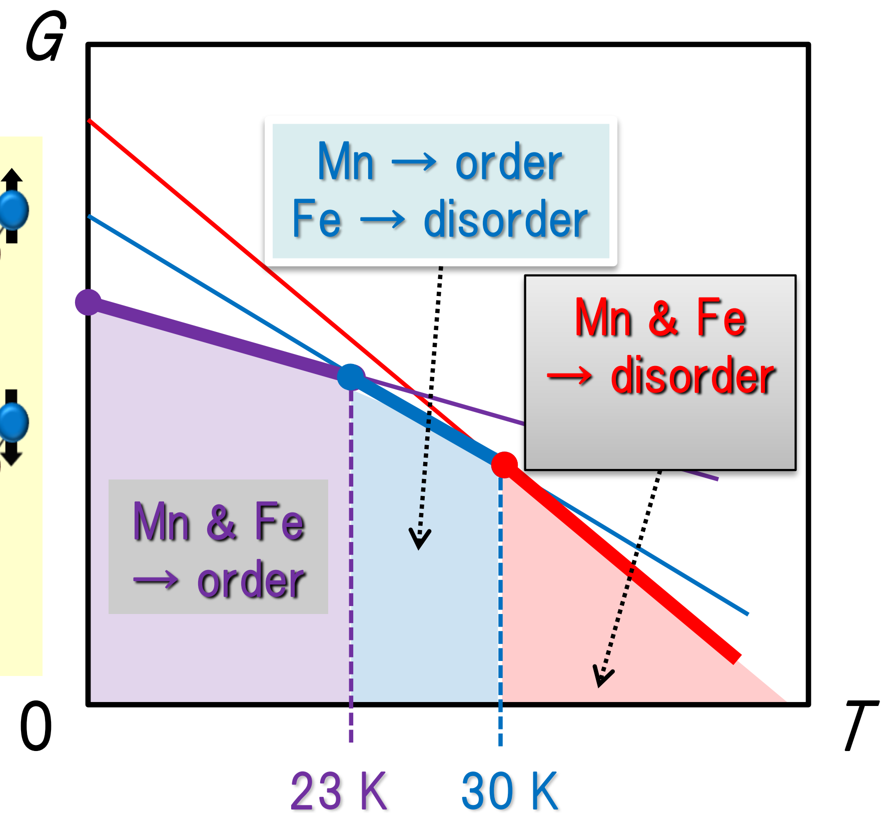
Successive magnetic phase transitions in $(C_6H_5)_4P[Mn^{II}Fe^{III}(mto)_3]$



K. Kagesawa, *Doctoral Thesis* (Univ. Tokyo, 2011)

Rapid Spin Equilibrium and Magnetic Ordering



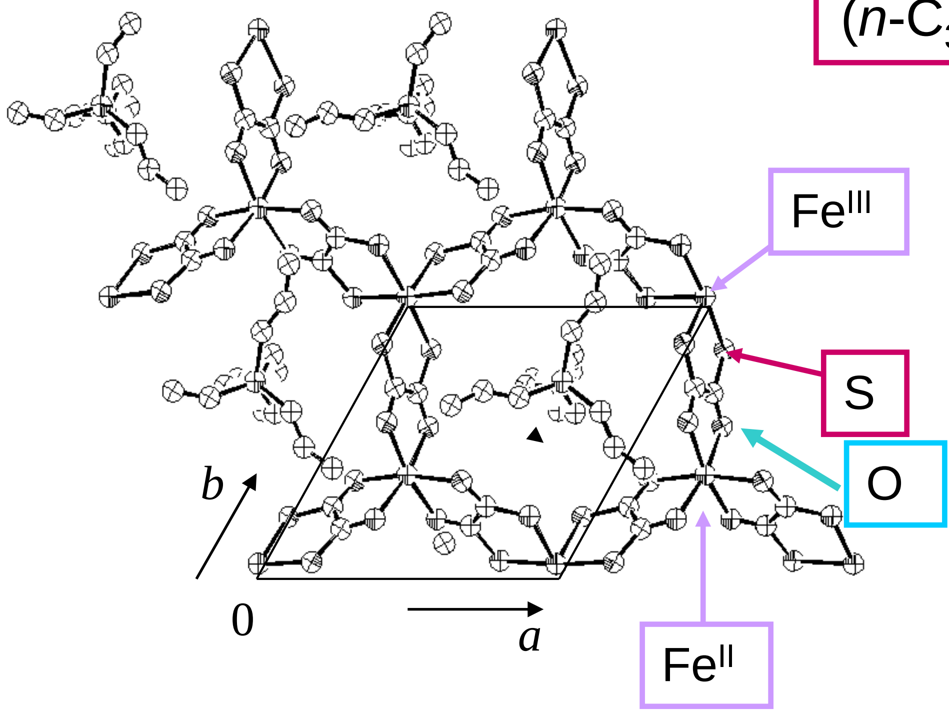


Multi-step magnetic phase transitions induced by rapid spin equilibrium in $(C_6H_5)_4P[Mn^{II}Fe^{III}(mto)_3]$

K. Kagesawa, *Doctoral Thesis* (Univ. Tokyo, 2011)

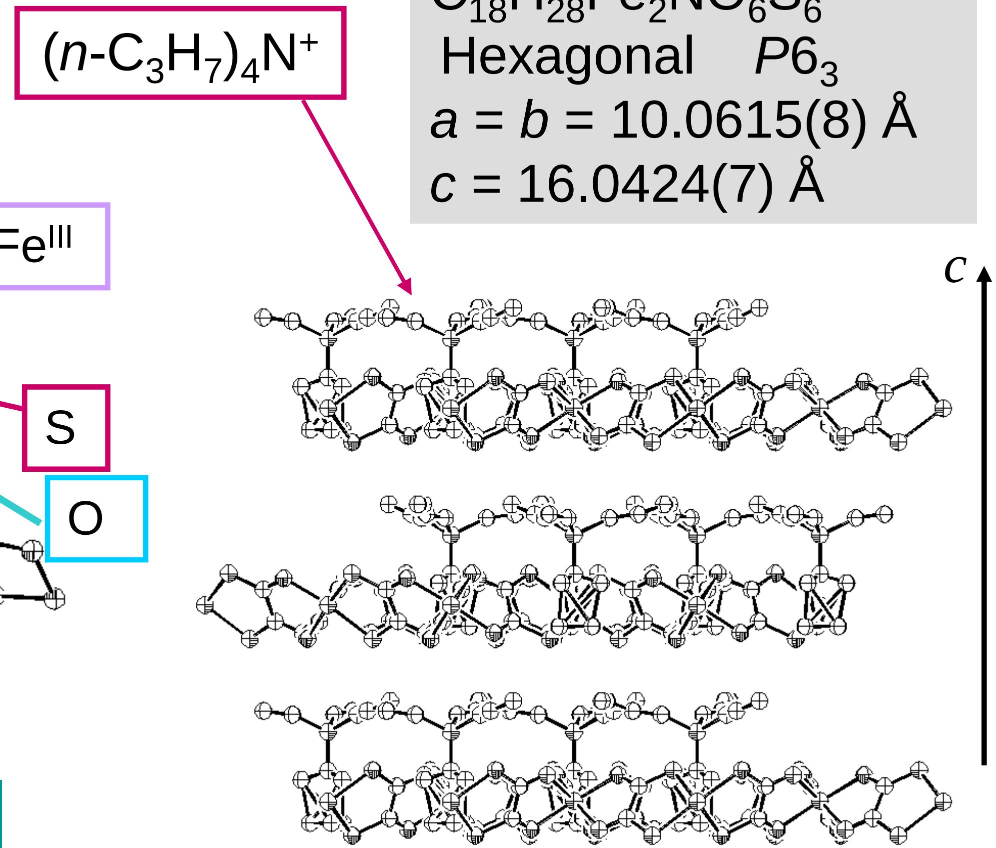
Charge transfer phase transition in $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$

Crystal structure of $(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$



Honeycomb structure

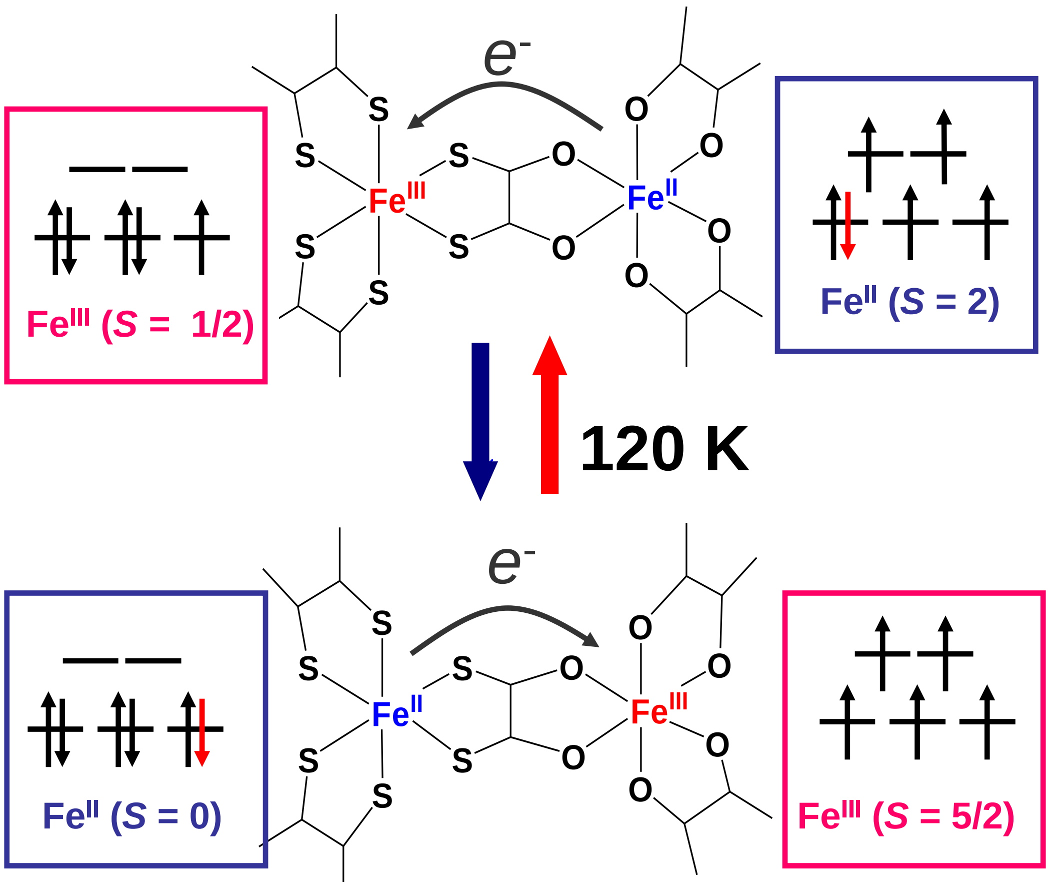
$C_{18}H_{28}Fe_2NO_6S_6$
Hexagonal $P6_3$
$a = b = 10.0615(8)$ Å
$c = 16.0424(7)$ Å



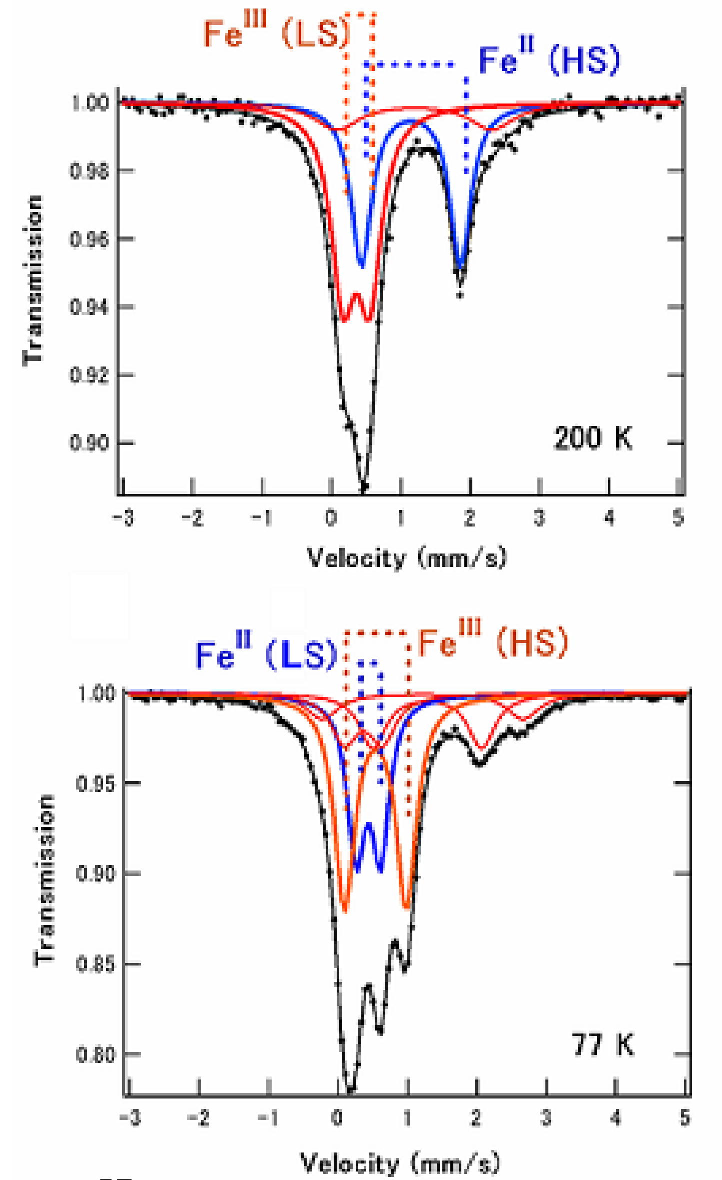
M. Itoi, M. Enomoto, N. Kojima, et al., *Solid State Commn.*, **2004**, *130*, 415.

Charge transfer phase transition in$(n\text{-}C_3H_7)_4N[Fe^{II}Fe^{III}(dto)_3]$

High Temperature Phase (HTP)
$S = R\ \ln(2\times 5)$



Low Temperature Phase (LTP)
$S = R\ \ln(1\times 6)$

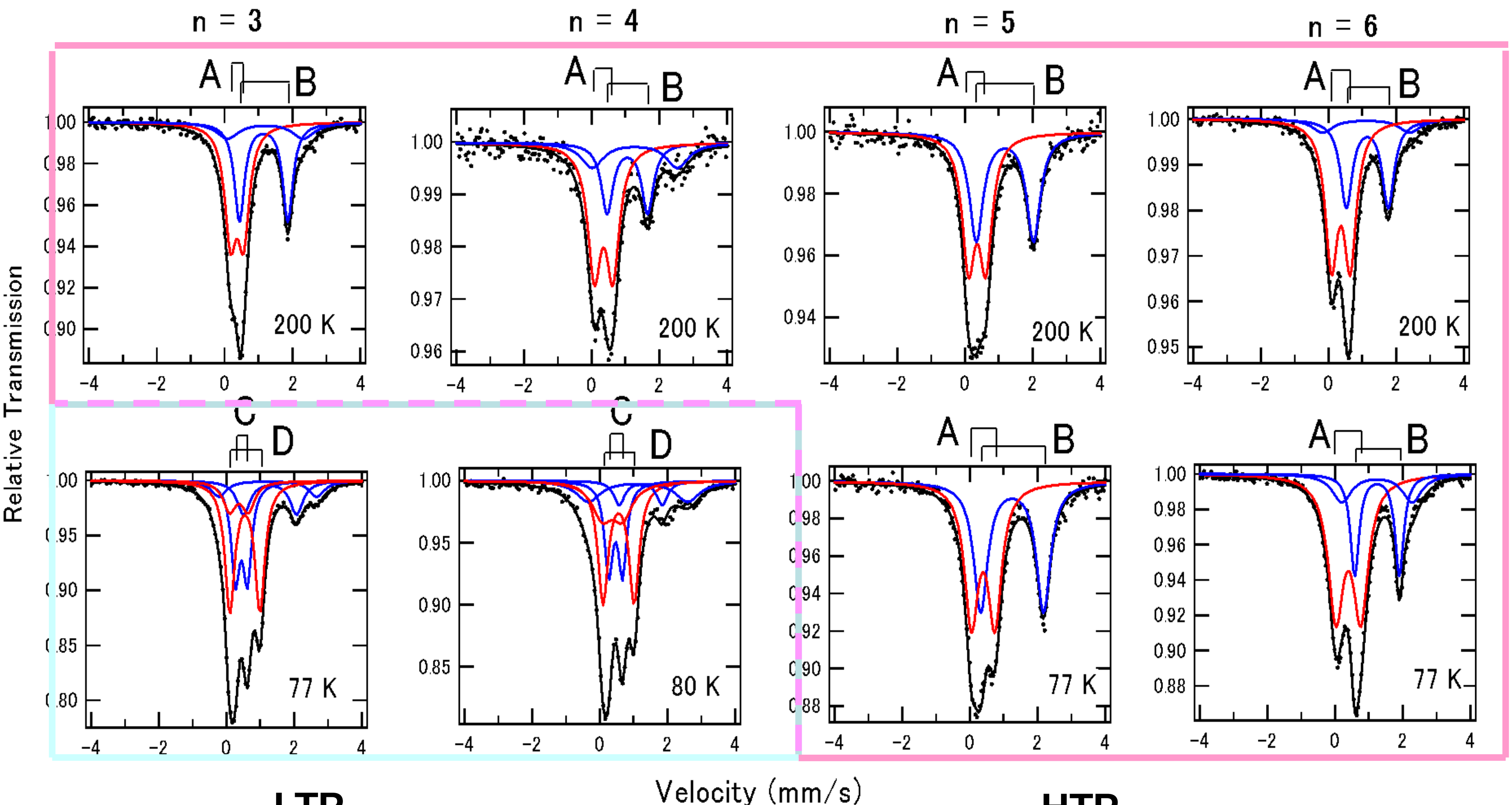


^{57}Fe Mössbauer spectra

N. Kojima, M. Seto, Yu. Maeda, *et al*., *Solid State Commun*. **2001**, 120, 165.

Mössbauer spectra of $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3](n = 3 - 6)$

n = 3,4**:** charge transfer phase transition (CTPT)   n = 5,6: no CTPT



LTP

C: $Fe^{II}(S = 0)$

D: $Fe^{III}(S = 5/2)$

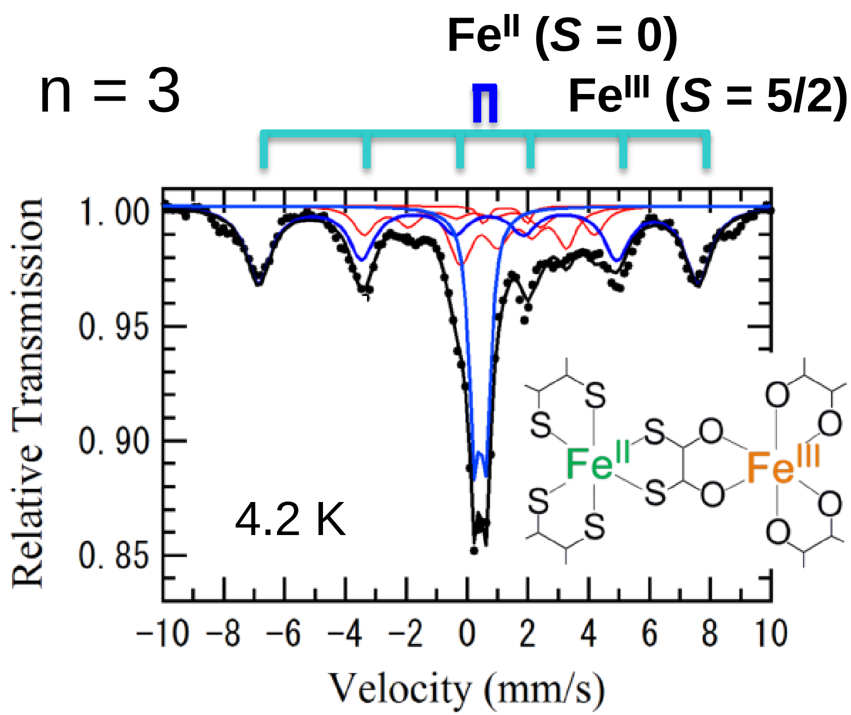
HTP

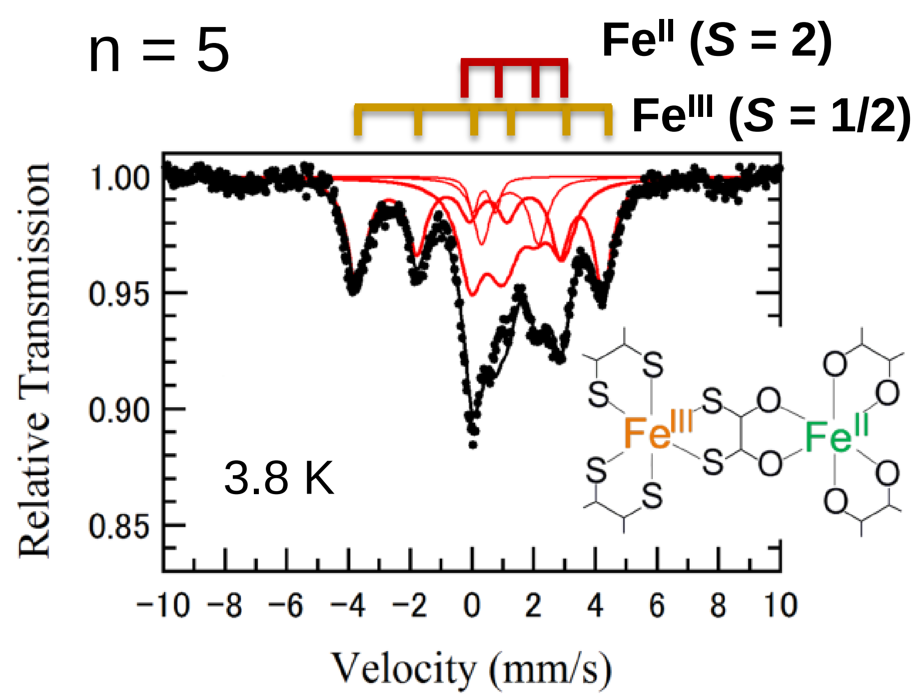
A: $Fe^{III}(S = 1/2)$

B: $Fe^{II}(S = 2)$

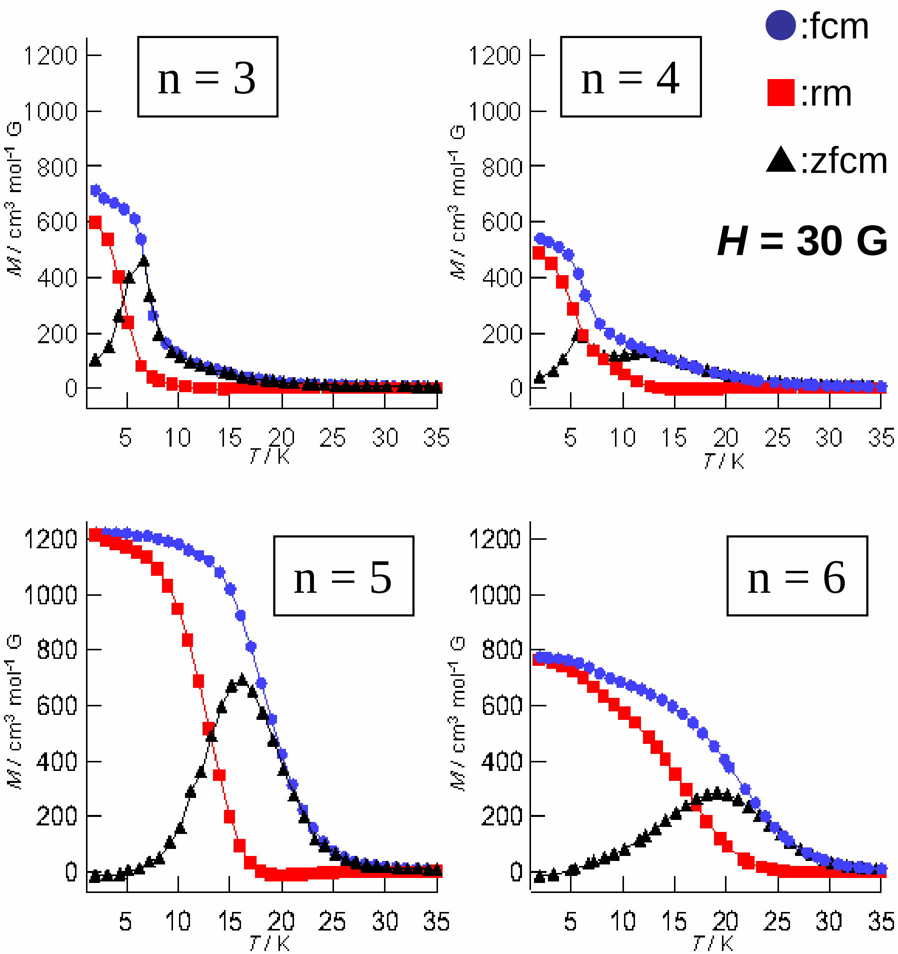
N. Kojima, et al., *Hyperfine Interactions*, **2004**, *156-157*, 175.

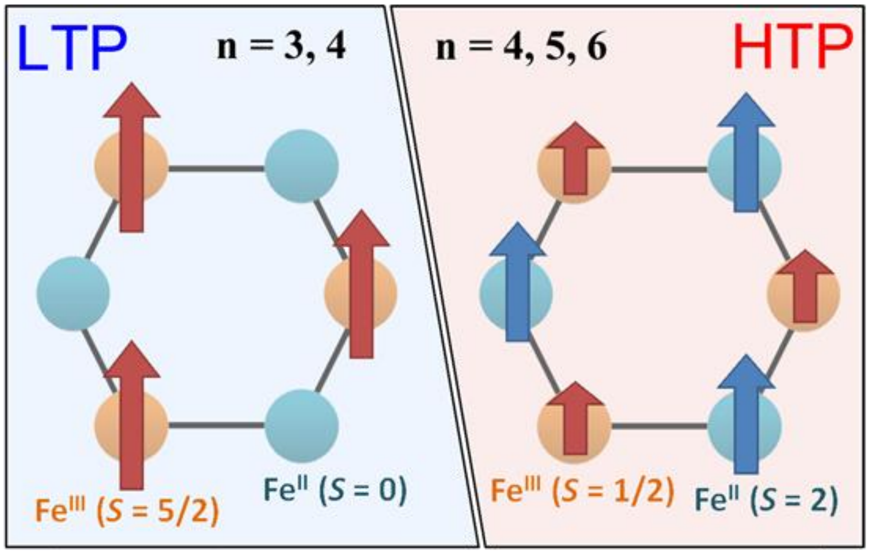
^{57}Fe Mössbauer spectra in the ferromagnetic phase of $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$(n = 3, 5)





Ferromagnetism of $(n\text{-}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$





n	3	4	5	6
T_c (K)	7	7 & 13	19.5	23
θ (K)	+12	+18	+23	+21
T_{CT} (K)	120	140	-	-

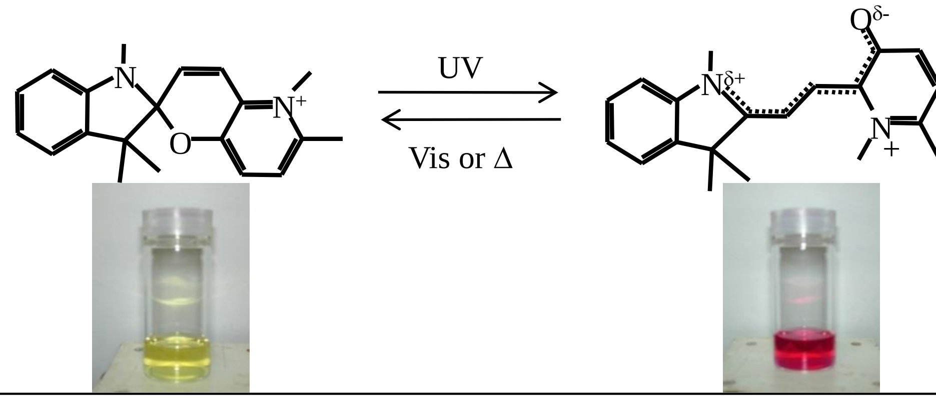
Organic-inorganic hybrid system with photochromic cation

(SP)[$Fe^{II}Fe^{III}(dto)_3$]

Cation

Photochromic spiropyran (SP)

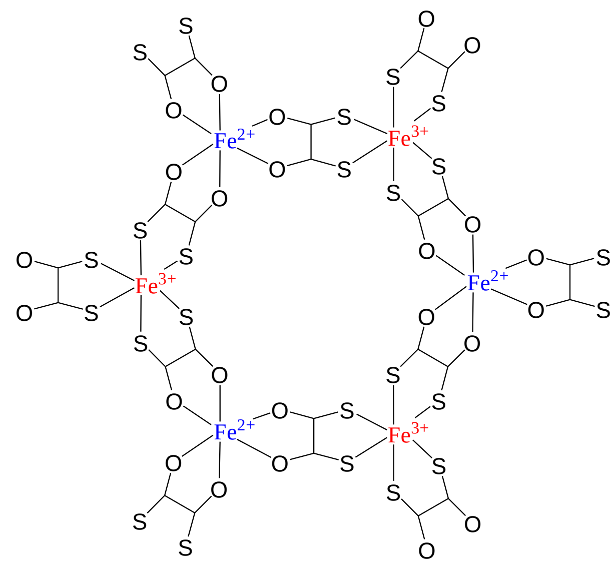
- **Reversible photo-isomerization**
- **Long life time in solids (several days in r.t.)**



Anion

Iron mixed valence complex with [$Fe^{II}Fe^{III}(dto)_3$]$^{-}_{\infty}$ 2D- honeycomb layers

- **Charge tarnsfer phase transition**
- **Ferromagnetic transition**

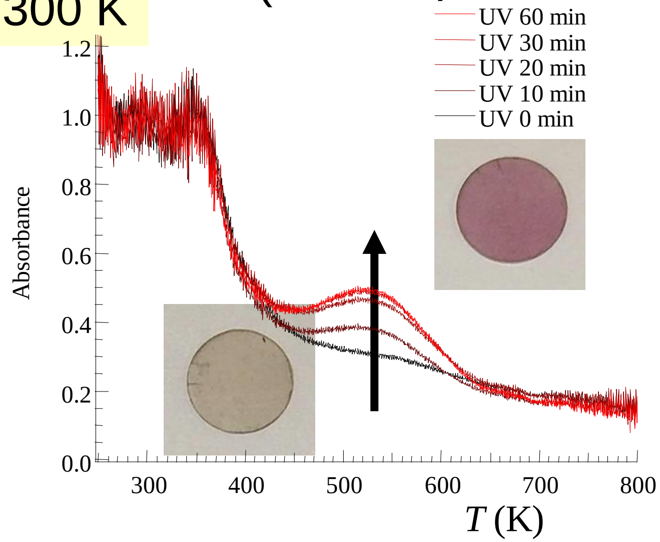


N. Kida, N. Kojima, et al., *J. Am. Chem. Soc.*, **2009**, 131, 212.

Photo-isomerization of spiropyran in (SP)[$Fe^{II}Fe^{III}(dto)_3$]

300 K

UV (350 nm) irradiation



After UV, Vis. (550 nm) irradiation

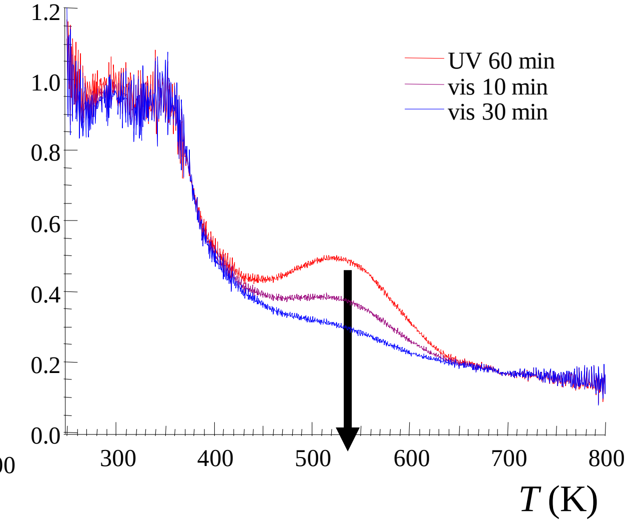
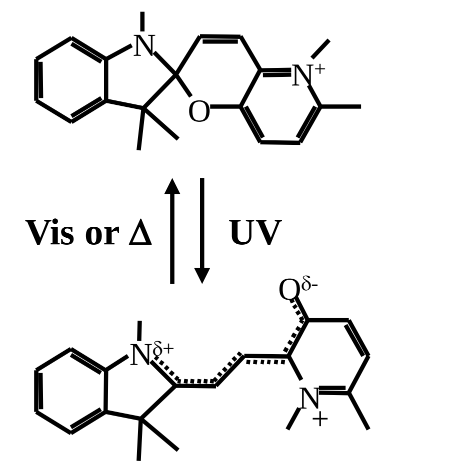
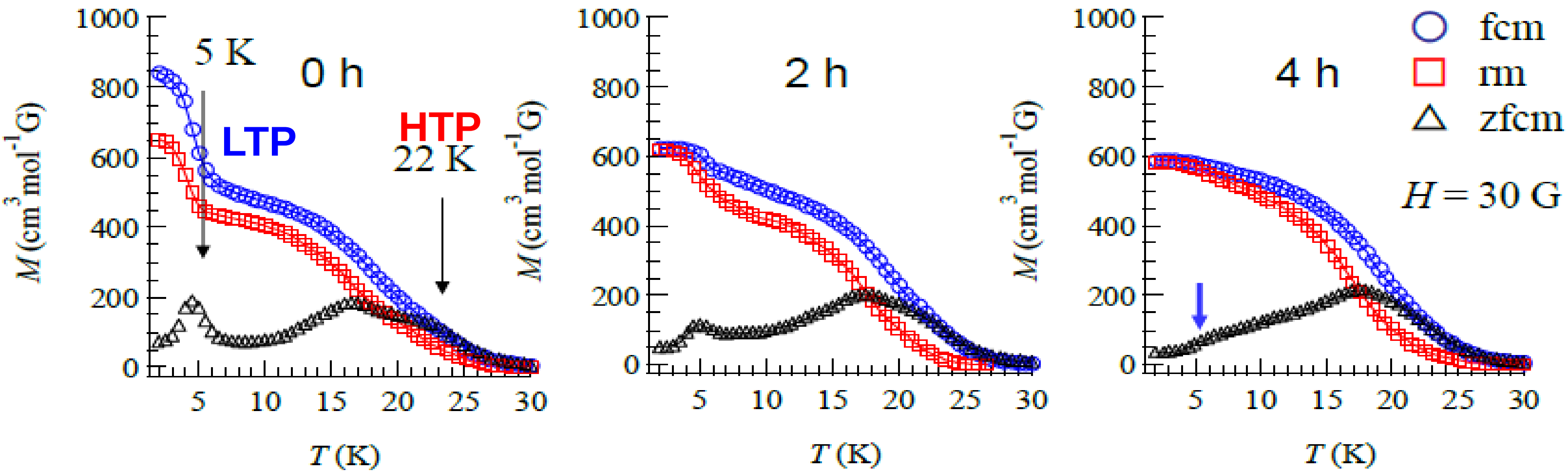


Photo-isomerization of SP



Photoinduced effect on the ferromagnetism

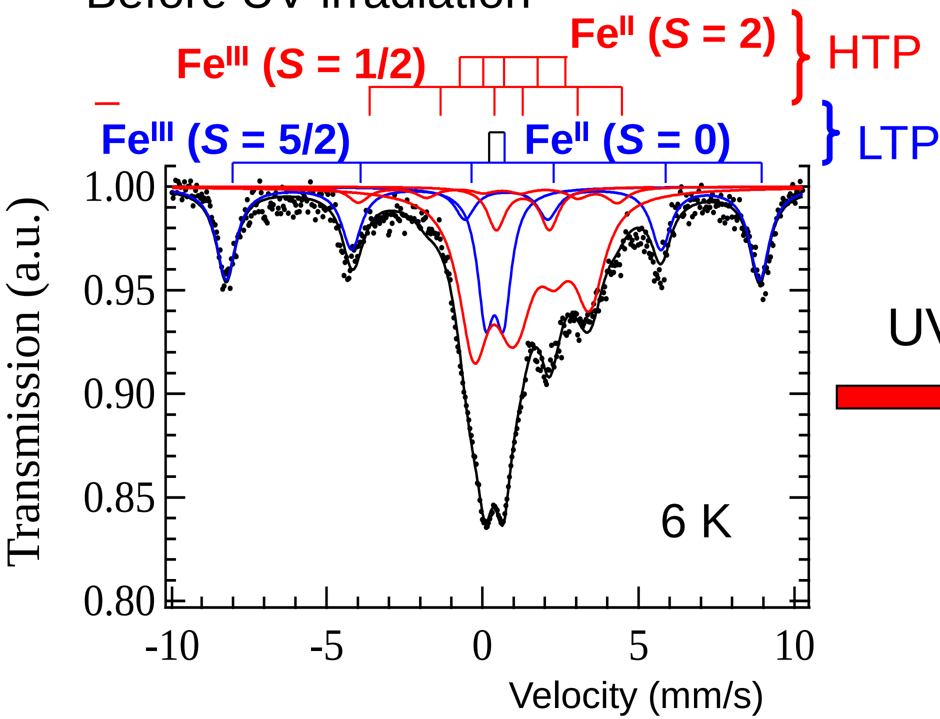
(after UV (350 nm, 40 mW/cm-1) irradiation at 300 K)



N. Kida, N. Kojima, et al., *J. Am. Chem. Soc.*, **2009**, 131, 212.

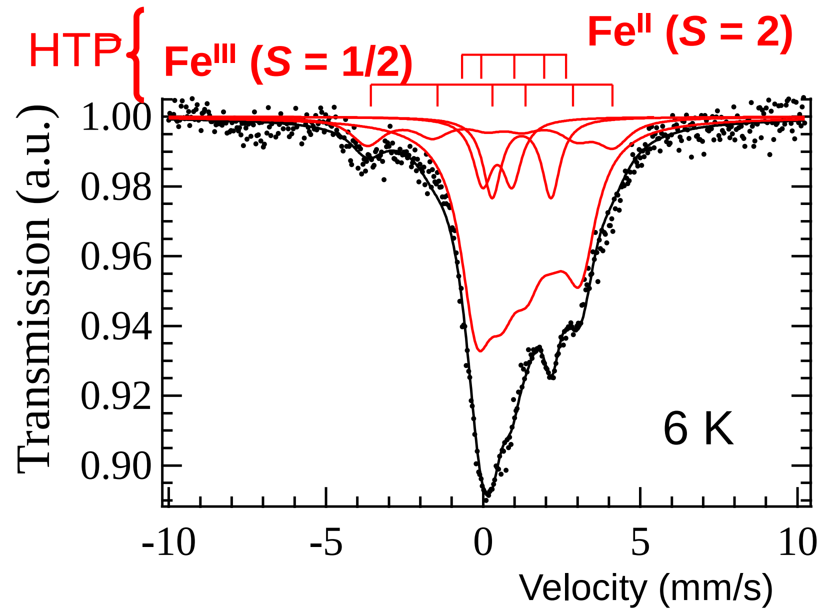
Disappearance of LTP under UV irradiation

Before UV irradiation



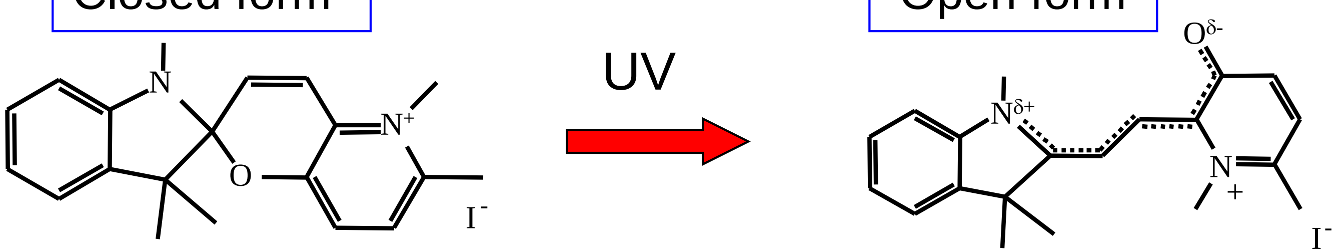
UV

After UV irradiation



Closed form

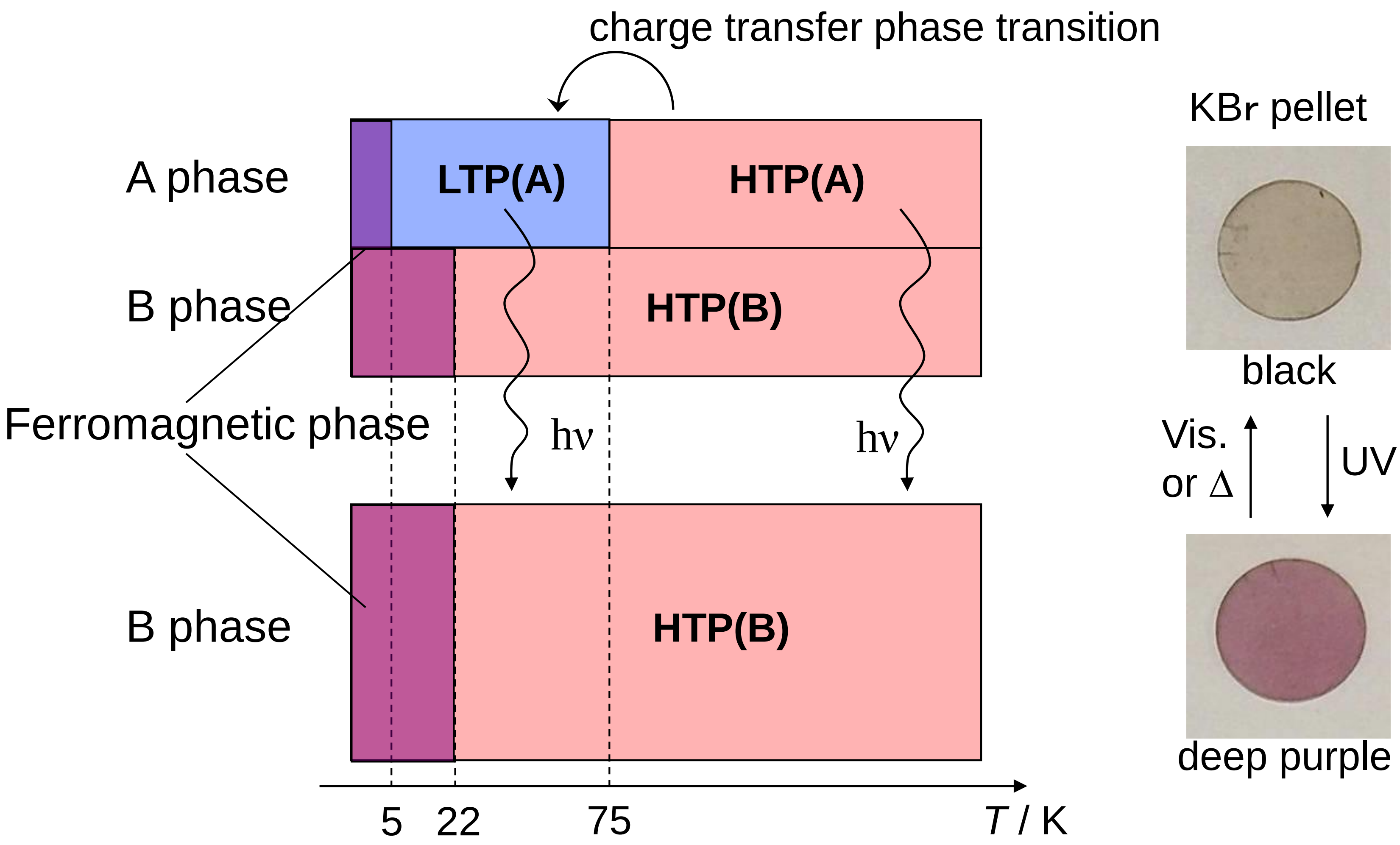
Open form



Expansion of the unit cell volume due to the photo-isomerization of SP

N. Kida, N. Kojima, et al., *Polyhedron*, **2009**, *28*, 1694.

Schematic diagram of spin states transition by photo-irradiation

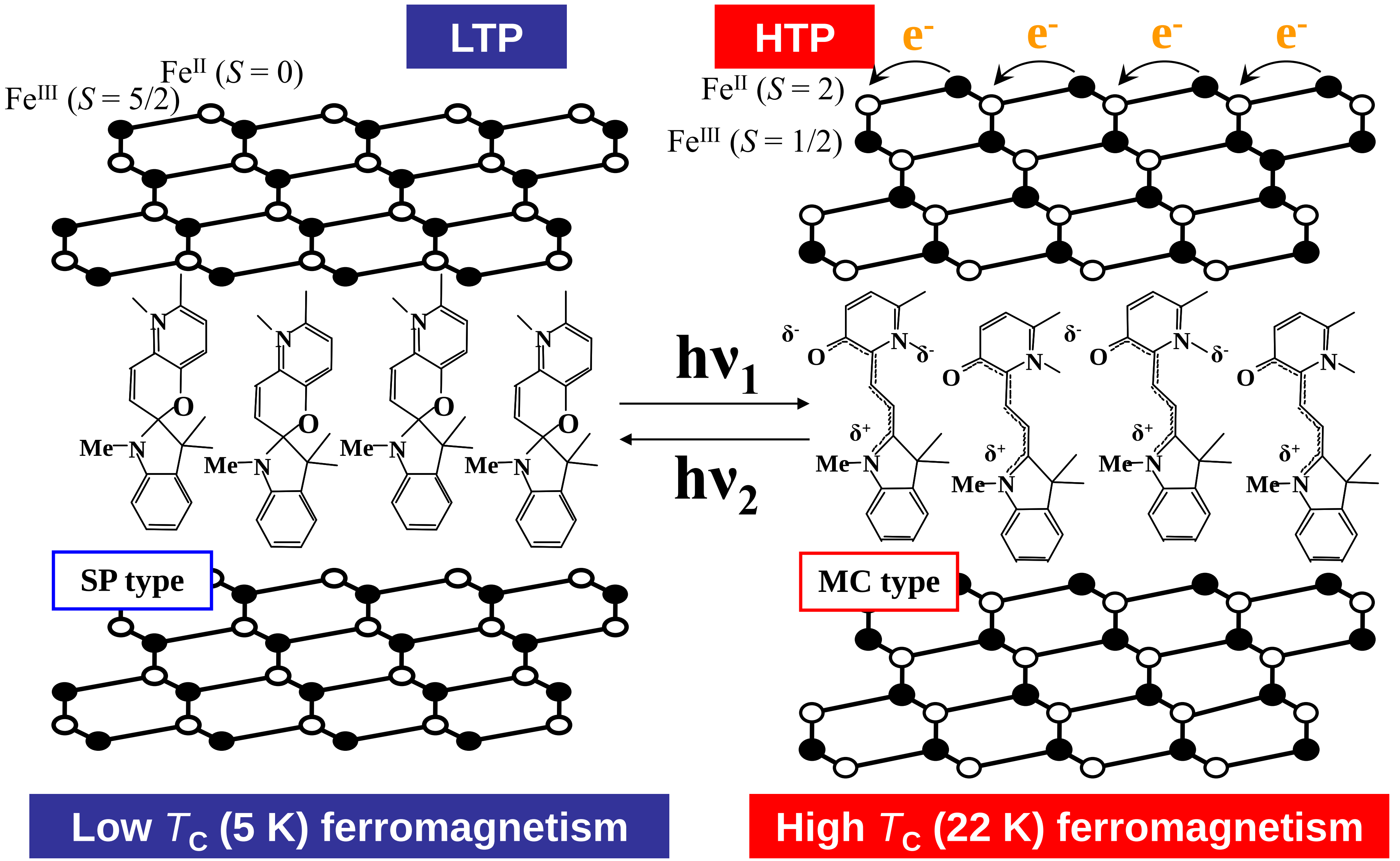


A phase Thermal charge transfer occurs

B phase No thermal charge transfer phase transition

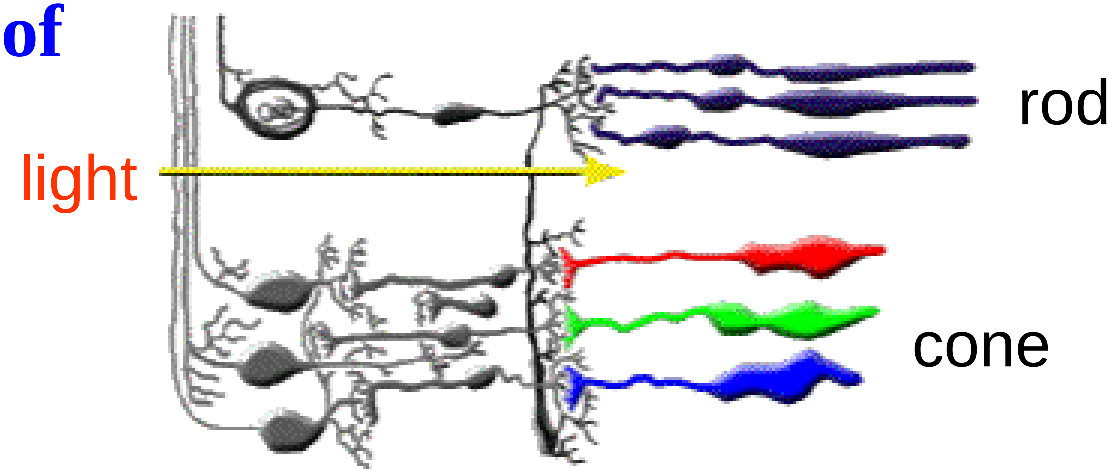
T_C shifts from 5 to 22 K by UV irradiation

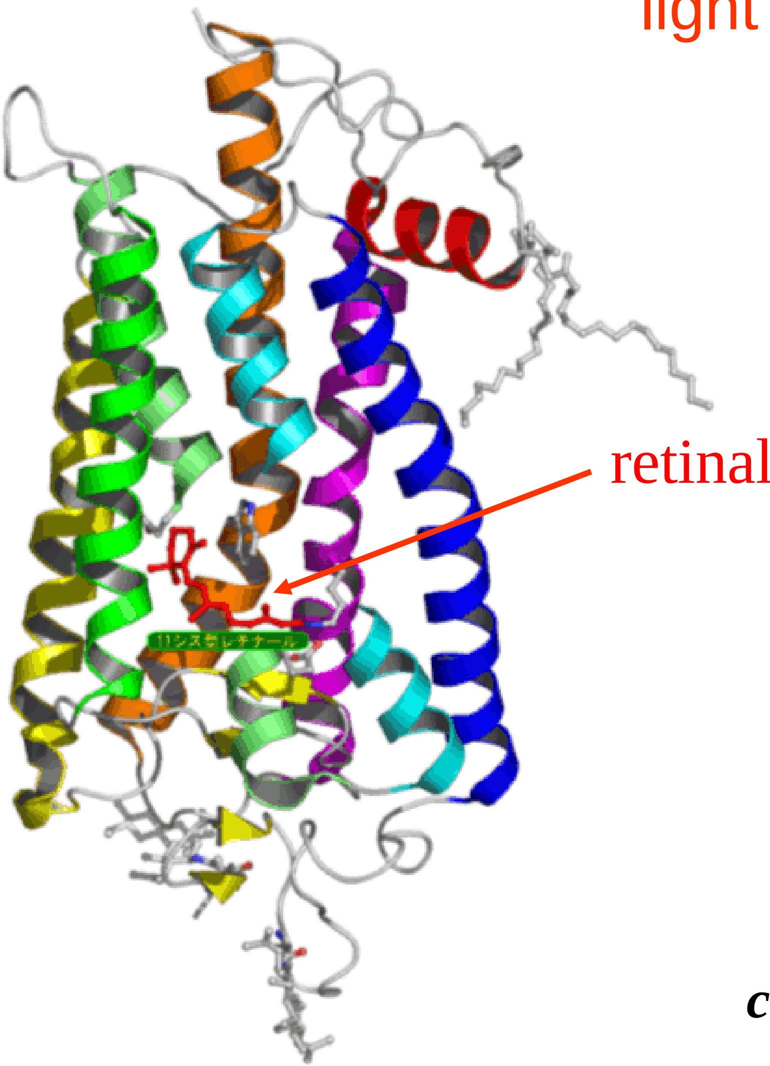
Photoinduced charge transfer phase transition at 70 K



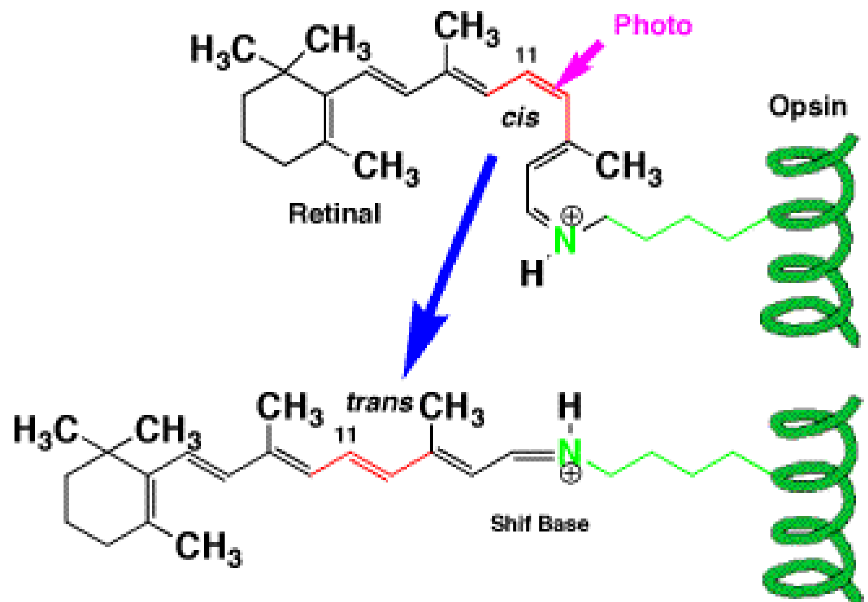
N. KIda, et al., *J. Am. Chem. Soc.*, **2009**, *131*, 212.

Photo-isomerization of retinal in visual cell





Structure of rhodopsin



cis-trans **photoisomerization of retinal**

http://www.kiriya-chem.co.jp/q&a/q52.html

Summary

(1) Development of transparent spin crossover complex film, $[Fe(Htrz)_3]$-Nafion and observation of LIESST

(2) Development of pH sensitive spin crossover complex film, $[Fe^{II}(diAMsar)]$-Nafion and the direct observation of proton flow in Nafion

(3) Concerted phenomenon between the rapid spin equilibrium and the successive magnetic phase transitions for $(n\text{-}C_nH_{2n+1})_4N[Mn^{II}Fe^{III}(mto)_3]$ (mto = C_2O_3S)

(4) Charge transfer phase transition (CTPT) for iron mixed- valence complex, $(C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ (dto = $C_2O_2S_2$)

(5) Concerted phenomenon between the photo-isomerization and charge transfer phase transition in a photo-reactive organic-inorganic hybrid complex, $(SP)[Fe^{II}Fe^{III}(dto)_3]$(SP = Spiropyran)