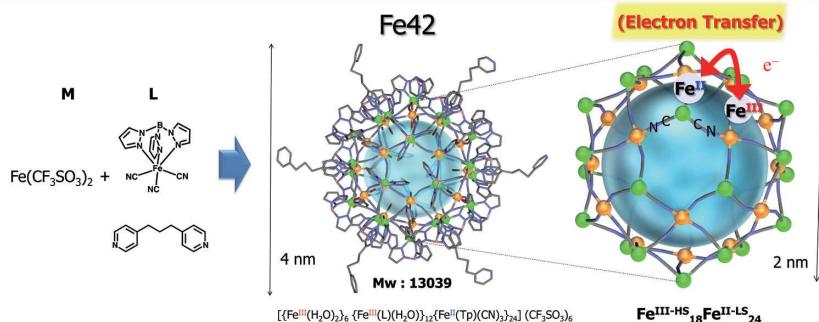


# 高スピン多核錯体の開発

## Cyanide-Bridged Fe<sub>42</sub> High-Spin Nanocage with $S = 90/2$

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1. The largest cyanide-bridged metal nanocage reported to date
2. Mixed valence state (Fe<sup>III</sup><sub>18</sub>Fe<sup>II</sup><sub>24</sub>)
3. High spin cluster [a Record  $S = 90/2$ ]
4. Metal-to-metal charge transfer upon reversible coordination bond formation/cleavage
5. Stalled-cuboctahedral structure

### 1. Introduction

Supramolecular Coordination Complex

Reaction:  $M + L \rightarrow M_{12-24}$  or  $M_{24-48}$

M: Pd<sup>2+</sup>, L:  $M_{12-24}$ ,  $M_{24-48}$

M. O'Keefe, O. M. Yaghi et al. *Angew. Chem. Int. Ed.* **2008**, 47, 5136.  
 M. Fujita et al. *Science*, **2010**, 328, 1144.  
 Angew. Chem. Int. Ed. **2012**, 51, 3161.

valence crossover: Metal (II) ↔ (III)

spin crossover:  $s, p, d, \sigma, \pi, \delta$

If we could utilize valence, spin and orbital of metals on metal-organic polyhedra...

1. Valence → Dynamic property
2. Spin → High-spin cluster nanocage

Charge Transfer:  $h\nu, \text{heat}$

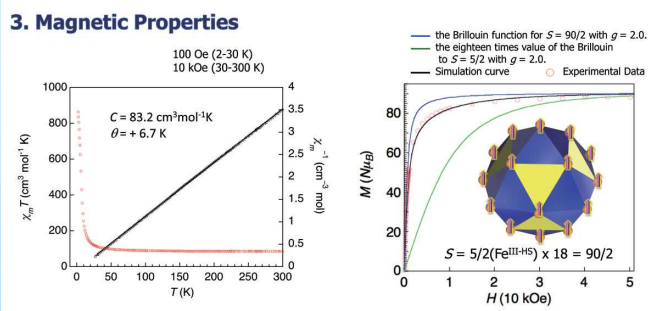
### 2. X-ray Crystal Structures

Packing structure, Asymmetric unit

Stalled Cuboctahedral Spin Nanocage

$a = 0.67 \text{ nm}$  Cuboctahedron

$Pn-3n$   
 $a = b = c = 30.7679(13) \text{ \AA}$   
 $\alpha = \beta = \gamma = 90.00 \text{ \AA}$   
 $V = 29126.9 \text{ \AA}^3$   
 $T = 100 \text{ K}$   
 $R1 = 0.0857$



### 4. Metal-to-Metal Charge Transfer

Weight change of heating and air exposure process

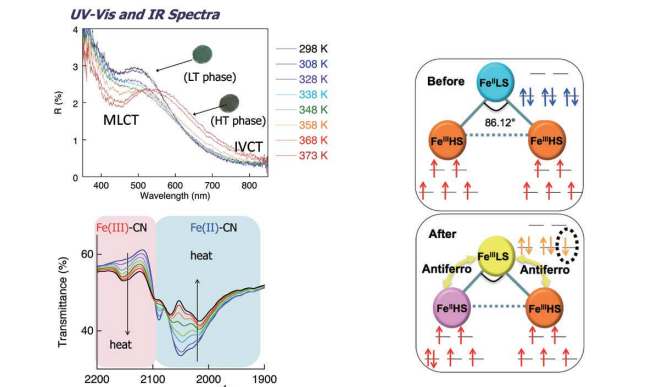
Dehydration, Charge Transfer

Heme, His

Reversible Coordination Bond Formation/Cleavage

300 K: Octahedral  $[Fe^{II}(CN)_6]^{4-}$  ↔ Square pyramidal  $[Fe^{III}(CN)_5]^{3-}$  (400 K)

Electron transfer



### 5. Other High Spin Molecules

$S = 83/2$  Mn<sub>19</sub>:  $[Mn^{III}_{12}Mn^{II}_7]$  (Ayuk M. Ako et al. *Angew. Chem. Int. Ed.* **2006**, 45, 4926.)

$S = 51/2$  Mn<sub>25</sub> (Muralee Murugesu et al. *J. Am. Chem. Soc.* **2004**, 126, 4766.)

$S = 31/2$  Mo<sub>3</sub>Mn<sub>14</sub> (X.-Y. Wang et al. *Angew. Chem. Int. Ed.* **2000**, 39, 1605.)

$S = 30/2$  Fe<sub>3</sub>Mn<sub>6</sub> (Z.-H. Ni, et al. *Angew. Chem. Int. Ed.* **2005**, 44, 7742.)

$S = 27/2$  CrMn<sub>6</sub> (Michel Verdaguer et al. *Chem. Eur. J.* **2003**, 9, 1677.)

$S = 39/2$  Mn<sub>3</sub>Mo<sub>6</sub> (Joulla Larionova et al. *Angew. Chem. Int. Ed.* **2000**, 39, 1605.)

$S = 90/2$  Fe<sub>42</sub> This study

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