



# Synthesis and Magnetic Properties of New Chromium(III)-Acetylide-TTF Type Complexes

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## 1. Introduction

Previously, we reported a promising magnetic properties of  $[\text{CrCyclam}(\text{C}\equiv\text{C}-\text{MeEDT-TTF})_2]^{n+}$  (Fig. 1). In the oxidation state of the complex, the magnetic moment of  $\text{Cr}^{3+}$  ( $S = 3/2$ ) strongly interacts with those of the TTF ligands ( $S = 1/2$ ), while the latter can bring the strong inter-molecular exchange interaction through  $\pi$ -stackings.

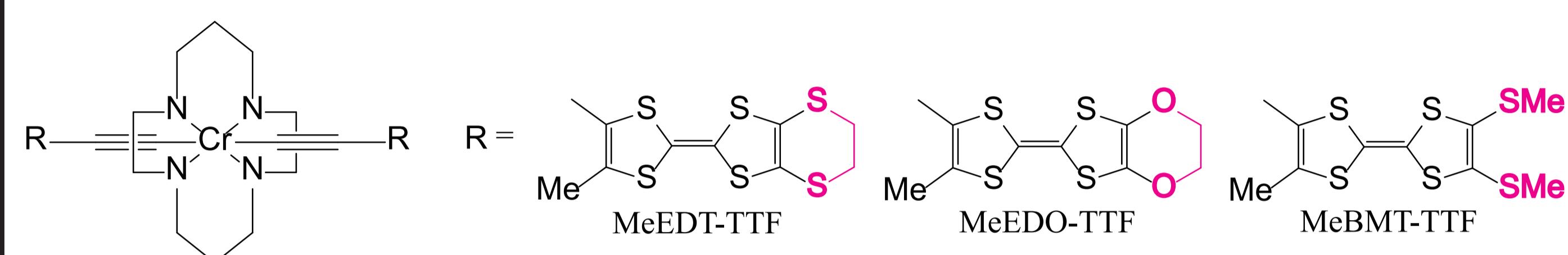
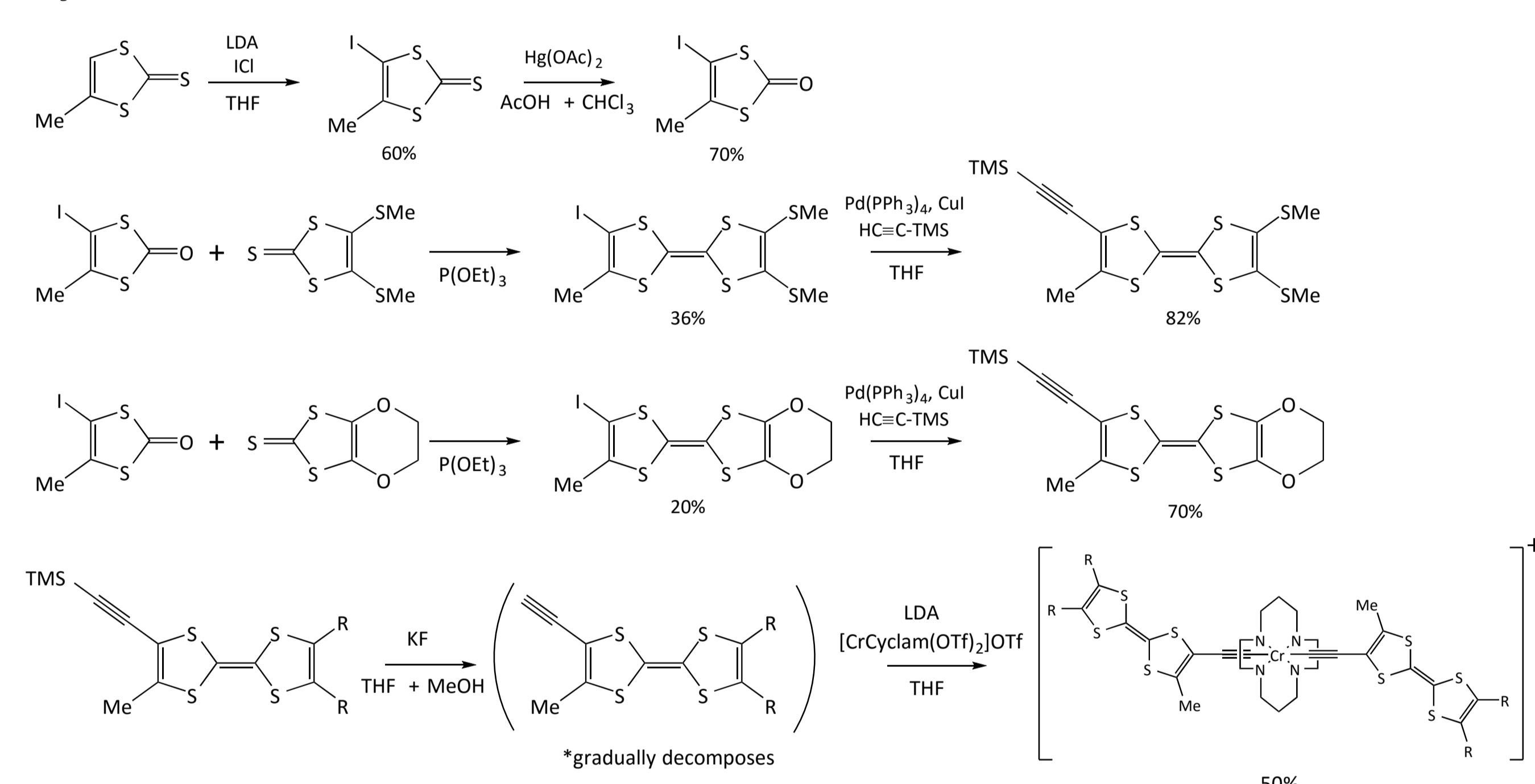


Figure 1. The molecular structures of Cr-acetylide-TTF type complexes.

Here, we report the synthesis of new Cr(III)-acetylide-TTF type complexes,  $[\text{CrCyclam}(\text{C}\equiv\text{C}-\text{MeEDO-TTF})_2]^{n+}$  and  $[\text{CrCyclam}(\text{C}\equiv\text{C}-\text{MeBMT-TTF})_2]^{n+}$ . The highly soluble functional groups of the complexes (ethylenedioxy and thiomethyl) make it easy to construct molecule-based magnetic materials. We also report the crystal structures and the magnetic properties of the crystals containing the complexes.

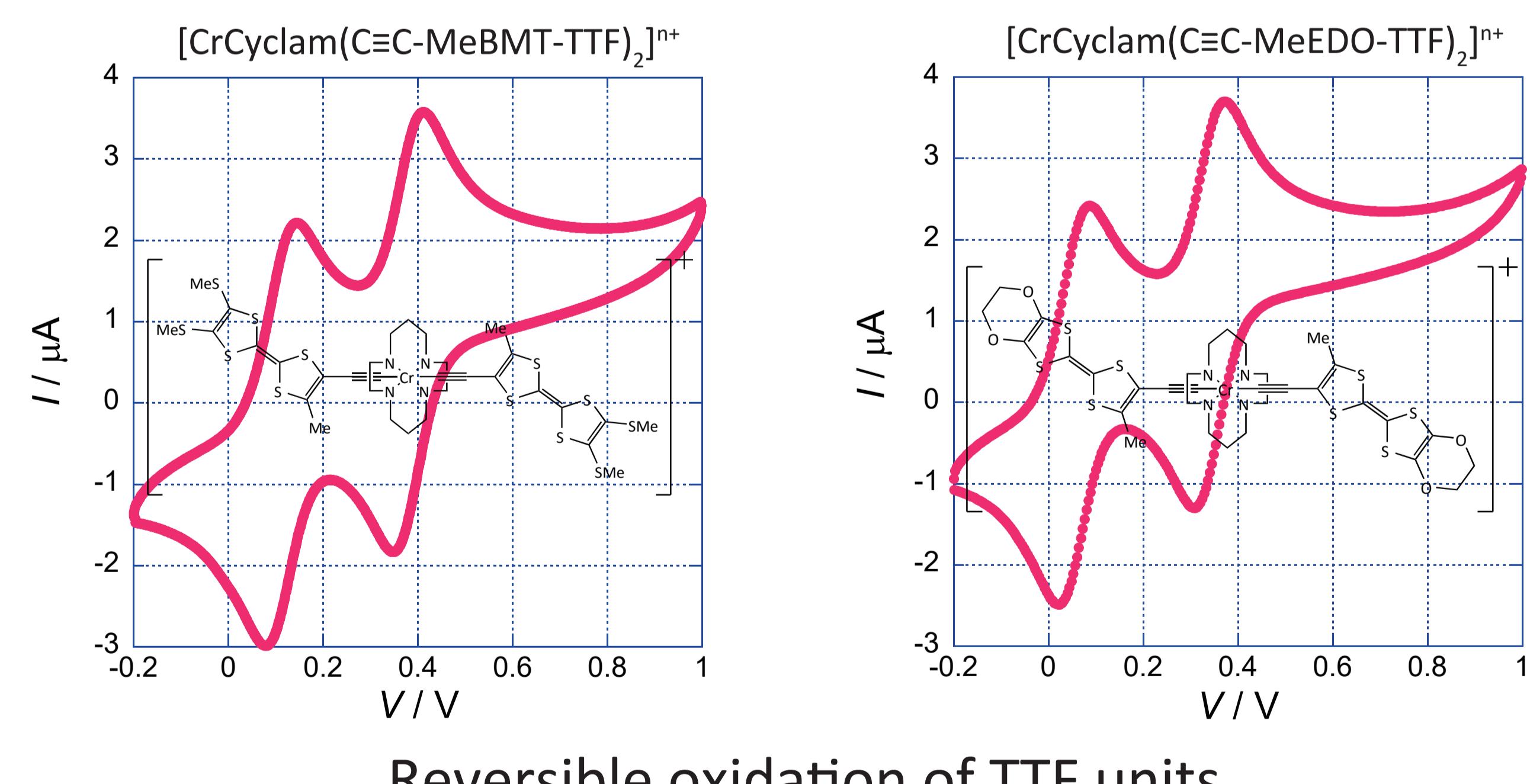
## 2. Synthesis and CV measurements

### Synthesis



### Cyclic Voltammetry

0.25 mM, 0.1 M  $(\text{Bu}_4\text{N})\text{ClO}_4$ , acetonitrile,  $\text{Ag}/\text{Ag}^+$ , 100 mV/s



Reversible oxidation of TTF units

## 4. Conclusion

Two new Cr-C≡C-TTF type complexes were synthesized.

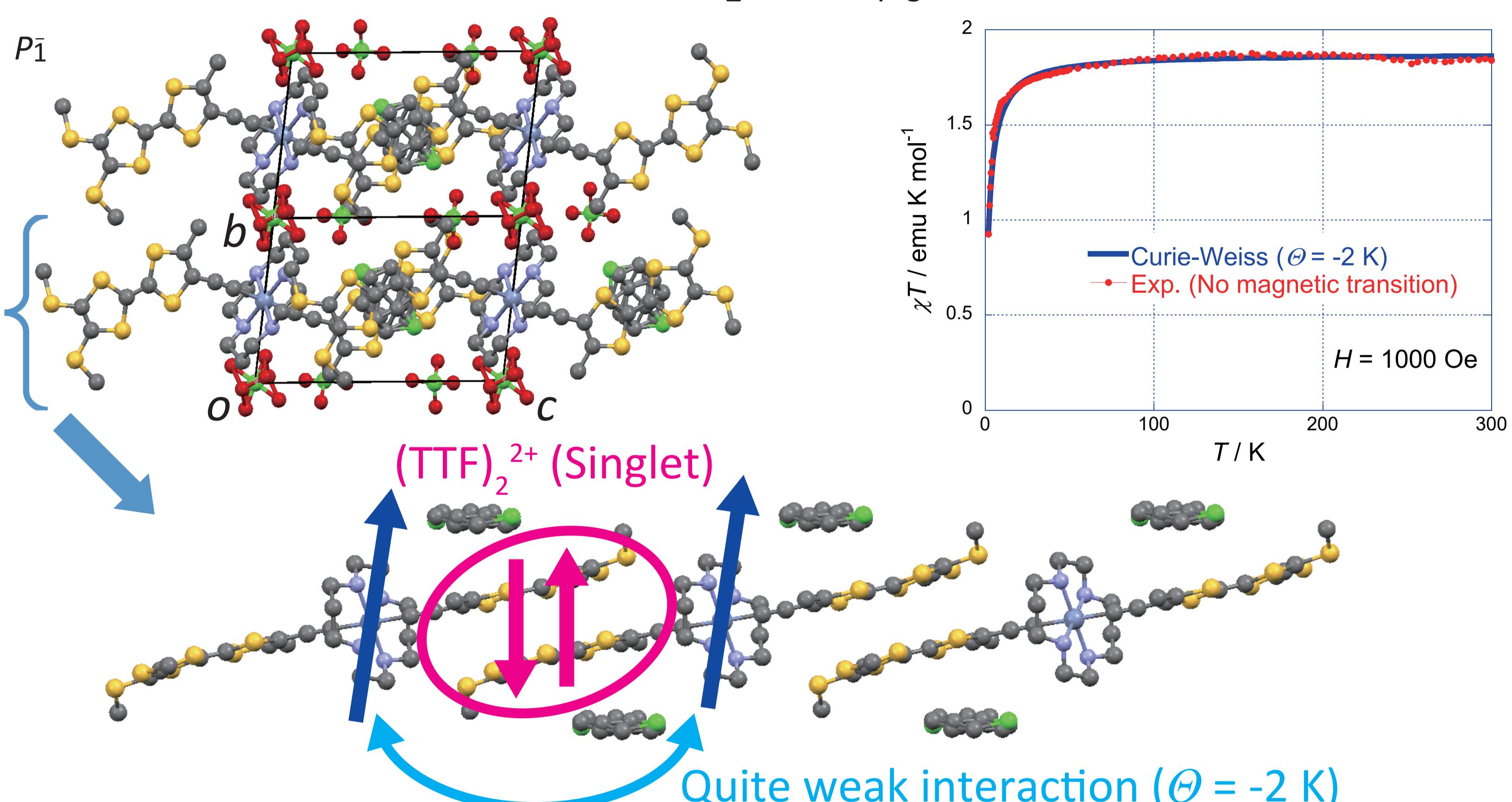
The  $[\text{CrCyclam}(\text{C}\equiv\text{C}-\text{MeEDO-TTF})_2]^{2+}$  salts are characterized by the ferrimagnetic chain of the complex with the strong intra-chain interaction of  $2J/k_B = -28$  ( $[\text{CrPhen}(\text{NCS})_4]^-$ ) and  $-24$  K ( $\text{ClO}_4^-$ ).

$[\text{CrCyclam}(\text{C}\equiv\text{C}-\text{MeEDO-TTF})_2](\text{ClO}_4)_2(\text{PhCl})_2(\text{H}_2\text{O})_2$  shows a weak ferromagnetic transition at 21 K.

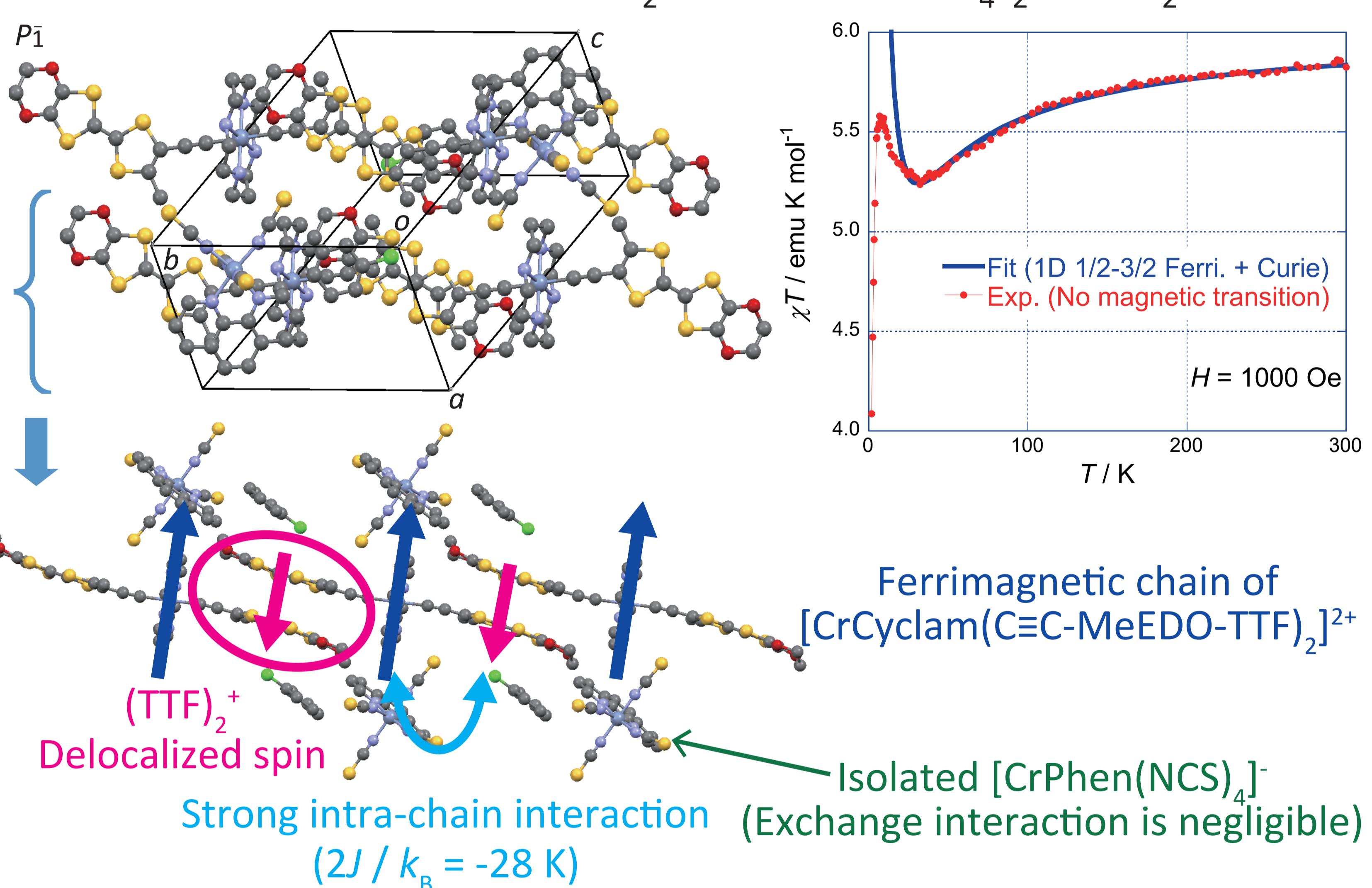
Cr-C≡C-TTF type complexes are promising for molecule-based magnetic materials owing to the strong intra- and inter-molecular interaction through the ethynyl group and the  $\pi$ -stacking of TTF-ligands, respectively.

## 3. Crystal structures and magnetic Properties

$[\text{CrCyclam}(\text{C}\equiv\text{C}-\text{MeBMT-TTF})_2](\text{ClO}_4)_3(\text{PhCl})$



$[\text{CrCyclam}(\text{C}\equiv\text{C}-\text{MeEDO-TTF})_2](\text{CrPhen}(\text{NCS})_4)_2(\text{PhCl})_2$



$[\text{CrCyclam}(\text{C}\equiv\text{C}-\text{MeEDO-TTF})_2](\text{ClO}_4)_2(\text{PhCl})_2(\text{H}_2\text{O})_2$

