Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Two-dimensional radical-cationic Mott insulator based on an electron donor containing neither tetrathiafulvalene nor tetrathiapentalene skeleton

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DFT calculation

To estimate the respective distribution maps of HOMO shown in Chart 1, density functional theory (DFT) calculations were performed with Gaussian09 program[S1] using the Becke, three-parameter, Lee–Yang–Parr (B3LYP) hybrid exchange-correlation functional[S2] and the 6-31G* basis set[S3] for a full geometry optimization. Molecular orbital composition analysis was conducted using the GaussSum Program.

Crystallographic data

Table S1 Crystallographic data of θ-(BEDT-BDT)PF_6.

Chemical formula	$C_{14}H_{10}F_6PS_6$
Formula weight	515.56
Crystal shape	red-brown plate
Crystal size (mm^3)	0.218×0.182×0.017
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	36.971(15)
b (Å)	4.3814(15)
c (Å)	11.483(5)
α (°)	90
β (°)	106.352(5)
γ (°)	90
V (Å^3)	1784.8(12)
Z	4
Unique reflections (R_{int})	1644 (0.0247)
D_{calc} (g/cm^3)	1.919
R_1 (I>2.00σ(I))	0.1069
wR_2 (All reflections)	0.3406
GOF	1.615
Temperature (K)	273
CCDC number	1983743

A Definition of the dihedral angle

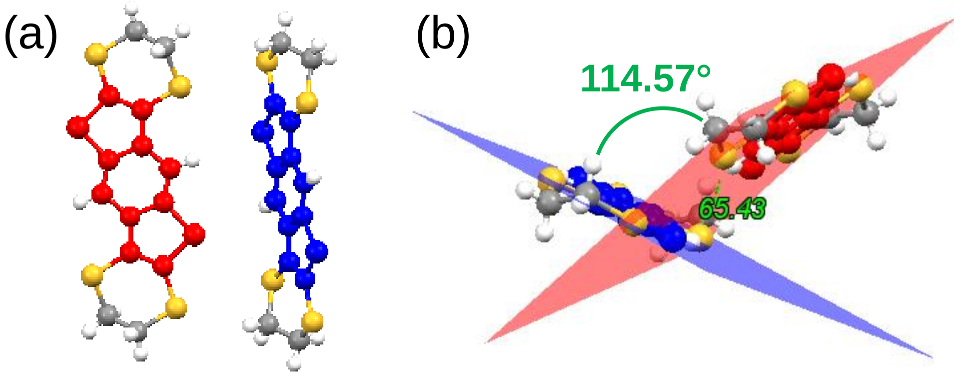

Fig. S1 (a) A plane definition of the benzodithiophene moiety and (b) a dihedral angle between the planes formed by two BEDT-BDT molecules on adjacent stacks.

As shown in Fig. S1a, flat benzodithiophene moieties (red and blue parts) were used to define the molecular plane because the whole molecular structure of BEDT-BDT is not perfectly planar. Fig. S1b shows the resulting dihedral angle, which is ~114.6°.

Optical image of sample

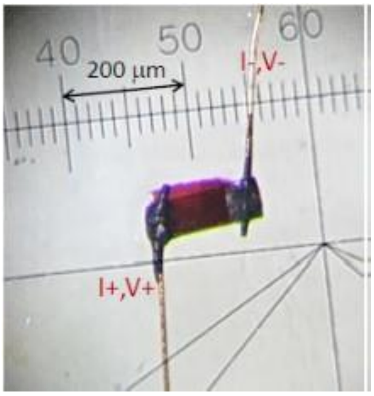

Fig. S2 Optical image of a single crystal of θ-(BEDT-BDT)PF_6 which used for the two probe measurement.

Spin concentration

The Curie constant C is given by the following equation:

$$C = \frac{NS(S+1)g^2{\mu_B}^2}{3k_B},$$

where N is spin density, S is a spin quantum number (S = 1/2), g is a g-factor (g = 2), μ_B is a Bohr magneton, and k_B is a Boltzmann constant. When C = 0.19 emu K/mol is used, N is determined to be 0.507.

Analyses of the magnetic properties

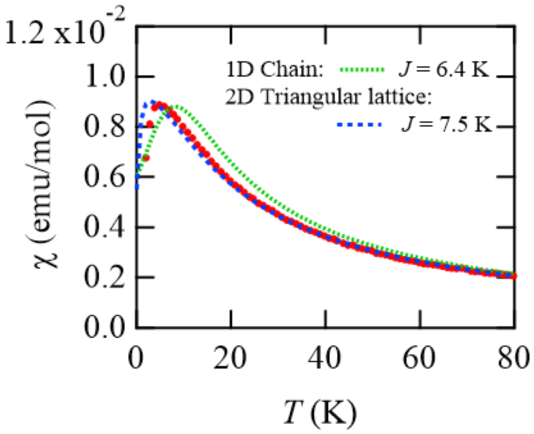

Fig. S3 Enlarged view of magnetic susceptibility below 80 K (Fig. 3a). Dotted and dashed curves are the calculated susceptibility by using Heisenberg model.

Figure S3 shows the temperature dependence of the magnetic susceptibility, which is the enlarged view of Fig. 3a at low temperature. The exchange coupling J in the spin Hamiltonian (Heisenberg model),

$$\hat{H} = \sum JS_i \cdot S_j,$$

was estimated as ~7.5 K by comparison with the calculated results (a blue dashed curve in Fig. S3). The result includes the spin concentration obtained by the Curie constant. Here, we have used the two-dimensional (2D) triangular lattice obtained from the extrapolation method using the [7/7] Padé approximation[15] as follows:

$$\chi = \frac{Ck_B 4x(1 + a_1 x + \cdots + a_6 x^6)}{J(1 + b_1 x + \cdots + b_7 x^7)},$$

where, $x = J/4k_\mathrm{B}T$ and $C = N_\mathrm{A}g^2\mu_\mathrm{B}^2/4k_\mathrm{B}$ (N_A is an Avogadro constant). The suggested coefficients are as follows:

$a_1 = 13.1382922$, $a_2 = 38.2639722$, $a_3 = 214.74454$,
$a_4 = 260.983171$, $a_5 = 622.734802$, $a_6 = 186.114208$,
and
$b_1 = 19.1382922$, $b_2 = 129.093725$, $b_3 = 597.98788$,
$b_4 = 1902.06491$, $b_5 = 3943.84464$, $b_6 = 5164.9974$,
$b_7 = 3452.67229$.

The calculated result for the one-dimensional (1D) Heisenberg chain[S4] is also shown in Fig. S3 (a green dotted curve). From the comparison of temperature dependence, where the magnetic susceptibility takes the maximum value, the 2D triangular lattice is more suitable than the 1D chain.

In Fig. 3d, the paramagnetic like magnetization curve, which is proportional to external magnetic field, was observed at low field region. Above ~ 2 T, the magnetization was gradually suppressed as the fields strengthened owing to the weak exchange coupling J between spins. This field dependence can be fitted (a dotted black curve) by using the modified Brillouin function $B_S(x)$[S5] as follows;

$$M_\mathrm{cal} = \alpha M_0 B_S(x) + \beta M_i,$$

where $M_0 = g\mu_\mathrm{B}SN_\mathrm{A}$ and impurity magnetization is M_i. Here, S is a spin value ($S = 1/2$), g is the g-factor ($g = 2$), μ_B is the Bohr magneton, and N_A is the Avogadro constant, respectively. The value of x is given by

$$x = \frac{g\mu_\mathrm{B}S}{k_B}\left(\frac{H}{T - T_0}\right),$$

where k_B is a Boltzmann constant. When we use the exchange coupling (J =7.5 K) as T_0, $\alpha = 0.3$ and $\beta = 0.15$ are determined.

Estimation of the transfer integrals *t* from the exchange coupling *J*

The transfer integrals are roughly calculated from the following equation:

$$|J| = \frac{2t^2}{U},$$

where t is the transfer integral and U is a Coulomb interaction. The above equation assumes a uniform triangular lattice. U is expected to be approximately 1 eV in the case of organic conductors. When J = 7.5 K and U = 1 eV are used, we can verify the small transfer integral t = 18 meV, which is the same order as the value calculated using the ADF program.

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