

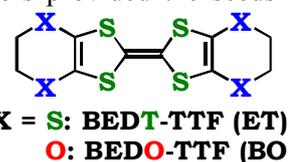
Development and Analysis of Functional Conducting Organic Materials

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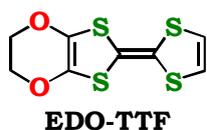


Born in 1957. He graduated from the Department of Chemistry, Faculty of Science, Kobe University in 1979 and received his Doctor of Science from Osaka University in 1984. From 1984 to 1990, he was a research associate in the Institute for Solid State Physics of the University of Tokyo. During this period, he worked as a post-doctoral fellow in University of California, Santa Barbara, U.S.A. for one year from 1988. He was a research associate (1990 - 1995) and an associate professor (1995 - 2004) in the Department of Chemistry, Faculty of Science, a professor (2004-2016) in Research Center for Low Temperature and Materials Sciences, and then a professor in the Division of Chemistry, Graduate School of Science, Kyoto University.

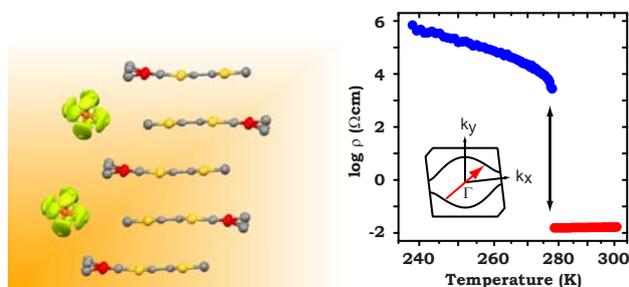
We design, synthesize, and analyze the condensed matters based on low molecular weight organic molecules aiming to derive the designing principles for further functional materials. Relatively small-sized π -conjugated systems are examined to provide molecular (super)conductors and related materials. The relationship between structure and physical properties are studied. The initial stage of our studies on BEDT-TTF (ET) and BEDO-TTF (BO) (super)conductors provided the seeds of recent investigations. In these days, we are focusing on the conducting charge-transfer (CT) complexes showing the multi-instability. The responses to the external stimuli e.g. light irradiation are also concerned along with the conventionally examined transport, magnetic, optical properties, etc.



(1) Metallic CT Complex having Multi-instabilities, (EDO-TTF)₂PF₆: Since the metallic state of BO complexes were too stable, the phase transition was observed only in a few numbers of complexes. Aiming to suppress the self-assembling nature partially, one of the ethylenedioxy groups was removed. As a result, the complete vanishing of the nature was observed for EDO-TTF. Among the complexes examined, (EDO-TTF)₂PF₆ exhibited the metal-insulator (MI)



transition at ca. 280 K with the some orders of resistivity jump as shown in Fig. 1. Although all the EDO-TTF molecules were almost planar at room temperature, half numbers of donor molecules showed distinct deformation in the low temperature phase in which bent (B) and flat (F) molecules were arranged in the order of [BBFF] (See, Fig. 2). The transition mechanism was attributed to the cooperation of Peierls transition, order-disorder (OD) transition of the counter anion and charge-ordering (CO) transition. Corresponding with the [BBFF] arrangement, the CO pattern was assigned to [0011]. The peculiarity of this complex was also demonstrated by the photo-induced phase transition (PIPT). The low temperature phase showed an ultra-fast and highly efficient metallization when irradiated by 120 fs laser pulse, the energy of which corresponded to the CT transition of $D^+D^+ \rightarrow D^{2+}D^0$. The time development of reflection spectra showed the coherent peaks and proved that one photon caused the transition of 50 - 500 donor molecules within ca. 0.1 ps followed by the relaxation to the metastable state within ca. 1.5 ps. The photo-conductivity spectra demonstrated the high conductivity of the resultant metastable state. (EDO-TTF)₂PF₆ is interested not only in the application but also in the



(Fig. 1) Crystal structure at room temperature (left) and temperature dependence of resistivity (right) of (EDO-TTF)₂PF₆. The inset for the right panel shows the calculated Fermi surface with the expected nesting vector (red arrow).

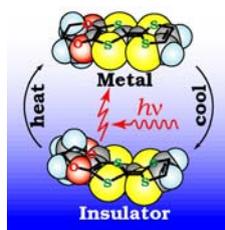
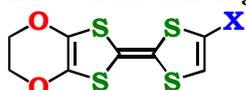


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non-equilibrium condensed matter physics which studies how the local phase transition develops into whole of the bulk. For example, the combination of time resolved reflectivity measurement and theoretical calculation revealed the CO pattern at 0.1 ps after the photo irradiation to be [0101] type with the lattice fluctuation.

(2) EDO-TTF Analogues and Selective Suppression of Multi-instability:

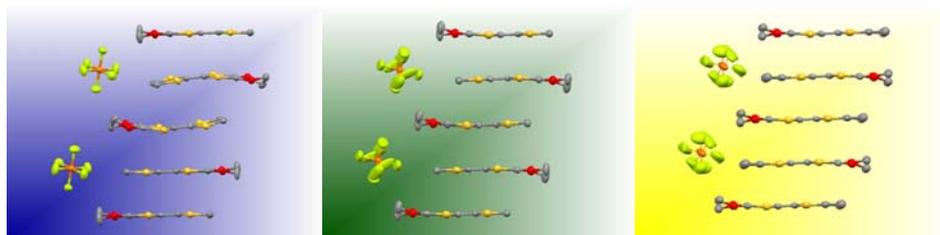
To understand the multi-instability of $(\text{EDO-TTF})_2\text{PF}_6$ and to obtain further multi-instability systems, deuterated EDO-TTF and EDO-TTF analogues (MeEDO-TTF, MeSEDO-TTF and CLEDO-TTF) are being studied. Along with the complexes of each donor molecule, the alloy of $[(\text{EDO-TTF})_{1-x}(\text{MeEDO-TTF})_x]_2\text{PF}_6$ was prepared despite the crystal structures of pristine complexes are different to each other. In the range of $x \leq 0.55$ and $x \geq 0.91$, the alloys were isostructural to the complexes of $x = 0.0$ and $x = 1.0$, respectively. The alloy of $x = 0.05$ exhibited MI transition at 242 K due to the same multi-instability to that of $x = 0$, while that of $x = 0.42$ showed no clear phase transition. In case of $x = 0.13$ alloy, CO was not observed while the MI transition was observed at 193 K. This means that the alloying selectively elimination a component of multi-instability.



X = CH₃: MeEDO-TTF

SCH₃: MeSEDO-TTF

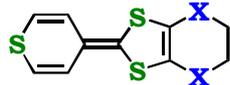
Cl: CLEDO-TTF



(Fig. 2) Crystal structures of $[(\text{EDO-TTF})_{1-x}(\text{MeEDO-TTF})_x]_2\text{PF}_6$ with $x = 0.05$ (left), 0.13 (middle) and 0.48 (right) at 150 K. Note that the molecular deformation and anion ordering observed for $x = 0.05$ are same to those for $x = 0$ (pristine EDO-TTF complex).

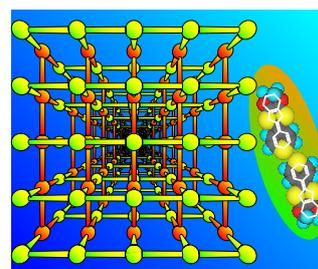
(3) π -conjugated System having Terminal Heteroatom (TP-EDXT):

TTF derivatives show the intermolecular interactions perpendicular to the molecular plane and along molecular lateral directions in general. To expand the directionality of the intermolecular interactions, TP-EDXT was examined in which a sulfur atom was located at the terminal of the molecule. Among the complexes obtained, a head-to-head type donor dimer was formed by using the terminal sulfur atoms in $(\text{TP-EDOT})_2\text{PF}_6$, which was a Mott insulator with a localized spin accommodated in the donor dimer. The temperature variation of magnetic susceptibility was reproduced by a two dimensional model (QLAF), while the localized spins were arranged three-dimensionally. The novel spin structure was interpreted by the anisotropy of inter-dimer interactions (Fig. 3). In case of the sulfur analogue, the coexistence of three kinds of differently charged donor molecules is suggested for $(\text{TP-EDTT})_3(\text{PF}_6)_2$.



X = O: TP-EDOT

S: TP-EDTT



(Fig. 3) Schematic representation of the donor dimer in $(\text{TP-EDOT})_2\text{PF}_6$ (right) and the arrangement in this complex (left). The intersection in left panel corresponds to a donor dimer and the beams between them indicate the significant interdimer interaction paths.

Publications (Complete list is available at http://mms.ltm.kyoto-u.ac.jp/yamochi/list_pub.pdf)

1. Synthesis and Charge-transfer Complexes of a New Donor Molecule, TP-EDOT, H. Yamochi, J.

- Hagiwara, M. Soeda, G. Saito, *J. Mater. Chem.*, **16**(6), 550-557 (2006)
2. Ink-jet Printing of Organic Metal Electrodes using Charge-transfer Compounds, M. Hiraoka, T. Hasegawa, Y. Abe, T. Yamada, Y. Tokura, H. Yamochi, G. Saito, T. Akutagawa, T. Nakamura, *Appl. Phys. Lett.*, **89**(17), 173504/1-3 (2006)
 3. Formation of Two-dimensional Metals by Weak Intermolecular Interactions Based on the Asymmetric EDO-TTF Derivatives, X.F. Shao, Y. Nakano, H. Yamochi, A.D. Dubrovskiy, A. Otsuka, T. Murata, Y. Yoshida, G. Saito, S. Koshihara, *J. Mater. Chem.*, **18**(18), 2131-2140 (2008)
 4. Photoinduced Change in the Charge Order Pattern in the Quarter-filled Organic Conductor (EDO-TTF)₂PF₆ with Strong Electron-Phonon Interaction, K. Onda, S. Ogihara, K. Yonemitsu, N. Maeshima, T. Ishikawa, Y. Okimoto, X.F. Shao, Y. Nakano, H. Yamochi, G. Saito, S. Koshihara, *Phys. Rev. Lett.*, **101**(6), 067403/1-4 (2008)
 5. Room-Temperature First-Order Phase Transition in a Charge-Disproportionated Molecular Conductor (MeEDO-TTF)₂PF₆, X.F. Shao, Y. Nakano, M. Sakata, H. Yamochi, Y. Yoshida, M. Maesato, M. Uruichi, K. Yakushi, T. Murata, A. Otsuka, G. Saito, S. Koshihara, K. Tanaka, *Chem. Mater.*, **20**(24), 7551-7562 (2008)
 6. Prediction of the Electronic Structure via Molecular Stacking Mode of Radical Cation Salts Based on Asymmetric Donor Molecule MeEDO-TTF, X.F. Shao, Y. Yoshida, Y. Nakano, H. Yamochi, M. Sakata, M. Maesato, A. Otsuka, G. Saito, S. Koshihara, *Chem. Mater.*, **21**(6), 1085-1095 (2009)
 7. Enantiomorph identification and stacking faults in κ -(BEDT-TTF)₂Cu(NCS)₂ by convergent-beam electron diffraction, S. Fujio, K. Tanaka, H. Inui, R. Ueji, N. Sumida, H. Yamochi, G. Saito, *J. Appl. Cryst.*, **42**(3), 433-441 (2009)
 8. Organic Metal (EDO-TTF)₂PF₆ with Multi-instability, H. Yamochi, S. Koshihara, *Sci. Technol. Adv. Mater.*, **10**(2), 024305/1-6 (2009)
 9. Tuning of Multi-instabilities in Organic Alloy, [(EDO-TTF)_{1-x}(MeEDO-TTF)_x]₂PF₆, T. Murata, X.F. Shao, Y. Nakano, H. Yamochi, M. Uruichi, K. Yakushi, G. Saito, K. Tanaka, *Chem. Mater.*, **22**(10), 3121-3132 (2010)