

Positional Order and Disorder of Symmetric and Unsymmetric BEDT-STF Salts

H. Mori,^{*,†,1} H. Suzuki,^{*,†,‡} T. Okano,^{†,§} H. Moriyama,[†] Y. Nishio,[§] K. Kajita,[§] M. Kodani,^{||} K. Takimiya,^{||} and T. Otsubo^{||}

^{*}Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa Chiba 277-8581, Japan; [†]International Superconductivity Technology Center (ISTEC), Tokyo 135-0062, Japan; [‡]Department of Chemistry, Faculty of Science, Toho University, Chiba 274-8510, Japan; [§]Department of Physics, Faculty of Science, Toho University, Chiba 274-8510, Japan; and ^{||}Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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The symmetric (*s*-) and unsymmetric (*us*-) BEDT-STF (= bis(ethylenedithio)diselenadithia-fulvalene) salts were prepared, and their crystal structures and electrical resistivities were investigated. Four *us*-BEDT-STF salts have the positional disorder of the Se atoms in the STF framework in crystals, whereas three *s*-BEDT-STF salts have no disorder. When κ -(*us*-BEDT-STF)₂GaCl₄ and κ -(*cis-s*-BEDT-STF)₂GaCl₄ are compared, the latter without the positional disorder of the Se atoms is more conductive than the former one with the disorder. © 2002

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INTRODUCTION

Organic superconductors have been usually obtained by the *bandwidth control* of antiferromagnetic insulators (1, 2) (Fig. 1). As shown in Fig. 2(a), λ -ET₂GaCl₄ (ET = bis(ethylenedithio)tetrathiafulvalene) is a semiconductor (i), whose electronic ground state is an antiferromagnetic one (3). By the introduction of the Se atoms in the TTF framework, λ -(*us*-BEDT-STF)₂GaCl₄ is a more conductive semiconductor at an ambient pressure (ii)(4), and has a constant resistivity down to 1.3 K with a hump around 30 K under 18 kbar (iii) (3). Moreover, λ -BETS₂GaCl₄ including four Se atoms affords a superconductivity at 6 K (iv) (4). The reason why the constant resistivity without superconductivity was obtained for λ -(*us*-BEDT-STF)₂GaCl₄ under 18 kbar might be the positional disorder of Se atoms in the salt as shown in Fig. 2(b) or an insufficient pressure. In order to get rid of the positional disorder, the possibility

of symmetric (*s*-)BEDT-STF (5) salts has been investigated and the comparison between the *s*- and *us*-BEDT-STF salts is reported in this paper.

EXPERIMENTAL

The donor molecule of *us*-BEDT-STF was synthesized by the cross coupling of ethylenedithio-1,3-diselenol-2-one (A) and bis(cyanoethylthio)-1,3-dithiole-2-thione and the introduction of an ethylene part by using ethylene dibromide. This method prohibits to include the symmetric donors, whereas it is difficult to exclude the symmetric ones completely by the cross coupling of (A) and ethylenedithio-1,3-dithiole-2-thione (4). The symmetric BEDT-STF was synthesized by the method of reference (5). The salts were prepared electrochemically by using TBA·GaCl₄, TBA·FeCl₄, TBA·I₃ or Ph₄P·CuCl₂ in chlorobenzene under N₂ atmosphere at a constant current of 0.5 μ A. The X-ray diffraction data were collected on a Rigaku AFC5R diffractometer ($T = 298$ K, $\lambda = 0.71073$ Å; 50 kV, 150 mA; $2\theta \leq 60^\circ$, ω - 2θ scan). The crystallographic data of *us*- and *s*-BEDT-STF salts are listed in Tables 1 and 2, respectively. The crystal structures were solved by a direct method (SHELXS86) (6). The non-hydrogen atoms were refined anisotropically by least-squares procedures. The population of S/Se atoms in the tetrachalcogenafulvalene frame is determined by the population analyses. The electrical resistivity is measured by the conventional four-probe method in the range of 300 and 1.3 K with gold paste as electrodes. Pressure dependence was measured by using a clamp-type cell with an oil (Daphne #7373) as a pressure medium. The pressure was determined from the resistance of a manganin wire.

¹To whom correspondence should be addressed. Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa Chiba 277-8581, Japan. Fax: +81 471 36 3444. E-mail: hmori@issp.u-tokyo.ac.jp.

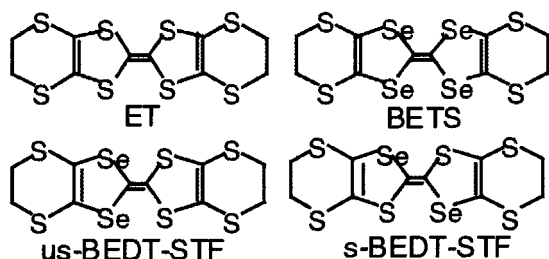


FIG. 1. Molecular structures of ET, BETS, and *us*-BEDT-STF, and *s*-BEDT-STF.

RESULTS AND DISCUSSION

Three *us*-BEDT-STF salts, κ -(*us*-BEDT-STF)₂GaCl₄, λ -(*us*-BEDT-STF)₂FeCl₄, and α -(*us*-BEDT-STF)₂I₃, have the positional disorder in the Se/S atoms in the STF framework like λ -(*us*-BEDT-STF)₂GaCl₄ as shown in Fig. 2(b) and Table 1. The possibilities of Se/S are 50/50 for these four salts. On the other hand, δ' -(*us*-BEDT-STF)₂GaCl₄ is the only *us*-BEDT-STF salt, which does not have the positional disorder as shown in Fig. 3. Two crystallographically independent *us*-BEDT-STF molecules make a twisted pair (Fig. 3(b), (c)), which stacks along the *a*-axis (Fig. 3(a)). The Se atoms in the *us*-BEDT-STF molecule are ordered in the crystal. The space group is $P\bar{1}$, which is centrosymmetric. The Se atoms between the *us*-BEDT-STF molecules are allocated close to each other (Fig. 3(c), (d)).

In order to obtain Se-ordered crystals, *s*-BEDT-STF (Fig. 1) is synthesized (5) and its salts are investigated. Fig. 4 shows the crystal structure of neutral *s*-BEDT-STF molecules, which is isostructural to BEDT-TTF ones. The

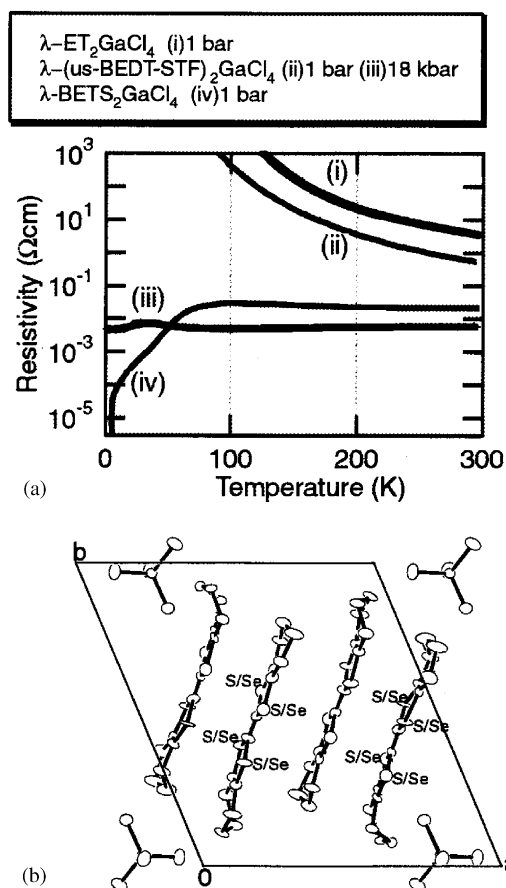


FIG. 2. (a) Electrical resistivities of λ -*D*₂GaCl₄ ((i) *D* = ET, *us*-BEDT-STF; (ii) 1 bar, (iii) 18 kbar, (iv) BETS) and (b) crystal structure of λ -ET₂GaCl₄.

TABLE 1
Crystal Data for *us*-BEDT-STF (*us*-*D*) Salts

	κ -(<i>us</i> - <i>D</i>) ₂ GaCl ₄	λ -(<i>us</i> - <i>D</i>) ₂ GaCl ₄	λ -(<i>us</i> - <i>D</i>) ₂ FeCl ₄	α -(<i>us</i> - <i>D</i>) ₂ I ₃	δ' -(<i>us</i> - <i>D</i>) ₂ GaCl ₄
Chemical formula	C ₂₀ H ₁₆ GaCl ₄ S ₁₂ Se ₄	C ₂₀ H ₁₆ GaCl ₄ S ₁₂ Se ₄	C ₂₀ H ₁₆ FeCl ₄ S ₁₂ Se ₄	C ₂₀ H ₁₆ I ₃ S ₁₂ Se ₄	C ₂₀ H ₁₆ GaCl ₄ S ₁₂ Se ₄
Formula wt	1168.4	1168.4	1154.6	1337.7	1168.4
Shape	Black plate	Black needle	Black needle	Black plate	Black plate
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>Pnma</i> (#62)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
<i>a</i> (Å)	11.587	16.203(8)	16.238(7)	9.198(2)	15.104(4)
<i>b</i> (Å)	35.696	18.316(9)	18.28(1)	10.802(3)	18.020(4)
<i>c</i> (Å)	8.493	6.573(2)	6.574(3)	17.607(5)	6.665(6)
α (deg)	90	98.41(4)	98.43(6)	96.86(2)	90.63(4)
β (deg)	90	97.03(3)	96.92(5)	97.88(2)	92.04(4)
γ (deg)	90	112.42(4)	112.37(4)	90.75(2)	82.31(2)
<i>V</i> (Å ³)	3512.8	1750(1)	1751(2)	1719.7	1796(2)
<i>Z</i>	4	2	2	2	2
<i>R</i> / <i>R</i> _w	—	0.073/0.064	0.067/0.050	—	0.059/0.046
<i>D</i> _c (g cm ⁻³)	2.21	2.22	2.19	2.58	2.16
Reflection used	—	2468/10213	2789/10145	—	2111/7950
Reference	4	<i>I</i> ₀ > 3σ <i>I</i> ₀ This work	<i>I</i> ₀ > 3σ <i>I</i> ₀ This work	4	<i>I</i> ₀ > 3σ <i>I</i> ₀ This work

TABLE 2
Crystal Data for *s*-BEDT-STF (*s*-D) and its Salts

	<i>s</i> -D	κ -(<i>cis-s</i> -D) ₂ GaCl ₄	λ' -(<i>trans-s</i> -D) ₂ GaCl ₄	κ -(<i>cis-s</i> -D) ₂ Cu _{1.6} Cl _{2.9}	α -(<i>s</i> -D) ₂ I ₃
Chemical formula	C ₁₀ H ₈ S ₆ Se ₂	C ₂₀ H ₁₆ GaCl ₄ S ₁₂ Se ₄	C ₂₀ H ₁₆ GaCl ₄ S ₁₂ Se ₄	C ₂₀ H ₁₆ Cu _{1.6} Cl _{2.9} S ₁₂ Se ₄	C ₂₀ H ₁₆ I ₃ S ₁₂ Se ₄
Formula wt	478.5	1168.4	1168.4	1161.5	1337.6
Shape	Orange plate	Black plate	Black needle	Black plate	Black plate
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>Pnma</i> (#62)	<i>P</i> 1̄(#2)	<i>Pccn</i> (#56)	<i>P</i> 1̄(#2)
<i>a</i> (Å)	6.669(5)	11.65(2)	16.15(1)	8.54(1)	9.229(5)
<i>b</i> (Å)	14.194(5)	35.74(2)	16.914(9)	34.776(8)	10.834(7)
<i>c</i> (Å)	15.997(5)	8.47(1)	6.563(4)	11.523(6)	17.585(8)
α (deg)	90	90	93.25(5)	90	97.16(4)
β (deg)	93.12(5)	90	98.90(6)	90	97.85(4)
λ (deg)	90	90	92.45(6)	90	90.82(5)
<i>V</i> (Å ³)	1512(1)	3527(8)	1765(2)	3421(4)	1727(2)
<i>Z</i>	4	4	2	4	2
<i>R</i> / <i>R</i> _w	0.073/0.062	0.126/0.113	0.068/0.052	0.138/0.103	0.178/0.1701
<i>D</i> _c (g cm ⁻³)	2.10	2.20	2.20	2.26	2.57
Reflection used	1332/4585	544/3861	1275/7357	1625/5610	2541/10543
Reference	This work	This work	This work	This work	This work

positional disorder of the Se/S (= 50/50) atoms is observed in the neutral crystal. However, as for its charge transfer salt, λ' -(*trans-s*-BEDT-STF)₂GaCl₄, the Se atoms are *trans*-ordered as shown in Fig. 5(a). Though the starting neutral

donors are mixtures of *cis*- and *trans*-BEDT-STF, the electrochemical preparation makes ionized donors *cis*- or *trans*-ordered in crystals. Two dimers (AA', BB') stack along the *b*-axis like four-fold ABB'A'. The room

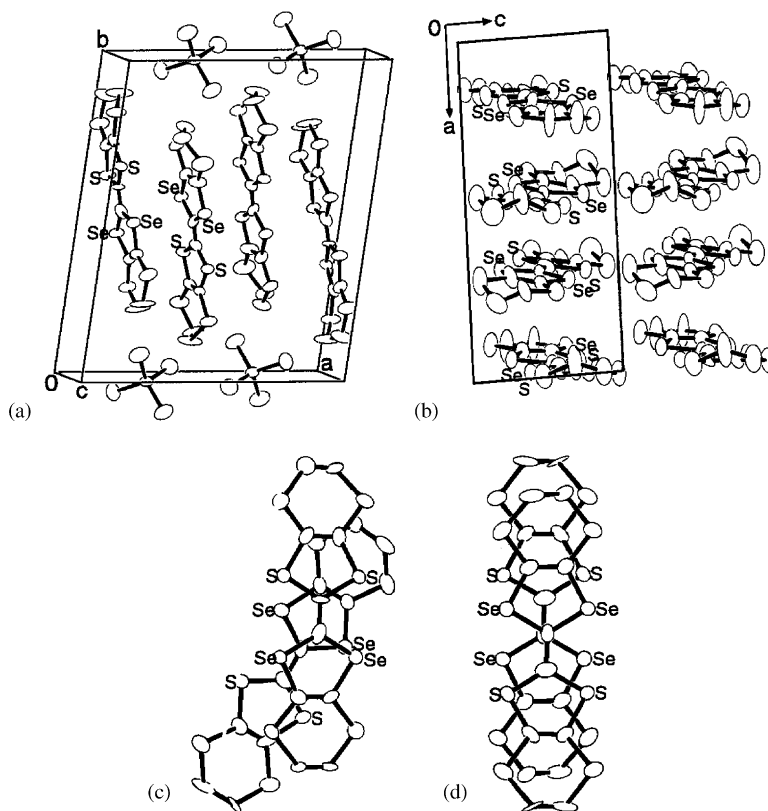


FIG. 3. (a) Crystal structure, (b) donor arrangement, and molecular arrangements (c) within and (d) between a dimer in δ' -(*us*-BEDT-STF)₂GaCl₄.

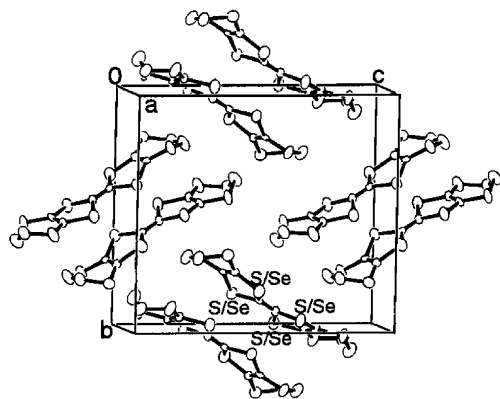


FIG. 4. Crystal structure of *s*-BEDT-STF molecules.

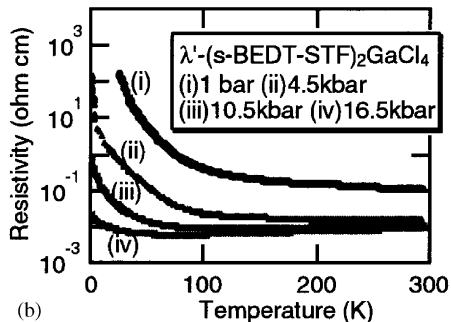
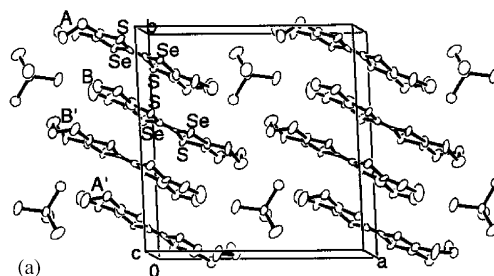


FIG. 5. (a) Crystal structure and (b) electrical resistivities at (i) 1 bar, (ii) 4.5 kbar, (iii) 10.5 kbar, and (iv) 16.5 kbar of λ' -(*s*-BEDT-STF)₂GaCl₄.

temperature resistivity is 0.1 Ω cm and increases gradually with lowering temperature. By applying pressure, the resistivity at room temperature decreases gradually and the rapid increase of resistivity at low temperatures is suppressed. The resistivity is almost constant with the minimum around 60 K under 16.5 kbar as shown in Fig. 5(b).

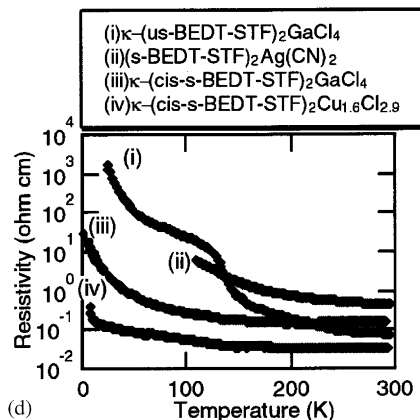
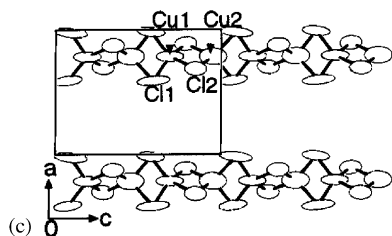
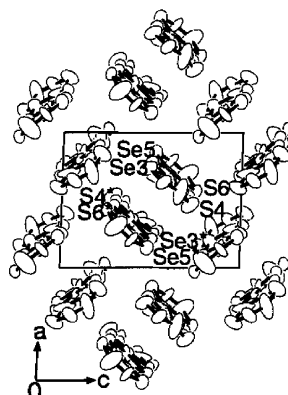
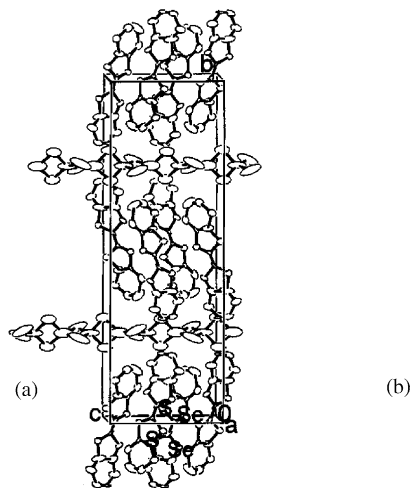


FIG. 6. (a) Crystal structure, (b) donor arrangement, (c) anion arrangement of κ -(*cis-s*-BEDT-STF)₂Cu_{1.6}Cl_{2.9}, and (d) electrical resistivities of (i) κ -(*us*-BEDT-STF)₂GaCl₄, (ii) (*s*-BEDT-STF)₂Ag(CN)₂, (iii) κ -(*cis-s*-BEDT-STF)₂GaCl₄, and (iv) κ -(*cis-s*-BEDT-STF)₂Cu_{1.6}Cl_{2.9}.

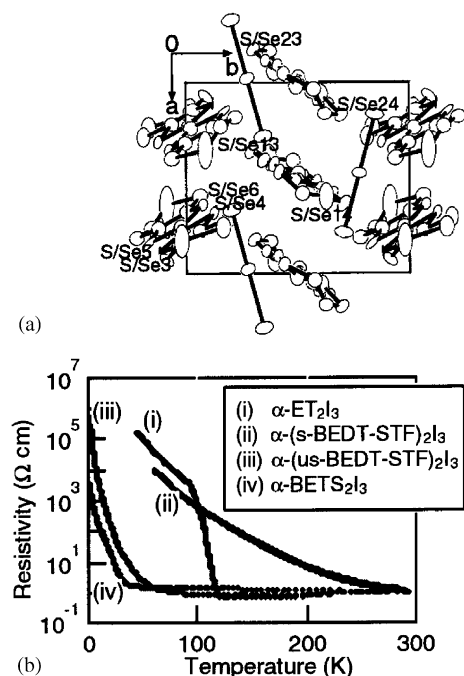


FIG. 7. (a) Crystal structure of α -(*s*-BEDT-STF) $_2$ I $_3$ and (b) electrical resistivities of (i) α -ET $_2$ I $_3$, (ii) α -(*s*-BEDT-STF) $_2$ I $_3$, (iii) α -(*us*-BEDT-STF) $_2$ I $_3$, and (iv) α -BETS $_2$ I $_3$.

Another Se-ordered salt is κ -(*cis-s*-BEDT-STF) $_2$ Cu $_{1.6}$ Cl $_{2.9}$ as shown in Fig. 6. The Se atoms in an *s*-BEDT-STF molecule are *cis*-ordered, and the space group of the crystal is *Pccn*, which is centrosymmetric; two donors in a dimer is connected by an inversion center. The anion arrangement is depicted in Fig. 6(c); two chlorines of a tetrahedral CuCl $_4$ share those of the neighboring CuCl $_4$. The populations of Cu1, Cu2, Cl1, and Cl2 are 0.42, 0.38, 0.75, and 0.72, namely, κ -(*cis-s*-BEDT-STF) $_2$ Cu $_{1.6}$ Cl $_{2.9}$. The resistivity at room temperature is 0.03 Ω cm and almost constant down to 13 K. Below that rapid increase is observed (Fig. 6(d)(iv)).

The other κ -phase is κ -(*cis-s*-BEDT-STF) $_2$ GaCl $_4$, in which the Se atoms are also *cis*-ordered. When we compare the ordered and disordered salts, κ -(*cis-s*-BEDT-STF) $_2$ GaCl $_4$ and κ -(*us*-BEDT-STF) $_2$ GaCl $_4$, the ordered one (Fig. 6(d)(iii)) is more conductive than the disordered one (Fig. 6(d)(i)) owing to a random potential from the disorder of the Se atoms. The ordered κ -(*cis-s*-BEDT-STF) $_2$ GaCl $_4$, however, still shows the semiconducting behavior at low temperatures. One of the explanations is its strong dimerization of donors or the quality of the crystal.

The exceptional example in the *s*-BEDT-STF salt is α -(*s*-BEDT-STF) $_2$ I $_3$. Although the Se atoms of other three *s*-BEDT-STF salts are ordered in a crystal, the Se/S atoms of I $_3$ salt are heavily disordered as shown in Fig. 7(a). The populations of S3, S4, S5, S6, S13, S14, S23, and S24 are

1.5, 1.1, 1.3, 1.4, 1.2, 1.5, 1.1, and 1.5, respectively. The resistivities of a series of α -type salts, (i) α -ET $_2$ I $_3$ (7), (ii) α -(*s*-BEDT-STF) $_2$ I $_3$, (iii) α -(*us*-BEDT-STF) $_2$ I $_3$, and (iv) α -BETS $_2$ I $_3$ (7), are depicted in Fig. 7(b). Since the Se atoms of (ii) is heavily disordered, the distinct metal-insulator transition is smeared out and the semiconducting behavior is observed.

CONCLUSION

In order to investigate a series of ET salts series, the unsymmetric (*us*-) and symmetric (*s*-) BEDT-STF salts, which is located between ET and BETS salts, were studied. The disorder of the Se atoms in *us*-BEDT-STF molecules is observed in four salts, κ -(*us*-BEDT-STF) $_2$ GaCl $_4$, λ -(*us*-BEDT-STF) $_2$ GaCl $_4$, λ' -(*us*-BEDT-STF) $_2$ FeCl $_4$, and α -(*us*-BEDT-STF) $_2$ I $_3$. The exceptional example is δ' -(*us*-BEDT-STF) $_2$ GaCl $_4$, in which the ordered Se atoms are observed. On the other hand, three of four *s*-BEDT-STF salts have the ordered Se atoms: κ -(*cis-s*-BEDT-STF) $_2$ GaCl $_4$, κ -(*cis-s*-BEDT-STF) $_2$ Cu $_{1.6}$ Cl $_{2.9}$, and λ' -(*trans-s*-BEDT-STF) $_2$ GaCl $_4$. Only the Se atoms of α -(*s*-BEDT-STF) $_2$ I $_3$ are heavily disordered without a distinct metal-insulator transition. When we compare the ordered and disordered salts, κ -(*cis-s*-BEDT-STF) $_2$ GaCl $_4$ and κ -(*us*-BEDT-STF) $_2$ GaCl $_4$, the ordered one is more conductive without a random potential.

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