Supplementary Data for

'Spin-crossover behavior and electrical conduction property in iron(II) complexes with tetrathiafulvalene moieties'

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Experimental details

All solvents and chemicals were purchased and used without further purification unless otherwise noted. Tetrahydrofuran was distilled from sodium and benzophenone. 2,6-bis(pyrazolyl)-4-hydroxymethylpyridine ($dppCH_2OH$),[1] formyltetrathiafulvalene,[2] and $(Bu_4N)[Ni(mnt)_2]$[3] were prepared according to the literature methods.

2,6-Bis(pyrazolyl)-4-bromomethylpyridine ($dppCH_2Br$)

Phosphorus tribromide (1.18 ml, 12.4 mmol) was added to $dppCH_2OH$ in dry THF (125 ml), and refluxed for 5 h under N_2. The resulting mixture was evaporated and the residue was extracted with dichloromethane and washed with water. The solvent was evaporated and the white solid was purified by silica gel column chromatography (CH_2Cl_2 :CH_3COOEt = 4 : 1 (v / v) as an eluent) affording a white solid of $dppCH_2Br$ (1.20 g, 3.95 mmol), yield: 92 %. Anal. Calcd for $C_{12}H_{10}N_5Br_1$: C, 47.39; H, 3.31; N, 23.03. Found: C, 47.64; H, 3.35; N, 22.90. ^{1}HNMR (270 MHz, $CDCl_3$): δ: 8.55 (2H, *dd, J* = 0.7, 2.6 Hz, pz), 7.89 (2H, *s*, py), 7.77 (2H, *dd*, *J* = 0.7, 1.6 Hz pz), 6.50 (2H, *dd*, *J* = 1.6, 2.6 Hz, pz), 4.49 (2H, *s*, CH_2).

1-{2-(1,3-dithiol-2ylinene)-1,3-dithiolyl}-2-{2,6-bis(1-pyrazolyl)pyridyl}-ethylene (dppTTF)

The mixture of $dppCH_2Br$ (1.00 g, 3.29 mmol) and triphenylphosphine (1.29 g, 4.91 mmol) in toluene (100 ml) was refluxed for 12 h, and cooled down to room temperature. The resulting white precipitate was filtered off to obtain triphenyl(2,6-bis(pyrazolyl)-4-pyridylmethyl)phosphonium bromide ($dppCH_2PPh_3^+Br^-$) (1.76 g, 3.11 mmol), yield: 95 %. The white solid of $dppCH_2PPh_3^+Br^-$ was used in the next synthesis without further purification. Potassium *t*-butoxide (143 mg, 1.27 mmol) was added to a stirred solution of $dppCH_2PPh_3^+Br^-$ (600 mg, 1.06 mmol) in dry tetrahydrofuran (420 mL) at 0°C and the resulting solution was stirred for 30 min. Formyltetrathiafulvalene (296 mg, 1.27 mmol) was added to the reaction mixture at room temperature and the solution was refluxed for one night. The reaction mixture was quenched with water and extracted with diethyl ether. The solvent was evaporated and the residue was purified by silica gel column chromatography (CH_2Cl_2 : CH_3COOEt_2 : hexane = 3:1:2 (v / v) as an eluent) affording a purple solid of dppTTF (280 mg, 0.64 mmol), yield: 61%. Anal. Calcd for

$C_{19}H_{13}N_5S_4 \cdot 0.3H_2O$: C, 51.28; H, 15.74; N, 3.08. Found: C, 51.27; H, 15.58; N, 3.02. ^{1}HNMR: (270 MHz $CDCl_3$): δ 8.56 (2H, d, *J* = 2.47 Hz, pz), 7.85 (2H, *s*, py), 7.77 (2H, *d*, *J* = 0.99 Hz, pz), 7.26 (1H, d, *J* = 15.7 Hz, CH = CH), 6.59 (2H, *s*, TTF), 6.50 (2H, *dd, J* = 0.99, 2.47 Hz, pz), 6.40 (2H, *d*, *J* = 15.7 Hz, CH = CH), 6.35 (2H, *s*, TTF).

References

1 M. A. Halcrow, *Coord. Chem. Rev.*, 2005, **249**, 2880;

2 J. Garín, J. Orduna, S. Uriel, A. J. Moore, M. R. Bryce, S. Wegener, D. S. Yufit, J. A. K. Howard, *Synthesis*, **1994**, 489.

3 A. Davidson, R and H. Holm, *Inorg. Synth.*, 1967, **10**, 8.

Table S1. Selected Interatomic and Interplanar Distances (Å) in **2**

		200K	300 K
The shortest S···S or S···Ni contacts			
[Ni1]-[Ni1]	S10-S11$^{\#1}$	3.463(6)	3.513(4)
[Ni1]-TTF1	Ni1-S1	3.548(4)	3.637(3)
TTF1-TTF1	S1-S4$^{\#2}$	3.646(5)	3.708(4)
[Ni2]-[Ni2]	S16-S15$^{\#3}$	4.170(5)	4.273(4)
TTF2-TTF2	S6-S5$^{\#4}$	3.573(5)	3.633(4)
TTF2-[Ni1]	S6-S12$^{\#5}$	3.603(5)	3.640(4)
TTF2-[Ni2]	S6-S14$^{\#4}$	3.403(5)	3.476(3)
[Ni2]-TTF1	S16-S2$^{\#6}$	3.670(5)	3.652(4)
Interplane distances			
[Ni1]-[Ni1]		3.396(5)	3.440(3)
[Ni1]-TTF1[a]		3.496(4)	3.550(3)
TTF1TTF1		3.400(5)	3.451(3)
[Ni2]-[Ni2]		3.457(7)	3.515(5)
TTF2-TTF2		3.53(1)	3.57(1)

[a] Distance between a mean plane of [Ni1] and S1 atom.

Key to symmetry operations: #1 = 2-x, 1-y, -z; #2 = 2-x, 2-y, -z; #3 = 1-x, 2-y, 2-z; #4 = 1-x, 1-y, 2-z; #5 = 2-x, 1-y, 1-z; #6 = -1+x, y, 1+z.

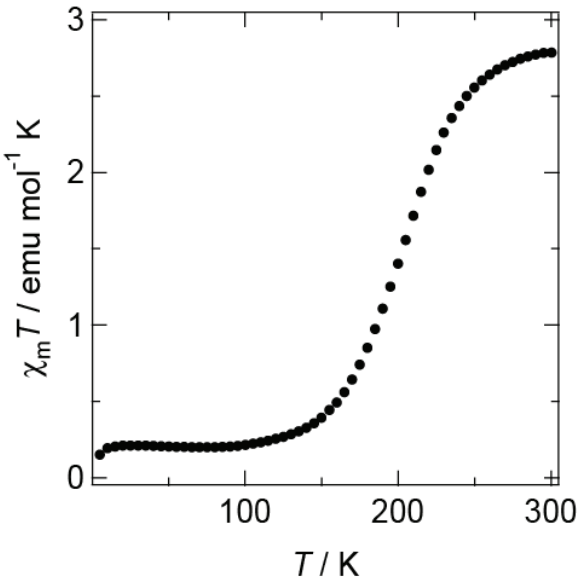

Fig. S1. $\chi_m T - T$ plot for **1**.

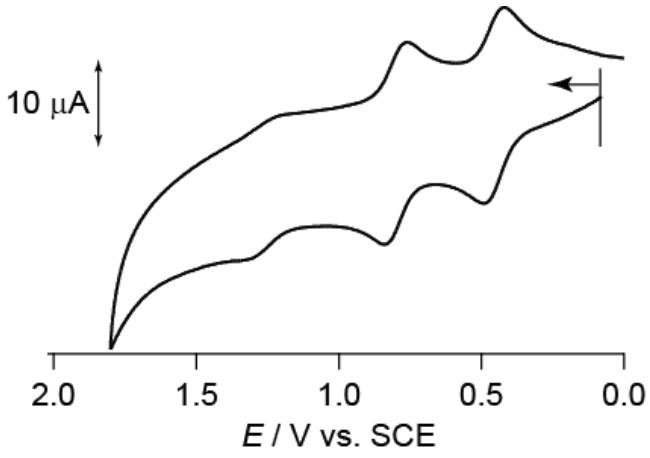

Fig. S2. Cyclic voltammogram for **1**.

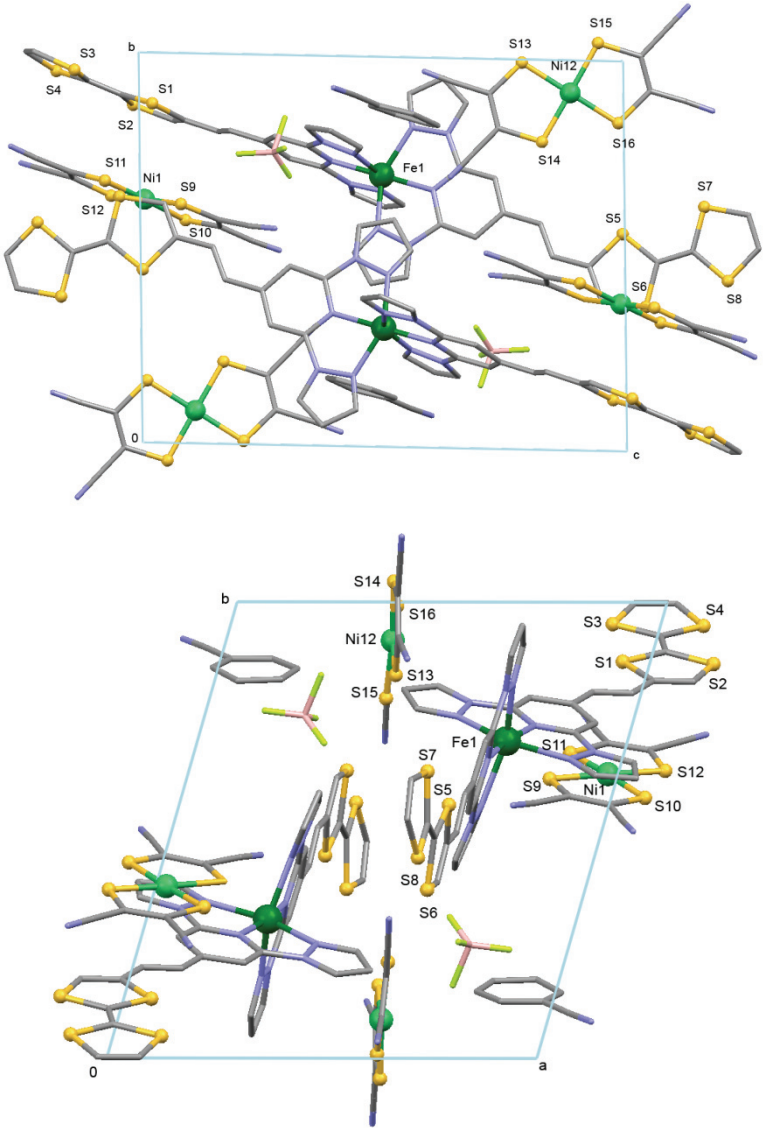

Fig. S3. Projection views of unit cell contents in **2** along (top) *bc* and (bottom) *ab* planes.

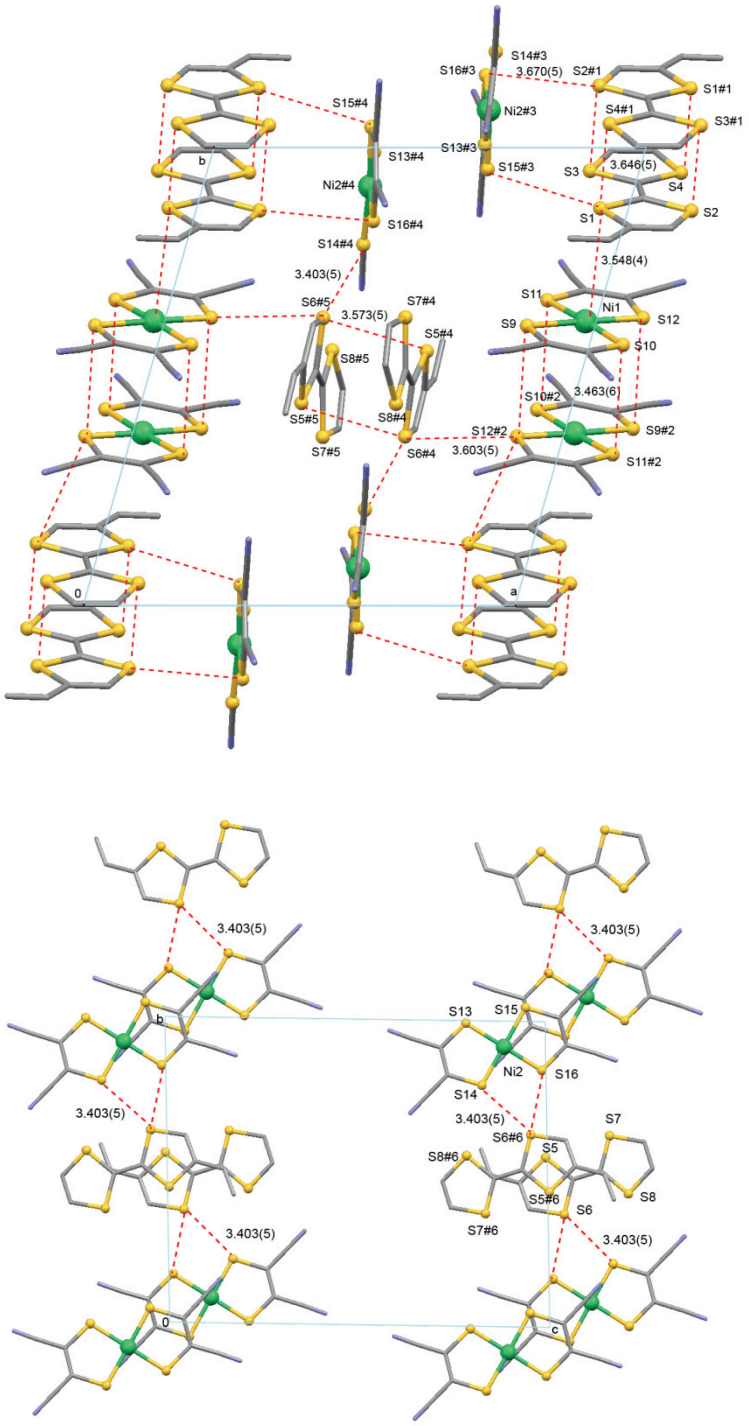

Fig. S4. Stacking diagram of TTF moieties and Ni complex anions in **2** at 200 K along (top) *ab* and (bottom) *bc* planes. Key to symmetry operations: #1 = 2-x, 2-y, -z; #2 = 2-x, 1-y, -z; #3 = 1-x, 2-y, 1-z; #4 = x, y, -1+z; #5 = 1-x, 1-y, 1-z; #6 1-x, 1-y, 2-z.

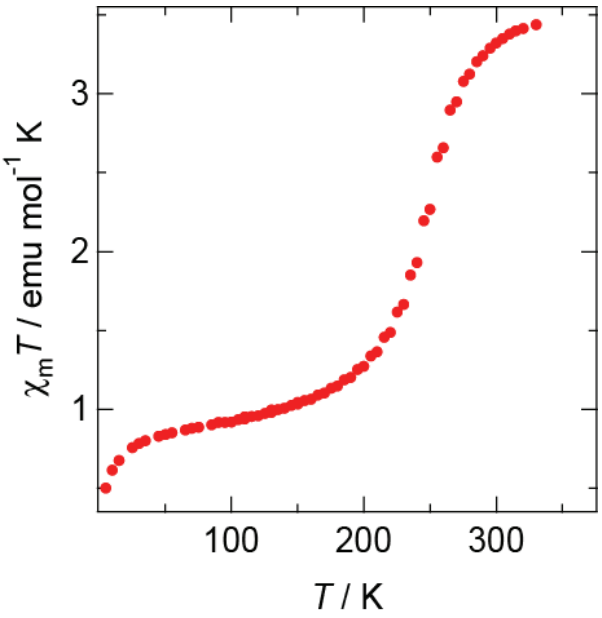

Fig. S5. $\chi_m T$ - T plot for **2**.