Chromium Acetylide Based Magnetic Materials

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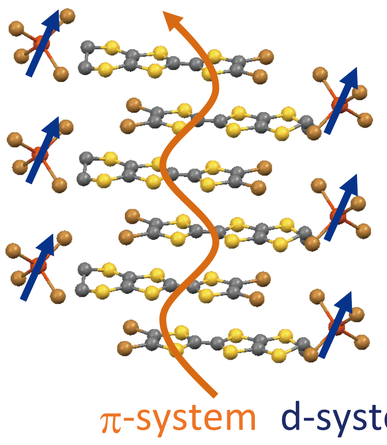
1. Introduction: π-d system



Conductive π-electron

⇕ Interact!

Magnetic d-electron

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Large magnetoresistance
Metal-Insulator transition
FIeld induced superconductivity
etc.

However, most of the π-d interaction is quite weak...

Why weak?

Magnetic d-electrons and conductive π-electrons are placed on distant molecules.

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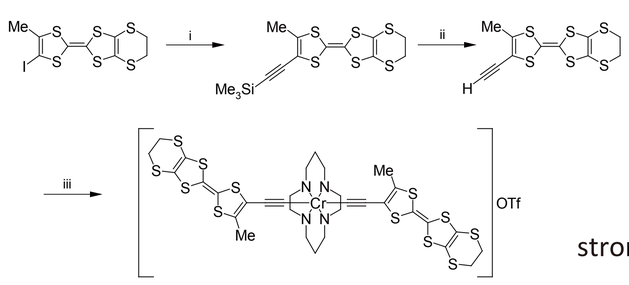
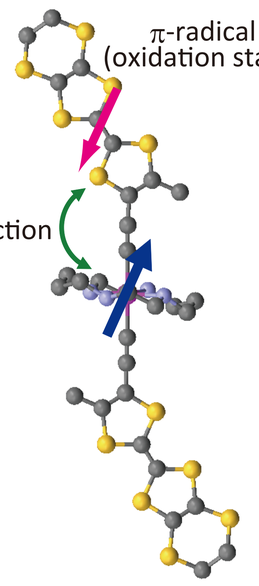
Integrate the π- and d-electrons into a molecule!

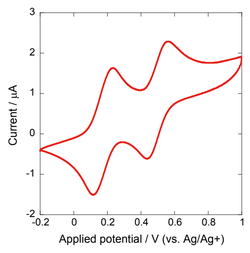
2. Cromium-Acetylide-TTF complex



(i)TMS-C≡C-H, $Pd(PPh_3)_4$, CuI, THF. (ii) KF, THF + MeOH.
(iii) LDA, $[CrCyclam(OTf)_2]OTf$, THF.



- Stable complex
- Redox active TTF-type ligand
- Strong intra-molecular interaction (oxidation state)



- Two reversible oxidation peaks
  → 1st and 2nd oxidation of TTF

Crystal growth of radical cation salts:
Standard galvanostatic oxidation inPhCl + MeCN (1:1) solution of Bu_4NClO_4 or Bu_4NBF_4.

5. Conclusion

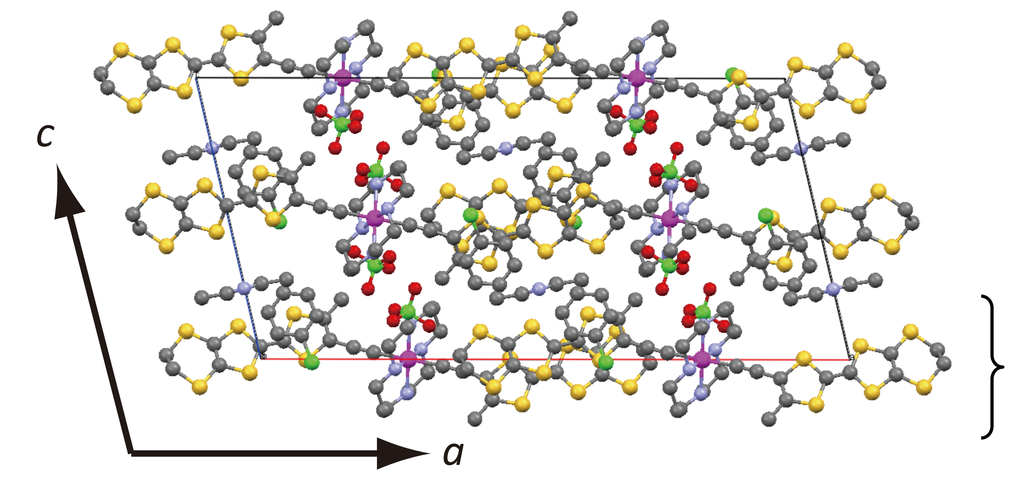
The first step toward the strongly interacted π-d system

We successfully synthesized a new complex with TTF ligand.
In the crystals obtained by electrochemical oxidation;
TTF backbones form mixed valence dimer (S = 1/2)
The complex forms 1D ferrimagnetic chain with strong intra-chain interaction ($2J \sim -30$ K)
Weakferromagnetic transition T_N = 23 K

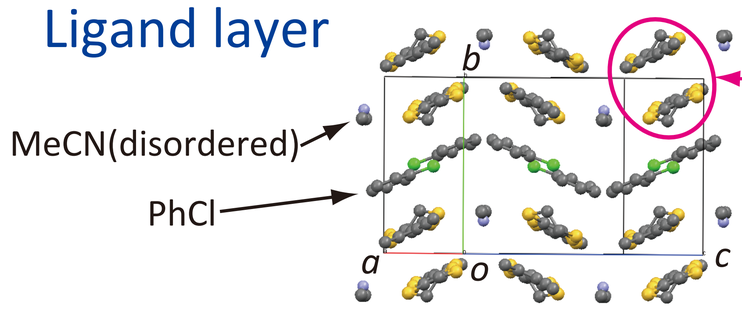
The strong intra-molecular π-d interaction of Chromium-Acetylide-TTF type complex is promising for constructing novel π-d systems.

3. Crystal structure of $[CrCyclam(C{\equiv}CMeEDT)_2][X]_2(PhCl)_2(MeCN)$

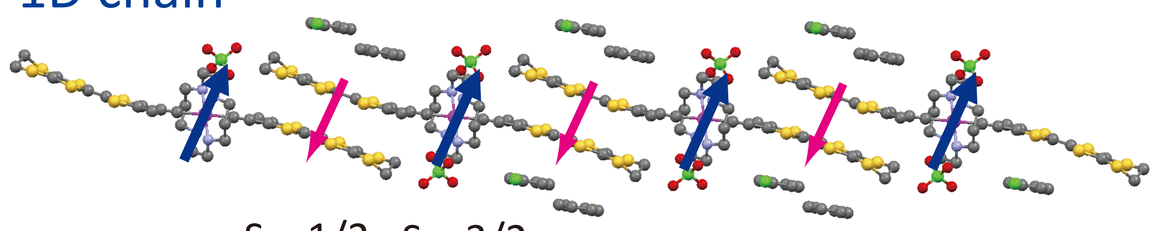
(same crystal structure regardless of anion X = $[ClO_4]^-$, $[BF_4]^-$)



Ligand layer



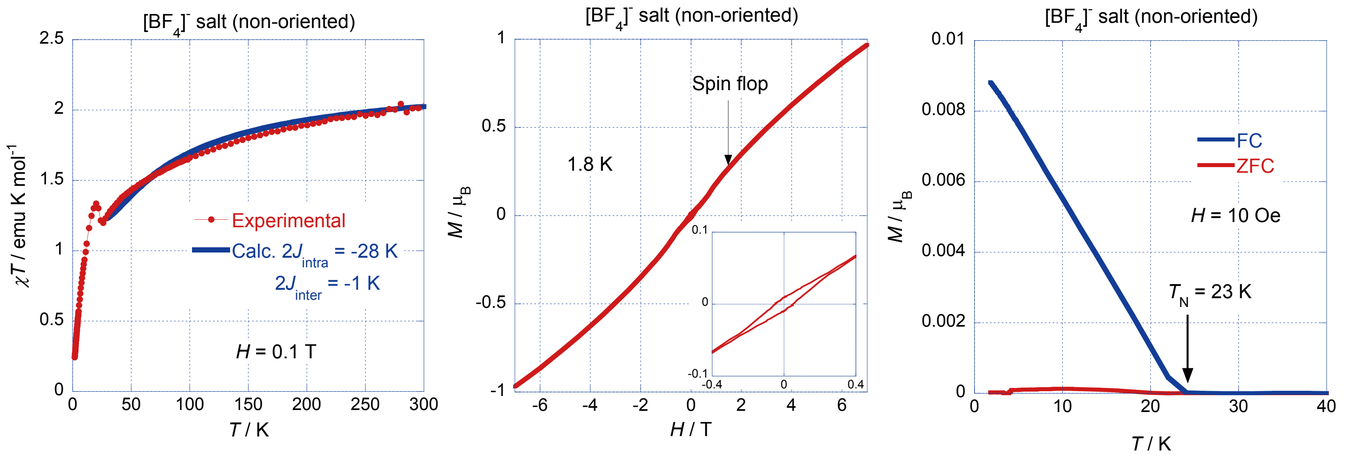
1D chain

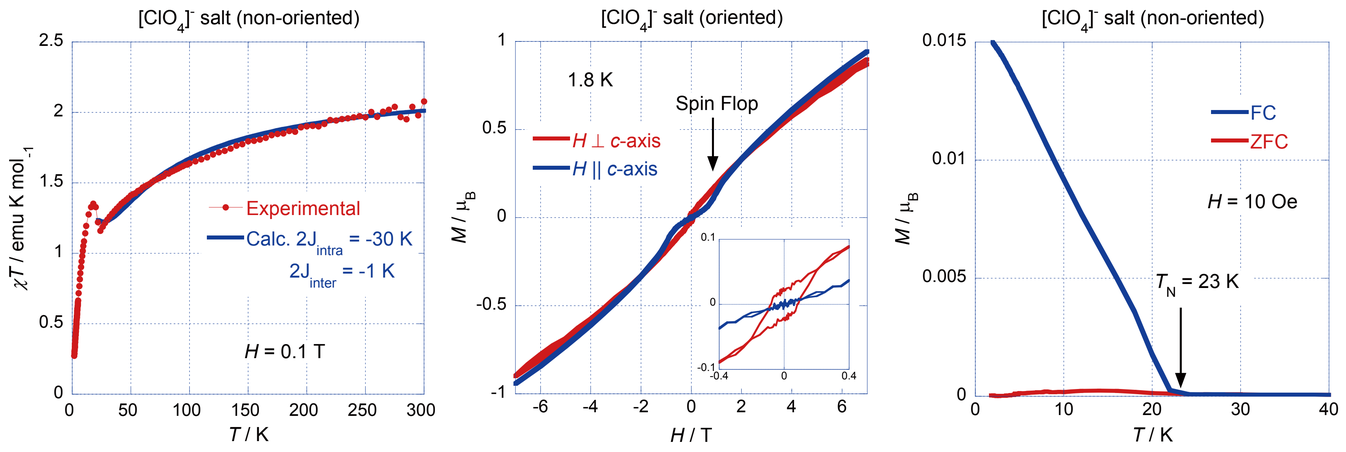


S = 1/2 (dimer) S = 3/2 (Cr^{3+})

1D ferrimagnetic chain

4. Magnetic properties





Strong intra-chain interaction $2J$ = -28 and -30 K
High weakferromagnetic transition temperature T_N = 23 K
Remanent magnetization: 0.009 μ_B for $[BF_4]^-$ salt (non-oriented)
0.023 μ_B for $[ClO_4]^-$ salt (oriented)
Coercive force: 50 mT for $[BF_4]^-$ salt (non-oriented)
85 mT for $[ClO_4]^-$ salt (oriented)
Origin of the weakferromagnetism:
Single ion anisotropy and / or Dzyaloshinsky-Moriya interaction