Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Ferromagnetic Ordering in the Organic Radical Cation Salt BBDTA•$Au(CN)_2$ at 8.2 K

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1. Crystal Structure Analyses.

X-ray diffraction data were collected with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation on a RIGAKU Mercury CCD diffractometer. Temperature control was carried out using Digital X-ray Cryo System XR-CS190D (Japan Thermal Engineering Co. Ltd.). All structures were solved by a direct method using the SHELXS-90 program[1] and refined by successive differential Fourier syntheses and a full-matrix least-squares procedure using the SHELXL-97 program.[2] Anisotropic thermal factors were applied to all non-hydrogen atoms. CCDC-1017180. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S1. Crystal structural parameters of BBDTA•$Au(CN)_2$ at 250 K.

CCDC ID code	1017180
Empirical formula	$C_8H_2AuN_4S_4$
Formula weight	479.34
Color, Shape, Size	black needle like, 0.3 × 0.1 × 0.01
Crystal system	orthorhombic
Space group	*Pnma*
a (Å)	14.1562(8)
b (Å)	15.315(9)
c (Å)	5.219(3)
V (Å^3)	1131.5(12)
Z	4
*D*calcd (g cm^{-3})	1.842
Reflections collected	2847
Goodness-of fit on F^2	1.024
*R*1, *wR*2 (all data)	0.0255, 0.0585

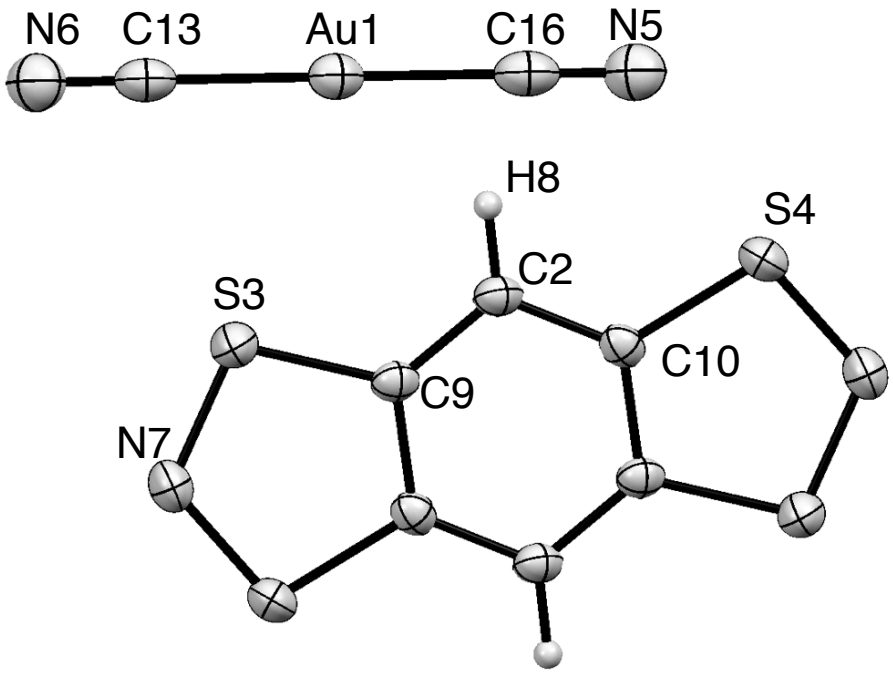

Figure S1. Molecular structures of $BBDTA^{+}$ and $Au(CN)_2^{-}$ for BBDTA•$Au(CN)_2$.

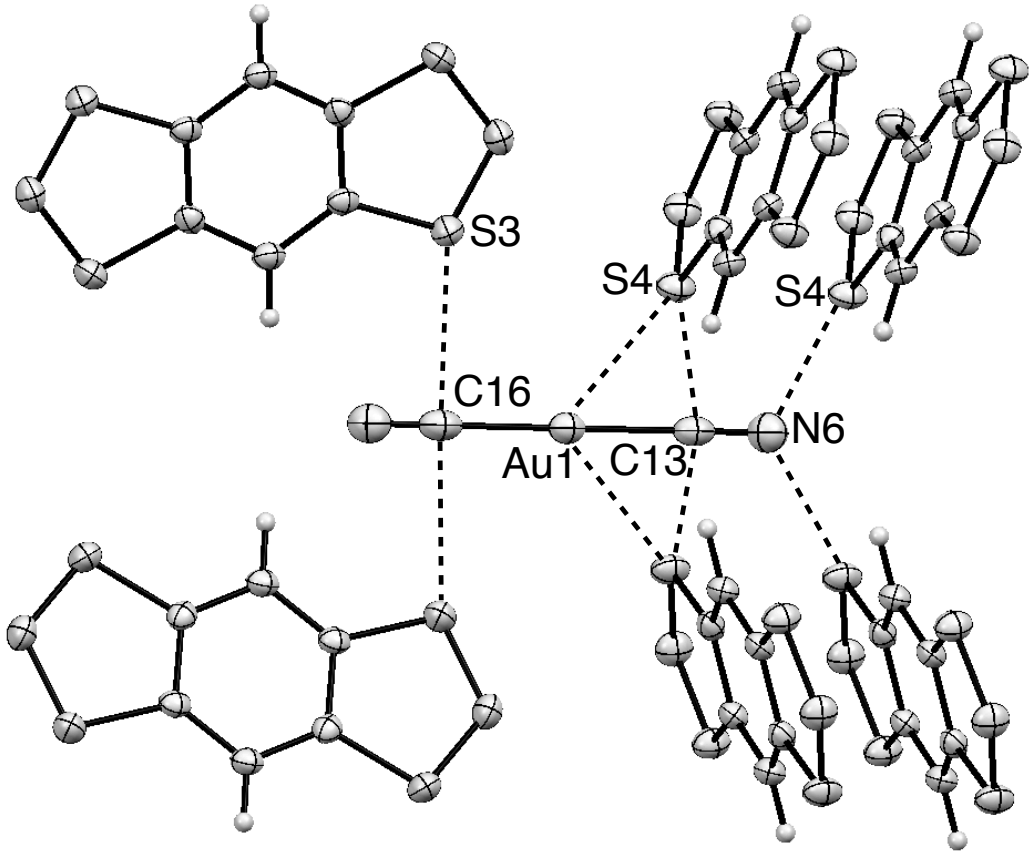

Figure S2. Interatomic short contacts between $BBDTA^{+}$ and $Au(CN)_2^{-}$ for BBDTA•$Au(CN)_2$.

Table S2. Bond lengths (Å) in $BBDTA^+$ and $Au(CN)_2^-$ for $BBDTA•Au(CN)_2$.

atom	atom	distance	atom	atom	distance
Au1	C13	1.978(6)	N5	C16	1.135(9)
Au1	C16	1.992(7)	N6	C13	1.130(9)
S3	N7	1.627(5)	C2	C9	1.394(6)
S3	C9	1.726(4)	C2	C10	1.409(6)
S4	N7	1.628(4)	C9	C10	1.424(6)
S4	C10	1.719(4)	C2	H8	0.97(5)

Table S3. Bond angles (°) in $BBDTA^+$ and $Au(CN)_2^-$ for $BBDTA•Au(CN)_2$.

atom	atom	atom	angle	atom	atom	atom	angle
C13	Au1	C16	177.2(3)	S4	C10	C2	125.6(3)
N7	S3	C9	99.75(19)	S4	C10	C9	113.2(3)
N7	S4	C10	99.5(2)	C2	C10	C9	121.2(4)
S3	N7	S4	115.4(3)	Au1	C13	N6	176.0(6)
C9	C2	C10	116.6(4)	Au1	C16	N5	177.5(6)
S3	C9	C2	125.7(3)	C9	C2	H8	124(3)
S3	C9	C10	112.2(3)	C10	C2	H8	120(3)
C2	C9	C10	122.1(4)				

Table S4. Interatomic short distances (Å) between $BBDTA^+$ and $Au(CN)_2^-$ for $BBDTA•Au(CN)_2$.

atom	atom	distance	atom	atom	distance
Au1	S4	3.4460(17)	S4	C13	3.409(5)
S3	C16	3.347(4)	S4	N6	2.975(5)

2. ESR Spectrum

ESR spectroscopy in polycrystalline samples was recorded on a Bruker E500 Spectrophotometer (X-band) at room temperature. Measurement conditions and parameters were as follows; Power 1 mW, Microwave Frequency 9.647198×10^9 Hz, Field Modulation 1 G, Time constant 0.02 s, g = 2.0083, ΔH_{pp} = 37.20 G.

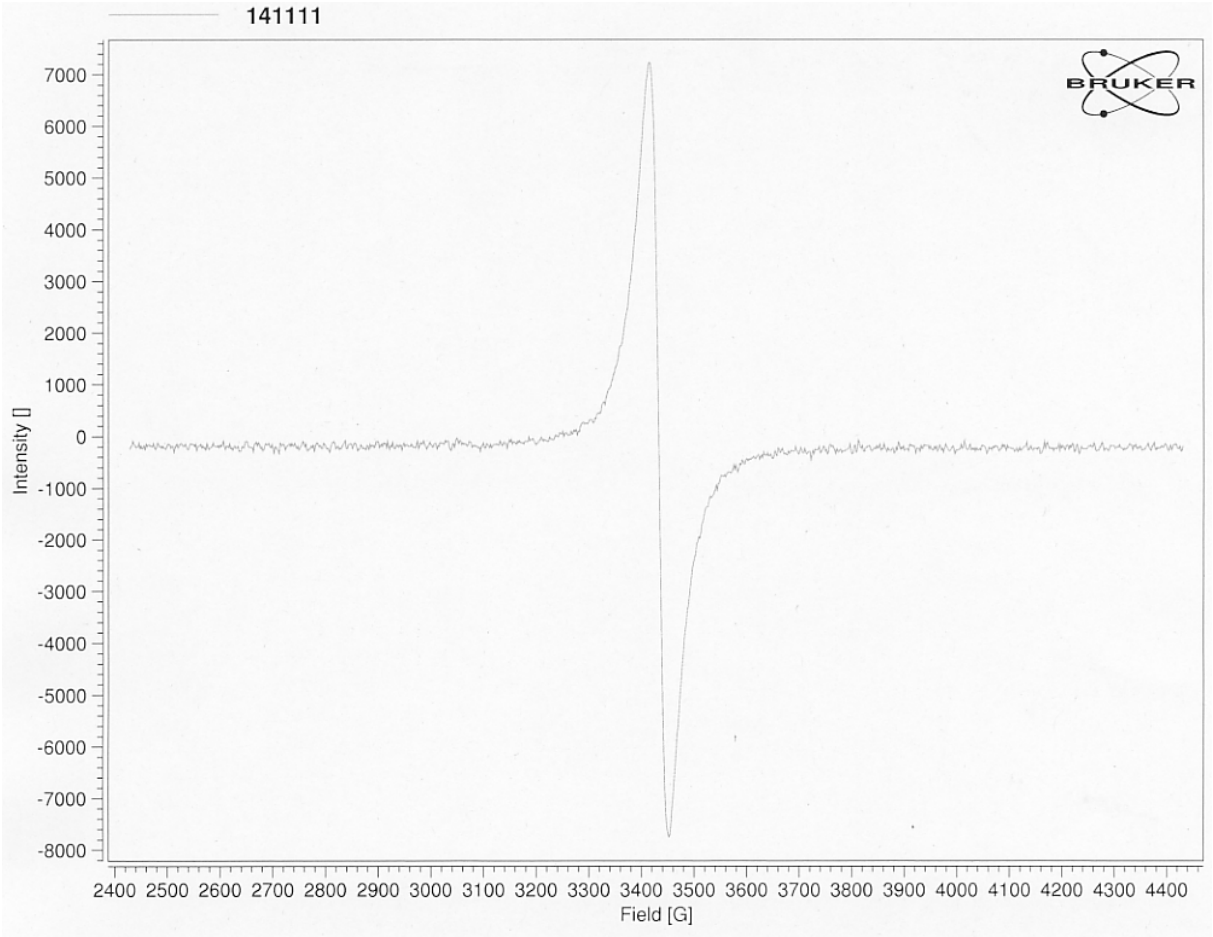

Figure S3. EPR spectrum for a powdered sample of BBDTA•$Au(CN)_2$ at room temperature.

3. Magnetic Measurements

Magnetic measurements were carried out for a microcrystalline sample with random orientation on a SQUID (Quantum Design MPMS XL) magnetometer down to 2 K. Temperature dependence of the dc susceptibility was measured under 500 Oe. The molar unit of the paramagnetic susceptibility χ_p was chosen as the quantity per one mole of BBDTA•$Au(CN)_2$. The experimental raw data were corrected for the diamagnetic contribution, which was estimated by assuming that the magnetic properties of this material obey the Curie-Weiss law at high temperatures.

4. Heat Capacity Measurements and its Analyses

Heat capacity measurements were carried out for total 2.20 mg of needle-like crystals on Quantum Design PPMS equipped a relaxation-type calorimeter option. The molar unit of the heat capacity C_p was chosen as the quantity per one mole of BBDTA•$Au(CN)_2$. The specific heat capacity C_{mag} was obtained by subtracting the lattice contribution $C_{lattice}$ from the total heat capacity C_p. The lattice heat capacity $C_{lattice}$ was estimated by the C_p data in the temperature range of 20 – 30 K using followed equation,[3]

$$C_p = aT^3 + bT^5 + cT^7 + dT^9 + eT^2 \qquad (1).$$

where the last term stands for the high-temperature limit of the specific heat capacity C_{mag}[4] and the other terms corresponds to lattice heat capacity $C_{lattice}$. The coefficients obtained from the fit were a = 0.0081605 J K^{-4} mol^{-1}, b = – 1.5355 × 10^{-5} J K^{-6} mol^{-1}, c = 1.3545 × 10^{-8} J K^{-8} mol^{-1}, d = – 4.4612 × 10^{-12} J K^{-10} $mol^{-1}$and e = 342.74 J K mol^{-1}. The specific heat capacity below the base temperature of 2.2 K was calculated assuming the three-dimensional ferromagnet

$$C_{mag}^{SW} = \alpha T^{3/2} \qquad (2)$$

in the spin-wave theory.[5] The adjustable parameter a was determined by fitting the C_{mag} data at zero magnetic field between 2.2 K and 5 K to be a = 0.11612 J $K^{-5/2}$ mol-1. The integration of C_{mag}^{SW} from 0 K to 2.2 K

$$S_{mag} = \int_0^{2.2} \frac{C_{mag}^{SW}}{T} dT \qquad (3)$$

gives the offset of the magnetic entropy. The definite integral

$$S_{mag} = \int_0^{2.2} \frac{C_{mag}^{SW}}{T} dT + \int_{2.2}^{30} \frac{C_{mag}}{T} dT \qquad (4)$$

affords 4.63 J K^{-1} mol^{-1}, 80.3 % of the total magnetic entropy for 1 mol of S = 1/2 spins, where C_{mag} represents the observed value.

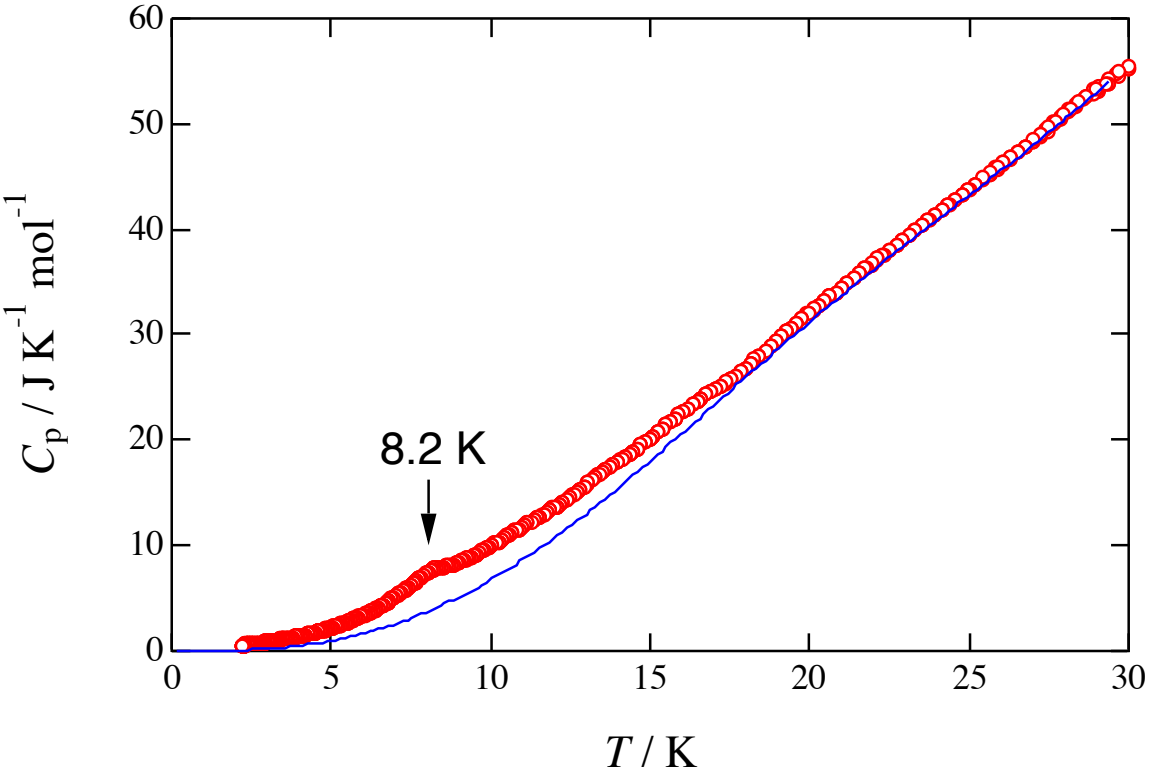

Figure S4. Temperature dependence of the total heat capacity C_{mag} in BBDTA•Au(CN)$_2$. The blue solid line expresses the contribution of the lattice, $C_{lattice}$.

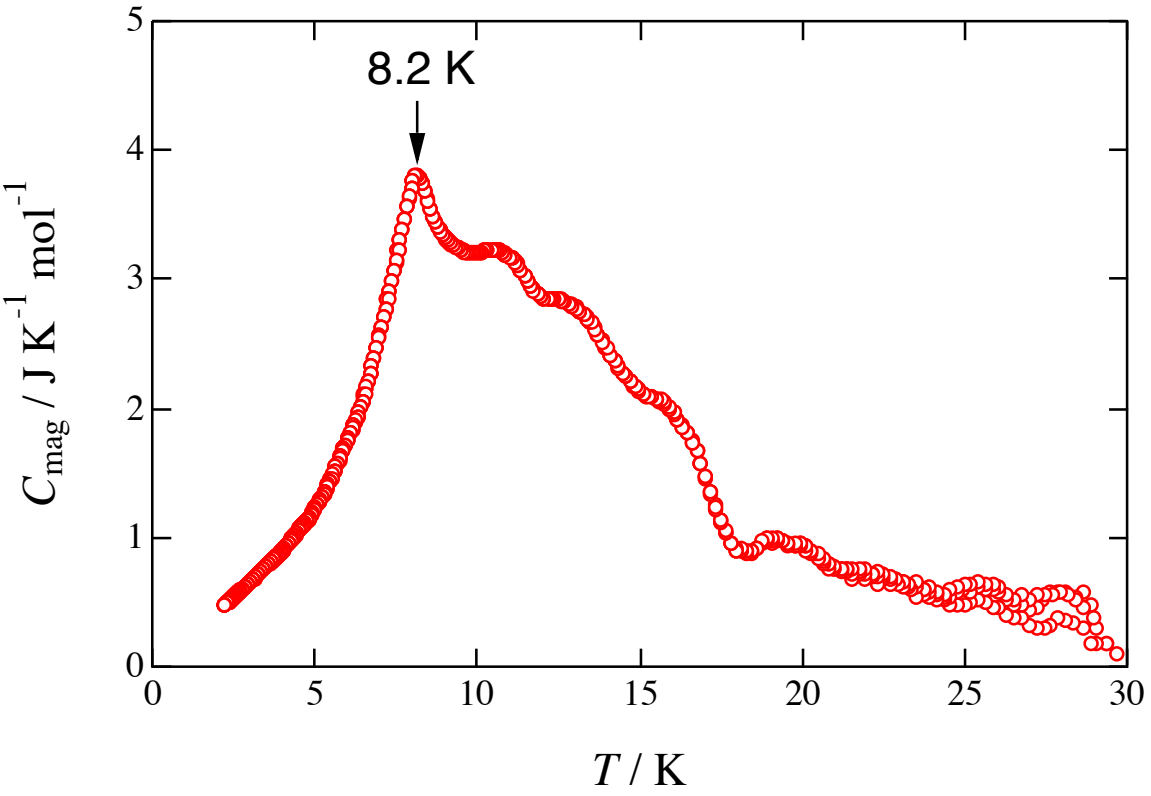

Figure S5. Temperature dependence of the specific heat capacity C_{mag} in BBDTA•Au(CN)$_2$.

5. References

1. G. M. Sheldrick, *Acta Crystallogr. A* 1990, **46**, 467.
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3. T. Sakakibara, Y. Miyazaki, T. Ishida, T. Nogami and M. Sorai, *J. Phys. Chem. B* 2002, **106**, 6390.
4. H. M. Blöte, *Physca B* 1975, **79**, 427.
5. L. J. de Jongh and A. R. Miedema, *Adv. Phys.* 1974, **23**, 1.