Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

From Spin-Crossover to Single Molecule Magnetism: Tuning Magnetic Properties of Co(II) bis-ferrocenylterpy Cations via Supramolecular Interactions with Organocyanide Radical Anions

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Section S1. Crystallographic data and SChMs analysis summary.

Table S1. Crystallographic and refinement parameters for [Co(FcTp)](TCNQ)$_2$ compounds.

Compound	**1**	**1'**	**2**	**3**
Empirical formula	C74H46CoFe2N14	C74H46 ZnFe2N14	C76H49CoFe2N15	C76H47CoF2Fe2N15
Formula weight	1301.88	1308.32	1342.93	1378.91
Temperature/K	100	110	120	120
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
a/Å	12.0595(5)	12.0572(3)	12.2917(3)	12.2558(5)
b/Å	12.6422(5)	12.6478(3)	15.1866(4)	15.3186(6)
c/Å	19.9814(8)	20.0264(5)	18.3369(4)	18.3379(7)
α/°	88.0990(10)	88.1340(10)	95.632(2)	96.059(2)
β/°	84.1870(10)	83.998(2)	100.2620(10)	99.428(2)
γ/°	71.5970(10)	71.4820(10)	113.4630(10)	113.636(2)
Volume/Å3	2875.7(2)	2879.97(12)	3035.00(13)	3055.0(2)
Z	2	2	2	2
ρcalcg/cm3	1.504	1.509	1.47	1.499
μ/mm-1	0.192	0.972	0.803	0.805
F(000)	1334	1340.0	1378	1410
Crystal size/mm3	0.053 × 0.045 × 0.04	0.2 × 0.15 × 0.1	0.2 × 0.1 × 0.02	0.15 × 0.14 × 0.06
Radiation	Synchrotron (λ= 0.41328)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.296 to 34.2820.	3.942 to 55.044	4.132 to 55.042	4.146 to 55.118
Index ranges	-17 ≤ h ≤ 16, -18 ≤ k ≤ 13, -28 ≤ l ≤ 28= 0.06	15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23
Reflections collected	56557	67792	106824	121984
Independent reflections	16730 [Rint = 0.0648, Rsigma = 0.0676]	13233 [R_{int} = 0.0614, R_{sigma} = 0.0414]	13900 [Rint = 0.0631, Rsigma = 0.0320]	14000 [Rint = 0.1183, Rsigma = 0.0571]
Data/restraints /parameters	16730/0/820	13233/0/820	13900/0/848	14000/0/911
Goodness-of-fit on F2	1.008	1.082	1.1	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0398, wR_2 = 0.0889=	R_1 = 0.0344, wR_2 = 0.0729	R_1 = 0.0438, wR2 = 0.1072	R_1 = 0.0453, wR_2 = 0.1055
Final R indexes [all data]	R_1 = 0.0645, wR_2 = 0.0972	R_1 = 0.0344, wR_2 = 0.0729	R_1 = 0.0547, wR2 = 0.1131	R_1 = 0.0598, wR_2 = 0.1135
Largest diff. peak/hole / e Å-3	0.41/-0.51	0.49/-0.53	1.43/-0.80	0.68/-0.74

$R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$. $wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$. $w = 0.75/(\sigma^2(F_o) + 0.00010\,F_o)$. Goodness-of-fit = $\{\sum [w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table S2. Continuous Shape Measure Analysis results from SHAPE v2.10

Symmetry	Shape	Deviation value (CShMs)			
		1	**1'**	**2**	**3**
D6h	Hexagon	33.793	33.603	32.841	32.642
C5v	Pentagonal pyramid	17.461	18.037	21.455	21.16
Oh	**Octahedron**	**5.283**	**5.413**	**2.771**	**2.819**
D3h	Trigonal prism	7.504	7.794	10.037	9.968
C5v	Johnson pentagonal pyramid J2	21.636	22.23	25.221	24.894

Section S2. Crystal packing and short contacts in the solid state structures.

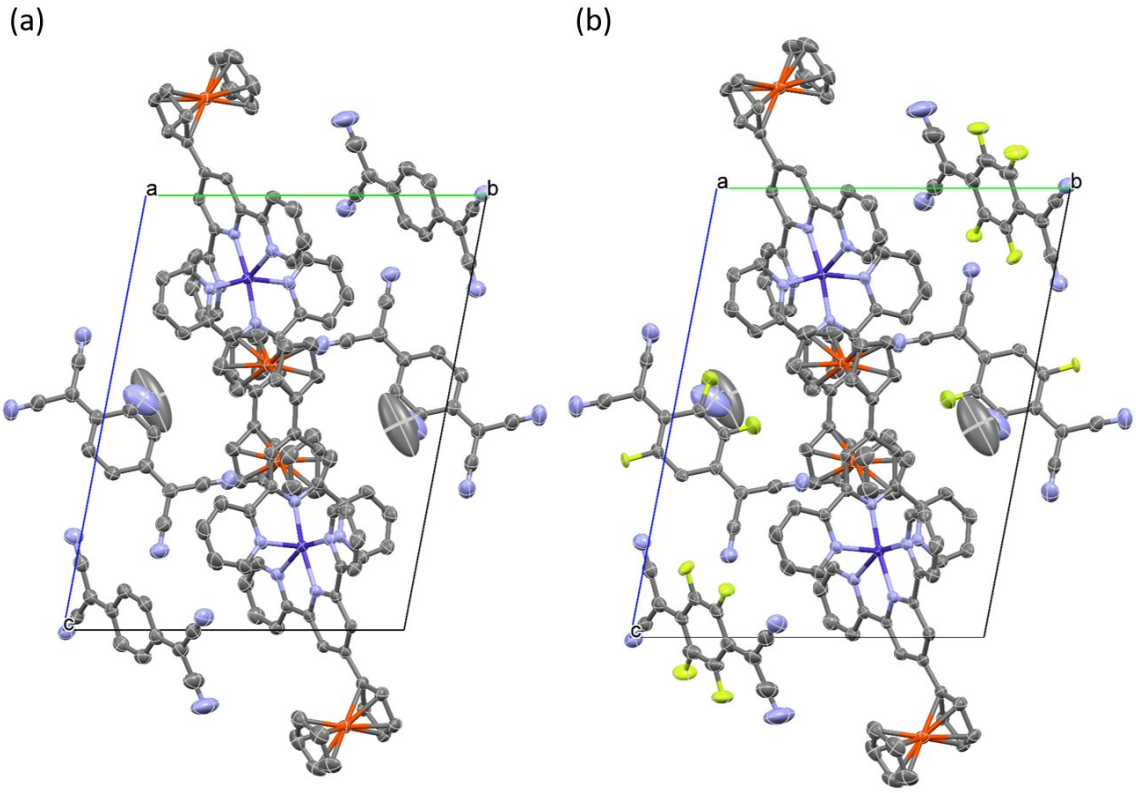
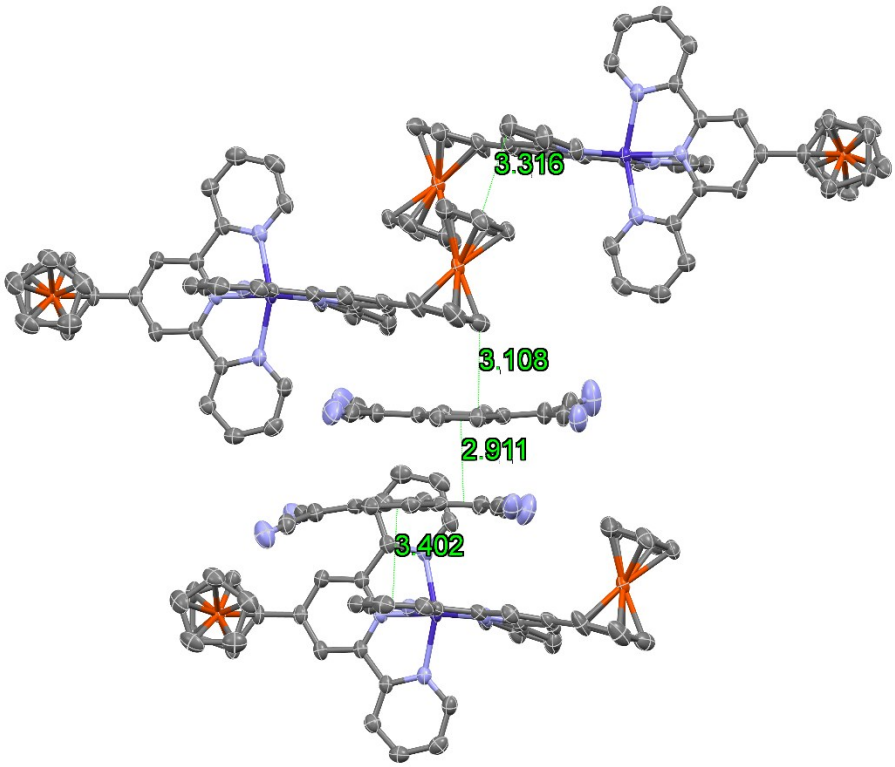
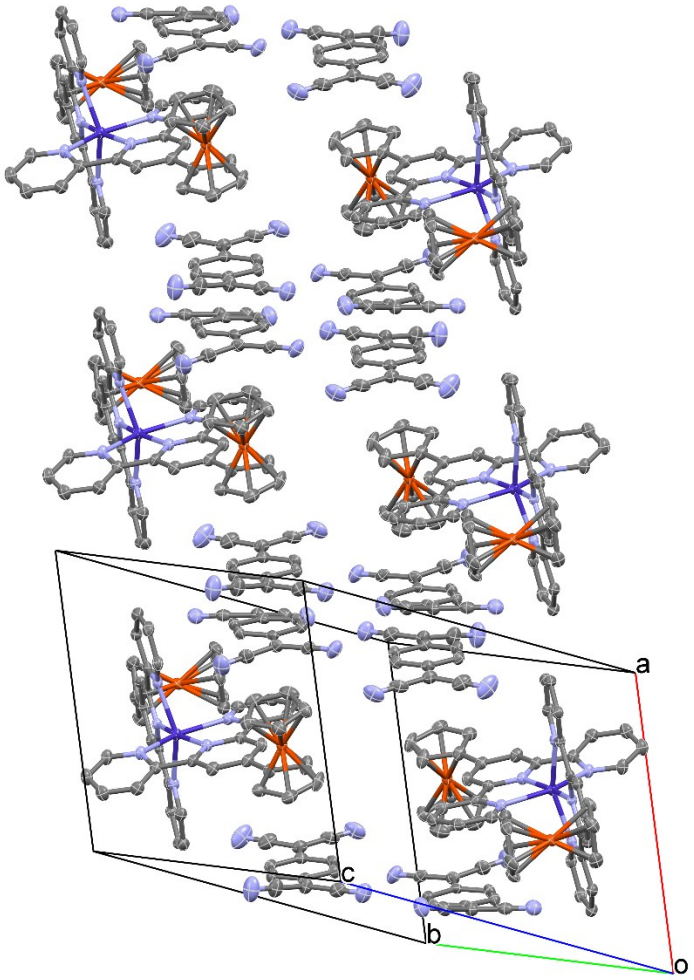


Figure S1. Views along the **a** crystal axis of (a) **2** and (b) **3**. The crystal origins of **3** were reset to the same position as **2** by a (1/2, 1/2, 1/2) translation. Hydrogen atoms were omitted for the sake of clarity. Colour code: carbon: grey; nitrogen: blue; cobalt: purple; iron: orange; fluorine: yellow.

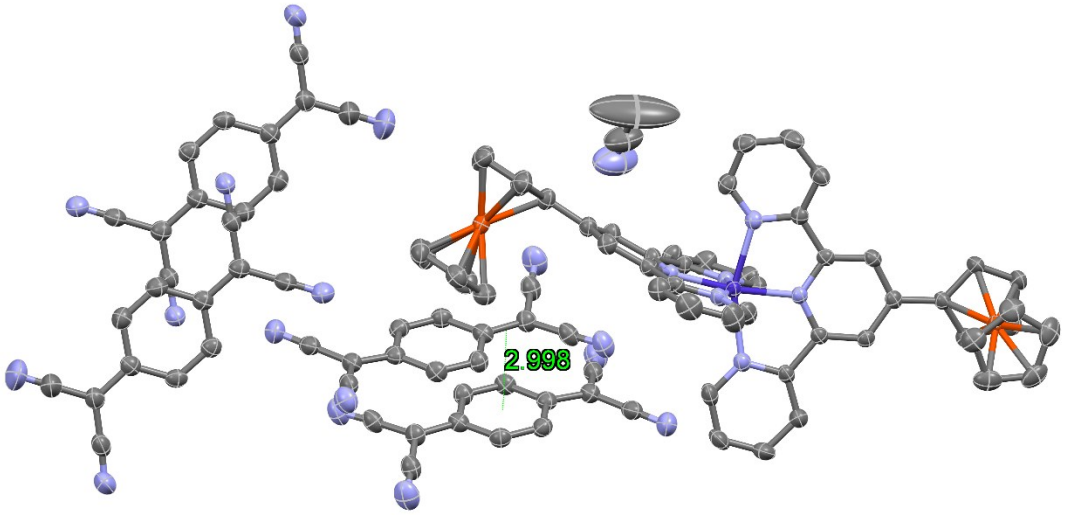


(a)

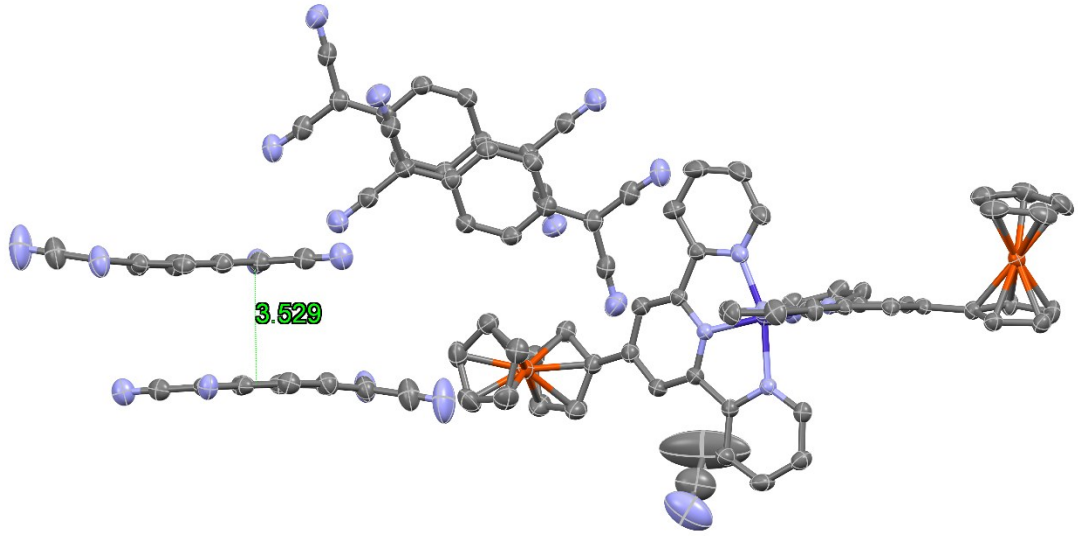


(b)

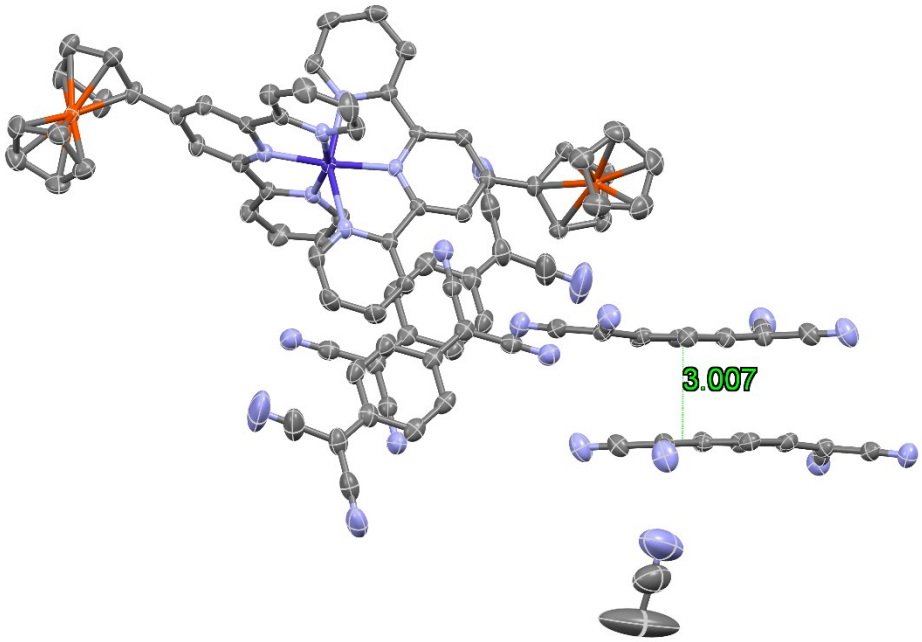
Figure S2. (a) Short contacts of TCNQ, pyridyl and ferrocenyl groups involved in intermolecular interactions in **1**. (b) The packing assemblies of **1** along the **a** axis of the unit cell with intermolecular interactions. Hydrogen atoms were omitted for the sake of clarity. Colour code: carbon: grey; nitrogen: blue; cobalt: purple; iron: orange.



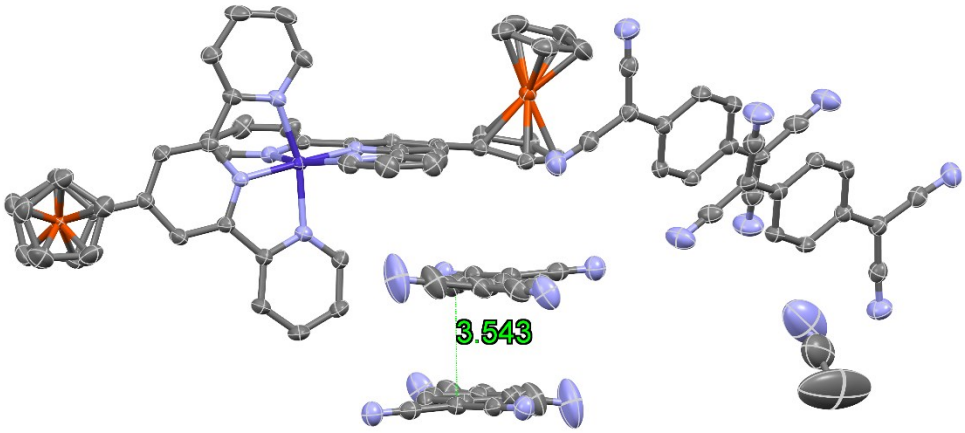
(a)



(b)



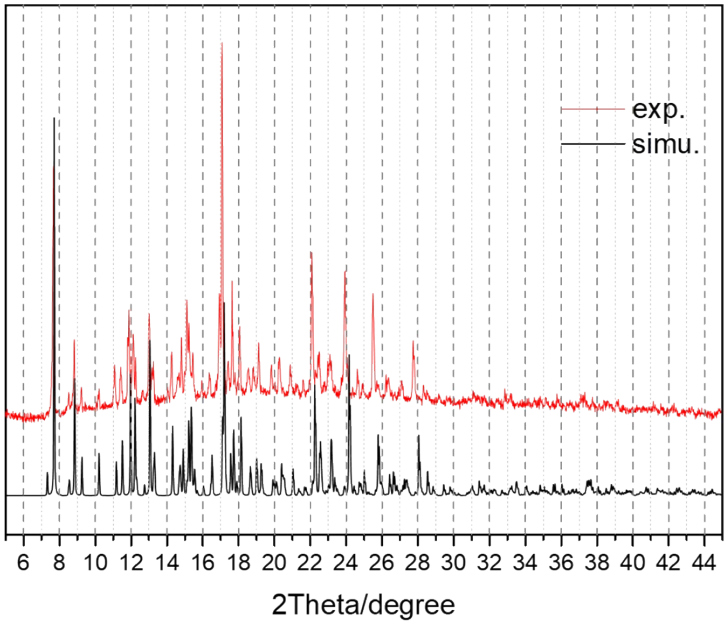
(c)



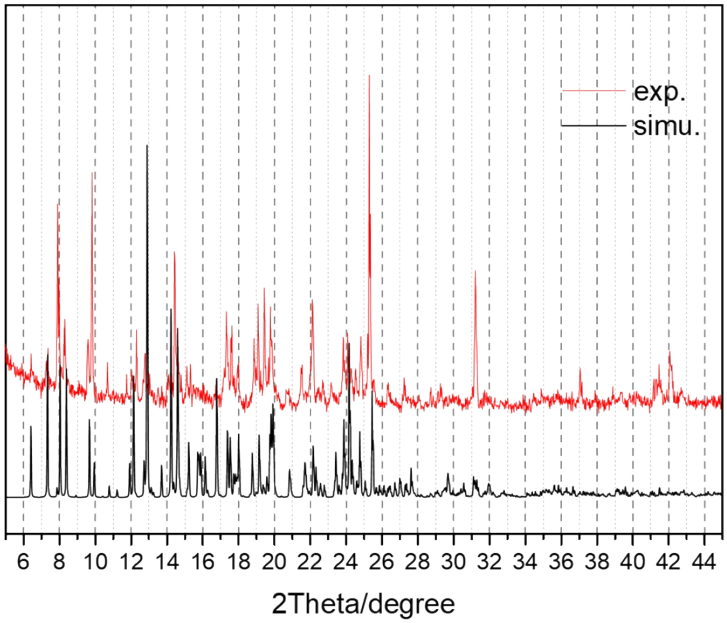
(d)

Figure S3. Interplanar distances of $TCNQ^{-\cdot}$ in **2**: (a) π-dimerized $TCNQ^{-}$, (b) undimerized $TCNQ^{-\cdot}$, and Inter-planar distance of $TCNQF^{-\cdot}$ in **3**: (c) π-dimerized $TCNQF^{-\cdot}$, (d) undimerized $TCNQF^{-\cdot}$. Hydrogen atoms and disordered fluorine atoms were omitted for the sake of clarity. Colour code: carbon: grey; nitrogen: blue; cobalt: purple; iron: orange.

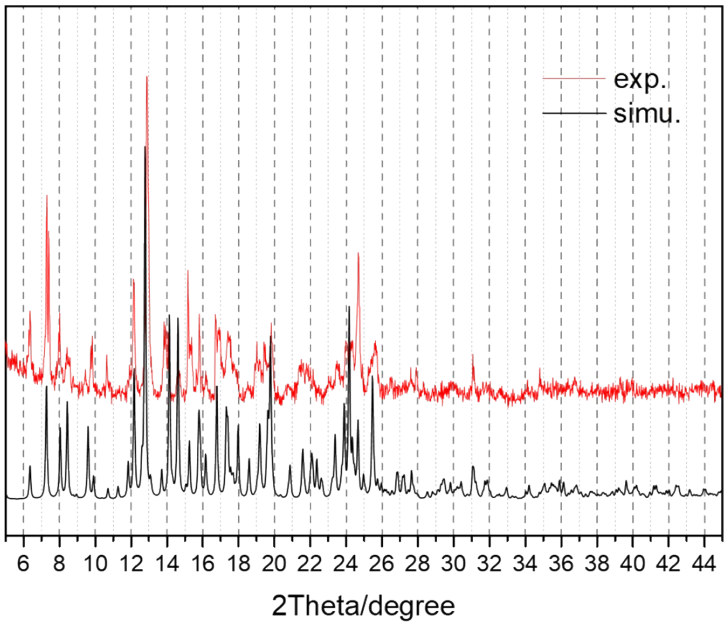
Section S3. **Powder X-ray diffraction data and simulations.**



(a)



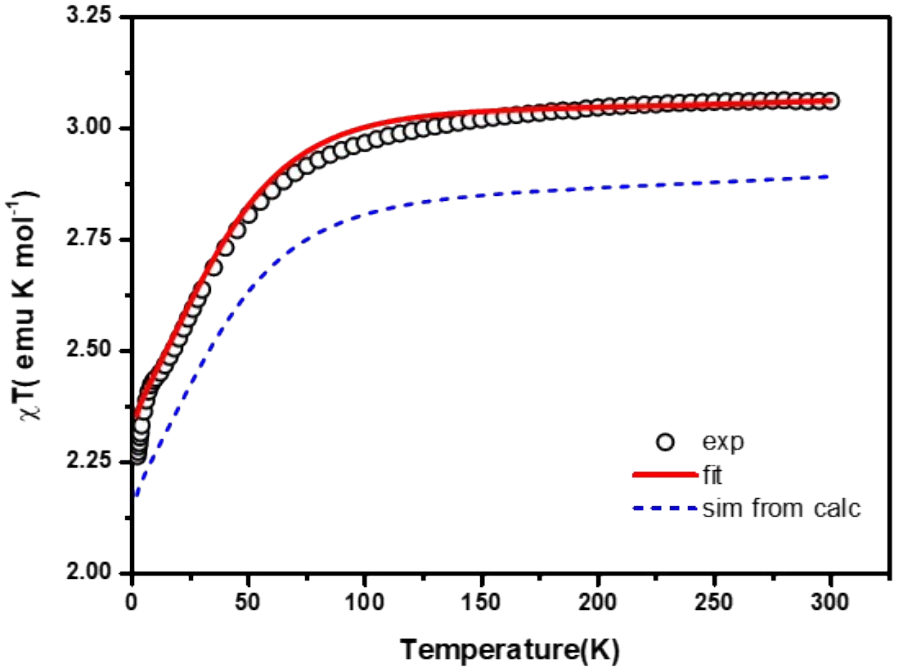
(b)



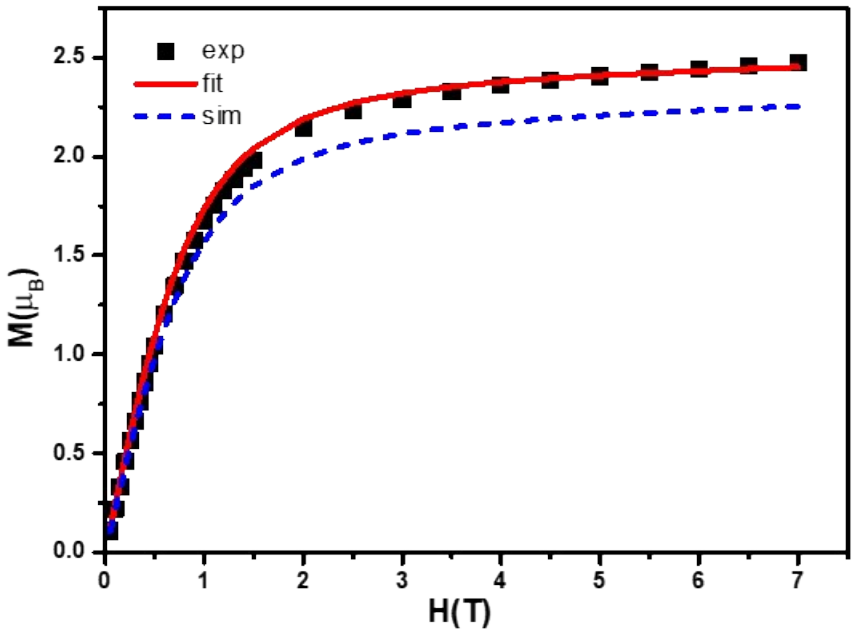
(c)

Figure S4. Powder X-ray diffraction for (a) **1**, (b) **2** and (c) **3**.

Section S4. Temperature- and field-dependent DC magnetization plots of 1



(a)



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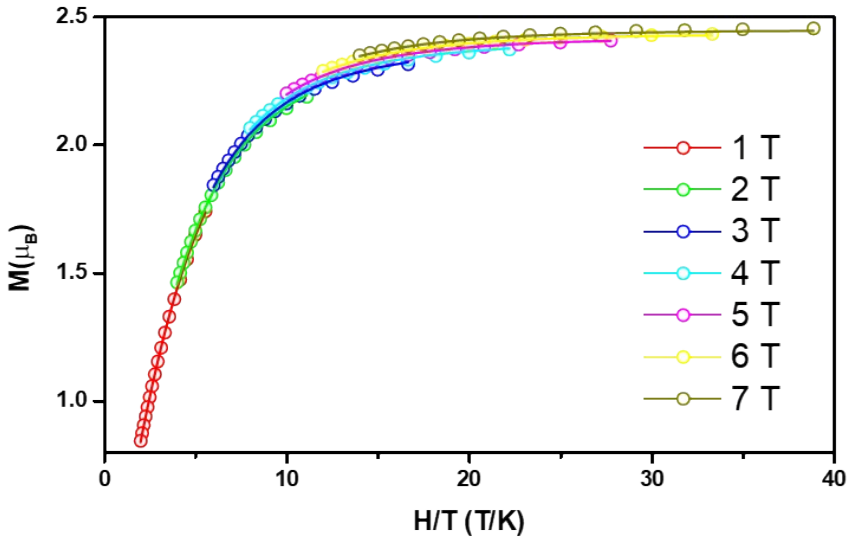


(c)

Figure S5. (a) χT vs T plot for **1** from 1.8-300 K under a 1000 Oe field (open circle) with fit (red line) and simulation with parameters from *ab initio* calculation (blue dashed line). (b) Magnetization data for **1** at 1.8 K from 0 - 7 T (solid block) with fit (red line) and simulation with parameters from *ab initio* calculations (blue dashed line). (c) Reduced magnetization data for **1** from 1.8-5K under 1-7 T magnetic fields and the fittings with the same parameters shown in the magnetic properties section.

Section S5. **Cole-Cole plot fittings.**

The Cole-Cole equation[1] below was used for the relaxation fittings of the AC data with the least squares method:

$$\chi^{*}(\omega) = \chi_s + \frac{\chi_T - \chi_s}{1 + (i\omega\tau)^{1-\alpha}} \qquad (S1)$$

Where $\chi^{*}(\omega)$ is the complex magnetic susceptibility, χ_T and χ_s are the "static" and "infinite frequency" magnetic susceptibilities, ω is angular frequency of alternating field. α is a parameter between 0 and 1.

Table S3. Fitting parameters of the Cole-Cole plots for variable-field AC magnetic susceptibilities data for **1** at *T* = 1.8 K.

H/Oe	χ_s / emu mol^{-1}	χ_T / emu mol^{-1}	τ / s	α
250	0.803029	1.513700	0.001505	0.079183
500	0.335141	1.560120	0.003292	0.132153
750	0.168002	1.556210	0.004961	0.162339
1000	0.095445	1.540634	0.006498	0.185753
1250	0.059656	1.512402	0.007815	0.202525
1500	0.036339	1.491969	0.009086	0.224662
1750	0.019631	1.439722	0.009915	0.244189
2000	0.021347	1.324544	0.009453	0.221707
2500	0.014191	1.143987	0.008248	0.215059
3000	0.005019	0.987262	0.006757	0.227973
3500	0.003641	0.795444	0.004431	0.212963
4000	0.002684	0.632542	0.002736	0.199705
5000	0.000000	0.422131	0.001042	0.210715
6000	0.000000	0.310067	0.000555	0.247732

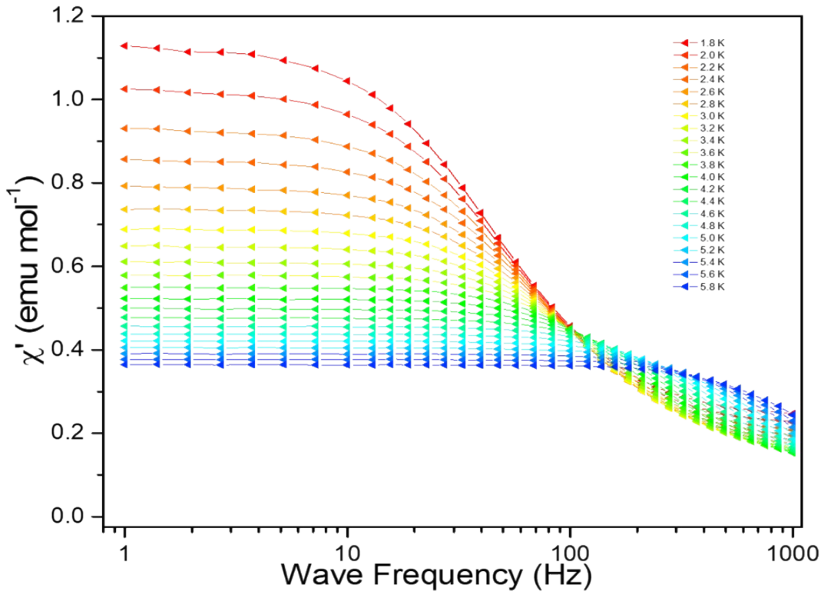
Table S4. Fitting parameters of the Cole-Cole plots for variable-field AC magnetic susceptibilities of 1 under H_{DC} = 500 Oe.

T/ K	χ_s / emu mol^{-1}	χ_T / emu mol^{-1}	τ / s	α
1.8	0.225751	1.138662	0.003434	0.136459
2.0	0.205087	1.034141	0.002908	0.134518
2.2	0.186434	0.937890	0.002444	0.131322
2.4	0.172673	0.863551	0.002102	0.126461
2.6	0.160589	0.798571	0.001814	0.122552
2.8	0.150670	0.744174	0.001581	0.117771
3.0	0.141917	0.695506	0.001376	0.112655
3.2	0.132523	0.658052	0.001205	0.115585
3.4	0.127941	0.615099	0.001031	0.099231
3.6	0.122480	0.582680	0.000890	0.090950
3.8	0.117484	0.552504	0.000760	0.082234
4.0	0.113100	0.525014	0.000646	0.072830
4.2	0.108839	0.500463	0.000546	0.064389
4.4	0.105106	0.478085	0.000460	0.055670
4.6	0.101473	0.457583	0.000386	0.047800
4.8	0.098021	0.438861	0.000324	0.040724
5.0	0.095132	0.421581	0.000273	0.033889
5.2	0.091647	0.405395	0.000229	0.028894
5.4	0.087712	0.390752	0.000192	0.025647
5.6	0.084745	0.377088	0.000162	0.020391
5.8	0.080182	0.364228	0.000136	0.020008

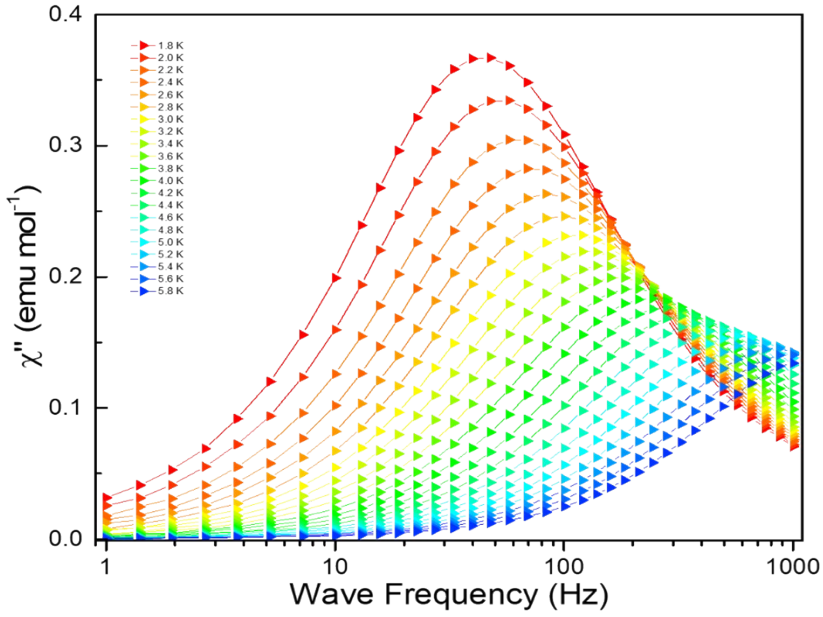
Table S5. Fitting parameters of the Cole-Cole plots for variable-field AC magnetic susceptibilities of 1 under H_{DC} = 1750 Oe.

T/ K	χ_s / emu mol^{-1}	χ_T / emu mol^{-1}	τ / s	α
1.8	0.017743	0.812731	0.006616	0.223733
2.0	0.016241	0.752787	0.005724	0.222138
2.2	0.017212	0.688890	0.004811	0.207378
2.4	0.018110	0.641018	0.004144	0.193241
2.6	0.019375	0.596736	0.003547	0.176140
2.8	0.020208	0.559781	0.003051	0.160736
3.0	0.020929	0.528463	0.002616	0.145613
3.2	0.020737	0.503347	0.002232	0.135550
3.4	0.022243	0.473873	0.001844	0.111759
3.6	0.022456	0.454479	0.001537	0.098005
3.8	0.022818	0.432519	0.001255	0.082040
4.0	0.022991	0.413782	0.001021	0.068815
4.2	0.022907	0.397285	0.000825	0.055039
4.4	0.022789	0.384167	0.000671	0.046723
4.6	0.022706	0.369304	0.000544	0.039098
4.8	0.022320	0.355687	0.000442	0.034189
5.0	0.021981	0.342535	0.000359	0.027009
5.2	0.022217	0.331465	0.000295	0.020961
5.4	0.022328	0.321776	0.000243	0.012717
5.6	0.022875	0.315234	0.000202	0.006265
5.8	0.021158	0.308997	0.000168	0.004965

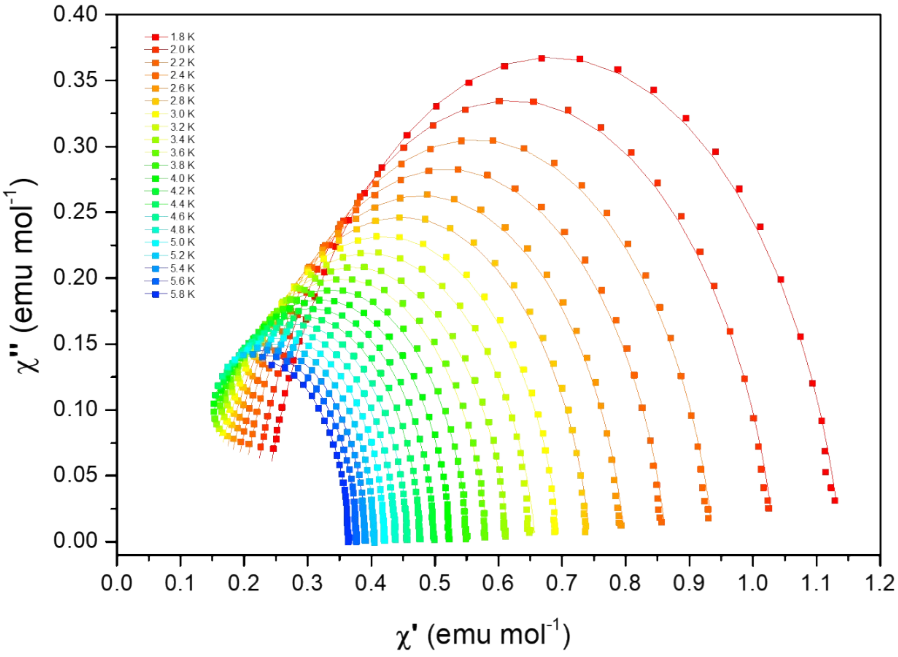
Section S6. Dynamic magnetic susceptibility data plots and fitting of different relaxation processes.



(a)

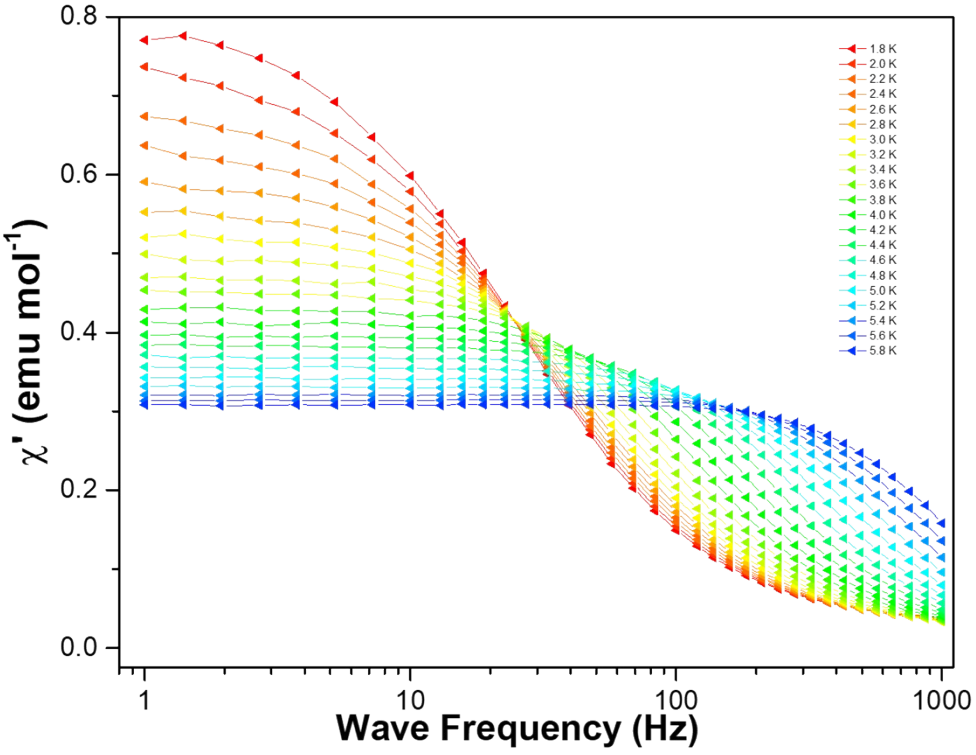


(b)

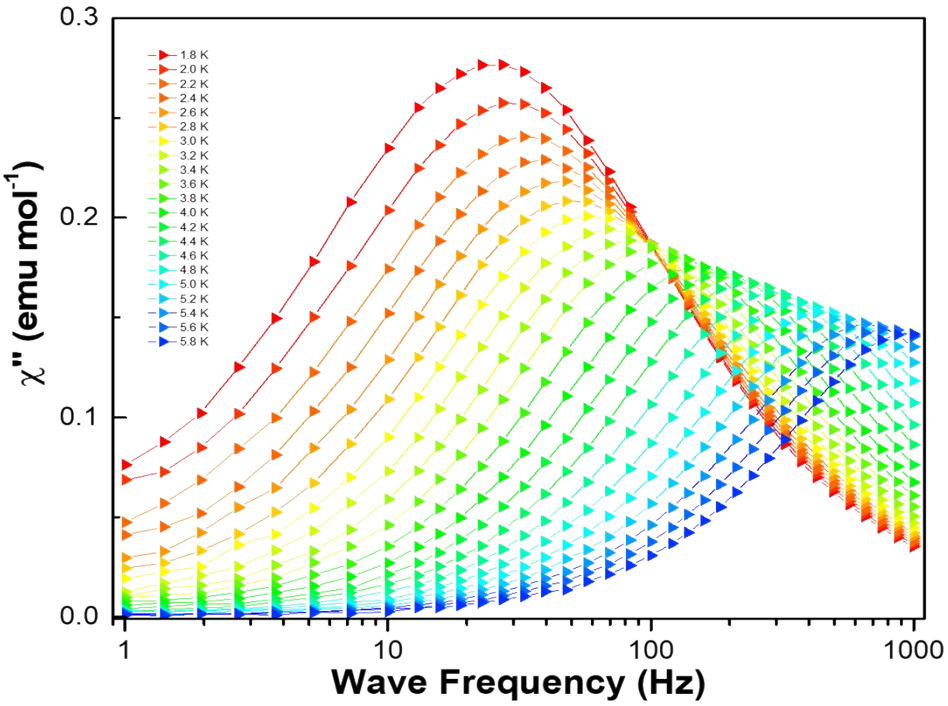


(c)

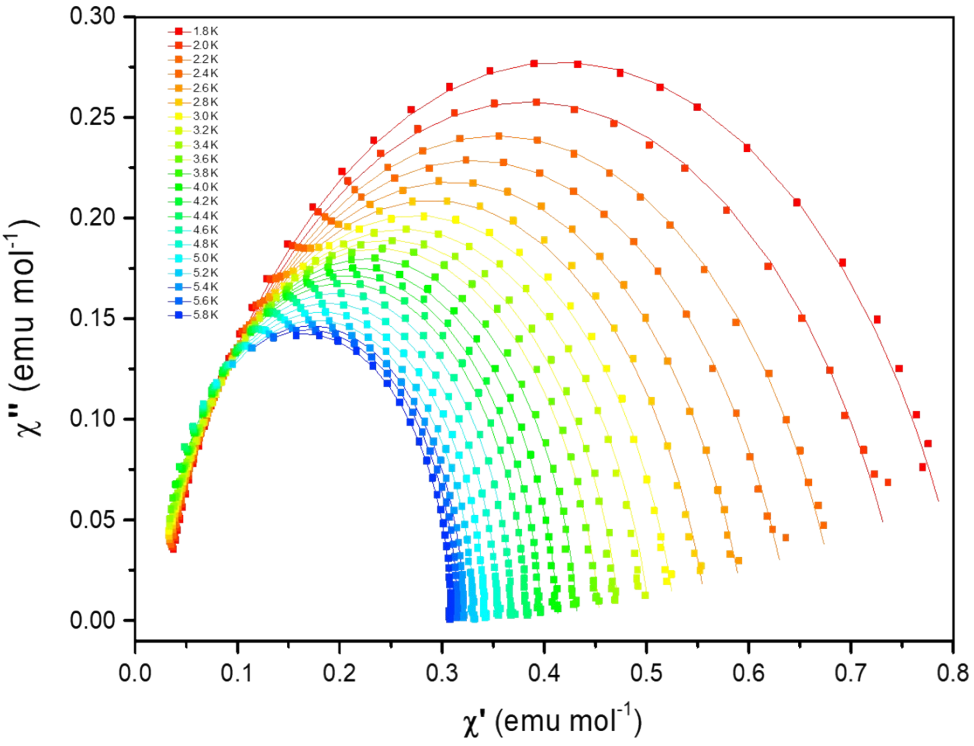
Figure S6. Frequency dependence of (a) in-phase and (b) out-of-phase ac susceptibility data from 1 Hz to 1000 Hz under H_{DC} = 500 Oe from 1.8 K to 5.8 K and (c) Cole-Cole plots with best fits (solid lines) for **1** from 1.8 to 5.8 K


0.8
0.6
0.4
0.2
0.0
χ' (emu mol-1)
1
10
100
1000
Wave Frequency (Hz)
1.8 K
2.0 K
2.2 K
2.4 K
2.6 K
2.8 K
3.0 K
3.2 K
3.4 K
3.6 K
3.8 K
4.0 K
4.2 K
4.4 K
4.6 K
4.8 K
5.0 K
5.2 K
5.4 K
5.6 K
5.8 K

(a)

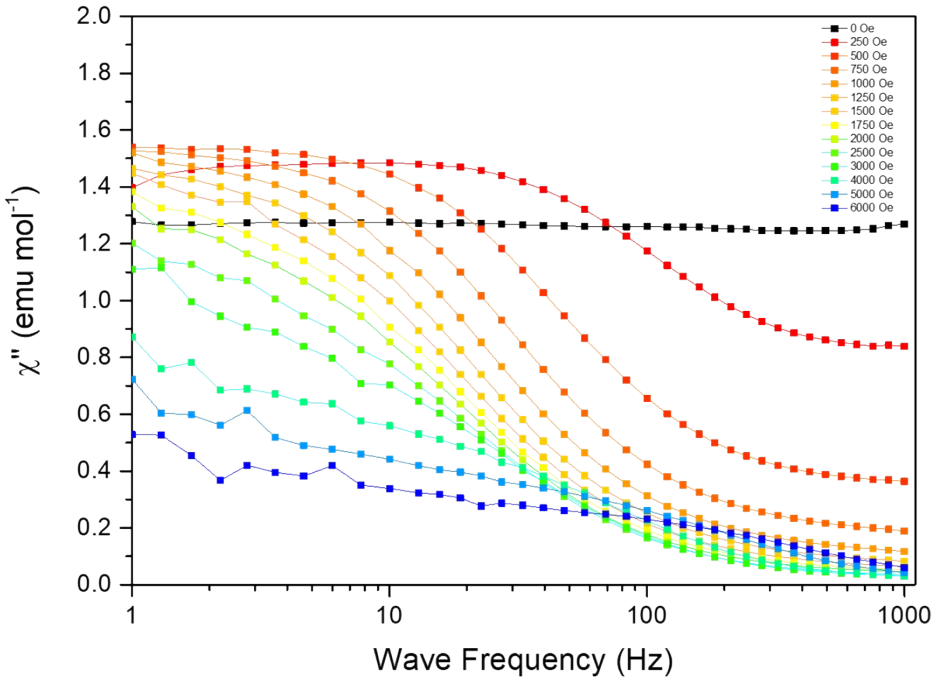

0.3
0.2
0.1
0.0
χ'' (emu mol-1)
1
10
100
1000
Wave Frequency (Hz)
1.8 K
2.0 K
2.2 K
2.4 K
2.6 K
2.8 K
3.0 K
3.2 K
3.4 K
3.6 K
3.8 K
4.0 K
4.2 K
4.4 K
4.6 K
4.8 K
5.0 K
5.2 K
5.4 K
5.6 K
5.8 K

(b)

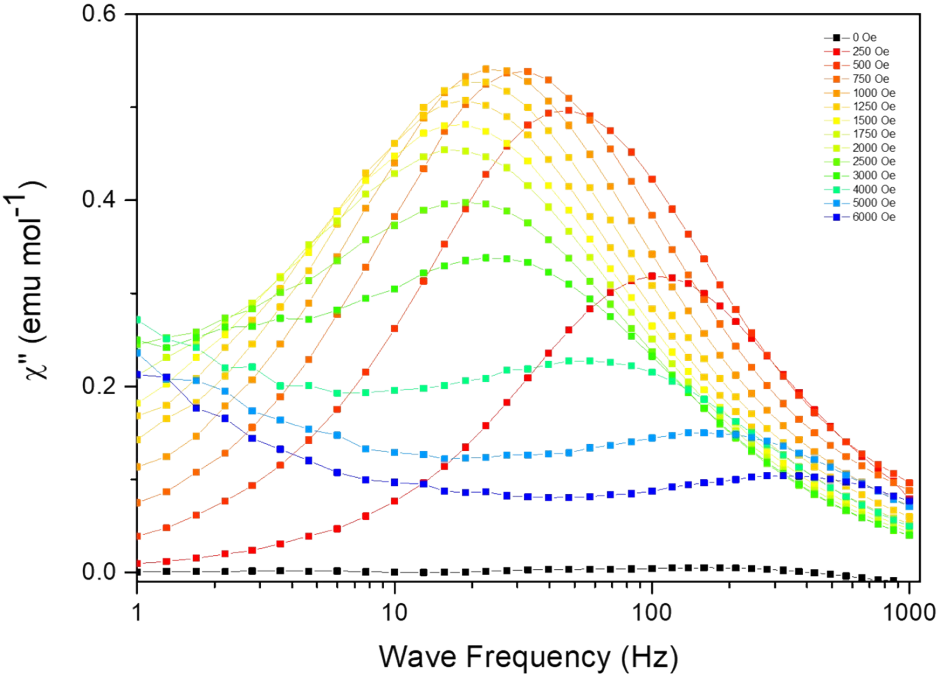


(c)

Figure S7. Frequency dependence of (a) in-phase and (b) out-of-phase ac susceptibility from 1 Hz to 1000 Hz under H_{DC} = 1750 Oe from 1.8 K to 5.8 K and (c) Cole-Cole plots with best fits (solid lines) for **1**


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
χ" (emu mol-1)
1
10
100
1000
Wave Frequency (Hz)
0 Oe
250 Oe
500 Oe
750 Oe
1000 Oe
1250 Oe
1500 Oe
1750 Oe
2000 Oe
2500 Oe
3000 Oe
4000 Oe
5000 Oe
6000 Oe

(a)


0.6
0.4
0.2
0.0
χ" (emu mol-1)
1
10
100
1000
Wave Frequency (Hz)
0 Oe
250 Oe
500 Oe
750 Oe
1000 Oe
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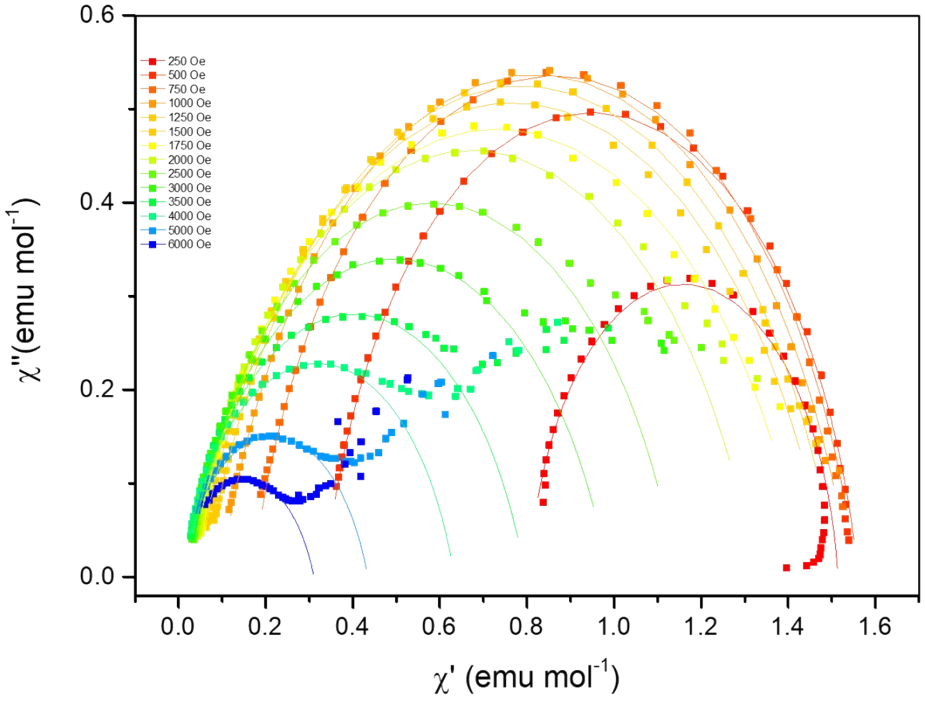
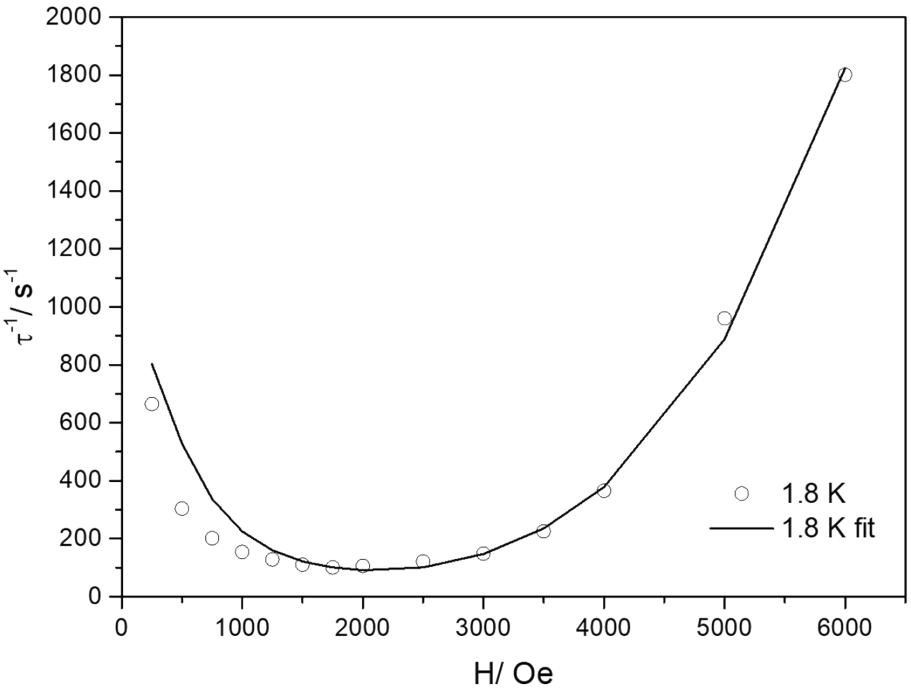
1500 Oe
1750 Oe
2000 Oe
2500 Oe
3000 Oe
4000 Oe
5000 Oe
6000 Oe

(b)

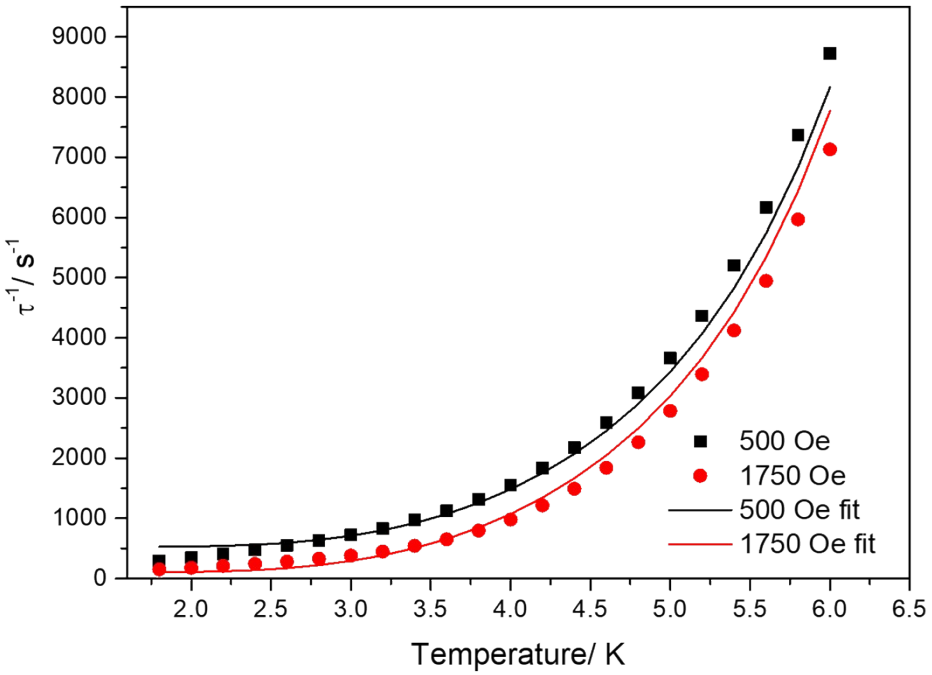


(c)

Figure S8. Frequency dependence of (a) in-phase and (b) out-of-phase ac susceptibility from 1 Hz to 1000 Hz at T = 1.8 K under H_{dc} fields from 0 Oe to 6000 Oe and (c) Cole-Cole plots with best fits (solid lines) for **1**.

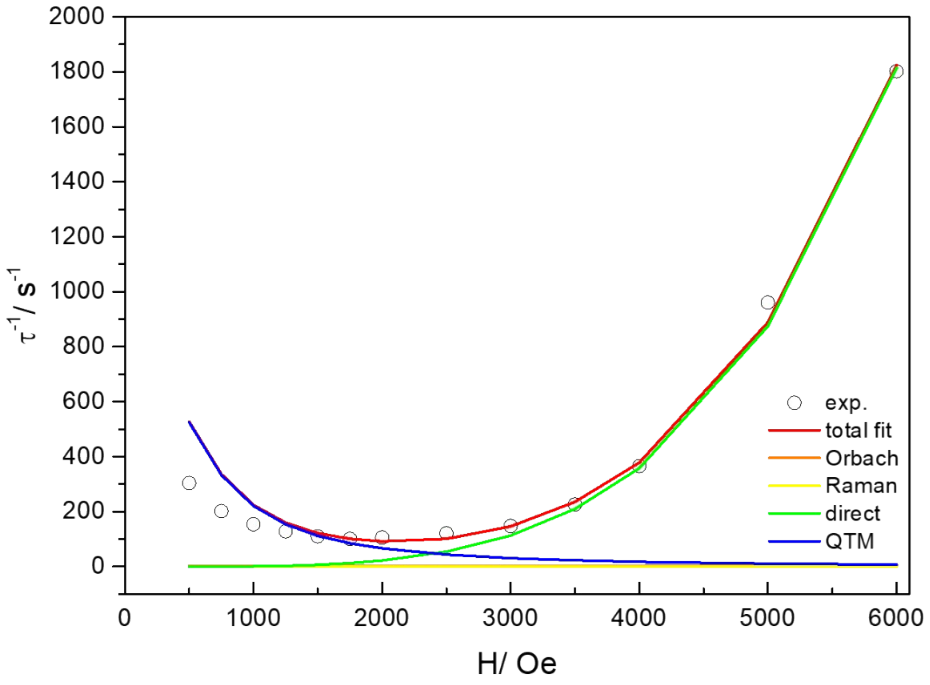

2000
1800
1600
1400
1200
1000
800
600
400
200
0
τ-1/ s-1
0
1000
2000
3000
4000
5000
6000
H/ Oe
1.8 K
1.8 K fit

(a)

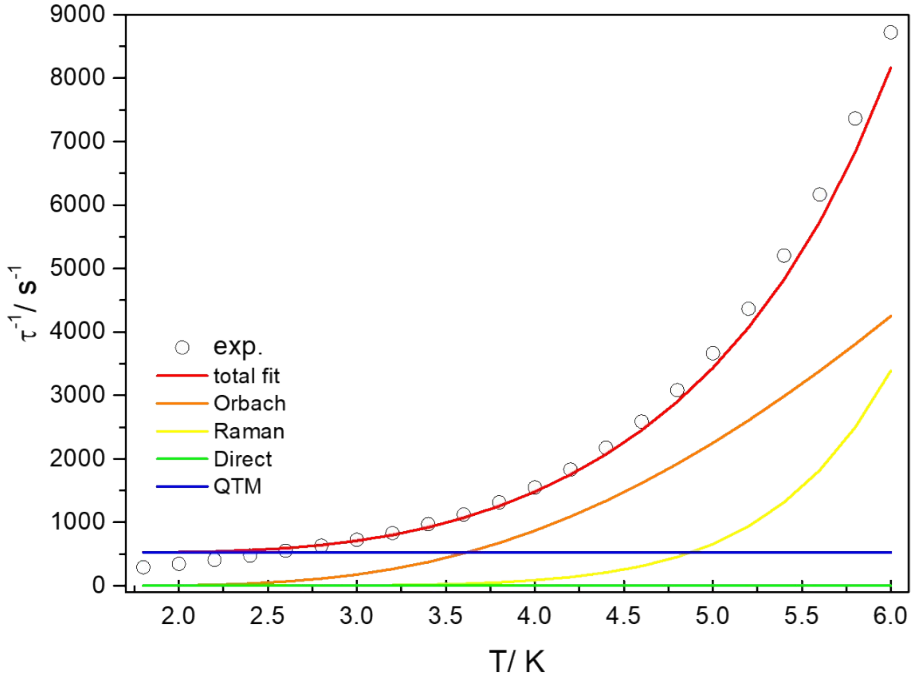


(b)

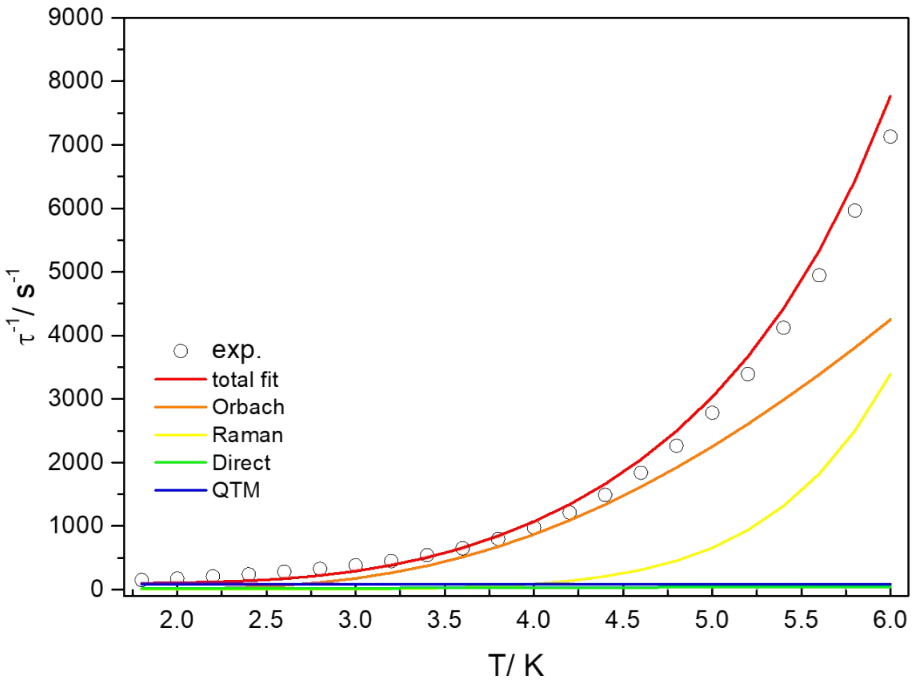
Figure S9. The fitting of (a) field-dependence and (b) temperature dependence of the inverse relaxation time (τ^{-1})


2000
1800
1600
1400
1200
1000
800
600
400
200
0
τ^{-1}/ s^{-1}
0
1000
2000
3000
4000
5000
6000
H/ Oe
exp.
total fit
Orbach
Raman
direct
QTM

(a)


9000
8000
7000
6000
5000
4000
3000
2000
1000
0
τ^{-1}/ s^{-1}
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
T/ K
exp.
total fit
Orbach
Raman
Direct
QTM

(b)



(c)

Figure S10. Contributions of different relaxation processes for the inverse relaxation time τ^{-1} for (a) field dependence of τ^{-1} at 1.8 K, (b) temperature dependence of τ^{-1} under H_{dc} = 500 Oe and (c) temperature dependence of τ^{-1} under H_{dc} = 1750 Oe for **1**.

Section S7. Spin-Crossover Fittings.

The equation[2] below was used for fitting the thermodynamic parameters of the SCO behaviour of **2** and **3**.

$$ln\left[\frac{1-n_{HS}}{n_{HS}}\right]=\frac{\left[\Delta H+\Gamma\left(1-2n_{HS}\right)\right]}{RT}-\frac{\Delta S}{R} \qquad (S2)$$

Where n_{HS} is the molar fraction of high-spin Co(II) species, ΔH, ΔS and Γ are the molar enthalpy, molar entropy and SCO cooperativity parameters, R is the gas constant. n_{HS} values at certain temperatures were calculated from the equation as follow:

$$n_{HS}(T)=\left[\chi T-(\chi T)_{LS}-(\chi T)_{rad}-(\chi T)_{TIP}\right]/\left[(\chi T)_{HS}-(\chi T)_{LS}\right] \qquad (S3)$$

Where $(\chi T)_{HS}$, $(\chi T)_{LS}$, $(\chi T)_{rad}$ and $(\chi T)_{TIP}$ are the χT values for high-spin Co(II), low-spin Co(II), $TCNQ^{\cdot-}$/ $TCNQF^{\cdot-}$ radical and temperature independent paramagnetism. The $(\chi T)_{HS}$, $(\chi T)_{LS}$ and $(\chi T)_{rad}$ values were fixed as $(\chi T)_{HS} = 3.00\ emu\ K\ mol^{-1}$ (*S* = 3/2, g_{iso} = 2.53 from **1**) and $(\chi T)_{LS} = (\chi T)_{rad} = 0.375\ emu\ K\ mol^{-1}$ (*S* = 1/2, *g* = 2.00). On the other hand, χT value at certain temperature can be expressed as:

$$\chi T = n_{HS}(\chi T)_{HS}+\left(1-n_{HS}\right)(\chi T)_{LS}+(\chi T)_{rad}+\chi_{TIP}T \qquad (S4)$$

The approximately linear relationships of the plots Figure. S11 (a) and (b) indicates that the Γ terms are negligible for **2** and **3** and that equation S2 can be rewritten as follow:

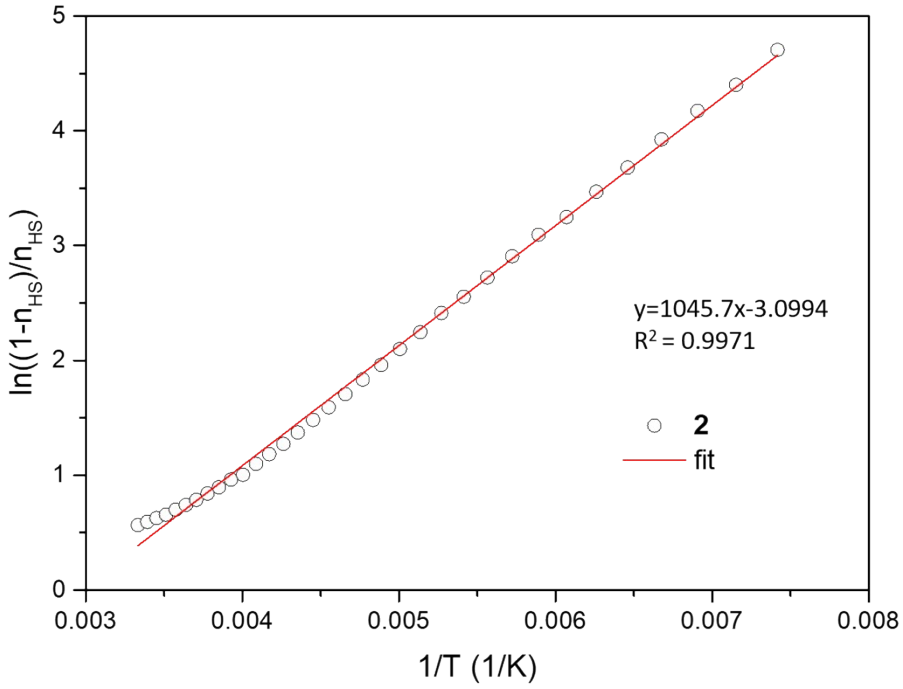
$$ln\left[\frac{1-n_{HS}}{n_{HS}}\right]=\frac{\Delta H}{RT}-\frac{\Delta S}{R} \qquad (S5)$$

The slope of $ln\left[\frac{1-n_{HS}}{n_{HS}}\right]$ vs 1/*T* plot is $\frac{\Delta H}{R}$ and the intersection with the y axis is $-\frac{\Delta S}{R}$.

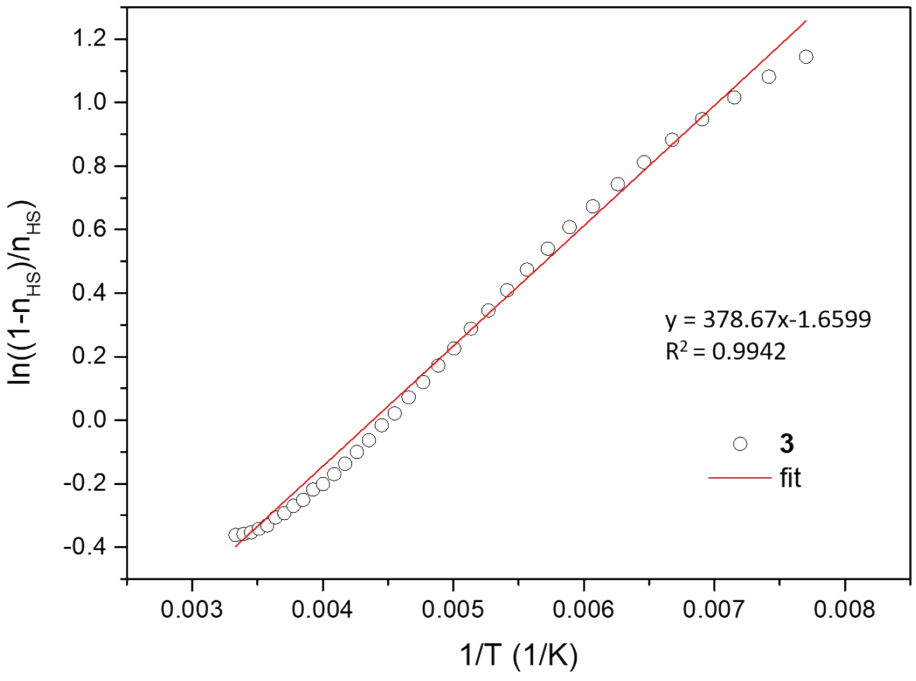
The parameters from least-squares fitting with equations S4 and S5 of χT vs T plots are summarized in Table S6. The transition temperature, $T_{1/2}$, is defined as the temperature at which $n_{HS} = n_{LS}$ so that the $T_{1/2}$ can be expressed as:

$$T_{1/2}=\frac{\Delta H}{\Delta S} \qquad (S6)$$

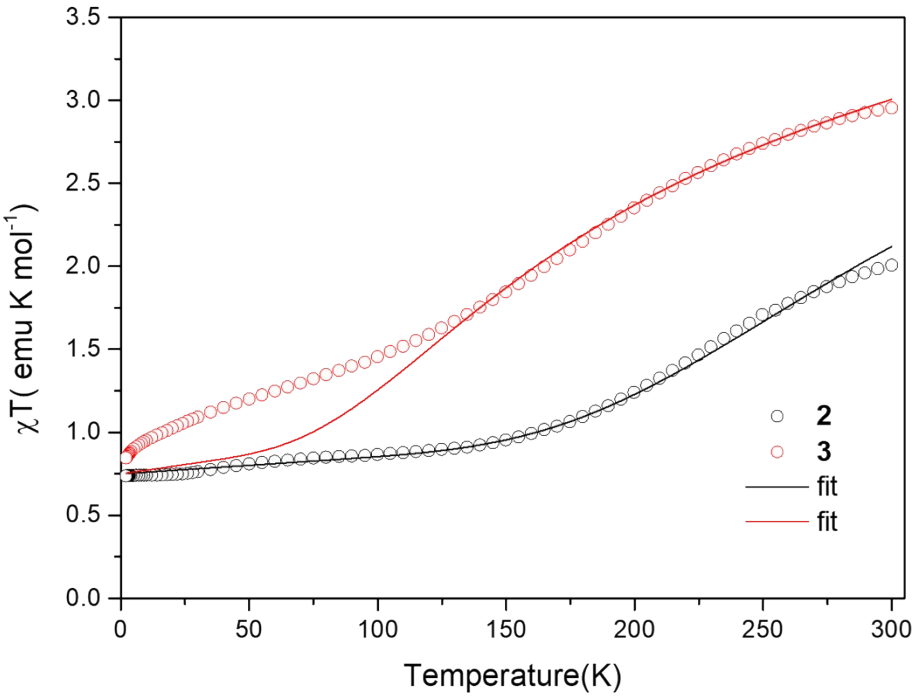
The best fits of χT vs T curves are shown in Figure S11(c). The fit matches well with experimental data for **2** from 2 - 300 K. Differences between the fitting and experimental data, however, were observed for **3** below 120 K. Similar phenomena have been observed for several SCO systems with geometric constraints of the crystal lattice and coordination sphere and/or supramolecular interactions.[3-6] Since the steric effect of the fluorine substitution on $TCNQF^{\cdot-}$ is insignificant, the incomplete SCO transition is attributed to the electric dipole interaction between the $TCNQF^{\cdot-}$ and $[Co(Fctp)_2]^{2+}$ moieties.


y=1045.7x-3.0994
R² = 0.9971
2
fit
ln((1-n_HS)/n_HS)
1/T (1/K)

(a)


y = 378.67x-1.6599
R² = 0.9942
3
fit
ln((1-n_HS)/n_HS)
1/T (1/K)

(b)



(c)

Figure S11. $ln\left[\frac{1-n_{HS}}{n_{HS}}\right]$ vs $1/T$ plots of (a) **2** and (b) **3** for fitting the SCO thermodynamic parameters and (c) fitting of the χT vs T plots of **2** and **3** with parameters from the fits of (a) and (b).

Table S6. Fitting parameters of χT vs T plots for **2** and **3** obtained from the least squares method.

Compound	**2**	**3**
ΔH (kJ mol^{-1})	8.69	3.12
ΔS (J K^{-1} mol^{-1})	25.8	13.8
χ_{TIP} (emu mol^{-1})	0.00102	0.00224
$T_{1/2}$(K)	336	226

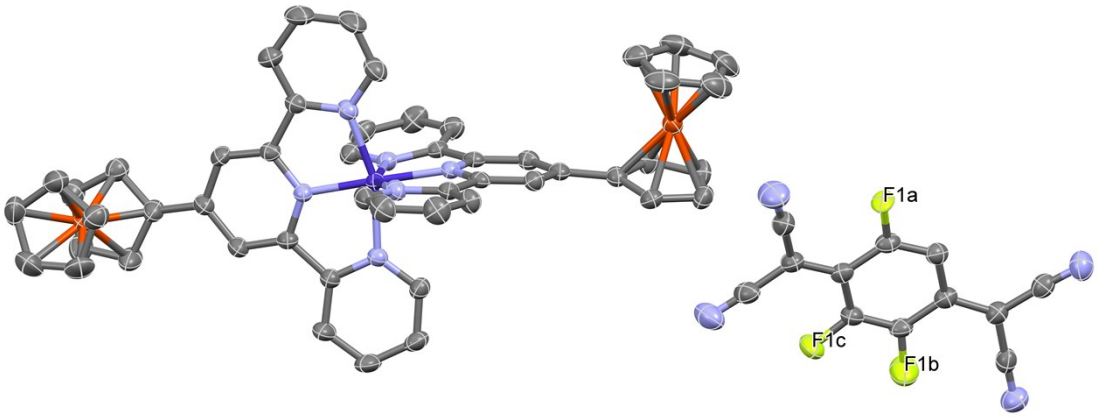
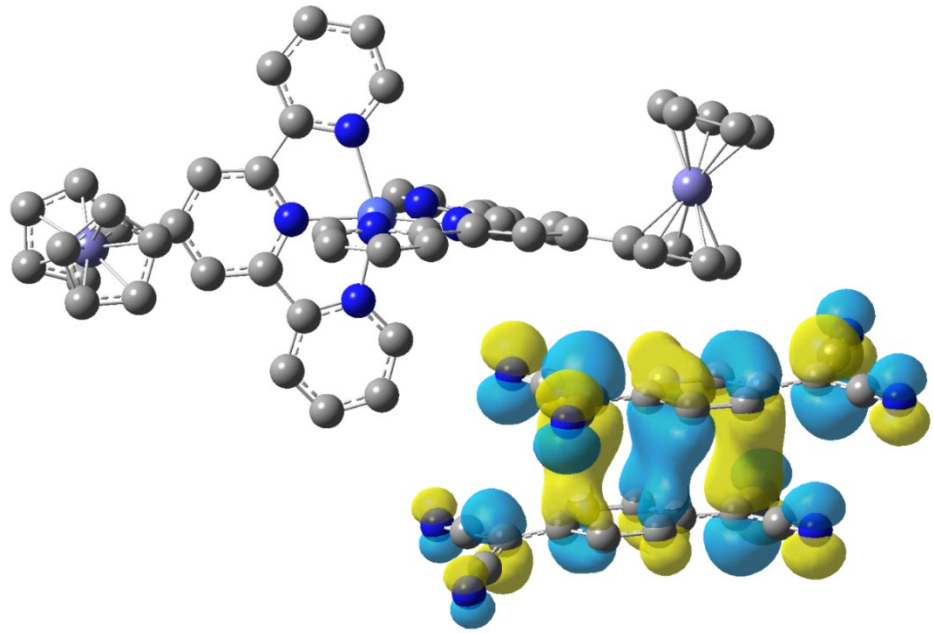
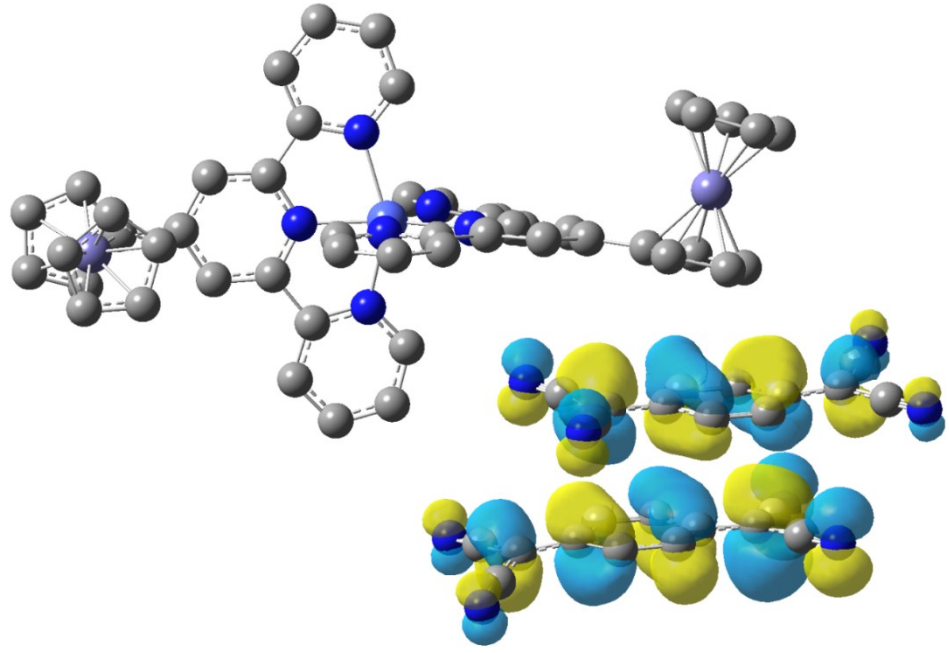


Figure S12. Asymmetric disordered fluorine substituent on $TCNQF^{-\cdot}$ in **3**. The refined occupancies for F1a, F1b, and F1c are 0.566, 0.099 and 0.335 respectively. Hydrogen atoms were omitted for the sake of clarity.

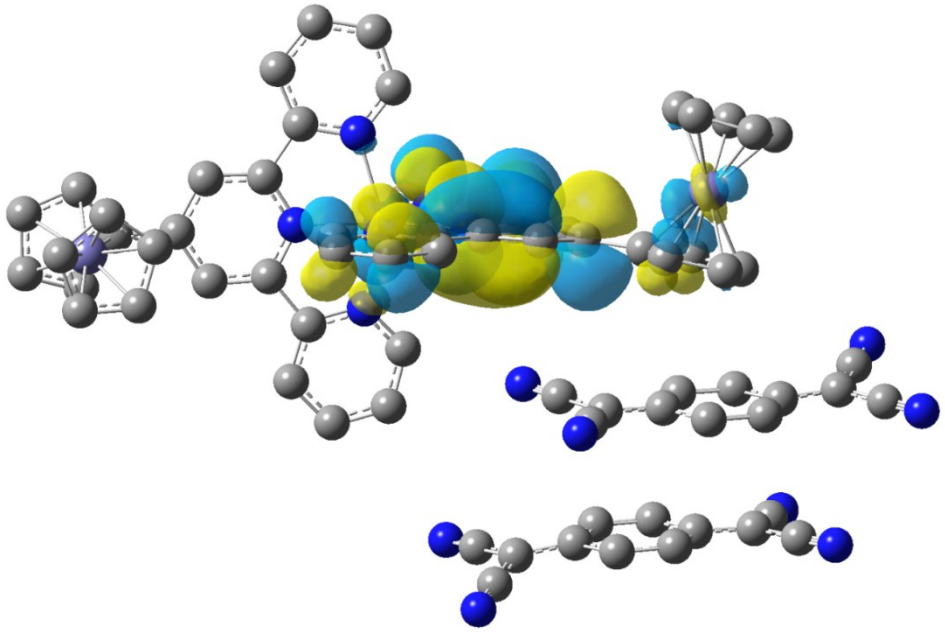
Section S8. Theoretical calculations.



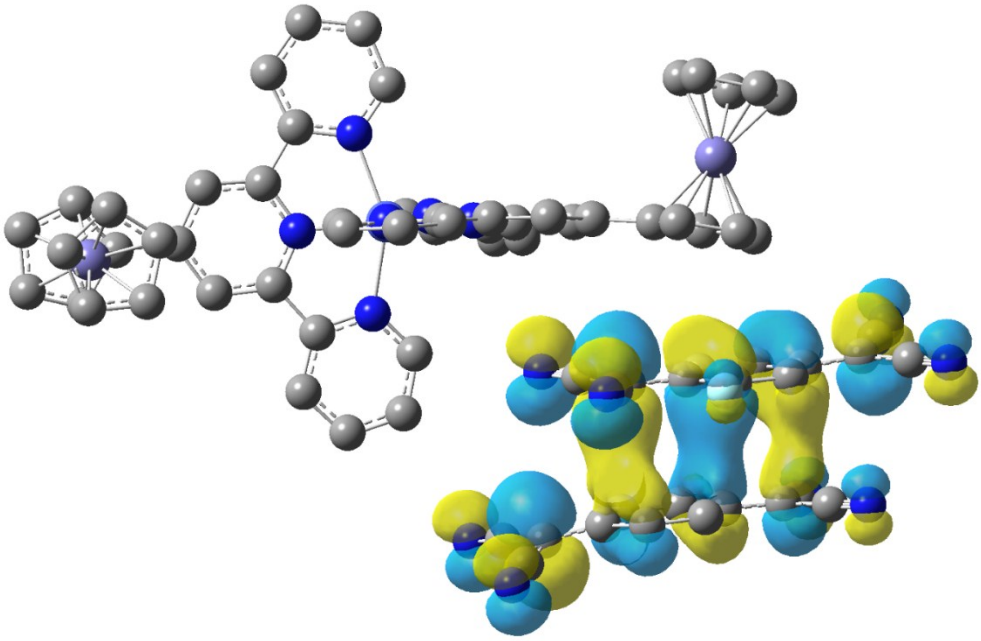
(a)



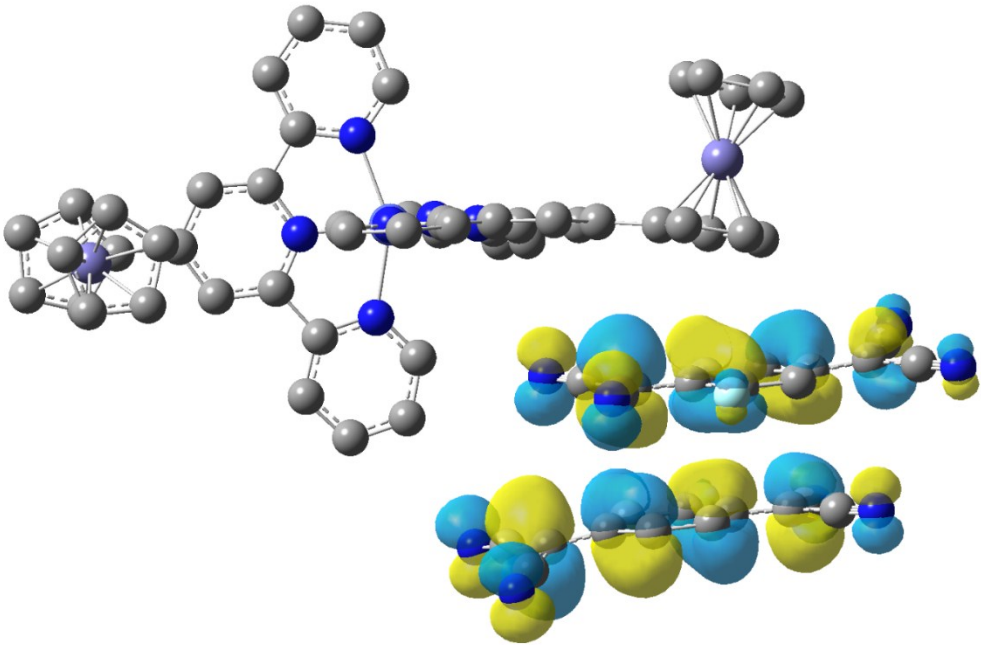
(b)



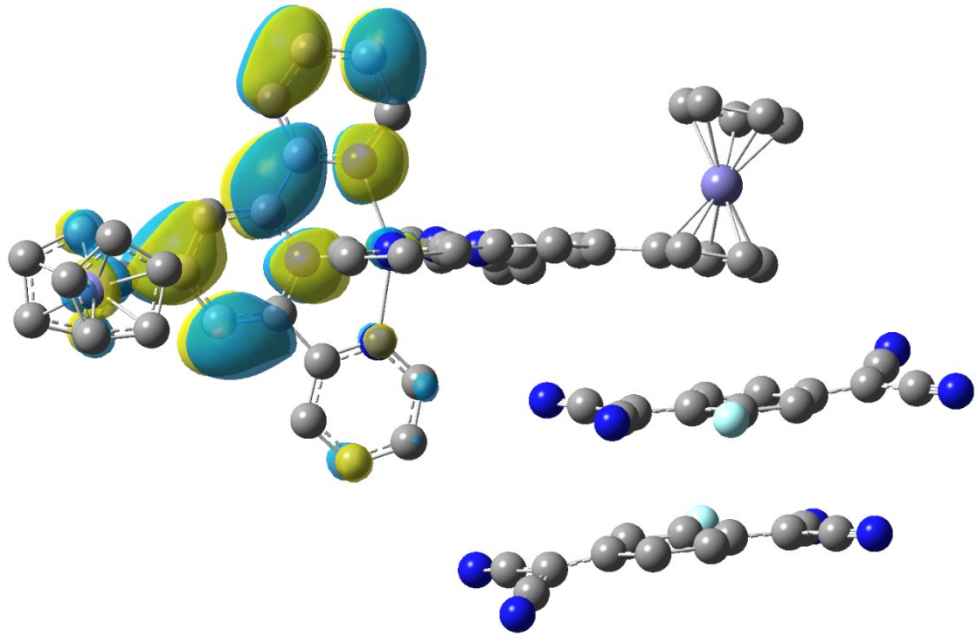
(c)



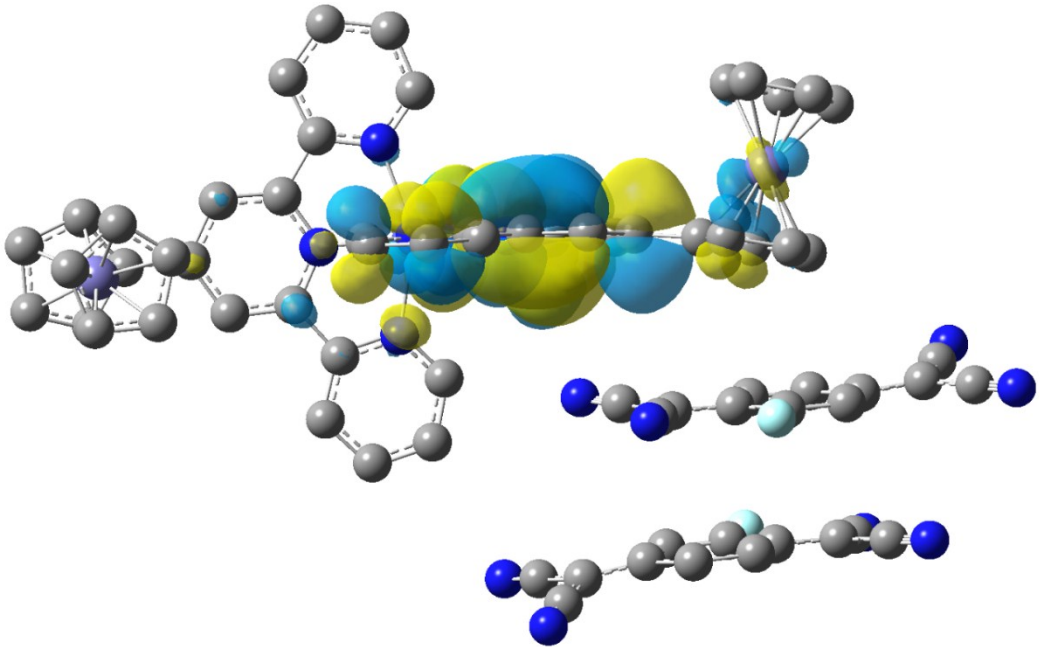
(d)



(e)



(f)



(g)

Figure S13. Plots of frontier molecular orbital surfaces of (a) HOMO (b) LUMO (c) LUMO+1 for {[Co(Fctp)$_2$](TCNQ)$_2$} and (d) HOMO (e) LUMO (f) LUMO+1 (g) LUMO+2 for {[Co(Fctp)$_2$](TCNQF)$_2$} with isovalues = 0.02 from DFT calculations. The yellow and blue regions indicate the positive and negative signs of the wavefunctions respectively.

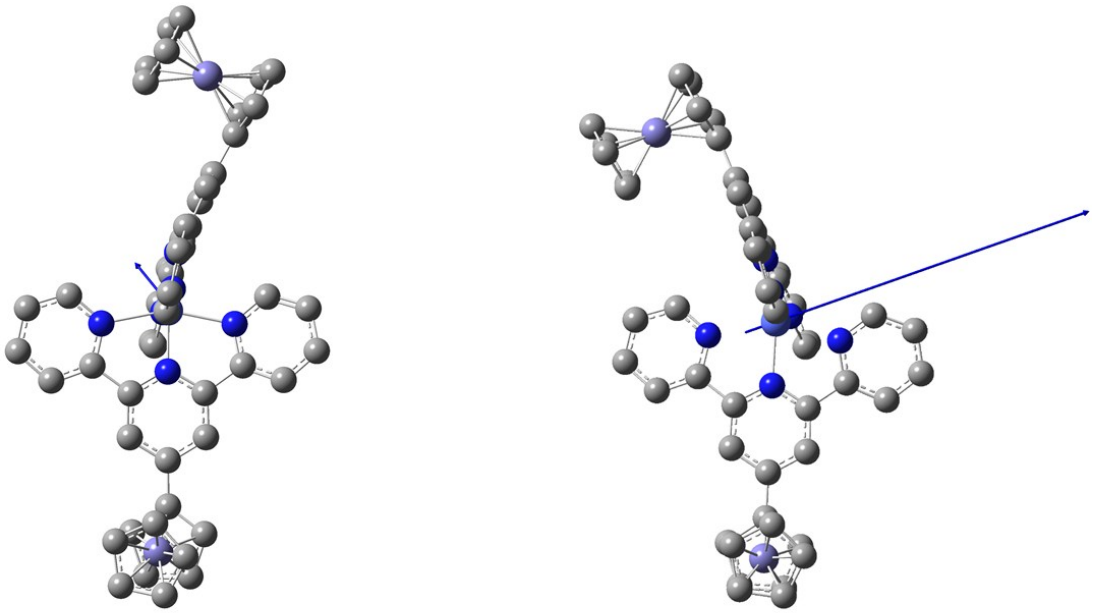


Figure S14. Dipole moments of (a) low-spin (0.7688 Debye) and (b) high-spin (4.0338 Debye) $[Co(Fctp)_2]^{2+}$ cations from the DFT calculation.

Table S7. Selected structural parameters of **2** computed using TPSSh functionals (see Figure 1 for labels).

2	Bond distances (Å) and angles(°)		
	X-ray	HS	LS
Co-N1	1.877	2.056	1.874
Co-N2	1.936	2.056	1.936
Co-N3	1.987	2.155	2.005
Co-N4	1.998	2.194	2.007
Co-N5	2.157	2.155	2.183
Co-N6	2.136	2.194	2.182
N1-Co-N2	171.1	173.0	179.5
N3-Co-N4	161.6	151.4	162.2
N5-Co-N6	156.8	151.3	157.2

Table S8. Energy of the spin states produced by the TPSSh/DFT calculations.

Spin State, S	E_s (Hartree)	$\Delta E = E_{3/2} - E_{1/2}$ (kJ/mol)
3/2	-6166.810104	13.55
1/2	-6166.815266	

Table S9. Atomic coordinates for DFT calculations of **1c**.

Atoms	x	y	z
Co	7.291425	1.254556	4.480644
Fe	9.572489	8.340265	2.012513
Fe	3.933206	-2.556003	9.763193
N	8.124887	0.935852	2.512659
N	8.180891	3.039181	4.03099
N	8.943707	0.149008	5.309981
N	6.810015	2.535353	6.197562
N	6.420841	-0.363818	5.396453
N	5.274223	1.240887	3.729629
C	8.979126	1.908191	2.110515
C	8.057094	4.091298	4.863308
C	8.915644	3.152793	2.90725
C	8.642043	5.305606	4.568707
H	8.528075	6.042766	5.156518
C	3.082	0.291783	4.008129
H	2.520153	-0.354262	4.41902
C	10.895285	-1.13995	6.804059
H	11.563086	-1.570536	7.323289
C	9.553528	-1.459773	6.97919
H	9.292781	-2.112364	7.619481
C	11.245578	-0.189763	5.86698
H	12.158089	0.032449	5.719083
C	10.239866	0.434895	5.144988
H	10.481843	1.094924	4.504499
C	11.041941	6.931182	2.050084
H	11.245152	6.327025	1.345784
C	2.564974	1.195082	3.082182
H	1.641273	1.182807	2.862523
C	9.404487	5.451193	3.402626
C	9.846566	1.728331	1.035478
H	10.450553	2.416925	0.785206
C	2.825414	-4.177481	9.177369
H	1.976341	-4.439522	9.511927
C	9.298425	9.573425	0.409301
H	9.983936	10.027098	-0.065599
C	11.594691	8.224298	2.22601
H	12.238981	8.634194	1.661854
C	3.048173	-3.295143	8.087623
H	2.379428	-2.864556	7.569784
C	6.544023	-2.056804	7.068047
H	7.070171	-2.587347	7.655262
C	7.296592	3.79659	6.112084
C	5.104626	-3.989487	8.910996
H	6.040654	-4.100652	9.032852
C	8.601088	-0.811908	6.205712

C	5.09233	-0.541582	5.310975
C	4.764369	2.092872	2.825152
H	5.35062	2.708069	2.399351
C	3.047439	-1.780989	11.443732
H	2.363802	-2.190824	11.960975
C	4.436009	0.354196	4.31923
C	10.118897	6.694912	3.12512
C	4.42123	-1.456806	6.103337
H	3.479679	-1.560183	6.02919
C	4.474207	-3.169654	7.910106
C	6.471584	4.332447	8.294162
H	6.355447	4.946453	9.008997
C	8.090353	-0.200912	1.808359
H	7.472189	-0.875462	2.06539
C	5.153741	-2.229605	7.018351
C	7.148234	-1.10574	6.254812
C	8.800894	8.276561	0.115892
H	9.093698	7.710071	-0.588408
C	9.540194	4.342931	2.566332
H	10.056162	4.40346	1.771186
C	3.419608	2.113913	2.486022
H	3.088796	2.744567	1.856664
C	2.849823	-0.912111	10.334107
H	2.010592	-0.641097	9.981062
C	5.980241	3.041474	8.389778
H	5.528916	2.749055	9.17399
C	8.594019	10.075556	1.537612
H	8.725196	10.922132	1.948106
C	6.161562	2.188182	7.318916
H	5.808478	1.308498	7.380937
C	8.915814	-0.437766	0.721594
H	8.862899	-1.259233	0.246495
C	11.020774	8.801085	3.387717
H	11.218742	9.662455	3.735195
C	4.080212	-4.603523	9.684672
H	4.213409	-5.196503	10.414417
C	7.659928	9.086067	1.942341
H	7.056277	9.153691	2.673676
C	5.114614	-1.144179	10.655743
H	6.055537	-1.055416	10.557543
C	4.440075	-1.926725	11.641326
H	4.855167	-2.454282	12.312826
C	7.134764	4.714002	7.138617
H	7.475462	5.596532	7.050952
C	9.818252	0.539514	0.33734
H	10.406934	0.394158	-0.393597
C	4.1198	-0.521189	9.848074
H	4.28153	0.055946	9.110378

C	10.10231	7.877044	3.943524
H	9.570217	8.014299	4.719188
C	7.786155	7.979432	1.064302
H	7.27899	7.177211	1.103264
N	14.231176	0.652537	7.350722
N	17.706309	9.103108	5.066865
N	14.629388	3.488263	10.713988
C	16.360338	5.842689	5.448933
C	17.415396	8.01001	4.836671
C	15.113336	4.032802	7.260473
C	15.413527	5.373438	7.638167
H	15.193587	5.669163	8.514019
C	16.013341	6.246818	6.767681
H	16.199442	7.134375	7.048964
C	17.050102	6.67595	4.536304
N	17.772985	5.65862	2.285844
C	14.412694	1.723408	7.742927
C	15.383826	3.665944	5.9129
H	15.13309	2.803305	5.605775
C	14.619631	3.29393	9.577129
C	15.995074	4.527946	5.056926
H	16.182643	4.242164	4.170538
C	14.657605	3.051043	8.179462
C	17.451872	6.145345	3.278384
N	16.103382	11.121842	2.406706
C	14.739927	7.900186	2.89592
N	15.469737	7.993677	-0.565746
C	13.389523	6.328948	4.845616
N	12.070279	6.594452	8.090604
C	12.188199	4.267602	5.499226
C	13.69202	5.80489	3.548138
H	13.436103	4.916456	3.331659
N	11.789071	3.230352	5.228081
C	15.309824	8.730815	1.894434
C	12.682522	5.564482	5.804959
C	14.460651	8.406137	4.198765
H	14.728019	9.29026	4.421008
C	15.750169	10.0519	2.179494
C	14.343963	6.563394	2.617221
H	14.536611	6.189608	1.765223
C	15.412358	8.307693	0.543879
C	13.817771	7.649074	5.131073
H	13.652443	8.014714	5.991421
C	12.341013	6.114056	7.075204

Table S10. Atomic coordinates for DFT calculations of **2c**.

Atoms	x	y	z
Co	-2.61149024	-1.25018486	0.98687792
Fe	4.40457247	-3.82307154	-1.3916349
Fe	-9.10818584	1.45838084	-1.05271645
N	-1.62068175	-1.95039442	2.77495005
N	-0.68589775	-1.5762873	0.38357343
N	-2.48513354	0.75737883	1.75745873
N	-2.64801042	-0.81434675	-1.16456721
N	-4.56500157	-0.64823912	1.17978326
N	-3.74873539	-3.06755455	0.79411941
C	-0.26974872	-1.99596662	2.67600267
C	-0.34492592	-1.43774395	-0.91241012
C	0.25054793	-1.90685241	1.29426421
C	0.94786851	-1.66500267	-1.33730462
H	1.16676889	-1.58240509	-2.25772612
C	-5.95346673	-3.98188697	0.49855345
H	-6.89350635	-3.84954649	0.47229994
C	-2.49070568	3.47510941	2.31981904
H	-2.48828013	4.40704377	2.4999714
C	-3.6695395	2.83163206	1.95987806
H	-4.48331371	3.31838679	1.89148153
C	-1.32423067	2.74406085	2.41245774
H	-0.51013529	3.16040668	2.67290547
C	-1.36291543	1.38954524	2.11797865
H	-0.5569265	0.88800454	2.17504202
C	4.46198298	-2.37472442	0.03847382
H	4.42894464	-2.52353244	0.9760791
C	-5.41071799	-5.25204275	0.31752508
H	-5.97550707	-5.99720249	0.1520719
C	1.93785686	-2.01725341	-0.41096554
C	0.54769695	-2.10930884	3.79825164
H	1.49261336	2.11858643	3.70527259
C	-10.74063934	0.87984074	0.04271556
H	-11.59808508	0.64565916	-0.2911488
C	5.5482138	-5.50920497	-1.26866094
H	6.46611005	-5.54102466	-1.028393
C	5.63310901	-2.32711034	-0.75828747
H	6.52292977	-2.43214677	-0.44430852
C	-9.65629579	-0.01576071	0.23710096
H	-9.65981058	-0.94735548	0.055714
C	-6.13628726	1.1401927	1.2702029
H	-6.31790591	2.06014013	1.42460687
C	-1.45855376	-0.97791347	-1.79164097
C	-8.98239512	2.11266633	0.87327128
H	-8.45905496	2.84004321	1.19011991
C	-3.64013277	1.46868211	1.70172653

C	-5.55715763	-1.508858	0.89905242
C	-3.24186087	-4.30125545	0.63610432
H	-2.30076661	-4.41769083	0.7012857
C	-9.74106162	1.77579263	-2.97837473
H	-10.64244463	1.82318928	-3.2752367
C	-5.09278023	-2.9118555	0.71826077
C	3.33247617	-2.15867819	-0.82238322
C	-6.87186485	-1.09652005	0.76725598
H	-7.55575474	-1.72328733	0.56192604
C	-8.54752953	0.74552829	0.75855036
C	-2.36952779	-0.19810642	-3.86317989
H	-2.27423953	0.0110855	-4.78439608
C	-2.1662968	-2.07575705	3.98987892
H	-3.11376744	-2.07572877	4.06410079
C	-7.17867658	0.26235644	0.94150523
C	-4.83666777	0.65824836	1.36850851
C	4.45001816	-5.60017122	-0.37357776
H	4.50267429	-5.70344805	0.5694201
C	1.56925141	-2.13207417	0.92955497
H	2.21610516	-2.36190706	1.58598554
C	-4.03221813	-5.41230123	0.38165007
H	-3.63831679	-6.26781929	0.2544367
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H	-9.22243156	-0.27763441	-3.14651123
C	-3.58509172	-0.02077607	-3.22432919
H	-4.33734964	0.32081072	-3.69509264
C	5.03676852	-5.36115308	-2.5869605
H	5.55151533	-5.27744633	-3.38095841
C	-3.67900385	-0.35157878	-1.8866146
H	-4.5187099	-0.24473868	-1.45552537
C	-1.41115504	-2.20534013	5.14379109
H	-1.83534853	-2.29089082	5.98999922
C	5.24875269	-2.09648843	-2.10391416
H	5.83894838	-2.01753627	-2.84372922
C	-10.33258399	2.18269986	0.42928429
H	-10.86828028	2.96622895	0.39756261
C	3.61944861	-5.35986829	-2.5055789
H	3.01807388	-5.27329278	-3.23679136
C	-7.66282492	2.36448478	-2.18210808
H	-6.93341473	2.8777636	-1.85444364
C	-8.95472693	2.86259214	-2.53086805
H	-9.23700632	3.76722098	-2.47174825
C	-1.29483947	-0.68619116	-3.13689154
H	-0.45340236	0.81956196	3.55738582
C	-0.02998952	-2.20906424	5.04637491
H	0.5098515	-2.27915353	5.82457995
C	-7.66757566	0.95895417	-2.41569339
H	-6.93939459	0.36649452	-2.26676117

C	3.83646779	-2.00349698	-2.16007073
H	3.31530817	-1.86340355	-2.94261987
C	3.25893733	-5.50994857	-1.14211471
H	2.37304796	-5.54462449	-0.80110055
N	0.75913754	5.45203808	1.81966836
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N	1.81418984	7.06648648	-2.15423361
C	6.23993756	3.80033404	0.29634286
C	8.58271541	3.34270158	-0.40169569
C	3.6156052	4.83511219	-0.09671871
C	4.58140481	4.84121419	-1.14422359
H	4.34445655	5.19943155	-1.99185535
C	5.84529553	4.34313987	-0.95762814
H	6.46603684	4.36036174	-1.67588638
C	7.5520843	3.34511731	0.56844357
N	8.09837429	2.61283908	2.97415079
C	1.46182312	5.48107769	0.90373817
C	3.9921329	4.21054423	1.12469224
H	3.35223848	4.12541858	1.82084542
C	2.04609089	6.3468938	-1.28318976
C	5.25161198	3.73360959	1.31339605
C	2.36252231	5.49594265	-0.19247313
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N	10.5808191	-0.3261201	-1.08816768
C	7.37325788	0.19890287	0.29505714
N	9.04703176	-1.72823449	2.74640761
C	4.79142573	1.18161314	-0.38473615
N	3.02370954	2.45856697	-3.13889928
C	2.40579672	1.53736965	0.16457724
C	5.0699271	0.66450126	0.92087596
H	4.3802784	0.64665571	1.57336196
N	1.53839393	1.43887657	0.90391617
C	8.63089085	-0.39397048	0.58585269
C	3.49784918	1.63468508	-0.73967774
C	7.09686643	0.74078193	-0.99388109
H	7.78959422	0.77143456	-1.64329604
C	9.70889338	-0.35387354	-0.33974528
C	6.3130021	0.19717305	1.24233141
H	6.47226366	-0.13638519	2.11760543
C	8.85719032	-1.11071912	1.78943257
C	5.86044977	1.21445799	-1.31410358
C	3.21844496	2.09935546	-2.05808487
F	5.67428583	1.66459451	-2.39764597
F	5.57618282	3.1711754	2.52085725

Section S9. **$[Zn(Fctp)_2](TCNQ)_2$(1') analogue synthesis and characterizations**

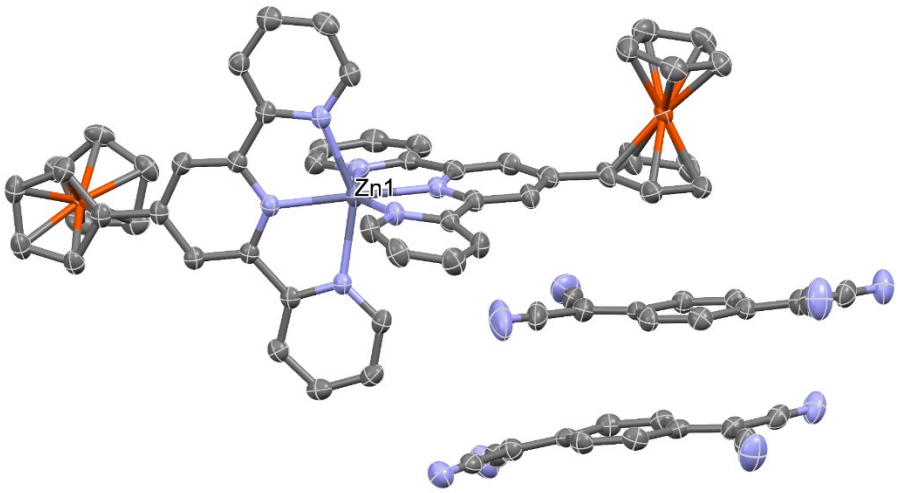
Synthesis of $[Zn^{II}(Fctp)_2](PF_6)_2$

The salt $[Zn^{II}(Fctp)_2](PF_6)_2$ was prepared by a modified literature method.[7] A sample of $Zn(OAc)_2{\cdot}4H_2O$ (0.25 mmol, 64 mg) was dissolved in 5 mL of methanol and Fctp (0.5 mmol, 209.5 mg) dissolved in 4 mL of $CHCl_3$ was gradually added which led to the formation of a dark purple solution. The mixture was stirred at room temperature for 30 minutes and 250 mg of a dark purple powder was obtained by adding an aqueous solution of KPF_6 (278 mg in 10 mL H_2O) which was collected and dried in air; 80 % yield. IR (KBr, cm^{-1}): 1612.5(m), 1600.9(m), 1572.0(m), 1548.8 (m), 1473.6 (m), 1431.2 (m), 1252.6 (m), 1030.0 (m), 1014.6 (m), 825.2 (vs), 792.7 (s), 767.7 (m), 671.2 (m), 655.8 (m), 555.5(m).

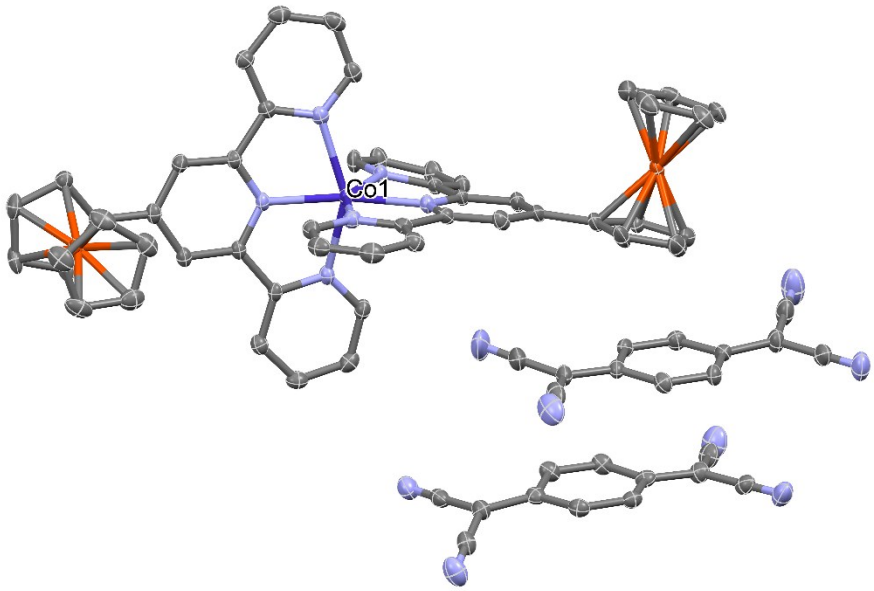
Synthesis of $[Zn^{II}(Fctp)_2](TCNQ)_2$

The salts $[Zn^{II}(Fctp)_2](PF_6)_2$(0.05 mmol, 60 mg) and LiTCNQ (0.1 mmol, 21 mg) were separately dissolved in 5 mL of MeCN/MeOH (1:1, v/v). The two solutions were layered in a 20 mL test tube for one week. A pure phase of dark block purple crystals that had formed during this period were filtered to give 25 mg of purple block crystals (**1'**, $[Zn^{II}(Fctp)_2](TCNQ)_2$) IR of **1'** (KBr, cm^{-1}): 3090.7 (w), 2164.9 (s), 2145.6 (s), 1610.5 (s), 1600.9 (s), 1572.0 (s), 1548.8 (m), 1501.3 (s), 1473.6 (m), 1431.2 (s), 1352.2 (s), 1252.7 (m), 1164.9 (m), 1030.0 (m), 1012.6 (m), 827.5 (s), 790.8 (s), 555.5(s). Elemental analysis of **1'**: calculated (%): C (67.93), H (3.54), N (14.98); found: C (67.73), H (3.56), N (15.01).

The isomorphic Zn analogue, $[Zn(Fctp)_2](TCNQ)_2$ (1'), of **1** (The asymmetric content and unit cell parameters are shown in Table S8 and Figure S14) was synthesized and characterized to evaluate the χT contribution of TCNQ at room temperature.



(a)



(b)

Figure S15. The asymmetric units in the crystal structures of (a) $[Zn^{II}(Fctp)_2](TCNQ)_2$ (**1'**), (b) $[Co^{II}(Fctp)_2](TCNQ)_2$ (**1**)

Table S9. Unit cell parameters of **1** and **1'**

	$[Co(Fctp)_2](TCNQ)_2$	$[Zn(Fctp)_2](TCNQ)_2$
a/Å	12.0595(5)	12.0572(3)
b/Å	12.6422(5)	12.6478(3)
c/Å	19.9814(8)	20.0264(5)
α/°	88.099(1)	88.134(1)
β/°	84.187(1)	83.998(2)
γ/°	71.597(1)	71.482(1)

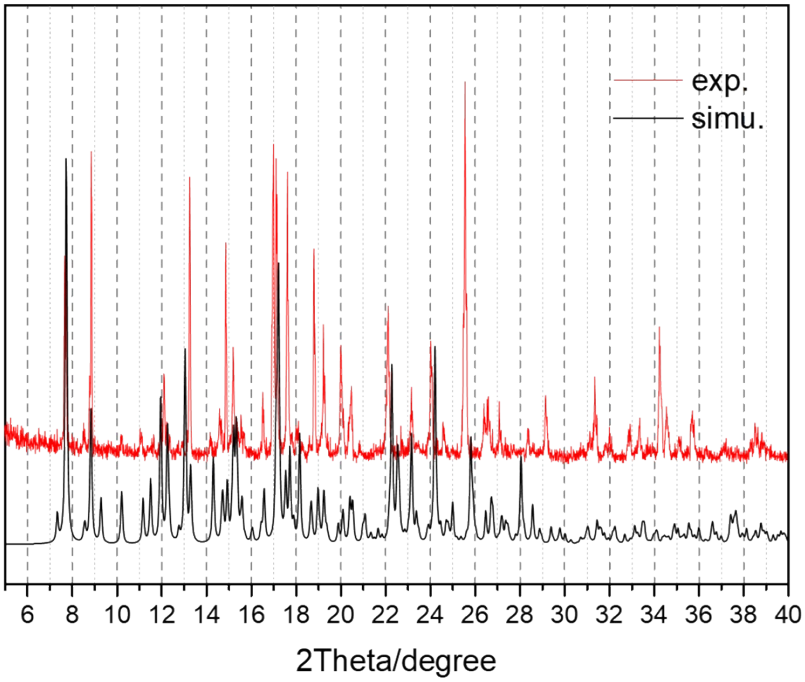
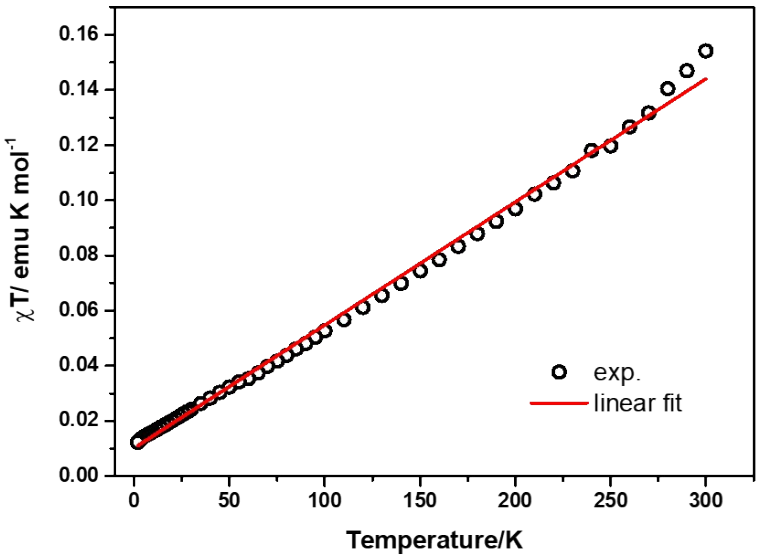
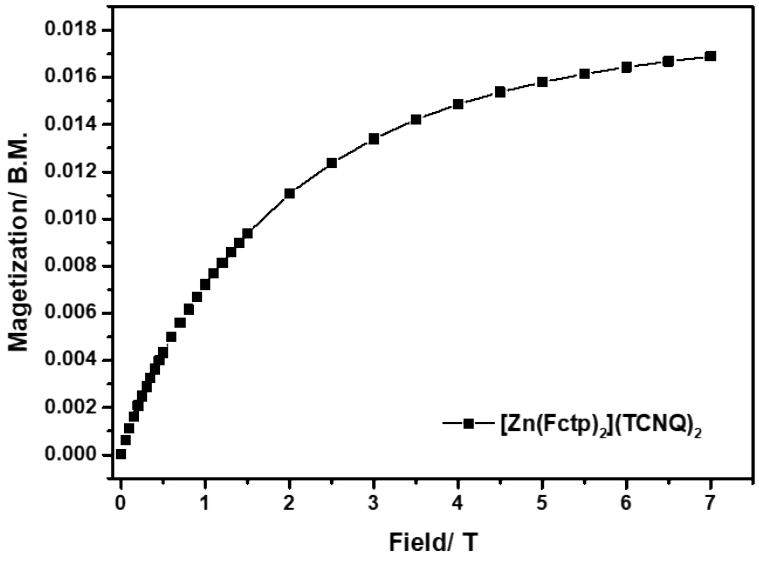


Figure S16. Powder X-ray diffraction and the simulation from single crystal structure of **1'**.

The magnetic susceptibility and magnetization measurements (Figure S16) indicate that the sample is almost diamagnetic. χT vs T plot shows only a small temperature independent paramagnetism (4.5×10^{-4} emu mol^{-1}). The magnetization at 2K is only ~0.017 μ_B at 7T which demonstrates the diamagnetic nature of the $(TCNQ)_2^{2-}$ dimer in the phase-I structure which corresponds well with results reported in the literature.[8]



(a)



(b)

Figure S17. (a) χT vs T plot and (b) magnetization plot for **1'**.

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