

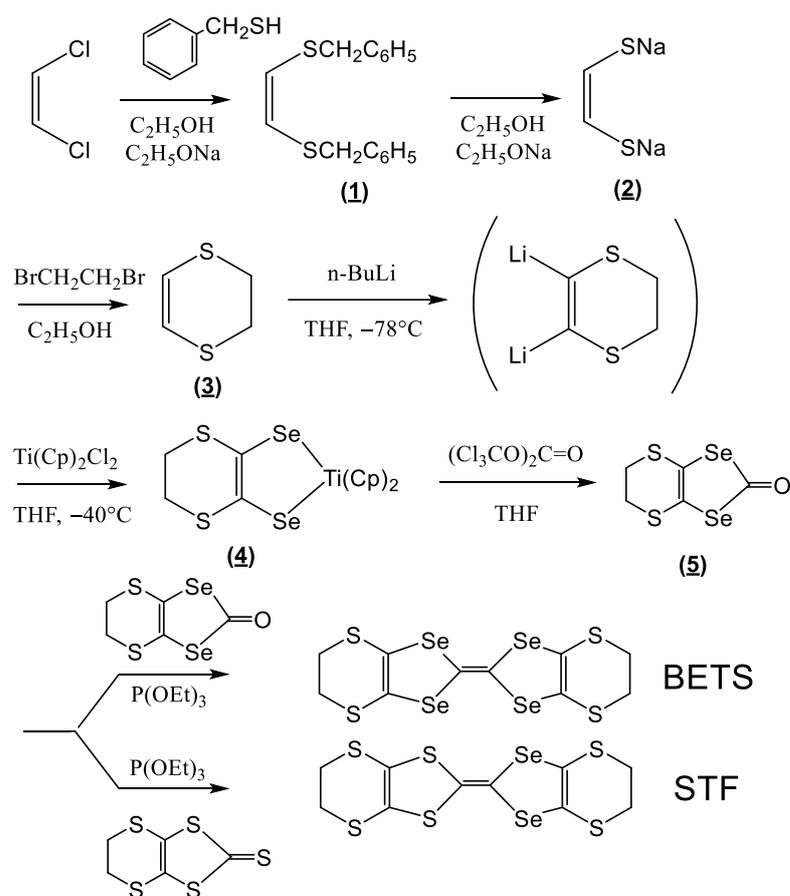
# Band structure evolution during reversible interconversion between Dirac and standard fermions in organic charge-transfer salts

## Electronic Supplementary Information

### 1. Sample Preparation

As stated in the main text, the sample preparation methods are reported previously for each compound (the neutral donor molecules and their CT salts) by independent groups from that of the present study. However, some of the detailed information on the syntheses of BETS and STF are not available in the previous papers. Thus, we describe the details here with citation of the previous papers. The reference numbers are identical with those in the main text.

### 1.1. Syntheses of neutral BETS and STF [45-47]



**Scheme S1.** Syntheses of neutral BETS and STF.

All syntheses were performed under inert ( $\text{N}_2$ ) atmosphere. The reagents were purchased in the purest grade available from the suppliers indicated and used as received unless noted otherwise. All solvents were sufficiently degassed (10–50 min depending on the volume and type of the solvents) in the dropping funnel with  $\text{N}_2$  prior to the addition to the reaction mixtures. UV-vis, IR, NMR, and mass spectra were recorded using a UV-Visible spectrophotometer V-630 (JASCO) with a temperature controller ETC-717 (JASCO), an FT-IR FT-720 (HORIBA) using a transmittance mode ( $400\text{--}4000\text{ cm}^{-1}$ ) and KBr disks or Nicolet iS5 FT-IR spectrometer with iD5 (Thermo Scientific) using an attenuated total reflection (ATR) mode ( $525\text{--}4000\text{ cm}^{-1}$ ) and a diamond crystal window, a Biospin AVANCE III 500 spectrometer (Bruker), and a JMS-700V (JEOL), respectively. Some compounds were unstable during the KBr pellets preparation, the IR spectra were measured in the ATR mode using the neat samples. For the peak wavenumbers of the IR spectra below, (w), (m), (s) indicate weak, medium, and strong absorption peaks, respectively.

#### 1.1.1. Preparation of (1) ( $\text{C}_{16}\text{H}_{16}\text{S}_2 = 272.428$ )

In a three-necked flask (1 L) equipped with a dropping funnel (500 mL), a condenser with a three-way valve on the top, a stopcock, and a magnetic stirring bar, sodium ethoxide was prepared by dissolving sodium metal (9.48 g; 0.41 mol; Wako Pure Chemicals) in absolute ethanol (380 mL; Wako Pure Chemicals). Then, benzyl mercaptan (50 g; 0.40 mol; Tokyo Chemical Industry Co., Ltd.) and *cis*-dichloroethylene (19.62 g; 0.20 mol; Sigma-Aldrich) each dissolved in absolute ethanol (210 mL) were added in the sodium ethoxide solution in this order. The mixture was refluxed for 19 h, then filtered. The colorless fine powder (NaCl) was washed with a minimum amount of hot ethanol, which was combined with the filtrate. Thus obtained reddish orange solution was stood for an hour at  $-40^\circ\text{C}$ . The colorless precipitates were filtered, washed with a small amount of cold ethanol,

filtered with suction, and dried in vacuo. The crude product was used in the synthesis of **(2)**. Yield: 34 g (62%).

UV (C<sub>2</sub>H<sub>5</sub>OH, 20°C)  $\lambda_{\text{max}}/\text{nm}$  ( $\log(\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1})$ ) = 259 (3.95)

IR (ATR; cm<sup>-1</sup>): 563(w), 578(w), 658(s), 695(s), 717(m), 761(m), 770(m), 815(s), 879(m), 1068(m), 1147(w), 1159(w), 1181(w), 1200(w), 1242(s), 1304(m), 1418(s), 1451(s), 1491(s), 1549(s), 2926(w), 2959(w), 3023(s), 3057(w), 3079(w).

#### 1.1.2. Preparation of **(2)** (C<sub>2</sub>H<sub>2</sub>S<sub>2</sub>Na<sub>2</sub> = 136.156)

In a three-necked flask (1 L) equipped with a dropping funnel (500 mL), a condenser with a three-way valve on the top, a stopcock, and a magnetic stirring bar, containing **(1)** (17.0 g; 0.062 mol) and sodium metal (10.24 g; 0.45 mol), absolute ethanol (80 mL) was added, and the reaction mixture was carefully stirred. A vigorous reaction immediately began, and the mixture was left to reflux without heating for a few minutes. When the reaction mixture was almost solidified, additional ethanol (80 mL) was added. After the vigorous reaction was slightly depressed (~ 10 min from the initial addition of ethanol), the reaction mixture was heated with an oil bath, which was kept 100°C in advance, to keep the reflux until the sodium metal pieces completely reacted to dissolve in the ethanol solution (~30 min). Then the mixture was left to slowly cool down to the room temperature in the oil bath (~2 h). Then, toluene (89 mL; Wako Pure Chemicals) was added and stirred for a few minutes. The colorless fine powder was filtered using a glass filter (G4) under purged N<sub>2</sub> gas, washed firstly with a mixed solvent of toluene:ethanol (2:1), then with ether, and dried in vacuo. Yield: 6.2 g (73%).

**(2)** was extremely unstable under air and moisture, and thus used in the next step of the synthesis without characterization or purification.

#### 1.1.3. Preparation of **(3)** (C<sub>4</sub>H<sub>6</sub>S<sub>2</sub> = 118.236)

In a three-necked flask (1 L) equipped with a dropping funnel (500 mL), a condenser with a three-way valve on the top, a stopcock, and a magnetic stirring bar, **(2)** (19.0 g; 0.14 mol) was dissolved in absolute ethanol (320 mL) as much as possible. 1,2-dibromoethane (39.3 g; 0.21 mol; Wako Pure Chemicals) dissolved in absolute ethanol (130 mL) was added, and the reaction mixture was stirred. A mild exothermic reaction commenced to yield pale brown suspension with colorless precipitates (NaBr fine powder). The reaction mixture was stirred firstly at room temperature overnight, then at 40–50°C for an hour. Then the reaction mixture was poured into the water (1.5 L) to yield suspension, which was extracted with diethyl ether (Wako Pure Chemicals) several times. The combined organic layer was washed with water and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> overnight. Then the ether was evaporated, and the residual oil was distilled under reduced pressure to obtain **(3)** (b.p. = 99°C (26 mmHg)) as pale yellow to colorless oil. Yield: 4.5 g (28%)

Elemental Analysis (%; calcd./found) : C (40.64/40.16), H (5.12/5.06), S (54.25/53.75)

UV (n-hexane, 20°C)  $\lambda_{\text{max}}/\text{nm}$  ( $\log(\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1})$ ) = 282 (3.59), 208 (3.70)

IR (liquid film between KBr disks; cm<sup>-1</sup>): 648(s), 684(s), 812(s), 885(s), 920(m), 995(w), 1125(m), 1158(m), 1190(w), 1252(m), 1287(s), 1322(w), 1416(s), 1550(s), 1627(w), 2817(w), 2918(s), 2961(m), 3026(s).

#### 1.1.4. Preparation of **(4)** (C<sub>14</sub>H<sub>14</sub>S<sub>2</sub>Se<sub>2</sub>Ti = 452.202)

In a three-necked flask (1 L) equipped with two dropping funnels (500 mL and 100 mL), a three-way valve, and a magnetic stirring bar, diisopropyl amine (3.30 g; 0.033 mol; Wako Pure Chemicals) was added to THF (220 mL; Super Dehydrated, Stabilizer Free, Wako Pure Chemicals). Then the solution was cooled at -78°C in a dry ice-acetone bath, n-BuLi (20 mL; 0.032 mol; Merck, 1.6 M in hexane) was added to this THF solution dropwise for 20-25 min and stirred for additional 30 min. The THF (60 mL) solution of **(3)** (1.90 g; 0.016 mol) was added dropwise during 45 min with stirring at -78°C and stirred for 15 min after completion of the addition of **(3)**. Then, elemental selenium (2.40 g; 0.030 mol; Wako Pure Chemicals; black fine powder) was added to the reaction mixture in one portion. The reaction mixture was gradually warmed to -40°C during 45-60 min and kept at

the temperature for 20 minutes to allow the selenium powder to be consumed almost completely. The resultant pale yellow to orange solution was cooled down to  $-78^{\circ}\text{C}$ , again, and was added with titanocene dichloride (3.66 g; 0.015 mol; Wako Pure Chemicals) in one portion. Then the mixture was stirred and left to warm gradually up to room temperature overnight in the dry ice-acetone bath. The mixture was filtered to remove insoluble solids, and the residual was washed with dichloromethane (Wako Pure Chemicals). The filtrate and washing liquid were combined and evaporated to dryness. The residual was extracted with dichloromethane and purified with column chromatography (Si gel/ $\text{CH}_2\text{Cl}_2$ ). The dark green portion was collected, which was evaporated to approximately a third to a fifth of the original volume and diluted with hexane (Wako Pure Chemicals) to double the volume. The obtained dark green fine needles were filtered with suction, washed with methanol and then with hexane, and dried in vacuo. Yield: 2.3 g (32%)

UV ( $\text{CH}_2\text{Cl}_2$ ,  $20^{\circ}\text{C}$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\log(\varepsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1})$ ) = 714.5 (3.12)

IR (ATR;  $\text{cm}^{-1}$ ): 814(s), 892(w), 919(w), 1014(m), 1063(w), 1120(w), 1279(m), 1365(w), 1409(s), 1504(w), 1538(w), 2911(w), 2960(w), 3067(w), 3101(w).

#### 1.1.5. Preparation of (5) ( $\text{C}_5\text{H}_4\text{S}_2\text{Se}_2\text{O} = 302.162$ )

In a three-necked flask (1 L) equipped with a dropping funnel (500 mL), a condenser with a three-way valve on the top, a stopcock, and a magnetic stirring bar, the THF (168 mL) solution of (4) (2.33 g; 5.15 mmol) was added with triphosgene (3.06 g; 10.3 mmol; Wako Pure Chemicals) dissolved in THF (84 mL; Super Dehydrated, Stabilizer Free, Wako Pure Chemicals) in one portion. The reaction dark green solution was refluxed for 25 min to yield a dark red solution. After the reflux, the heater was turned off and the reaction mixture was left cooling down to room temperature with stirring overnight. The residual triphosgene was treated with distilled water (10 mL), and the mixture was filtered to remove insoluble solids, and the residual was washed with dichloromethane (Wako Pure Chemicals). The filtrate and washing liquid were combined and evaporated to dryness. The residual was extracted with dichloromethane and purified with column chromatography (Si gel/ $\text{CH}_2\text{Cl}_2$ ). The yellow-orange portion was collected to yield the crude product of (5) after evaporation. The yellowish orange irregular platelets were recrystallized from hot acetonitrile ( $\sim 30$  mL; Wako Pure Chemicals) and dried in vacuo. Recrystallization from hot toluene yielded reddish dark brown fine needles. Yield: 0.96 g (62%)

Elemental Analysis (%; calcd./found) : C (19.87/19.91), H (1.33/1.79), N (0.00/0.00)

UV ( $\text{CHCl}_3$ ,  $20^{\circ}\text{C}$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\log(\varepsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1})$ ) = 296 (3.53)

IR (ATR;  $\text{cm}^{-1}$ ): 696(w), 760(w), 803(m), 884(w), 922(w), 949(w), 1129(w), 1175(w), 1263(w), 1286(w), 1414(s), 1499(s), 1588(s), 1651(s), 2819(w), 2919(m), 2968(m), 3252(br, w), 3308(br, w).

#### 1.1.6. Preparation of BETS ( $\text{C}_{10}\text{H}_8\text{S}_4\text{Se}_4 = 572.324$ )

In a two-necked flask (200 mL) equipped with a dropping funnel (100 mL) and a condenser with a three-way valve on the top, and a magnetic stirring bar, freshly distilled triethyl phosphite (96 mL; Wako Pure Chemicals) was added to (5) (0.96 g; 3.18 mmol) and slowly heated to  $110-120^{\circ}\text{C}$  with stirring. The mixture soon turned to dark red solution, then dark brown fine needles precipitated immediately. After the mixture was stirred for 10–15 min at  $110-120^{\circ}\text{C}$ , the heater was turned off to leave the reaction mixture to slowly cool in the oil bath down to room temperature. The precipitates were filtered with suction, washed with acetone and then with hexane, and dried in vacuo. The crude product was recrystallized from hot toluene. Yield; 444 mg (49%)

Elemental Analysis (%; calcd./found) : C (20.99/21.64), H (1.41/1.56), S (22.41/22.56)

UV ( $\text{C}_6\text{H}_5\text{CH}_3$ ,  $20^{\circ}\text{C}$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\log(\varepsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1})$ ) = 324.5 (3.92), 504 (2.03)

MS (EI)  $m/z$  = 572 ( $\text{M}^+$ , 12%), 570 ( $\text{M}^+ - 2\text{H}$ , 10%)

IR (ATR;  $\text{cm}^{-1}$ ): 840(w), 877(w), 918(w), 1171(w), 1281(m), 1406(m), 2918(w), 2959(w).

#### 1.1.7. Preparation of STF ( $\text{C}_{10}\text{H}_8\text{S}_6\text{Se}_2 = 478.524$ )

The procedure of the synthesis from (5) and the corresponding thione in Scheme 1 is described in detail in Ref. 45 in the main text.

UV ( $\text{C}_6\text{H}_5\text{Cl}$ ,  $50^\circ\text{C}$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\log(\varepsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1})$ ) = 326 (4.18)

$^1\text{H-NMR}$  ( $\text{CS}_2$  with a trace amount of  $\text{CDCl}_3/\text{TMS}$ ,  $20^\circ\text{C}$ )  $\delta$  = 3.26 (singlet)

$^{13}\text{C-NMR}$  ( $\text{CS}_2$  with a trace amount of  $\text{CDCl}_3/\text{TMS}$ ,  $30^\circ\text{C}$ )  $\delta$  = 30.31, 31.06 (C atoms in the ethylene groups)

MS (EI)  $m/z$  = 478 ( $\text{M}^+$ , 21%), 476 ( $\text{M}^+ - 2\text{H}$ , 12%)

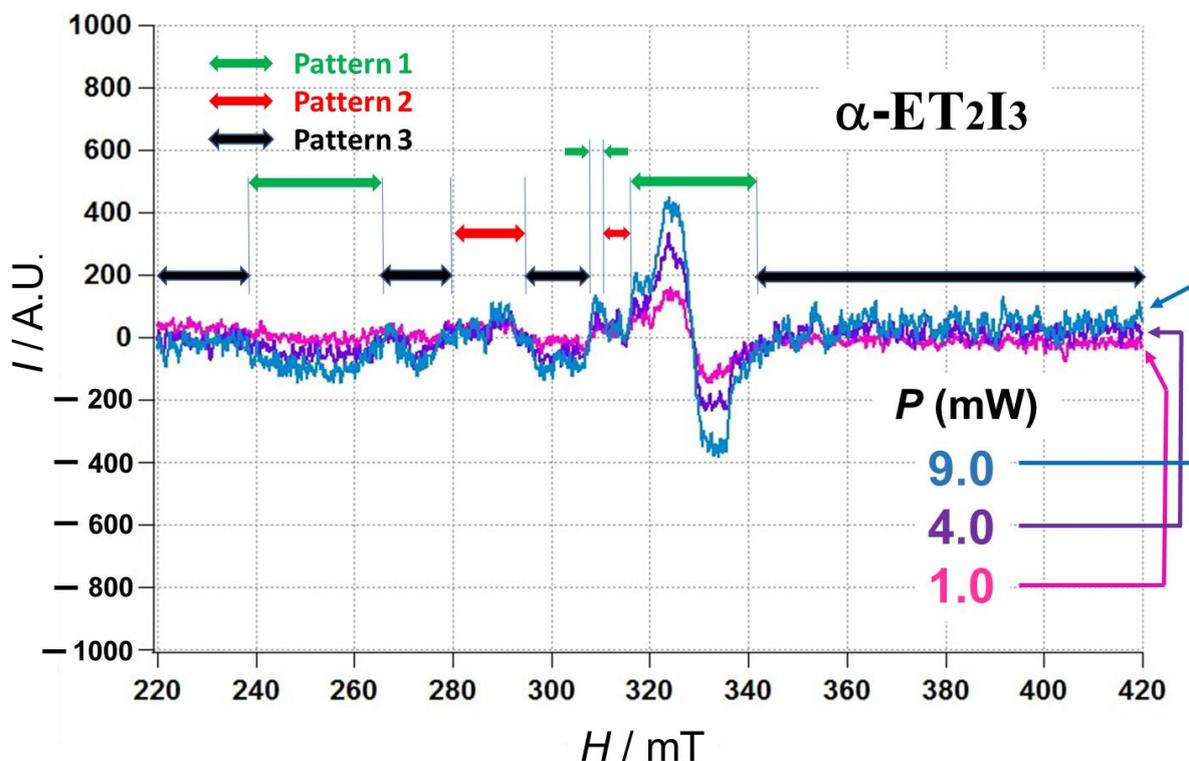
### 1.2. Syntheses of single crystals of $\alpha\text{-D}_2\text{I}_3$ ( $D = \text{ET}$ , BETS and STF) [45-47]

The single crystals of  $\alpha\text{-D}_2\text{I}_3$  were prepared using a standard electrocrystallization method. In H-tube cells, the neutral D species (*ca.* 5 mg; 0.01 mmol) and  $(\text{n-C}_4\text{H}_9)_4\text{NI}_3$  (50.5 mg; 0.08 mmol) were placed in the anode and cathode compartments, respectively. They were dissolved as much as possible in distilled and degassed  $\text{C}_6\text{H}_5\text{Cl}$  (10 mL) under inert ( $\text{N}_2$ ) atmosphere. The constant current of  $1.4 \mu\text{A}$  was applied for 7–10 days at  $43^\circ\text{C}$  using platinum electrodes (each 1 mm in diameter). Usually, the single crystals as black platelets produced on the anode.

### References (selected from the main text)

1. Naito, T.; Kobayashi, H.; Kobayashi, A. The electrical behavior of charge-transfer salts based on an unsymmetrical donor bis(ethylenedithio)diselenadithiafulvalene (STF): Disorder effect on the transport properties. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 107–114, <https://doi.org/10.1246/bcsj.70.107>.
2. Inokuchi, M.; Tajima, H.; Kobayashi, A.; Ohta, T.; Kuroda, H.; Kato, R.; Naito, T.; Kobayashi, H. Electrical and optical properties of  $\alpha\text{-(BETS)}_2\text{I}_3$  and  $\alpha\text{-(BEDT-STF)}_2\text{I}_3$ . *Bull. Chem. Soc. Jpn.* **1995**, *68*, 547–553, <https://doi.org/10.1246/bcsj.68.547>.
3. Kato, R.; Kobayashi, H.; Kobayashi, A. Synthesis and properties of bis(ethylenedithio)tetraselenafulvalene (BEDT-TSeF) compounds. *Synth. Met.* **1991**, *42*, 2093–2096, [https://doi.org/10.1016/0379-6779\(91\)92024-C](https://doi.org/10.1016/0379-6779(91)92024-C).

### 2. Evidence for the hidden peaks of the CT interactions driving the band reshaping: Microwave-power dependencies of ESR



**Figure S1.** Microwave-power ( $P$ ) dependencies of ESR spectra of  $\alpha\text{-ET}_2\text{I}_3$  (single crystal,  $B // a$ -axis) at 296 K. Generally, unless saturation occurs, the peak intensity ( $I$ ) increases proportionally to  $\sqrt{P}$ . The main peak at  $\sim 328$  mT, together with the broad peak at  $\sim 240\text{--}260$  mT, obeys this law (Pattern 1, green arrows). However, the spectral parts marked with red and black arrows respectively exhibit

different  $P$ -dependencies from the main peak. Red arrows: the parts hardly differ from each other between 1 and 9 mW (Pattern 2).<sup>a)</sup> Black arrows: the parts differ from each other between 1 and 4 mW, but do not between 4 and 9 mW (Pattern 3).<sup>b)</sup>

- a) Such a pattern is explained that the signals were practically saturated at  $P \leq 1$  mW and only noises were observed.
- b) Such a pattern is explained as follows.

Firstly, we assume that the signal contained three independent signals (A, B, and C) overlapped with each other. Then the total intensity  $I_0$  at  $P = 1$  mW,  $I_0(1)$ , is described as follows using each intensity  $I_A$ ,  $I_B$ , and  $I_C$ ,

$$I_0(1) = I_A + I_B + I_C \quad (\text{S1})$$

Similarly, if saturation does not occur at  $P = 4$  mW

$$I_0(4) = 2(I_A + I_B + I_C) \quad (\text{S2})$$

If saturation occurs at  $P = 9$  mW only for the signal C,

$$I_0(9) = 3(I_A + I_B) \quad (\text{S3})$$

If

$$I_0(4) = I_0(9)$$

then

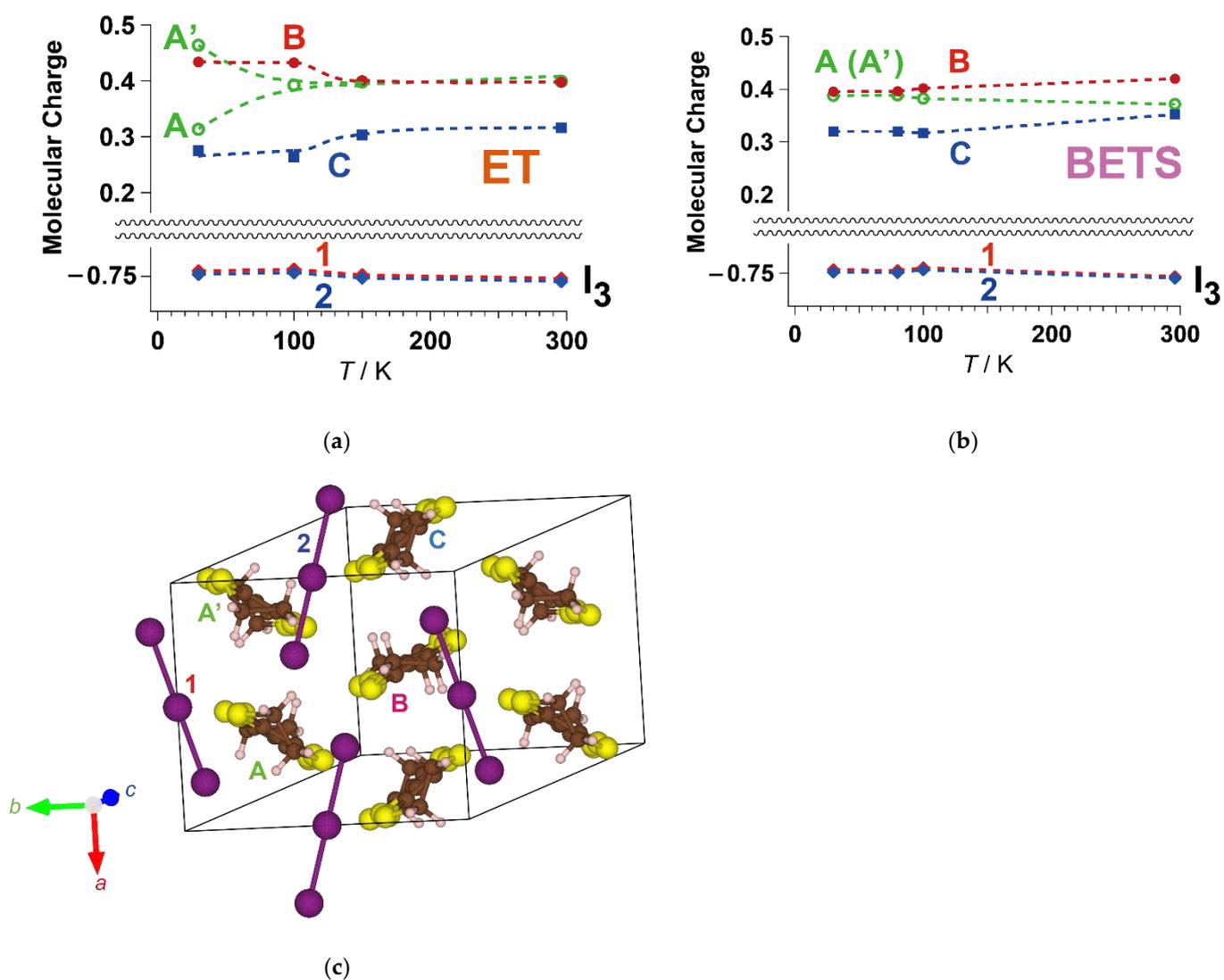
$$2(I_A + I_B + I_C) = 3(I_A + I_B) \quad (\because \text{Eqs. 2 and 3}) \quad (\text{S4})$$

$$\therefore I_C = \frac{I_A + I_B}{2} \quad (\text{S5})$$

Accordingly, when Eq (S5) is true, Pattern 3 is observed. The observation of Pattern 3 proves that the ESR originated from three different spin systems corresponding to Patterns 1–3, i.e., massive (standard) fermions mainly on the donor molecules (Pattern 1), massless (Dirac) fermions, and massive (standard) fermions mainly on the I atoms.

### 3. Molecular charges *vs* temperature in $\alpha$ -ET<sub>2</sub>I<sub>3</sub> and $\alpha$ -BETS<sub>2</sub>I<sub>3</sub>

**Supplementary Figure S2** shows the temperature-dependence of molecular charges in  $\alpha$ -ET<sub>2</sub>I<sub>3</sub> and  $\alpha$ -BETS<sub>2</sub>I<sub>3</sub> based on the Bader charges from the VASP calculation. In the respective salt, the charges on the crystallographically independent D molecules are different from each other at all the temperatures and temperature-dependent. In other words, there are temperature-dependent D-D CT interactions in  $\alpha$ -D<sub>2</sub>I<sub>3</sub>. These qualitative features are consistent with the observed physical properties. Additionally, it is consistent with our observation that the charges on both I<sub>3</sub> anions are deviated from -1 at all the temperatures, reflecting the D-I<sub>3</sub> CT interactions. Accordingly, the calculated Bader charges are qualitatively consistent with the observed physical and structural properties. However, quantitatively, the charge on both I<sub>3</sub> anions ( $\sim -0.75$ ) are significantly deviated from -1 at all the temperatures and practically temperature-independent. This is inconsistent not only with the observation but also with the band structures based on the same calculation, where the Fermi levels moves depending on the temperature. This inconsistency originates from coarse assumption of Bader charges on the assignment of electron densities to atoms, which is not always suitable for quantitative discussion. Thus, we did not discuss the Bader charges in **Supplementary Figure S2**.



**Figure S2.** Temperature-dependence of the molecular (Bader) charges on the crystallographically independent D (A, A', B, and C) and I<sub>3</sub> (1 and 2) species in (a)  $\alpha$ -ET<sub>2</sub>I<sub>3</sub> and (b)  $\alpha$ -BETS<sub>2</sub>I<sub>3</sub>. (c) Unit cell showing molecular numbering for (a) and (b).