

Redox-activity control in a conducting single-molecule magnet compound

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1 Introduction

Single-molecule magnets (SMMs) are molecular compounds with a significant energy barrier for the spin reversal behaviour at the molecular level and can be used for information storage, spin-valves or quantum computing, etc. Since the discovery of SMM, researchers have perceived several potential applications, which have become key research topics in the area of molecular quantum spintronics. Combining SIM behavior and electrical conductivity may bring about the giant-magnetoresistance and be advantageous for the next generation of high-density information storage media. Hybrids of SMM and electrical conductors with layered structures have been reported, synergy between magnetic lattice and conducting lattice is still challenging for materials chemists. Herein, we introduce a strategy to incorporate strong interactions between π -conjugated redox-active SIM and conducting sublattice with the use of TTF molecule to afford the conductive SIM (TTF)₂[Co(pdms)₂] (**2-Co**) and the isostructural (TTF)₂[Zn(pdms)₂] (**2-Zn**). Introduction of redox-activity on ligand is the first time to prepare conducting SIM material. The H₂pdms ligand is a σ and π electron donor with quite similar redox activity to TTF upon formation of metal complex, causing the frontier orbitals of the ligand and TTF to overlap, yielding electrical conductivity down to 2 K. Moreover, the tetrahedrally coordination geometry of [M(pdms)₂], combined with TTF, leads to an unusual 3D mixed stacking framework compared to those reported 2D layered conductive SMM compounds.

2 Experiment

H₂pdms, CoCl₂, ZnCl₂, TTF and organic solvents were commercially purchased and used without further purification. The precursors (HNEt₃)₂[Co(pdms)₂] (**1-Co**) and (HNEt₃)₂[Zn(pdms)₂] (**1-Zn**) were synthesised following a reported procedure.

Preparation of (TTF)₂[M(pdms)₂]: A solution of 20 mg TTF and 80 mg of **1-Co** (or **1-Zn**) in 15 mL of dry acetonitrile was filtered, and the resulting clear solution was placed in an electrocrystallization cell under a N₂ gas atmosphere. A 0.5 μ A dc current was then applied. Small black needle-shaped crystals of size typically 50 μ m \times 5 μ m \times 5 μ m grew on the anode over 10 days, and then they were collected, washed with a small amount of ethanol and dried in air. Yield: 20 mg (36% based on TTF).

3 Results and Discussion

The TTF^{•+} and Co(pdms)₂ units electrocrystallized in the C2/c space group with one TTF^{•+} and 0.5 Co(pdms)₂ molecules per asymmetric unit. The Co ion is coordinated to two pdms ligands through the N atoms in a tetrahedral geometry. Each TTF dimer is surrounded by six Co(pdms)₂ molecules (behaves as SMM) and interacts with them through several short contacts and weak hydrogen bonds, forming a zig-zag structure along the [101] direction with the Co(pdms)₂ molecules at the corner and the TTF^{•+} dimer as segment (Figure 1a). The zig-zag chains interact with each other in the (10 $\bar{1}$) plane through hydrogen bonds and O2 \cdots S3 (2.953 Å) and O2 \cdots C9 (2.887 Å) short contacts to form a 2D sheet. Finally, the sheets interact with each other through various O \cdots S, S \cdots C and O \cdots C short contacts to give a fully interacting 3D structure (Figure 1b). Figure 1c shows the theoretical calculation of charge transfer between Co(pdms)₂ and TTF dimer. 0.73e⁻ electrons was transferred from pdms ligand to (TTF)²⁺, meanwhile, 0.76e⁻ transferred from pdms ligand to Co ion, affording a total mix-valence state.^[1]

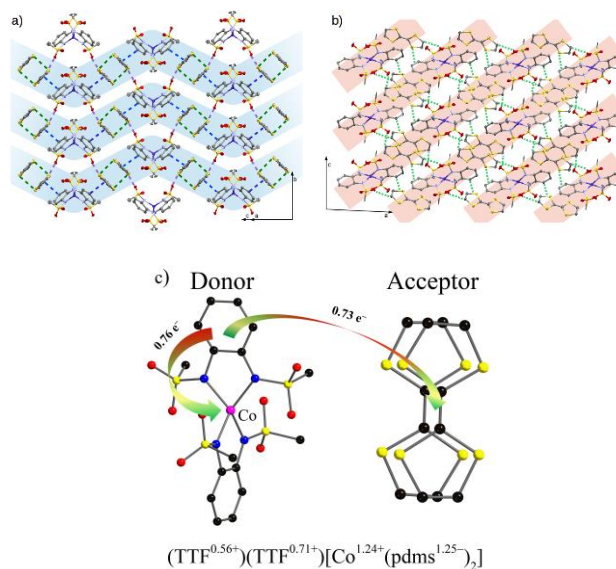


Figure 1. a) crystal packing in ab plane b) crystal packing in ac plane. c) charge transfer between Co(pdms)₂ and TTF dimer.

References

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