Electronic Supplementary Information

Solid-Solid Phase Interconversion in an Organic Conductor Crystal: Hydrogen-bond-mediated Dynamic Changes of π-Stacked Molecular Arrangement and Physical Properties

Junya Yoshida[†], Akira Ueda^{*,†}, Akiko Nakao[‡], Reiji Kumai[§], Hironori Nakao[§], Youichi Murakami[§], Hatsumi Mori^{*,†}

Email: hmori@issp.u-tokyo.ac.jp, a-ueda@issp.u-tokyo.ac.jp

[†]The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan.

[‡]Comprehensive Research Organization for Science and Society (CROSS), Tokai, Ibaraki 319-1106, Japan

[§]CMRC and Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan.

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General information

The parent H₂Cat-EDO-TTF (Catechol-fused ethylenedioxy tetrathiafulvalene) donor molecule (Figure S1) was prepared according to the literature.^{S2} Other commercially available materials were used as received. X-ray crystallographic measurements were made on a Rigaku imaging plate at the BL-8A in the Photon Factory at KEK, Japan (synchrotron, $\lambda = 1.0000$ Å) for β '- $[H_3(Cat-EDO-TTF)_2]BF_4$ and α - $[H_3(Cat-EDO-TTF)_2]BF_4$ or on a Rigaku Mercury70 CCD (Mo-K α , $\lambda = 0.71073$ Å) for H₂Cat-EDO-TTF donor molecule, respectively. We note that the synchrotron X-ray radiation provided very high quality crystal structure data, although the completeness seems to be low, which is due to the large 2θ angle (~91.4°) as well as the small sample size. The direct current electrical conductivity measurement was made by the conventional four-probe method using carbon paste and gold wires. The magnetic susceptibility was measured on a Quantum Design SQUID magnetometer MPMS-XL in the temperature range of 2–300 K at the static field of 1 T. The magnetic responses were corrected with blank data of the sample holder obtained separately. The diamagnetic contribution of the sample itself was estimated to be 3.70×10^{-4} emu/mol from Pascal's constants. The intermolecular transfer integrals were calculated with the tight-binding approximation using the extended Hückel molecular orbital method.^{S3} DFT calculations of the molecular orbitals, electrostatic surfaces, exchange interactions, and potential energy curves were performed with: M. J. Frisch et al. Gaussian 03, revision E.01; Gaussian Inc.: Wallingford CT, 2004.^{S4}

Material preparation

Catechol-fused ethylenedioxytetrathiafulvalene (H₂Cat-EDO-TTF) molecule (Figure S1)
 H₂Cat-EDO-TTF was prepared according to the literature.^{S2} Recrystallization from a CH₃CN solution at room temperature gave a red plate crystal suitable for X-ray analysis.



Figure S1. Chemical structure of the H₂Cat-EDO-TTF molecule

• β' -[H₃(Cat-EDO-TTF)₂]BF₄ (Figure S2)

The H₂Cat-EDO-TTF donor molecule (3.0 mg, 8.7 mmol) was placed in one side of an Hshaped cell equipped with a glass filter. Then, *n*-Bu₄NBF₄ (5.7 mg, 17.3 mmol) was placed in each side and the H-shaped cell was purged by argon gas. These materials were dissolved in anhydrous EtOH (1.5 mL) and degassed PhCl (9.5 mL) by sonication, and then two Pt electrodes were inserted into the solution. A constant current of 0.3 μ A was applied for 1 week, to give black plate crystals (~0.2 mg) of β '-[H₃(Cat-EDO-TTF)₂]BF₄, through deprotonation of one of the catechol protons, formation of the H-bond, and oxidation of the TTF skeletons.

The replacement of the EDT group in the previous system^{S1} with the EDO one enhances the electron-donating ability of the TTF skeleton,^{S2} which enables to form this higher oxidized TTF⁺¹ state in the present system.



Figure S2. Chemical structure of β '-[H₃(Cat-EDO-TTF)₂]BF₄.

Crystal structure of κ-H₃(Cat-EDT-TTF)₂^{S1}



Figure S3. Packing structure of the H-bonded molecular unit, H_3 (Cat-EDT-TTF)₂, in κ -H₃(Cat-EDT-TTF)₂^{S1}. The κ -type conducting layers, composed of π -dimers of the Cat-EDT-TTF^{+0.5} skeletons, are connected by the intra-unit H-bond.

Supporting crystal structural data

	β' -[H ₃ (Cat-EDO-TTF) ₂]BF ₄	α -[H ₃ (Cat-EDO-TTF) ₂]BF ₄	H ₂ Cat-EDO-TTF
Formula	$C_{24}H_{15}O_8S_8B_1F_4$	$C_{24}H_{15}O_8S_8B_1F_4$	$C_{12}H_8O_4S_4$
Formula Weight	774.66	774.66	352.50
Crystal System	triclinic	triclinic	Orthorhombic
Space Group	<i>P</i> -1 (#2)	<i>P</i> -1 (#2)	C222 ₁ (#20)
Temperature / K	270	150	293
λ / Å	1.00000	1.00000	0.71073
<i>a</i> / Å	7.2409(3)	7.1203(2)	3.999(3)
<i>b</i> / Å	9.7683(5)	10.9390(4)	29.96(3)
<i>c</i> / Å	10.8941(6)	18.0093(7)	10.493(9)
α / °	66.6688(13)	78.1857(8)	90
β / °	85.6578(18)	82.3285(10)	90
γ / °	79.0863(19)	89.7204(11)	90
$V/ Å^3$	695.62(6)	1358.06(8)	1257(2)
Z value	1	2	4
$d_{ m calc}$ / g cm ⁻³	1.849	1.894	1.863
GOF	1.060	1.048	1.144
<i>R</i> 1 (I >2.00σ(I))	0.0435	0.0330	0.0559
wR2 (All data)	0.1348	0.0958	0.1363
# of observations	2452	3304	1440
# of variables	232	473	96
CCDC	997839	997837	997838

Table S1. Crystallographic data for β '- and α -[H₃(Cat-EDO-TTF)₂]BF₄ and H₂Cat-EDO-TTF.



Figure S4. (a) Molecular structure and (b) molecular arrangement of the neutral donor, $H_2Cat-EDO-TTF$ (See also Figure S1). The thermal ellipsoids are scaled to the 50% probability level.



Figure S5. X-ray structure of β '-[H₃(Cat-EDO-TTF)₂]BF₄ at 270 K. (a) Arrangement of the Hbonded molecular units and BF₄⁻ anions. The yellow- and pink-colored H-bonded units are in the same plane, and the blue one is located above the pink one. (b) Molecular arrangement of the Cat-EDO-TTF skeletons in the conducting layer. The pink and blue molecules are π -dimerized. (c) Top view of the π -dimer arranged in a head-to-tail manner. (d) Side-by-side intermolecular short contacts in the C direction with the second largest transfer integral.



Figure S6. X-ray structure of α -[H₃(Cat-EDO-TTF)₂]BF₄ at 150 K. (a) Arrangement of the Hbonded molecular units and BF₄⁻ anions. The crystallographically non-equivalent molecules A and B are shown by green and red, respectively. (b) Molecular arrangement of the Cat-EDO-TTF skeletons in the conducting layer. The A1 and B1 molecules correspond to the yellow and pink ones in Figure S4b. (c) Top views of two kinds of the π -dimers. (d) Side-by-side intermolecular short contacts in the C' direction.



Figure S7. Comparison of the intermolecular contacts between the Cat-EDO-TTF skeletons in the *bc* plane. (a) β' -[H₃(Cat-EDO-TTF)₂]BF₄ at 270 K and (b) α -[H₃(Cat-EDO-TTF)₂]BF₄ at 150 K (Molecules A and B are shown in green and red, respectively). See also Figures 2e,f, S4a, and S5a.



Figure S8. Comparison of the intermolecular contacts around the disordered BF_4^- anion in the *bc* plane. (a) β' -[H₃(Cat-EDO-TTF)₂]BF₄ at 270 K and (b) α -[H₃(Cat-EDO-TTF)₂]BF₄ at 150 K (Molecules A and B are shown in green and red, respectively). See also Figures 2e,f, S4a, and S5a.

	H ₂ C ₂ t_FDOTTE	B'-calt	α-salt	α-salt
		p -san	(molecule A)	(molecule B)
a / Å	1.347(8)	1.386(3)	1.382(3)	1.384(3)
b / Å	1.755(3), 1.755(3)	1.728(2), 1.714(3)	1.728(3), 1.725(3)	1.724(3), 1.726(3)
b' / Å	1.770(3), 1.770(3)	1.722(3), 1.723(2)	1.729(3), 1.724(3)	1.723(3), 1.729(3)
c / Å	1.760(4), 1.760(4)	1.740(3), 1.729(2)	1.734(2),1.736(3)	1.734(3), 1.744(2)
c' / Å	1.756(4), 1.756(4)	1.722(3), 1.731(3)	1.728(3), 1.737(2)	1.724(3), 1.731(2)
d / Å	1.394(6)	1.404(4)	1.403(5)	1.411(4)
d' / Å	1.315(6)	1.338(5)	1.336(5)	1.343(5)
δ^a / Å	0.774(6)	0.666(3)	0.677(4)	0.669(3)
$\delta^{\prime b}$ / Å	0.864(6)	0.725(3)	0.741(4)	0.727(4)
Q ^c	0.235(6)	1.158(3)	1.058(4)	1.140(3)
Q'^d	0	0.924(3)	0.823(4)	0.905(3)
Q" ^e	-	-	0.953(3)	1.047(3)

Table S2. Charge estimation of the TTF skeleton in β '- and α -[H₃(Cat-EDO-TTF)₂]BF₄, based on its bond lengths (Figure S8, see below).^{S1} Q, Q', and Q'' represent the tentative, net, and normalized charges, respectively.

^{*a*} $\delta = b+c-a-d$, ^{*b*} $\delta' = b'+c'-a'-d'$, ^{*c*} $Q = 6.347-7.463 \cdot (\delta+\delta')/2$, ^{*d*} Q' = Q-0.235, ^{*e*} Q'' (molecule A) = [Q'(molecule A)/(Q'(molecule A)+Q'(molecule B))]×2, Q'' (molecule B) = [Q'(molecule B)/(Q'(molecule A)+Q'(molecule B))]×2

According to the EDT case,^{S1} the tentative charge Q for the neutral donor H₂Cat-EDO-TTF molecule in the crystal (Q = 0.235(6)) was calculated and defined as the internal standard for the neutral species (Q' = 0) in this system. Then, the net charge Q' for the TTF skeleton in β '- and α -[H₃(Cat-EDO-TTF)₂]BF₄ was calculated by the equation Q' = Q–0.235, to give 0.924(3) for the

 β '-crystal and 0.823(4) and 0.905(3) for the molecules A and B (Figure 2b, see the text page) in the α -crystal, respectively. The Q' value for the β '-crystal (0.924(3)) well corresponds to the +1.0 mono-oxidized state predicted from the crystal composition. Thus, the net charge Q' for the molecules A (0.823(4)) and B (0.905(3)) in the α -crystal was further corrected as Q", 0.953(3) and 1.047(3), respectively, by normalizing of the sum of Q" to 2. These Q" values suggest that both the two kinds of the TTF skeletons in the α -crystal are in a +1.0 oxidized state, namely, unchanged from those in the HTP β '-crystal.



Figure S9. Bond numbering scheme for the TTF skeleton.

DFT calculations



Figure S10. HOMO (highest occupied molecular orbital) distribution maps of the H-bonded molecular unit, $[H_3(Cat-EDO-TTF)_2]^+$, in (a) β '- $[H_3(Cat-EDO-TTF)_2]BF_4$ at 270 K (HTP) and (b) α - $[H_3(Cat-EDO-TTF)_2]BF_4$ at 150 K (LTP), calculated at the ROB3LYP/6-31G(d) level of theory.^{S4} The molecular geometries were taken from the X-ray data.

Each Cat-EDO-TTF skeleton in (a) shows the same HOMO distribution, due to the crystallographic equivalence. In contrast, the two Cat-EDO-TTF skeletons in (b) are crystallographically non-equivalent, however, the amount of their HOMO coefficient looks like similar. These results suggest that the charge on the Cat-EDO-TTF skeleton is unchanged upon the phase transition, as estimated from the bond length analysis (Table S2).



Figure S11. Electrostatic potential surfaces of the H-bonded molecular unit, $[H_3(Cat-EDO-TTF)_2]^+$, in (a) $\beta'-[H_3(Cat-EDO-TTF)_2]BF_4$ at 270 K and (b) α - $[H_3(Cat-EDO-TTF)_2]BF_4$ at 150 K, calculated at the broken-symmetry (BS) UB3LYP/6-31G(d) level of theory.^{S4} The molecular geometries were taken from the X-ray data.

There are no noticeable differences in the charge distribution of (a) and (b), suggesting that the oxidized state and electronic structure of each Cat-EDO-TTF skeleton is unchanged upon the phase transition, as mentioned in Table S2 and Figure S9.

Table S3. Calculation of the exchange coupling parameters for the π -dimers in β '- and α -[H₃(Cat-EDO-TTF)₂]BF₄. The spin expectation values and total energies for the brokensymmetry (BS) singlet ($\langle S^2 \rangle_{BS}$ and E_{BS}) and triplet states ($\langle S^2 \rangle_T$ and E_T), energy gap between BS singlet and triplet states ($E_{BS} - E_T$), and exchange interaction parameters ($2Jk_B^{-1}$) were calculated at the UB3LYP/6-31G(d) level of theory.^{S4} The molecular geometries were taken from the X-ray data.

The *intra*-dimer antiferromagnetic coupling $2Jk_{\rm B}^{-1}$, obtained by the equation $Jk_{\rm B}^{-1} = (E_{\rm BS} - E_{\rm T})/(\langle S^2 \rangle_{\rm T} - \langle S^2 \rangle_{\rm BS})^{\rm S5}$, is significantly stronger in the α -salt (-2139 and -2095 K) than in the β '-salt (-1848 K), suggesting the enhancement of the intra-dimer interaction in the low-temperature α -salt.

		molecule A (green-	molecule B (red-
Compound	β'-salt (270 K)	colored) dimer in α -salt	colored) dimer in α -salt
		(150 K)	(150 K)
$\langle S^2 \rangle_{BS}$	0.7647	0.72965	0.72956
$< S^{2} >_{T}$	2.0317	2.0340	2.0339
$E_{\rm BS}$ / hartree	-4709.7664	-4709.7703	-4709.7470
$E_{\rm T}$ / hartree	-4709.7627	-4709.7658	-4709.7427
$E_{\rm BS}-E_{\rm T}$ / K	-1170.6	-1395.4	-1366.5
$2Jk_{\rm B}^{-1}$ / K	-1847.9	-2139.5	-2095.3



Figure S12. Theoretical potential energy curves for the H-bonded unit, $[H_3(Cat-EDO-TTF)_2]^+$, in (a) β '- $[H_3(Cat-EDO-TTF)_2]BF_4$ at 270 K and (b) α - $[H_3(Cat-EDO-TTF)_2]BF_4$ at 150 K. The total energy profiles (ΔE , in eV) as a function of the distance between the O1…O2 center position and the H-bonded hydrogen atom, which moves linearly between O1…O2. The calculations were performed at the UB3LYP/6-31G(d) level of theory by using the X-ray structural data with changing the H-bonded hydrogen atom position. In the inset, each H-bonded molecular unit structure in the crystal is shown.

At (a) 270 K, a symmetric double-well (nearly a single-well) potential curve is obtained, in which the energy barrier for hydrogen transfer is calculated to be 0.01 eV. This very low barrier, ascribable to the very short O1···O2 distance (2.455(3) Å), allowed to form the H-centered structure in the crystal. On cooling down to (b) 150 K, the potential curve desymmetrizes and the potential minimum is located at the O1 side, corresponding to the experimental asymmetric Hbond structure (O1···H = 1.17(4) Å, H···O2 = 1.31(4) Å). Consequently, the energy barrier at 150 K is very higher (0.07 eV) than that at 270 K (0.01 eV). However, the valence on each Cat-EDO-TTF skeleton is fundamentally unchanged upon the phase transition, which means that there is no relationship between the hydrogen atom position and the electronic structure of the Cat-EDO-TTF skeletons, in contrast to the [ODO] deuterated Cat-EDT-TTF system.^{S6}

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