Controlling Interchain Interaction in Weak-Ferromagnet [CrCyclam(C≡C-MeEDT-TTF)$_2$](Anion)$_2$(Solvent1)(Solvent2)$_2$

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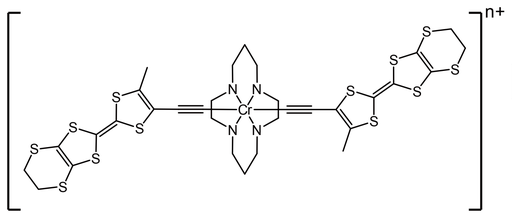
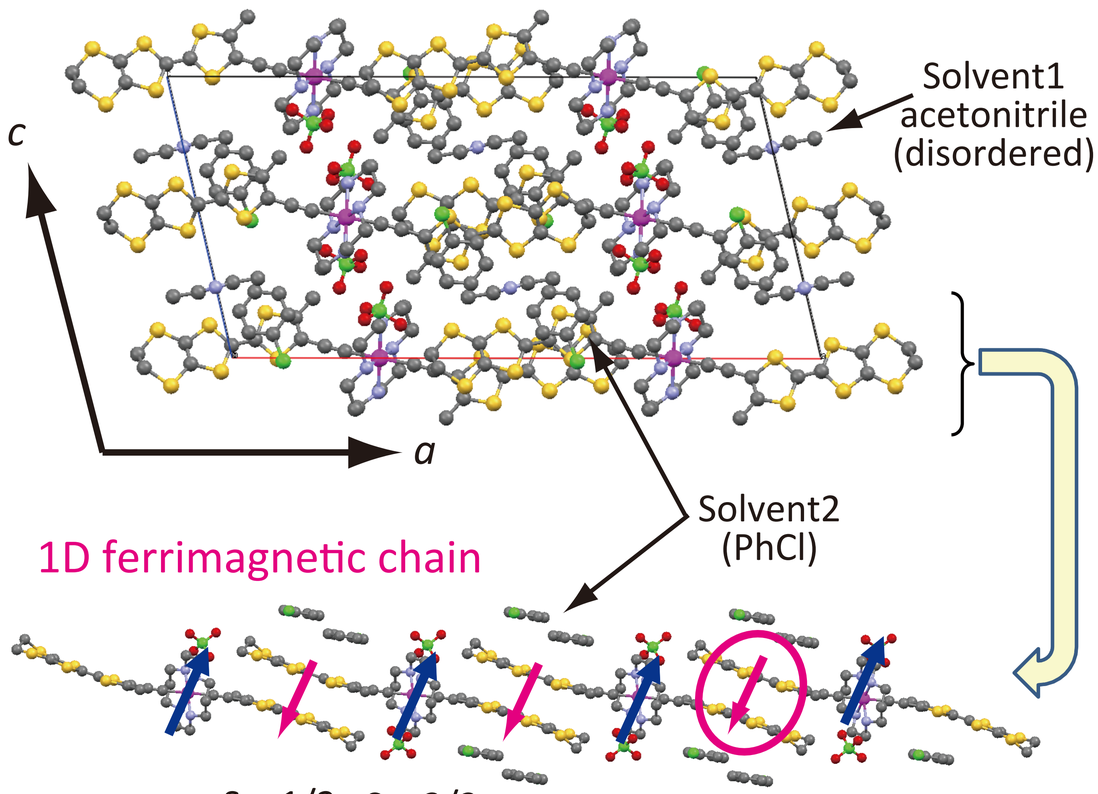
1. Introduction

Weak Ferromagnets [CrCyclam(C≡C-MeEDT-TTF)$_2$](Anion)$_2$(MeCN)(PhCl)$_2$
(Anion = $[BF_4]^-$, $[ClO_4]^-$) J. Nishijo et al., *Inorg. Chem.*, **50**, 3464-3470 (2011).



$[CrCyclam(C{\equiv}C\text{-}MeEDT\text{-}TTF)_2]^{n+}$
(denoted as $[\mathbf{1}]^{n+}$)



- Redox-active TTF-type ligand
- Inter-molecular charge and spin delocalization
- Strong intra-chain exchange interaction ($2J \sim -30$ K)
- High transition temperature ($T_N \sim 23$ K)

There are two unsolved questions:

·What is the origin of the weak ferromagnetism?

·The remanet magnetization of the $[ClO_4]^-$ salt is about twice that of the $[BF_4]^-$ salt. Why?

To answer these questions, 8 isostructural crystals were investigated, where inter-chain interaction was controlled by the solvent and anion substitution.

2. Experimental

Crystal preparation: electrochemical oxidation of $[\mathbf{1}]^+$

Solvent: acetonitrile + PhX (X = F, Cl, Br, I)

Anion: $[BF_4]^-$, $[ClO_4]^-$, $[ReO_4]^-$

Obtained crystal: [1][Anion]$_2$(Solvent1)(Solvent2)$_2$

For PhX = PhF and PhCl

Solvent1 = acetonitrile, Solvent2 = PhX

For PhX = PhBr and PhI

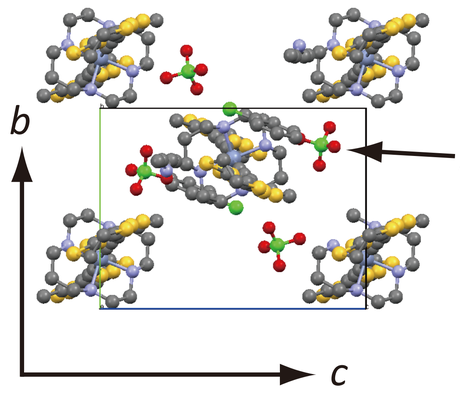
Solvent1 = Solvent2 = PhX

Obtained crystals and their inter-chain S-S distances

	PhF	PhCl	PhBr	PhI
$[BF_4]^-$	✓ 3.959 Å	✓ 3.827 Å	low quality	low quality
$[ClO_4]^-$	✓ 3.997 Å	✓ 3.854 Å	✓ 3.813 Å	✓ 3.803 Å
$[ReO_4]^-$	no crystal	✓ 3.911 Å	✓ 3.898 Å	low quality

3. Structural change and magnetism

Effect of the anion size

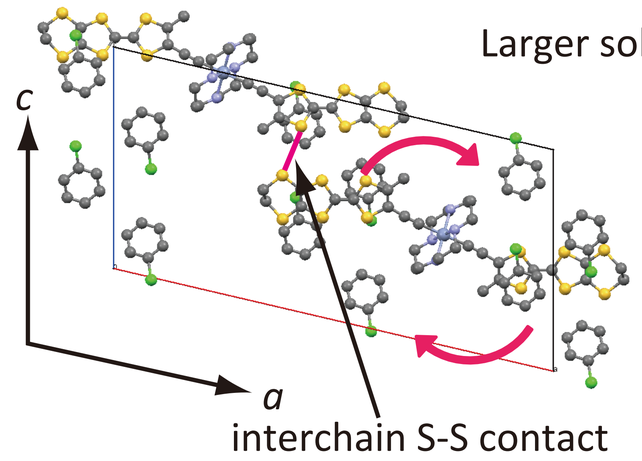


Anions are located between ferrimagnetic chains.

larger anion = longer inter-chain distance

(anion size: $[ReO_4]^- > [ClO_4]^- > [BF_4]^-$)

Effect of the solvent size

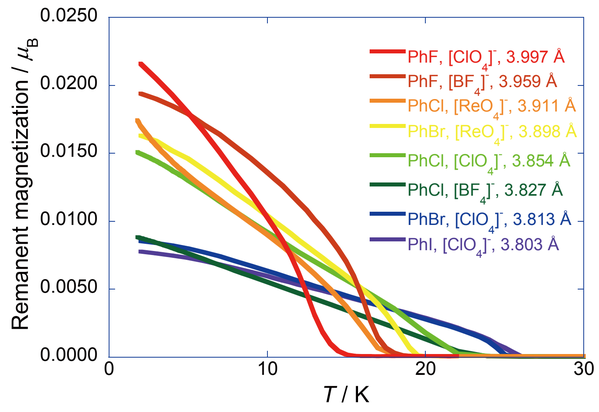


Larger solvent brings not only a longer *c*-axis, but also a small rotation of $[\mathbf{1}]^{2+}$.

As a result, larger solvent indicates shorter inter-chain distance.

(solvent size: PhI > PhBr > PhCl > PhF)

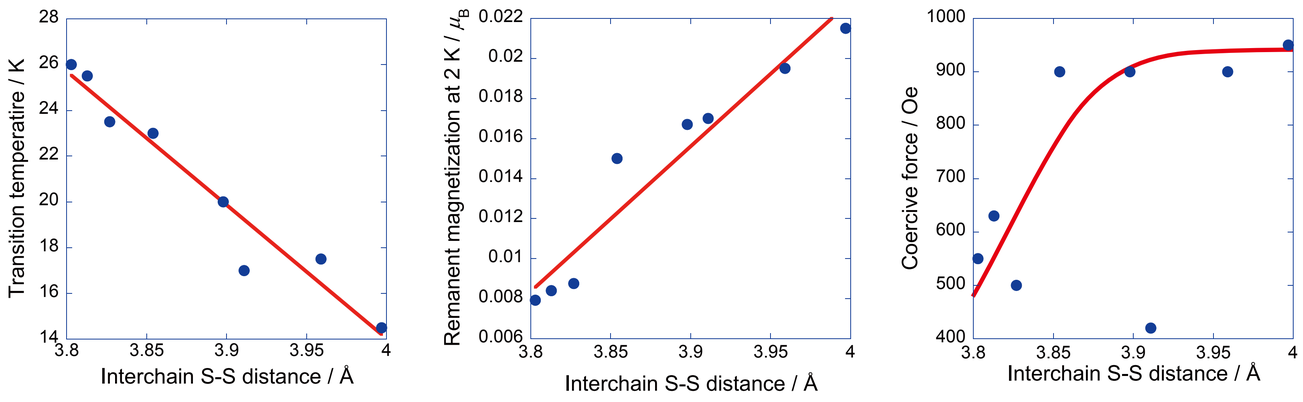
Magnetic properties



Longer interchain distance brings

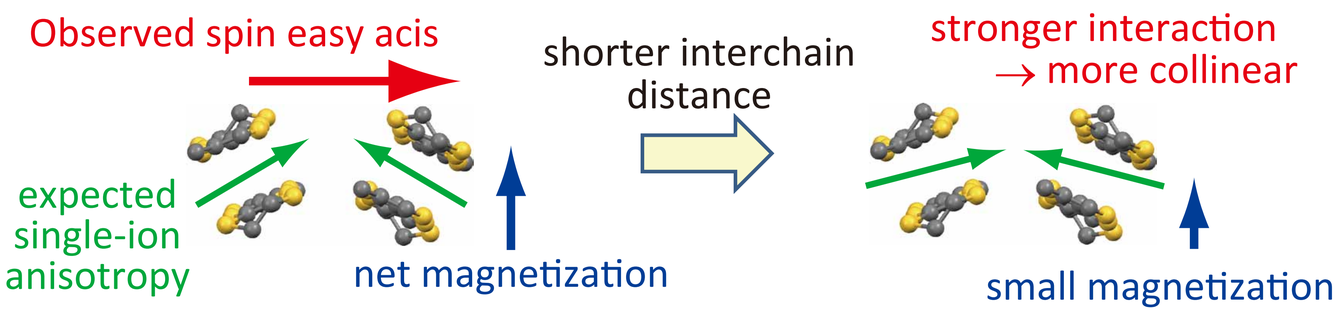
- higher transition temperature
- smaller remanent magnetization

The results indicate that interchain interaction diminishs the weak ferromagnetism.



Origin of the weak ferromagnetism

The results can be explained by assuming that the weak ferromagnetism is originated from a single ion anisotropy.



4. Conclusion

Controlling the Interchain exchange interaction of weak ferromagnet $[\mathbf{1}](Anion)_2(Solvent1)(Solvent2)_2$ was achieved.

The transition temperature increases as the inter-chain interaction increases, while the remanent magnetization decreases remarkably.

The results indicate that the origin of the weak ferromagnetism is single-ion anisotropy of $[1]^{2+}$.