

Structural Investigation on H/D Isotope Effect in a Hydrogen-bonded Purely Organic Conductor

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1 Introduction

Hydrogen bonds (H-bonds) are one of the most fundamental and important non-covalent interactions in materials, and thus have attracted much attention in a wide range of scientific fields. Notably, H-bonded protons (or hydrogen atoms) can be thermally transferred or displaced within the H-bond. This unique dynamic behavior is known to play crucial roles in (bio)chemical reactions/processes and some kinds of functional solids/materials, such as dielectrics and proton conductors.

Recently, our group has explored H-bonded organic conductors, whose H-bond dynamics and conductive π -electrons are cooperatively coupled in the crystal. Among them, κ -H₃(Cat-EDT-TTF)₂ (κ -H) is a new class of H-bonded conductors whose conducting layers are connected by strong H-bonds (Fig. 1) [1], which anticipates the emergence of interplay between the π -electrons and H-bond dynamics and the resulting novel electronic properties and functionalities [2]. Therefore, in this work, we have prepared the deuterated analogue of κ -H, κ -D₃(Cat-EDT-TTF)₂ (κ -D), and investigated its structure and properties, to gain insight into how the difference in the H-bond dynamics by the H/D substitution affects the electronic structure of this unique molecular system [3].

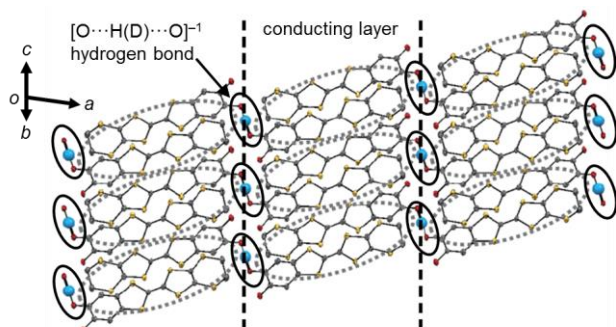


Fig. 1: Crystal structures of κ -X₃(Cat-EDT-TTF)₂ (κ -H: X = H, κ -D: X = D) at room temperature.

2 Results and Discussion

The synchrotron X-ray structural analysis at BL-8A, KEK-PF reveals that κ -D is isostructural to the parent

hydrogen crystal κ -H at room temperature. Namely, the H-bonded molecular unit, shown in the top left of Fig. 2, is assembled (Fig. 1), to form the two-dimensional conducting layer (Fig. 2, bottom left), in which the π -dimers with $S = 1/2$ spins are arranged two dimensionally. On the other hand, their low-temperature structures are fundamentally different from each other: Although κ -H maintains the room temperature structure, κ -D undergoes a phase transition at 185 K, originating from deuterium transfer or displacement within the H-bond accompanied by electron transfer between the Cat-EDT-TTF π -systems (Fig. 2, top). As a result, significant charge disproportionation occurs within the H-bonded unit, which leads to the transformation from the dimer-Mott state at high temperatures to a charge-ordered state with spin-singlet pairs (Fig. 2, bottom). Reflecting this electronic structure change, the physical properties of κ -D are drastically switched (paramagnetic semiconductor \leftrightarrow nonmagnetic insulator). Therefore, we have concluded that the present system is a truly new type of molecular conductors, whose electronic structures and physical properties are coupled to the structural degree of freedom of hydrogen (deuterium) in H-bonds [3].

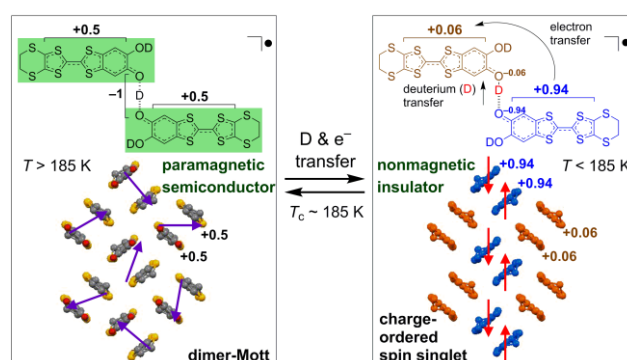


Fig. 2: Schematic drawing of the phase transition of κ -D.

References

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