Supplementary Information

Dihedral-Angle Dependence of Intermolecular Transfer Integrals in BEDT-BDT-based Radical-Cation Salts with _θ_-type Molecular Arrangements

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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)AsF$_6$ and θ-(BEDT-BDT)PF$_6$.

Chemical formula	$C_{14}H_{10}S_6AsF_6$		$C_{14}H_{10}S_6PF_6$
Formula weight	559.51		515.56
Crystal shape	brown plate		red-brown plate
Crystal size (mm^3)	0.231×0.114×0.008		0.134×0.061×0.018
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$
a (Å)	37.322(8)	37.42(6)	37.07(2)
b (Å)	4.3105(8)	4.191(7)	4.278(2)
c (Å)	11.680(3)	11.85(2)	11.556(8)
α (°)	90	90	90
β (°)	106.927(3)	107.99(3)	106.681(11)
γ (°)	90	90	90
V (Å^3)	1797.7(6)	1768(5)	1755.3(19)
Z	4	4	4
Unique reflections (R_{int})	2036 (0.0268)	1513 (0.0565)	1994 (0.0462)
D_{calc} (g/cm^3)	2.067	2.101	1.951
R_1 (I>2.00$\sigma(I)$)	0.1046	0.1353	0.1284
wR_2 (All reflections)	0.3491	0.4408	0.3902
GOF	1.639	1.612	1.761
Temperature (K)	270	93	93
CCDC number	2092710	2092712	2092714

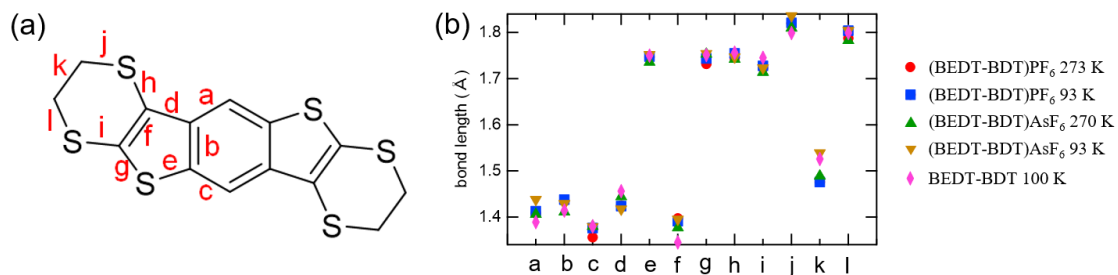**Bond-length analysis**

(a)

(b)

Figure S1. (a) Definition of label at each bond of BEDT-BDS molecule. (b) Relationship between bond length and molecular valence.

Table S2 List of bond lengths of BEDT-BDT and their charge-transfer salts.

	(BEDTBDT)PF$_6$	(BEDTBDT)PF$_6$	(BEDTBDT)AsF$_6$	(BEDTBDT)AsF$_6$	BEDT-BDT
T (K)	273	93	270	93	100
a (Å)	1.408	1.413	1.406	1.438	1.389
b (Å)	1.434	1.438	1.411	1.429	1.414
c (Å)	1.356	1.376	1.380	1.379	1.38
d (Å)	1.425	1.424	1.444	1.417	1.456
e (Å)	1.747	1.748	1.736	1.752	1.75
f (Å)	1.397	1.391	1.377	1.395	1.345
g (Å)	1.732	1.744	1.753	1.754	1.751
h (Å)	1.745	1.755	1.742	1.747	1.756
i (Å)	1.723	1.728	1.714	1.723	1.745
j (Å)	1.820	1.821	1.810	1.836	1.799
k (Å)	1.476	1.476	1.489	1.539	1.526
l (Å)	1.788	1.804	1.783	1.804	1.799

Crystallographic data for (BEDT-BDT)PF$_6$ at 273 K and BEDT-BDT at 100 K were taken from Refs. 12 and 13, respectively.

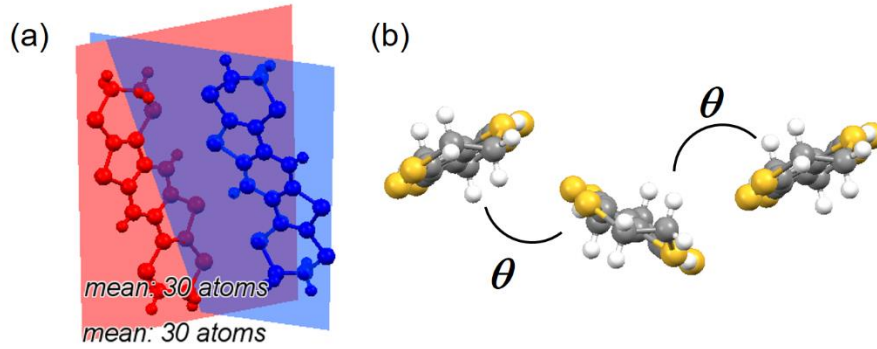## A Definition of the dihedral angle θ

Figure S2 (a) A plane definition of the BEDT-BDT and (b) a dihedral angle θ between the planes formed by two BEDT-BDT molecules on adjacent stacks.

Magnetic-susceptibility analyses

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 $C = 0.14$ emu K/mol is used, N is determined to be 0.373.

Two model calculations were performed to analyze the magnetic susceptibility at low temperatures below 150 K; calculations were performed using the same 2D triangular lattice as the PF$_6$ salt of the previous study[12,S4] and the 1D chain model[18].
The magnetic Hamiltonians is,

$$\widehat{H} = \sum JS_i \cdot S_j.$$

2D triangular lattice model was calculated from the extrapolation method using the [7/7] Padé approximation 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, $x = J/4k_B T$ and $C = N_A g^2 \mu_B{}^2/4k_B$ (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

$b_1 = 19.1382922,$ $b_2 = 129.093725,$ $b_3 = 597.98788,$

$b_4 = 1902.06491,$ $b_5 = 3943.84464,$ $b_6 = 5164.9974,$

$b_7 = 3452.67229.$

1D chain model was calculated as follows,

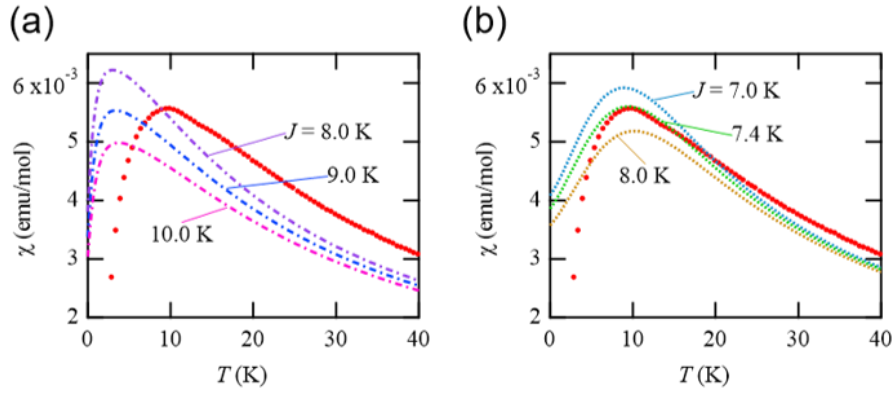$$\chi = \frac{Ng^2\mu_B^2}{k_BT}\frac{(1 + 0.14995x + 0.30094x^2)}{(1 + 1.9862x + 0.68854x^2 + 6.0626x^3)}.$$

Figure S3 Exchange coupling J dependence of the calculation results for (a) 2D triangular lattice and (b) 1D chain model. Red curves are experimental data of the AsF$_6$ salt.

The calculation results and experimental data are shown in Figure S3. From the comparison of temperature dependence, where the magnetic susceptibility takes the maximum value, the 1D chain model at $J = 7.4$ K is most suitable to the experimental data.

References

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