Ambient pressure Dirac electron system in quasi-two-dimensional molecular conductor \(\alpha\)-(BETS)\(_2\)I\(_3\)

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We investigated the precise crystal structures and electronic states in a quasi-two-dimensional molecular conductor \(\alpha\)-(BETS)\(_2\)I\(_3\) at ambient pressure. The electronic resistivity of this molecular solid shows a metal-to-insulator (MI) crossover at \(T_{MI} = 50\) K. Our x-ray diffraction and \(^{13}\)C nuclear magnetic resonance experiments revealed that \(\alpha\)-(BETS)\(_2\)I\(_3\) maintains the inversion symmetry below \(T_{MI}\). The first-principles calculations found a pair of anisotropic Dirac cones at a general \(k\)-point, where the degenerated contact points are located at the Fermi level. Furthermore, the origin of the insulating state in this system is explained by a small energy gap of \(\sim 2\) meV opened by a spin–orbit interaction, in which the \(Z_2\) topological invariants indicate a weak topological insulator. Our results suggest that \(\alpha\)-(BETS)\(_2\)I\(_3\) is a promising material for studying the bulk Dirac electron system in two-dimension.

**Introduction.** A massless Dirac electron system, in which two linear band dispersions intersect at the Fermi level \((E_F)\), is one of the central themes of modern physics [1-6]. When a system has such emergent band structure, the electron behavior, such as the electronic transport, follows a relativistic Dirac equation, and the charge carriers move, as if they had no mass, at the speed of light in a material. However, there are very few material systems, in which the Dirac point is located at the \(E_F\), and the band gap is zero, that can be named massless Dirac electron system. Such an electronic state is realized in two-dimensional (2D) layer of graphene [1], bismuth [7-9], and the surface of topological insulators [10,11]. In these systems, unique physical properties such as quantum Hall effect [1], quantum spin Hall effect [2], and unscreened long-range Coulomb interaction [6] attributed to the Dirac cone band structure have been proposed. In addition, potential applications to a high mobility electronic device have been reported [12,13].

Recently, the existence of massless Dirac electron systems has been suggested in some organic molecular solids [14-30], in which Dirac cones are formed by the bands of the same character of wavefunctions as frontier orbitals of consistent molecules at different sites. The massless Dirac electron system in bulk was first realized in a quasi-2D molecular conductor, \(\alpha\)-(ET)\(_2\)I\(_3\) \([ET = \text{BEDT-TTF} = \text{bis(ethylenedithio)tetrathiafulvalene}]\) [Fig. 2(a)] [16]. Unlike graphene [1], \(\alpha\)-(ET)\(_2\)I\(_3\) has a pair of anisotropic Dirac cones [16]. However, the massless Dirac state in \(\alpha\)-(ET)\(_2\)I\(_3\) is realized only under high-pressure \((P > 1.2\) GPa\) [30]. At ambient pressure and \(T_{MI} = 135\) K, \(\alpha\)-(ET)\(_2\)I\(_3\) shows a metal–insulator (MI) transition, which causes a charge ordering (CO) associated with the lack of inversion center, and the system turns to a nonmagnetic ferroelectric phase [31-39]. Further, the CO transition can be suppressed by applying pressure, and an anomalous electronic conducting phase including the massless Dirac electron system can be realized under high-pressure [15-17]. Although the quantum Hall effect [25], discrete Landau levels [26], and unscreened long-range Coulomb interactions [28,29] are observed under high-pressure in \(\alpha\)-(ET)\(_2\)I\(_3\), experimental determination of the detailed crystal structure and physical property measurements in the Dirac state are still limited.

To address the above-mentioned limitations, we searched for a bulk Dirac electron system at ambient pressure and found a promising candidate in the selenium-substituted analog of \(\alpha\)-(ET)\(_2\)I\(_3\), \(\alpha\)-(BETS)\(_2\)I\(_3\) \([\text{BETS} = \text{BETS-TSF} = \text{bis(ethylenedithio)tetrathiafulvalene}]\) [Fig. 2(b)], where the central four S atoms in the ET molecule were replaced with Se atoms. \(\alpha\)-(BETS)\(_2\)I\(_3\) shows a resistivity behavior similar to that of \(\alpha\)-(ET)\(_2\)I\(_3\), and the MI crossover temperature of \(\alpha\)-(BETS)\(_2\)I\(_3\) \(T_{MI} = 50\) K [40] is less than the CO transition temperature of \(\alpha\)-(ET)\(_2\)I\(_3\) [31]. As the temperature decreases from room temperature to low-temperature (LT), the magnetic susceptibility of \(\alpha\)-(BETS)\(_2\)I\(_3\) gradually decreases, and no anomaly is observed at \(T_{MI}\) [41]. These electronic properties are different from \(\alpha\)-(ET)\(_2\)I\(_3\), and the origin of the insulating state
in α-(BETS)$_2$I$_3$ has not been understood yet.

To verify the existence of the bulk Dirac electron system at ambient pressure, we investigate the crystal structures and electronic states of α-(BETS)$_2$I$_3$ by performing synchrotron x-ray diffraction (XRD) and $^{13}$C nuclear magnetic resonance (NMR) experiments. For our analyzed structure at LT, first-principles density-functional-theory (DFT) calculations are performed. Our results strongly suggest the existence of the bulk Dirac electron system in α-(BETS)$_2$I$_3$ at ambient pressure.

**Experiments.** XRD experiments were performed using a BL02B1 beamline at the synchrotron facility SPring-8 [42] in Japan. The dimensions of the α-(BETS)$_2$I$_3$ and α-(ET)$_2$I$_3$ crystals for the XRD experiments were $150 \times 150 \times 15 \, \mu m^3$ and $140 \times 90 \times 20 \, \mu m^3$, respectively. A helium-gas-blowing device was employed to cool the samples to 30 K. A 2D imaging-plate was used as the detector. The wavelength of the x-ray was 0.39054 Å to avoid energy at the $K$-edge absorption of iodine (0.3738 Å). For the crystal structural analysis, we used original software for extracting the diffraction intensity [43]. SORTAV [44] and Jana2006 [45,46] were used for diffraction intensity averaging and crystal structural analysis, respectively. Single crystal $^{13}$C NMR measurements were performed in a same way as the earlier report of α-(ET)$_2$I$_3$ [47]. The central double-bonded carbon atoms in BETS were selectively enriched with $^{13}$C isotope. An NMR spectrum was obtained by the fast Fourier transformation of the spin echo signal induced by a π/2-π pulse sequence. The assignment of each peak to the molecular site was performed as follows. First, we measured the NMR spectra in the $ab$-plane at metallic state and we found that the angular dependence of the peak positions is quite similar to that of α-(ET)$_2$I$_3$. This is reasonable because the molecular arrangements in the unit cell of α-(BETS)$_2$I$_3$ are similar to that of α-(ET)$_2$I$_3$. The peak assignments were easily done in the $ab$-plane. Then, we tilted the field direction to the $c$-axis from the $a$-axis with keeping the peak assignment. Temperature dependence of the NMR spectrum was obtained by the field direction $B \parallel c$ in which the chemical shift is reported to be sensitive to the fractional molecular charge in the case of α-(ET)$_2$I$_3$ [48]. The present first-principles DFT calculations [49,50] are based on the exchange-correlation functional of generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [51]. For scalar-relativistic calculations, Kohn–Sham equations are self-consistently solved using all-electron full-potential linearized augmented plane wave (FLAPW) method [52]. We also performed the calculations with a scheme based on plane waves and pseudopotentials generated with projected augmented wave (PAW) formalism [53], which was implemented in Quantum Espresso (Q.E.) 6.3 [54,55]. The dimensions of the $k$-point meshes used were $6 \times 6 \times 2$. The results of both the methods agree well. In addition, we performed nonmagnetic band structure calculations including the spin–orbit coupling (SOC) effect with full-relativistic pseudopotentials. Further, $Z_2$ topological invariants were calculated by using OpenMX code [56-58]. We summarized the detailed computational conditions in Supplemental Material (SM) [59].

**Result and discussion.** First, we investigated the crystal structure of α-(BETS)$_2$I$_3$ in the high-temperature (HT) phase at 80 K. To determine the bond length in the molecule (i.e., the amount of the molecular charge) with high accuracy, high-angle analysis, which is an effective method for the analysis of molecular crystals [60], was performed. The structural analysis shows that α-(BETS)$_2$I$_3$ and α-(ET)$_2$I$_3$ have similar crystal structures in the HT phase (Fig. 1(a)), and the space group is P1̅. Detailed analysis results are shown in SM [59]. There are four BETS molecules (i.e., molecule A, A’, B, and C) in a unit cell. Because there are inversion points at the center of the molecule A and A’, these two are crystallographically equivalent.

To investigate any potential change in symmetry at $T_M$, $^{13}$C NMR experiments were performed in α-(BETS)$_2$I$_3$. Figure 1(b) shows the NMR spectra for α-(BETS)$_2$I$_3$ at 100 K and 30 K obtained by the field direction $B \parallel c$. Maximum three doublets were observed even at 30 K. The splitting of the peak of the molecule A and A’ due to the lack of the inversion center, which was observed at $T_M$ of α-(ET)$_2$I$_3$ [48], is not observed in the LT phase of α-(BETS)$_2$I$_3$.

![Fig. 1. (a) Crystal structure of α-(BETS)$_2$I$_3$ in the bc-plane. (b) $^{13}$C NMR spectra for α-(BETS)$_2$I$_3$ at 100 K and 30 K. The external field of 7 T was applied parallel to the c-axis. The origin of the horizontal axis is zero-Knight shift frequency.](image)

In the LT phase of α-(BETS)$_2$I$_3$, additional superlattice reflections and/or splitting of the diffraction peaks were not confirmed from the XRD data. In addition, the lack of the inversion center was not confirmed at 30 K from the structural analysis (Fig. S2 [59]), which is consistent with the result of NMR measurement (Fig. 1(b)). Therefore, we conclude that the space group is P1̅ in the LT phase. Further, we discuss the temperature dependence of the charge amount based on the bond length in BETS in α-(BETS)$_2$I$_3$. To use as references, XRD experiments at SPring-8 and high-angle analysis were performed on α-(ET)$_2$I$_3$. Figure 2(c) shows the experimental evaluation
of the charge amount $Q$ of $\alpha$-(ET)$_2$I$_3$, which is calculated from the change in intra-molecular bond lengths corresponding to the C=C bonding and C–S antibonding orbitals [61]. The definition of $Q$ is given in the inset of Fig. 2(c). The charge amount $Q$ varied largely due to the MI transition with a lack of the inversion center. In the LT phase, molecule A' and B are hole-rich, and molecule A and C are hole-poor suggesting the existence of a horizontal-stripe-type CO state. This result is consistent with the results of several previous reports using infrared spectra [35], Raman spectra [36], NMR [37], XRD [38], and various theoretical calculations [33,34,62].

Next, in Fig. 2(d), we show the temperature dependence of the charge amount on each BETS molecule in $\alpha$-(BETS)$_2$I$_3$. Because a coefficient of $\delta$ (database) has not been reported for calculating the $Q$ value in BETS, a comparison is made using the $\delta$ value itself. For reference, Fig. 2(e) shows the temperature variation of $\delta$ for $\alpha$-(ET)$_2$I$_3$. For $\alpha$-(BETS)$_2$I$_3$, the amount of charge of BETS shows an insignificant change due to the MI crossover. The changes in bond length within BETS are less than 0.2% between 80 K and 30 K. Furthermore, the changes in the distance and angle between the BETS molecules are insignificant (Figs. S3 and S4 [59]). It implies that not only the symmetry but also the intra- and inter-molecular structures hardly change at the MI crossover of $\alpha$-(BETS)$_2$I$_3$.

In molecular solids, the valence and conduction bands, which control the physical properties, are made up of frontier orbitals of the constituent molecules [63]. Here, we focused on the valence electron density (VED) distribution to investigate the difference between $\alpha$-(ET)$_2$I$_3$ and $\alpha$-(BETS)$_2$I$_3$. The electron density (ED) analysis using a core differential Fourier synthesis (CDFS) method [60,64], which efficiently extracts only the valence electron contribution, was performed in these two compounds.

![Fig. 3](image.png)

FIG. 3. VED distribution of molecule A in $\alpha$-(ET)$_2$I$_3$ at (a) 150 K and (c) 30 K, and in $\alpha$-(BETS)$_2$I$_3$ at (b) 80 K and (d) 30 K, which are obtained from the CDFS analysis. These VED distributions are calculated by the XRD data in the limit $0 \, \text{Å}^{-1} \leq \sin \theta / \lambda \leq 0.5 \, \text{Å}^{-1}$. VED distributions of molecule A, obtained from the DFT calculations including SOC effect and semicore $d$ states, in (e) $\alpha$-(ET)$_2$I$_3$ and (f) $\alpha$-(BETS)$_2$I$_3$ using the present structural parameters at 30 K, respectively.

We compared the VED distributions of molecule A in $\alpha$-(ET)$_2$I$_3$ and $\alpha$-(BETS)$_2$I$_3$ as shown in Figs. 3(a)–3(d). Here, valence electrons of C, S, and Se constituting the ET and BETS molecules correspond to $2s^22p^2$, $3s^23p^4$, and $4s^24p^5$ configurations, respectively. The VED distributions of molecule A', B, and C were approximately identical to that of molecule A in real space (Figs. S6–S8 [59]). In the HT phase, differentiating the contribution of the thermal vibrations from the VED is difficult due to the large temperature contribution factor. Indeed, the VED distribution of ET at 150 K is blurred [Fig. 3(a)]. However, relatively localized VED distributions are observed at 80 K [Fig. 3(b)] and 30 K [Figs. 3(c) and 3(d)]. There is a trade-off between the resolution of XRD data and the statistical error of the weak reflection intensity. We confirmed the reliability of the VED distributions by changing the resolution (Fig. S9 [59]).

The change in the VED is observed between the CDFS analysis results at 80 K and 30 K [Figs. 3(b) and 3(d)]. The ED around Se sites is higher in the LT phase than in
the HT phase although there is no significant change in the structural parameters at the MI crossover. Comparing ET and BETS molecules at 30 K, the ED near the C=C bonds in BETS is higher than that in ET. Furthermore, although the number of valence electrons is the same (6e per atom), the VED around Se sites in BETS [Fig. 3(c)] is higher than that around S sites near the center in ET [Fig. 3(d)]. These results indicate that the VED is more localized in BETS than in ET.

To evaluate the importance of the difference between the VED distributions of the ET and BETS molecules observed by the CDFS analysis, we performed first-principles DFT calculations for the experimental structures considering the SOC. Figures 3(e) and 3(f) show the VED distributions of ET and BETS molecules in crystalline solids, respectively. These 2D ED maps show the all-electron valence charge density, which is calculated from pseudopotentials based on the PAW method, where the valence electron configuration of Se and I atoms are set to be $4s^24p^53d^0$ and $5s^25p^54d^0$, respectively. Therefore, Fig. 3(f) includes the contribution of semicore $d$ states in Se and I atoms. The calculated VED distributions agree well with the experimental results for the differences between the ET and BETS molecules [Figs. 3(c) and 3(d)].

(Fig. 4) First-principles DFT calculated band structure and (b) LDOS of $\alpha$-(BETS)$_2$I$_3$ in the LT phase (30 K) (without the SOC effect calculated with the FLAPW method). The dashed horizontal line at the origin shows the $E_F$. Green, red, and blue solid curves indicate the LDOS of molecule A, B, and C, respectively. (c) Band dispersion seen from two directions close to the Dirac cone on the $\mathbf{k} = (k_x, k_y, 0)$ plane, where a pair of Dirac points are located at $\mathbf{k} = (\pm 0.2958, \mp 0.3392, 0)$.

Figures 4(a) and 4(b) show a calculated band structure and local density of states (LDOS) of $\alpha$-(BETS)$_2$I$_3$ at 30 K without the SOC effect. We find the Dirac cones at general $k$-points of $(\pm 0.2958, \mp 0.3392, 0)$, not at high symmetric points. No over-tilting of the Dirac cones is observed in Fig. 4(c). Near the $E_F$ in Fig. 4(b), the variations in DOSs of molecule A and C, which have a steep downward slope toward the $E_F$, are similar. On the other hand, the DOS of molecule B has a relatively gentle downward slope near the $E_F$. These trends of the DOSs of $\alpha$-(BETS)$_2$I$_3$ near the $E_F$ are similar to those of $\alpha$-(ET)$_2$I$_3$ at high-pressure [62].

Within the no SOC limit, massless Dirac electron system is realized where two linear bands intersect at the $E_F$ (the Dirac points are located at the $E_F$) [Fig. 5(a)]. However, with the SOC, we observe a finite (indirect) energy gap of ~2 meV around the Dirac points, and the $E_F$ is located inside the energy gap as plotted in Fig. 5(b). This insulator band dispersion is consistent with the increase in the electrical resistivity below $T_{MI} = 50$ K [40] and the decrease in the magnetic susceptibility with decrease in temperature from room temperature [41]. Therefore, the insulating mechanism of $\alpha$-(BETS)$_2$I$_3$ is quite different from that of $\alpha$-(ET)$_2$I$_3$ showing the structural phase transition associated with CO [38]. However, because the energy gap of this system is quite small, unique physical properties, such as the massless Dirac electron system, are expected.

Barring a few reports [65-68], the SOC has been mostly ignored in theoretical studies for molecular solids because most of them are composed of light elements. However, we observe that the SOC critically changes low-energy band structure from massless Dirac electron system to a small band gap insulator in the present system. In addition, we calculate $Z_2$ topological invariants from first-principles for bulk $\alpha$-(BETS)$_2$I$_3$ with the experimental structure at 30 K using the parity eigenvalues at the time-reversal invariant momenta [69] and the parity method [10] implemented in OpenMX code [70]. We confirm that the calculated topological invariants ($\nu_1, \nu_2, \nu_3$) are (0, 0, 0) indicating a weak topological insulator.

In addition, to investigate whether the noncentrosymmetric CO phase in $\alpha$-(ET)$_2$I$_3$ is a topological insulating state, we calculate $Z_2$ topological invariant [69] for the experimental structure of $\alpha$-(ET)$_2$I$_3$ at 30 K using the Fukui-Hatsugai method [71] implemented in OpenMX code [72]. The calculated topological invariant for the CO phase is $Z_2 = 0$ implying a trivial insulator phase. On the other hand, the topological invariant for the HT phase with centrosymmetric structure is $Z_2 = 1$ which indicates a topological semimetal phase [73]. These results suggest that the $Z_2$ topological phase transition occurs in $\alpha$-(ET)$_2$I$_3$ associated with the CO phase transition. We summarized the detailed computational conditions in SM [59].

As discussed above, our study of $\alpha$-(BETS)$_2$I$_3$ reveals that the crystal structure, differently from $\alpha$-(ET)$_2$I$_3$, is centrosymmetric even at 30 K, and the energy bands are
Kramers degenerate. Moreover, the degeneracies are removed by the SOC, resulting in an energy gap of ~2 meV near the Dirac points. Thus, spin–orbit interaction converts \( \alpha \)-\((\text{BETS})_2\)I from a zero-gap massless Dirac electron system to a weak topological insulator. This phenomenon is similar to that occurring in graphene which has smaller energy gap than \( \alpha \)-\((\text{BETS})_2\)I resulting from the SOC \((-0.8 \times 10^{-3} \text{ meV})\) [74]. Thus, as in graphene [2] and surface states of topological insulators, quantum spin Hall effect is also expected in \( \alpha \)-\((\text{BETS})_2\)I.

![Band dispersion of \( \alpha \)-\((\text{BETS})_2\)I along \((-0.2995, 0)\) line (a) without SOC and (b) with SOC near the \( E_F \) calculated with Q.E. code. In (b), the zero energy is at the top of the valence bands.](image)

In summary, we studied the precise crystal and electronic structures of \( \alpha \)-\((\text{BETS})_2\)I at ambient pressure. No significant change in the lattice system was observed at \( T_{MI} \) of \( \alpha \)-\((\text{BETS})_2\)I, and the inversion center remained even in the LT phase. The bulk Dirac electron system was realized at ambient pressure in \( \alpha \)-\((\text{BETS})_2\)I. Further, the insulating mechanism in this system could be explained by the energy gap caused by the SOC. However, because the energy gap is very small, the unique physical properties, such as the massless Dirac state, are expected. Our results have the potential to contribute significantly in the study of the Dirac electron system. In the near future, experimental results based on our expectations will be reported.

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Supplemental Material for

Ambient pressure Dirac electron system in quasi-two-dimensional molecular conductor \( \alpha\)-(BETS)\(_2\)I\(_3\)

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1. Crystal structural analysis

The results of the crystal structural analysis of \(\alpha\)-(ET)\(_2\)I\(_3\) and \(\alpha\)-(BETS)\(_2\)I\(_3\) are shown in Fig. S1 and Table S1–S4.

FIG. S1. Results of the crystal structural analysis (high-angle analysis) of (a) \(\alpha\)-(ET)\(_2\)I\(_3\) at 30 K and (b) \(\alpha\)-(BETS)\(_2\)I\(_3\) at 30 K using only high-angle reflections (0.5 Å\(^{-1}\) ≤ sin \(\theta\) /\(\lambda\) ≤ 1.42 Å\(^{-1}\)). \(|F_c(hkl)|^2 - |F_o(hkl)|^2\) plots are shown as a double logarithmic. Here, \(F_o(hkl)\) is the experimentally observed crystal structure factor, and \(F_c(hkl)\) is the calculated crystal structure factor. The number of reflections is (a) 90754 and (b) 65572, respectively.
Table S1. Summary of crystallographic data of α-(ET)$_2$I$_3$ at the high-temperature phase.

| Chemical Formula       | C20 H16 I3 S16          |
|------------------------|--------------------------|
| Temperature (K)         | 150                      |
| Wavelength (Å)          | 0.39054                  |
| Crystal dimension (µm$^3$) | 140 × 90 × 20            |
| Space group             | P 1                      |
| $a$ (Å)                 | 9.0983(18)               |
| $b$ (Å)                 | 10.724(2)                |
| $c$ (Å)                 | 17.388(4)                |
| $\alpha$ (°)           | 96.654(7)                |
| $\beta$ (°)            | 97.961(7)                |
| $\gamma$ (°)           | 90.864(8)                |
| $V$ (Å$^3$)             | 1668.0(6)                |
| $Z$                     | 2                        |
| $F$ (000)               | 1102                     |
| (sinθ/λ)$_{\text{Max}}$ (Å$^{-1}$) | 1.42               |
| $N_{\text{Total,obs}}$ | 193468                   |
| $N_{\text{Unique,obs}}$ | 63054                    |
| Average redundancy      | 3.1                      |
| Completeness            | 0.775                    |

High-angle analysis [$0.5$ Å$^{-1}$ ≤ sin θ / λ ≤ 1.42 Å$^{-1}$] ($N_{\text{Parameters}} = 229$)

- $R_1$ [# of reflections] = 0.1485 [44887]
- $R_1$ ($I > 1.5\sigma$) [# of reflections] = 0.0604 [22589]
- GOF [# of reflections] = 1.04 [44887]

Normal analysis [$0$ Å$^{-1}$ ≤ sin θ / λ ≤ 1.42 Å$^{-1}$] ($N_{\text{Parameters}} = 0$)

- $R_1$ [# of reflections] = 0.1131 [48039]
- $R_1$ ($I > 3\sigma$) [# of reflections] = 0.0328 [19805]
- GOF [# of reflections] = 1.07 [48039]
Table S2. Summary of crystallographic data of α-(ET)$_2$I$_3$ at the low-temperature phase.

| Parameter                                      | Value                                      |
|------------------------------------------------|--------------------------------------------|
| Chemical Formula                               | C20 H16 I3 S16                             |
| Temperature (K)                                | 30                                         |
| Wavelength (Å)                                 | 0.39054                                    |
| Crystal dimension (µm$^3$)                     | 140 × 90 × 20                              |
| Space group                                    | P1                                         |
| $a$ (Å)                                        | 9.0352(2)                                  |
| $b$ (Å)                                        | 10.6734(2)                                 |
| $c$ (Å)                                        | 17.3547(12)                                |
| $\alpha$ (°)                                   | 96.541(7)                                  |
| $\beta$ (°)                                    | 97.752(7)                                  |
| $\gamma$ (°)                                   | 91.216(6)                                  |
| $V$ (Å$^3$)                                     | 1646.40(13)                                |
| $Z$                                            | 2                                          |
| $F$ (000)                                      | 1102                                       |
| $(\sin \theta/\lambda)_{\text{Max}}$ (Å$^{-1}$) | 1.42                                       |
| $N_{\text{Total,obs}}$                        | 327060                                     |
| $N_{\text{Unique,obs}}$                       | 130278                                     |
| Average redundancy                             | 2.5                                        |
| Completeness                                   | 0.810                                      |
| High-angle analysis $[0.5 \text{ Å}^{-1} \leq \sin \theta /\lambda \leq 1.42 \text{ Å}^{-1}]$ ($N_{\text{Parameters}} = 347$) |  |
| $R_1$ [$\#$ of reflections]                   | 0.0522 [90754]                             |
| $R_1$ ($I > 1.5\sigma$) [$\#$ of reflections] | 0.0353 [74900]                             |
| GOF [$\#$ of reflections]                     | 0.88 [90754]                               |
| Normal analysis $[0. \text{ Å}^{-1} \leq \sin \theta /\lambda \leq 1.42 \text{ Å}^{-1}]$ ($N_{\text{Parameters}} = 0$) |  |
| $R_1$ [$\#$ of reflections]                   | 0.0465 [97167]                             |
| $R_1$ ($I > 3\sigma$) [$\#$ of reflections]   | 0.0268 [70334]                             |
| GOF [$\#$ of reflections]                     | 0.91 [97167]                               |
Table S3. Summary of crystallographic data of $\alpha$-(BETS)$_2$I$_3$ at the high-temperature phase.

| Chemical Formula | C20 H16 I3 S8 Se8 |
|------------------|--------------------|
| Temperature (K)  | 80                 |
| Wavelength (Å)   | 0.39054            |
| Crystal dimension ($\mu$m$^3$) | 150 × 150 × 15 |
| Space group      | P1                 |
| $a$ (Å)          | 9.0996(2)          |
| $b$ (Å)          | 10.7301(2)         |
| $c$ (Å)          | 17.7313(12)        |
| $\alpha$ (°)     | 96.356(7)          |
| $\beta$ (°)      | 97.739(7)          |
| $\gamma$ (°)     | 90.777(6)          |
| $V$ (Å$^3$)      | 1704.25(13)        |
| $Z$              | 2                  |
| $F$ (000)        | 1390               |
| $(\sin\theta/\lambda)_{\text{Max}}$ (Å$^{-1}$) | 1.42 |
| $N_{\text{Total,obs}}$ | 205480           |
| $N_{\text{Unique,obs}}$ | 73729           |
| Average redundancy | 2.8              |
| Completeness     | 0.886              |

High-angle analysis [$0.5$ Å$^{-1}$ ≤ $\sin \theta / \lambda$ ≤ 1.42 Å$^{-1}$] ($N_{\text{Parameters}} = 229$)

| $R_1$ [# of reflections] | 0.0751 [54921] |
| $R_1$ ($I > 1.5\sigma$) [# of reflections] | 0.0409 [38378] |
| GOF [# of reflections] | 0.94 [54921] |

Normal analysis [$0$ Å$^{-1}$ ≤ $\sin \theta / \lambda$ ≤ 1.42 Å$^{-1}$] ($N_{\text{Parameters}} = 0$)

| $R_1$ [# of reflections] | 0.0646 [58389] |
| $R_1$ ($I > 3\sigma$) [# of reflections] | 0.0274 [34639] |
| GOF [# of reflections] | 0.95 [58389] |
Table S4. Summary of crystallographic data of α-(BETS)$_2$I$_3$ at the low-temperature phase.

|                           | C20 H16 I3 S8 Se8 |
|---------------------------|-------------------|
| Chemical Formula          |                   |
| Temperature (K)           | 30                |
| Wavelength (Å)            | 0.39054           |
| Crystal dimension (µm$^3$)| 150 × 150 × 15    |
| Space group               | P1                |
| a (Å)                     | 9.0922(2)         |
| b (Å)                     | 10.7221(2)        |
| c (Å)                     | 17.7377(12)       |
| α (°)                     | 96.310(7)         |
| β (°)                     | 97.706(7)         |
| γ (°)                     | 90.794(6)         |
| V (Å$^3$)                 | 1702.49(13)       |
| Z                         | 2                 |
| F (000)                   | 1390              |
| (sinθ/λ)$_{Max}$ (Å$^{-1}$)| 1.42              |
| N$_{Total,obs}$           | 353053            |
| N$_{Unique,obs}$          | 77235             |
| Average redundancy        | 4.6               |
| Completeness              | 0.929             |
| High-angle analysis [0.5 Å$^{-1}$ ≤ sin θ / λ ≤ 1.42 Å$^{-1}$] (N$_{Parameters}$ = 229) |
| $R_1$ [# of reflections]  | 0.0554 [65572]    |
| $R_1$ (I > 1.5σ) [# of reflections] | 0.0359 [51466]    |
| GOF [# of reflections]    | 1.03 [65572]      |
| Normal analysis [0 Å$^{-1}$ ≤ sin θ / λ ≤ 1.42 Å$^{-1}$] (N$_{Parameters}$ = 0) |
| $R_1$ [# of reflections]  | 0.0505 [69116]    |
| $R_1$ (I > 3σ) [# of reflections] | 0.0274 [47938]    |
| GOF [# of reflections]    | 1.06 [69116]      |
Figure S2 shows the difference in intensities of the Friedel pairs \( I(hkℓ) \) and \( I(\overline{hkℓ}) \). In \( α-(ET)_2I_3 \) at 30 K, there is no inversion center. In this case, when comparing the intensities of the Friedel pairs for \( |F_o|^2 (α I) \) and \( |F_c|^2 \) [Fig. S2(b)], \( |F_o(hkℓ)|^2 - |F_o(\overline{hkℓ})|^2 \) and \( |F_c(hkℓ)|^2 - |F_c(\overline{hkℓ})|^2 \) has a positive correlation, whose slope is \(~1\). This result indicates the lack of the inversion center, i.e., the space group is \( P1 \). When the result of \( |F_o(hkℓ)|^2 - |F_o(\overline{hkℓ})|^2 \) at 150 K is plotted using the \( |F_c(hkℓ)|^2 - |F_c(\overline{hkℓ})|^2 \) at 30 K on the horizontal axis [Fig. S2(a)], the slope is almost zero, which indicates the existence of the inversion center, i.e., the space group is \( P1 \). We applied this analogy to \( α-(BETS)_2I_3 \). When the crystal structural analysis of \( α-(BETS)_2I_3 \) at 30 K was performed assuming \( P1 \) [Fig. S2(d)], we found that the slope was almost zero. This result indicates that the inversion center exists in the low-temperature phase, which is consistent with the result of the \( ^{13}C \) NMR experiment [Fig. 1(b)].

FIG. S2. Difference in intensities of the Friedel pairs. \( |F_c|^2 \) in (a) and (b) is the result of the crystal structural analysis of \( α-(ET)_2I_3 \) at 30 K, in which \( P1 \) (no inversion) is assumed for the space group. \( |F_c|^2 \) in (c) and (d) is the result of the crystal structural analysis of \( α-(BETS)_2I_3 \) at 30 K, in which \( P1 \) (no inversion) is assumed for the space group. In these figures, only reflections which have the intensity of less than 0.25% of the maximum intensity are plotted.
Figures S3 and S4 show the results of the crystal structural analysis of $\alpha$-(BETS)$_2$I$_3$ at 80 K and 30 K. The inter-molecular distances in the $a$-axis direction hardly changed between 80 K and 30 K (the ratio of change is 0.16% or less) (Fig. S3). The angles between the BETS molecules also hardly changed between 80 K and 30 K (Fig. S4). As a reference, the results of $\alpha$-(ET)$_2$I$_3$ at 150 K and 30 K are shown in a dotted box in Fig. S4.

FIG. S3. Distances between the BETS molecules in $\alpha$-(BETS)$_2$I$_3$ at 80 K and 30 K.
FIG. S4. Angles between the BETS molecules in $\alpha$-(BETS)$_2$I$_3$ at 80 K and 30 K. The plane through which central ten atoms (six C and four Se) in BETS pass was calculated by the method of least squares. The angle between two planes was calculated from the normal vectors $\mathbf{n}$ of the planes.

$$\cos \theta_{BC} = \mathbf{n}_B \cdot \mathbf{n}_C$$

($|\mathbf{n}_B| = |\mathbf{n}_C| = 1$)

$\theta_{BC}(80 \text{ K}) = 12.545^\circ$

$\theta_{BC}(30 \text{ K}) = 12.521^\circ$

$\begin{array}{|c|c|c|}
\hline
\text{cf.) } \alpha-(ET)_2$I$_3$ & \hline
\theta_{AA'}(150 \text{ K}) = 0^\circ & \theta_{BC}(150 \text{ K}) = 12.387^\circ \\
\theta_{AA'}(30 \text{ K}) = 1.969^\circ & \theta_{BC}(30 \text{ K}) = 13.179^\circ \\
\hline
\end{array}$
2. Electron density analysis

To investigate the valence electron density (VED) distribution in \( \alpha-(\text{ET})_2\text{I}_3 \) and \( \alpha-(\text{BETS})_2\text{I}_3 \), we performed the electron density analysis using the core differential Fourier synthesis (CDFS) method [S1]. The equation of the inverse Fourier transform by the CDFS method is described as

\[
\rho_v(r) = \frac{1}{V} \sum_k \left[ \left( |F_o(K)| - \sum_i f_i^{\text{core}} T_i e^{-i\mathbf{K} \cdot \mathbf{r}_i} \right) P e^{i\mathbf{K} \cdot \mathbf{r}} \right] + \frac{n_v}{V}.
\]  

(S1)

Here, \( \rho_v(r) \) corresponds the VED, \( V \) is the cell volume, \( \mathbf{r}_j \) is the \( j \)th atomic position, \( T_j \) is the \( j \)th atomic displacement parameter. \( f_j^{\text{core}} \) is the \( j \)th atomic scattering factor with only the core electrons contribution [S2,S3], which corresponds to the blue line in Fig. S5. \( P \) is the phase term, which is calculated as \( P = F_c(K) / |F_o(K)| \). \( n_v \) is the total number of valence electrons contained in the unit cell. It is noted here that the 000 Bragg reflection intensity cannot be observed experimentally. When ignoring the second term \( n_v/V \), the total number of electrons in the unit cell becomes zero. Therefore, the VED distribution data is corrected by adding the \( n_v/V \) term.

![Diagram](image)

FIG. S5. (a) Electron configurations of C, S, and Se. Atomic scattering factor of (b) C, (c) S, and (d) Se [S3]. Black, blue, and orange lines indicate the contribution of the total, core, and valence electrons, respectively.

Figures S6 and S7 show the VED distributions of molecule B and C, respectively. Figure S8 shows the difference between the VED distributions of molecule A (hole-poor) and A’ (hole-rich) in \( \alpha-(\text{ET})_2\text{I}_3 \) at 30 K, where there are no clear differences in the electron density distribution. Figure S9 shows the VED distributions calculated by the diffraction data with the different \((\sin \theta / \lambda)_{\text{max}}\) range corresponding to the real space resolution \( d (= \lambda / 2 \sin \theta) \). These VED distributions are qualitatively the same regardless of the resolution, but especially in Fig. S9(c), the electron density appears to be disturbed due to the influence of high-angle reflections, whose intensities are weak (bad S/N ratio).
FIG. S6. VED distribution on of molecule B in (a) $\alpha$-(ET)$_2$I$_3$ at 30 K, and in (b) $\alpha$-(BETS)$_2$I$_3$ at 30 K, which are obtained from the CDFS analysis. These VED distributions are calculated by the diffraction data in the limit $0 \, \text{Å}^{-1} \leq \sin \theta / \lambda \leq 0.5 \, \text{Å}^{-1}$. VED distribution of molecule B in (c) $\alpha$-(ET)$_2$I$_3$ and (d) $\alpha$-(BETS)$_2$I$_3$, which are obtained from the DFT calculations (with spin-orbit coupling effect and semicore $d$ states) using the present structural parameters at 30 K, respectively.

FIG. S7. VED distribution on of molecule C in (a) $\alpha$-(ET)$_2$I$_3$ at 30 K, and in (b) $\alpha$-(BETS)$_2$I$_3$ at 30 K, which are obtained from the CDFS analysis. These VED distributions are calculated by the diffraction data in the limit $0 \, \text{Å}^{-1} \leq \sin \theta / \lambda \leq 0.5 \, \text{Å}^{-1}$. VED distribution of molecule C in (c) $\alpha$-(ET)$_2$I$_3$ and (d) $\alpha$-(BETS)$_2$I$_3$, which are obtained from the DFT calculations (with spin-orbit coupling effect and semicore $d$ states) using the present structural parameters at 30 K, respectively.
FIG. S8. Difference of the experimental VED distributions between (a) molecule A (hole-poor) and (b) molecule A’ (hole-rich) in α-(ET)$_2$I$_3$ at 30 K. These VED distributions are calculated by the diffraction data in the limit $0 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 0.5 \text{ Å}^{-1}$.

FIG. S9. VED distribution obtained by the CDFS analysis in α-(BETS)$_2$I$_3$ at 30 K, which are calculated by the diffraction data in the limit (a) $0 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 0.5 \text{ Å}^{-1}$, (b) $0 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 1 \text{ Å}^{-1}$, and (c) $0 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 1.42 \text{ Å}^{-1}$, respectively.
3. Computational details for electronic structures

The band structures shown in Fig. 4 are calculated by first-principles density functional theory within the generalized gradient approximation (GGA) to the exchange-correlation functional proposed by PBE [S4]. Kohn-Sham equations are self-consistently solved in a scalar-relativistic fashion using the all-electron full-potential linearized augmented plane wave (FLAPW) method implemented in the QMD-FLAPW12 code [S5-S7]. The LAPW basis functions in the interstitial region have a cutoff energy of 20.3 Ry. The angular momentum expansion inside the muffin-tin (MT) sphere is truncated at $l = 8$ for all the atoms. The cutoff energy for the potential and density is 282 Ry. The MT sphere radii are set as 1.26, 0.75, 2.00, and 2.27 Bohr for C, H, S, and Se atoms, respectively. The electronic states up to C ($2s^2, 2p^6$), S ($3s^2, 3p^6$), and I ($4d^{10}$) are treated as core electrons, which are predominantly confined to the MT spheres. $k$-point meshes used are 6 × 6 × 2 for both self-consistent field and the density of states (DOS) calculations. The local density of states (LDOS) shown in Fig.4(b) are obtained as a summation of projected DOS on C $p$, S $p$, and Se $p$ states in the respective monomer units. We used a high-dense $k$-mesh for plotting the 3D band structures shown in Fig.4(c).

The band structure calculations are also performed using the pseudopotential method based on the projector augmented wave (PAW) formalism [S8] with plane wave basis sets implemented in the Quantum Espresso (version 6.3) [S9]. The results of the scalar relativistic calculations are fairly in agreement with each other. The cutoff energies for plane waves and charge densities are set to be 55 (48) and 488 (488) Ry in the scalar (full) relativistic calculations, respectively. We used $4 \times 4 \times 2$ uniform $k$-point mesh with a gaussian smearing method during self-consistent loops. In both scalar and full relativistic pseudopotentials, the valence configurations of the pseudopotentials are C: ($2s^2, 2p^6$), H: ($1s^1$), S: ($3s^2, 3p^4$), Se: ($4s^2, 4p^4, 3d^{10}$), and I: ($5s^2, 5p^5, 4d^{10}$). The pseudopotentials are generated using "atomic" code by A. Dal Corso v.6.3 [S10], where the pseudization algorithm proposed by Troullier and Martins [S11] and non-linear core correction [S12] are used.

4. Computational details for $Z_2$ topological invariants

The density functional calculations of $Z_2$ topological invariants are performed by computing parity eigenvalues and Fukui-Hatsugai method using OpenMX code [S13]. The computational details are summarized in Table S5. We used GGA-PBE as the exchange correlation functional [S4]. We adapt norm-conserving pseudopotentials with an energy cutoff of 300 Ry for the charge density, including the 2$s$ and 2$p$-states as states for C; 1$s$ for H; 5$s$ and 5$p$ for I; 3$s$ and 3$p$ for S; 4$s$ and 4$p$ for Se. The wavefunctions were expanded by the linear combination of numerical pseudoatomic orbitals [S14,S15]. Spin-orbit interactions were included by a fully relativistic $j$-dependent pseudopotential, where $j$ is the total angular momentum. The numerical pseudo atomic orbitals are as follows: the numbers of the $s$, $p$, and $d$-character orbitals are 2, 2, and 1, respectively, for C, S, and Se; 2, 1, and 0, respectively, for H; 2, 2, and 2, respectively, for I. The cutoff radii of C, S, Se, H, and I are 5.0, 7.0, 7.0, 5.0, and 5.0, respectively, in units of Bohr. The regular $k$-point mesh $7 \times 7 \times 7$ was used for self-consistent field calculations. The $20 \times 20$
A $k$-point mesh for four independent two-dimensional tori was used for computing $Z_2$ topological invariants by Fukui-Hatsugai method [S16].

Table S5. The computational details for the $Z_2$ topological invariants

| Atom | Basis set | Cutoff radius (Bohr) |
|------|-----------|----------------------|
| C    | $s^2p^3d^1$ | 5.0                  |
| H    | $s^2p^1$    | 5.0                  |
| I    | $s^2p^2d^2$ | 5.0                  |
| S    | $s^2p^2d^2$ | 7.0                  |
| Se   | $s^3p^3d^1$ | 7.0                  |

$k$-space sampling points for self-consistent field calculations

| Cutoff energy |
|---------------|
| 300 Ry        |

$k$-space sampling points for Fukui-Hatsugai method

| 20 $\times$ 20 $\times$ 1 |

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