

Structural Study of a Purely Organic Single-Component Metal with Symmetric Hydrogen Bond

Purely organic materials are generally insulating. Here, we report a new type of purely organic single-component molecular conductor that utilizes strong hydrogen-bonding interactions between tetrathiafulvalene-based electron-donor molecules. We found that these conductors are composed of highly symmetric molecular units constructed by strong intra-unit hydrogen bonding, and that charge carriers are produced by the partial oxidation of the donor molecules and delocalized through the formation of symmetric intra-unit hydrogen bonds. To the best of our knowledge, our conductors show the highest room-temperature electrical conductivity and the metallic state under the lowest physical pressure among purely organic single-component systems.

The realization of purely organic single-component molecular metals has been a long-standing open problem in chemistry, physics, and materials science. As is well known, purely organic materials are normally insulating. Recently, we unveiled a new type of purely organic single-component molecular conductor based on a catechol-fused ethylenedithiotetrathiafulvalene, H₂Cat-EDT-TTF, and its diseleno analogue, H₂Cat-EDT-ST, which were designed and synthesized by us [1]. These conductors are unprecedented single-component systems composed of molecular units, H₃(Cat-EDT-TTF)₂ and H₃(Cat-EDT-ST)₂, with a highly symmetric intra-unit hydrogen bond. The higher electrical conductivity observed in our systems is attributed to the hydrogen bond-promoted delocalization of charge carriers, which are generated through the partial oxidation of the H₂Cat-EDT-TTF and H₂Cat-EDT-ST molecules [2].

A new type of purely organic single-component molecular conductors, κ-H₃(Cat-EDT-TTF)₂ and κ-H₃(Cat-EDTST)₂, hereinafter described as κ-S and κ-Se, respectively, were obtained as black plate-like crystals

by electrochemical oxidation of the corresponding donor molecules, H₂Cat-EDT-TTF and H₂Cat-EDT-ST, in the presence of the base, 2,2'-bipyridine. Crystal structure analysis was carried out at PF BL-8A. The minimal molecular unit, the H₃(Cat-EDT-TTF)₂ composition (Fig. 1), is established by the formation of an intra-unit hydrogen bond, O..H..O, between the catechol moieties of the donor molecules, where the one hydroxyl proton is deprotonated. The oxygen–oxygen distance in the hydrogen bond, d(O..O), is 2.486(5) Å and 2.509(8) Å at room temperature, and 2.453(5) Å and 2.443(8) Å at 50 K and 30 K for κ-S and κ-Se, respectively, which are much shorter than the length of the normal O–H..O type hydrogen bond, d(O..O) 2.7–3.0 Å. Because of this strong hydrogen bonding nature, the bonded hydrogen atom is located at nearly the center between two oxygen atoms, in contrast to the asymmetric hydrogen distribution in normal hydrogen bonds. The minimal molecular units are assembled into the purely organic single-component crystal.

The electrical conductivity at room temperature is significantly high, 3.5 and 19 S cm⁻¹ for κ-S and κ-Se, respectively. To the best of our knowledge, these values are one or two orders of magnitude higher than the highest reported value, σ_π = 10⁻¹ S cm⁻¹, among purely organic single-component systems. We observed dramatic changes in the temperature variation in the electrical resistivity under pressure for κ-Se. At pressures above 1.3 GPa, the electrical resistivity monotonically decreases with reducing temperature down to around 150 K, in striking contrast with the semiconducting behavior at ambient pressure, although the resistive curve starts to increase at low temperature. Thus, the metallic states emerge with suppression of the semiconducting energy gap by applying a pressure of only ~1 GPa. We believe this is the lowest metallization pressure among purely organic single-component systems.

Our system demonstrates that the symmetric hydrogen bond constructs a new type of purely organic single-component molecular conductor composed of highly symmetric molecular units. Moreover, we found that the formation of the symmetric hydrogen bond promoted the intermolecular delocalization of the generated carriers, associated with the enhancement of the electrical

conductivity. We believe that our new type of molecular conductors with symmetric intra-unit hydrogen bond will lead to the first purely organic single-component molecular metal at ambient pressure. A tetraselenafulvalene (TSF)-type analogue, in which all the sulfur atoms in the TTF part of the present system are replaced with selenium atoms, is a promising candidate for the ambient-pressure metal, because the intermolecular interactions are expected to be further enhanced.

REFERENCES

- [1] H. Kamo, A. Ueda, T. Isono, K. Takahashi and H. Mori, *Tetrahedron Lett.*, **53**, 4385 (2012).
- [2] T. Isono, H. Kamo, A. Ueda, K. Takahashi, A. Nakao, R. Kumai, H. Nakao, K. Kobayashi, Y. Murakami and H. Mori, *Nature Commun.*, **4**, 1344 (2013).

BEAMLINE

BL-8A

H. Mori¹, T. Isono¹, A. Ueda¹, K. Takahashi², A. Nakao³, R. Kumai⁴, H. Nakao⁴, K. Kobayashi⁴ and Y. Murakami⁴ (¹The Univ. of Tokyo, ²Kobe Univ., ³CROSS, ⁴KEK-PF/CMRC)

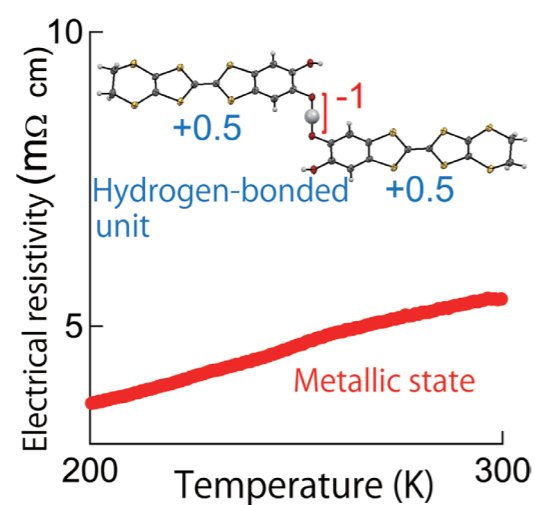


Figure 1: Structure of the molecular unit and the metallic state under ~1 GPa in the purely organic single-component conductor, κ-H₃(Cat-EDT-ST)₂. The hydrogen bonding unit is open-shell and neutral since the oxidized TTF parts are +0.5 and the [O..H..O] hydrogen bonding part is -1.