

## Hydrogen Bonds can Switch Electrical Conductivity and Magnetism

Hydrogen-bonds (H-bonds) are one of the most fundamental and important non-covalent interactions in materials, thus attracting 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 plays a crucial role in the (bio)chemical reactions/processes and certain kinds of functional solids/materials. Herein, a new kind of H-bond-dynamics-based phase transition in a purely organic conductor crystal is described. Interestingly, an interplay between the H-bond dynamics and organic  $\pi$ -electrons plays an essential role in this dynamic behavior with switching of physical properties.

Hydrogen bonds (H-bonds) are one of the most fundamental and important non-covalent interactions in materials, and as such have attracted significant 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 plays crucial roles in the (bio)chemical reactions/processes and some kinds of functional solids/materials, such as dielectrics and proton conductors. For example, in an H-bonded material, such a displacement varies the polarity not only of the H-bond part, but also the whole material, resulting in switching of the dielectric properties (i.e., the paraelectric-to-(anti)ferroelectric transition). The control and switching of such physical properties and functions utilizing H-bond dynamics is of great interest not just in the basic science but also from the perspective of the applied science and its practical applications. However, successful examples of such switching based on H-bonding are limited.

In 2014, we discovered unprecedented H-bond-dynamics-based switching of electrical conductivity and magnetism [1]. The material they focused on in this study is a purely organic conductor crystal,  $\kappa$ -H<sub>3</sub>(Cat-EDT-TTF)<sub>2</sub> (abbreviated as  $\kappa$ -H), synthesized by the same research group in 2013 [2]. The  $\kappa$ -H conductor has a peculiar crystal structure, in which the conducting layers are connected by [O...H...O]<sup>-1</sup> H-bonds (Fig. 1), suggesting the emergence of coupling between

the  $\pi$ -electrons and H-bond dynamics that results in novel electronic properties and functionalities. In this study, the research group performed deuteration of the H-bonds of  $\kappa$ -H, to modulate the H-bond dynamics. As a result, a unique phase transition triggered by deuterium transfer accompanied by electron transfer occurred, leading to the switching of electrical conductivity and magnetism.

The present deuterated analogue,  $\kappa$ -D<sub>3</sub>(Cat-EDT-TTF)<sub>2</sub> (abbreviated as  $\kappa$ -D), at room temperature is isostructural to the parent hydrogen crystal  $\kappa$ -H. The H-bonded molecular unit, shown in the top left of Fig. 2, is assembled [Fig. 1(a)] to form the two-dimensional conducting layer [Fig. 1(b)], in which the  $\pi$ -dimers with  $S = 1/2$  spins are arranged in a triangular pattern. The temperature dependence of electrical resistivity  $\rho$  of  $\kappa$ -D exhibited semiconducting behavior similar to  $\kappa$ -H, cooling down to 185 K, and then rapidly increasing [blue circles in Fig. 3(a)]. Such an anomaly was also observed in the magnetic susceptibility  $\chi_p$  of  $\kappa$ -D: After recording paramagnetic behavior similar to that of  $\kappa$ -H,  $\chi_p$  of  $\kappa$ -D abruptly dropped at 185 K, to approach  $\chi_p \sim 0.0$  emu mol<sup>-1</sup> with decreasing temperature. This result suggests that spin-singlet pairs were formed upon the phase transition, which leads to a singlet ground state. This is in contrast to the fact that the hydrogen compound  $\kappa$ -H assumes a quantum spin liquid ground state [3].

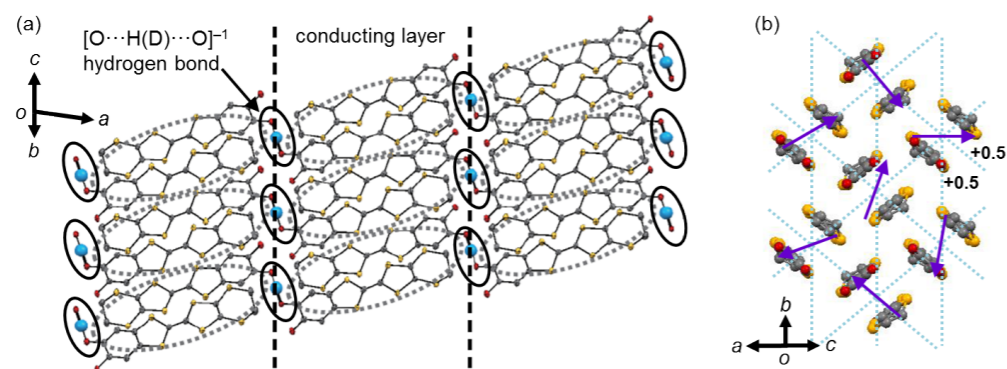


Figure 1: Crystal structures of  $\kappa$ -X<sub>3</sub>(Cat-EDT-TTF)<sub>2</sub> ( $\kappa$ -H: X = H,  $\kappa$ -D: X = D) at room temperature. (a) H-bonding manner and (b) molecular arrangement in the conducting layer shown in (a). Purple arrows represent  $S = 1/2$  spins.

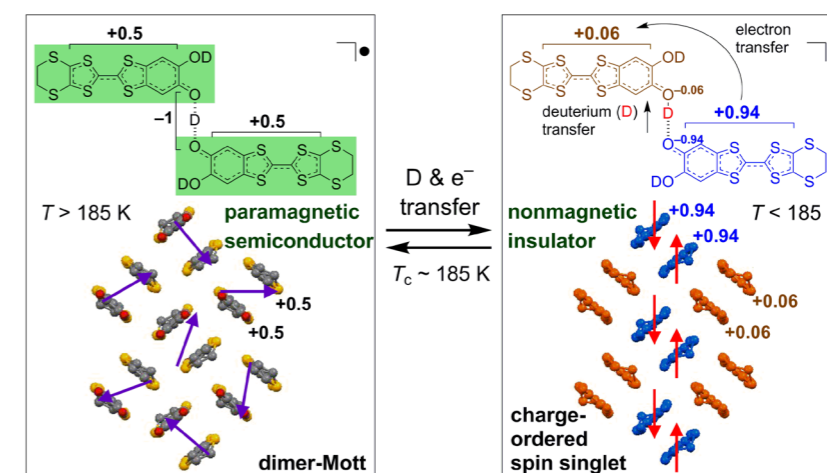


Figure 2: Schematic drawing of the phase transition of  $\kappa$ -D (top: H-bonded molecular unit, bottom: conducting layer). The chemical structures shown in green (top left) represent the Cat-EDT-TTF molecule. The black circles in top right of the top panels represent the fact that the H-bonded molecular unit has an unpaired electron.

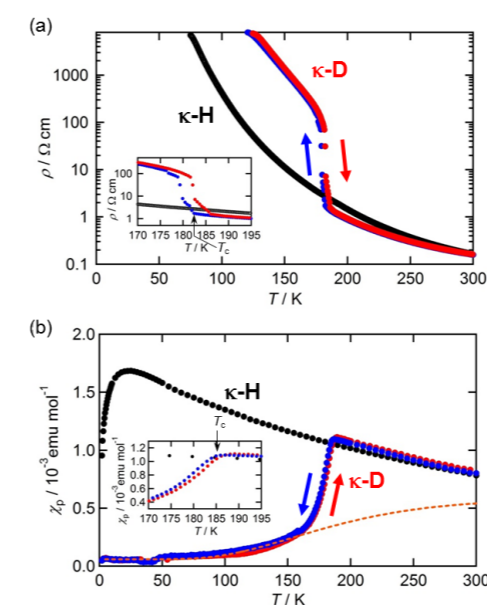


Figure 3: Temperature dependence of (a) electrical resistivity and (b) magnetic susceptibility of  $\kappa$ -D (the blue and red circles represent the cooling and heating processes, respectively) and  $\kappa$ -H (black circles).

Then, to reveal the origin of this phase transition, the temperature dependence of the X-ray crystal structure was examined by using synchrotron radiation at KEK-PF. As a result, it turned out that, below 185 K, the H-bonded deuterium is displaced from the center to one side between the two oxygen atoms, which induced an electron transfer between the Cat-EDT-TTF  $\pi$ -skeletons, to give a charge-disproportionated state composed of the +0.06 and +0.94 species (Fig. 2 top). Consequently, the high-temperature dimer-Mott state was transformed into a charge-ordered spin-singlet state, to give rise to the switching from the paramagnetic semiconductor to the nonmagnetic insulator (Fig. 2 bottom). Generally, charge ordering in molecular conductors is caused by

the intermolecular Coulomb interactions. On the other hand, the present charge ordering is triggered by the H-bonded deuterium transfer. Specifically, the present system consists of 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. In addition, it is also of interest that only  $\kappa$ -D exhibited the transition; this is qualitatively interpreted as a result of the combination of the geometrical and quantum isotope effects.

In summary, this study has demonstrated that the H-bond dynamics can switch electrical conductivity and magnetism in the crystal [1]. This switching or phase transition is an extremely rare event not only in the organic materials but also in the inorganic ones; thus, the further investigation of the mechanism and H/D isotope effect and application to organic electronic materials/devices with switching functionality is of great interest.

## REFERENCES

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## BEAMLINE

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