Compound	**1**·2H_2O	**2**·2H_2O	**2**

Hydrogen Bond-Induced Abrupt Spin Crossover Behaviour in 1-D Cobalt(II) Complexes - the Key Role of Solvate Water Molecules

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Formula	$C_{20}H_{18}Cl_2CoN_4O_2$		$C_{22}H_{18}Cl_2CoN_4O_2$	$C_{22}H_{14}Cl_2CoN_4$
Temperature (K)	123	250	123	173
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	Pcca	Pcca	P2/n	P2/n
a (Å)	11.1222(8)	10.7848(18)	8.377(2)	8.6789(5)
b (Å)	7.8437(8)	7.5554(18)	13.222(3)	13.825(5)
c (Å)	21.7183(2)	21.527(4)	9.678(3)	10.2562(6)
α (°)	90.0000	90.0000	90.0000	90.0000
B (°)	90.0000	90.0000	114.9678(3)	113.333(7)
γ (°)	90.0000	90.0000	90.0000	90.0000
V (Å^3)	1894.7(3)	1754.1(6)	998.8(5)	1130.25(12)
Z	4	4	2	2
R1	0.0545	0.0891	0.0558	0.0314
wR2	0.1202	0.2017	0.1108	0.0700
R1(all)	0.0665	0.1678	0.1256	0.0746
wR2(all)	0.1240	0.2397	0.1372	0.0453
CCDC	2059287	2059289	2059288	2059290

Table. S1 Crystal parameters.

Table S2. Representative bond distances (Å) around cobalt(II) centers.

Compound	**1**·2H_2O		**2**·2H_2O	**2**
Temperature (K)	123	250	123	173
Co-N(1)	1.976(3)	2.060(6)	2.072(4)	2.1686(16)
Co-N(2)	1.856(4)	1.967(8)	1.973(5)	2.060(2)
Co-N(3)	1.967(4)	2.034(8)	2.017(6)	2.158(2)
Co-Cl	2.6232(9)	2.409(2)	2.3681(13)	2.4401(5)

Table S3. Selected intermolecular separations (Å) for the interactions.

	1·2H$_2$O		
	123 K		250
	Hydrogen bond		Hydrogen bond
Cl-O1 (Å)	3.305	Cl-O1 (Å)	3.093
Cl-O2 (Å)	3.227	Cl-O2 (Å)	3.224
Cl-C4 (Å)	3.760	Cl-C4 (Å)	3.648
Cl-C7 (Å)	3.712	Cl-C7 (Å)	3.675
Cl-C10 (Å)	3.567	Cl-C10 (Å)	3.447
	2		**2**·2H$_2$O
	173 K		123 K
	Hydrogen bond		Hydrogen bond
Cl-C2 (Å)	3.441	Cl-C2 (Å)	3.552
Cl-C3 (Å)	3.485	Cl-C4 (Å)	3.732
Cl-C4 (Å)	3.621	Cl-H7 (Å)	3.527
Cl-C7 (Å)	3.376		
	π-π stacking		
py-py (Å)	3.581		

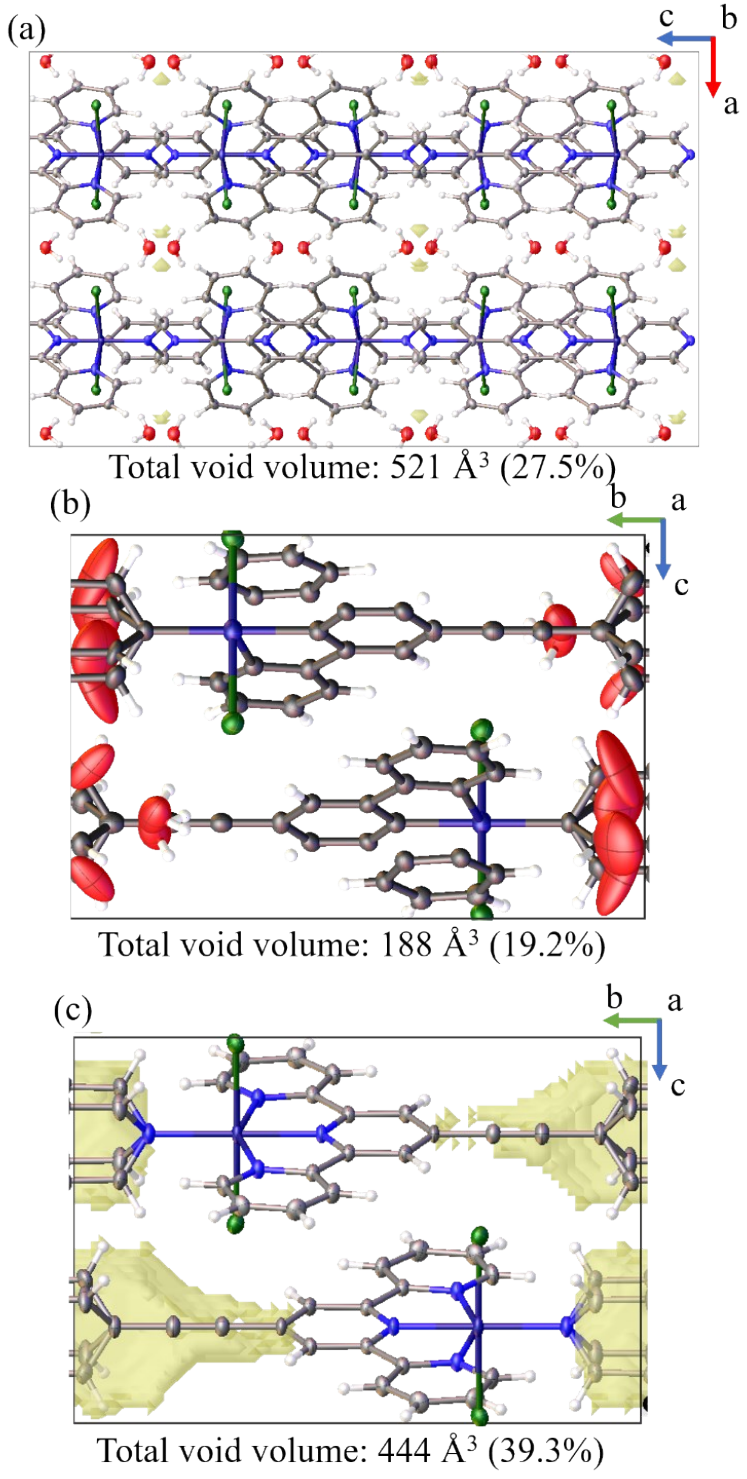

Figure S1. Single crystal void volumes for (a) **1**·2H_2O at 173 K, (b) **2**·2H_2O at 123 K and (c) **2** at 173 K. Yellow "fog" in (c) represents the voids.

Compound	**1**·2H_2O		**2**·2H_2O	**2**
Temperature (K)	123	250	123	173
Cl(1)-Co-N(1)	87.99	90.3	92.03	88.91
Cl(1)-Co-N(2)	85.18	87.53	90.10	90.855
Cl(1)-Co-N(3)	94.82	92.47	89.90	89.145
Cl(1)-Co-N(1′)	90.68	88.6	88.02	91.49
N(1)-Co-N(2)	82.06	76.93	76.45	76.38
N(1)-Co-N(3)	97.94	103.07	103.55	103.62
Σ (°)	**56.42**	**65.56**	**62.62**	**63.06**

Table S4. Bond angles (°) and distortion Σ values (°) around cobalt(II) centers.

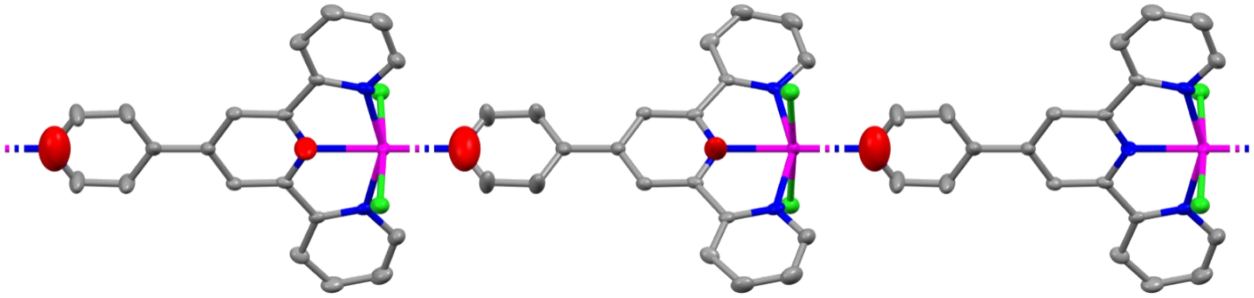

Figure S2. Single crystal structure of **1**·2H_2O at 250 K. Hydrogen atoms are omitted for clarity. Color code: Color code: C, gray; N, blue; O, red; Cl, green; Co, Magenta.

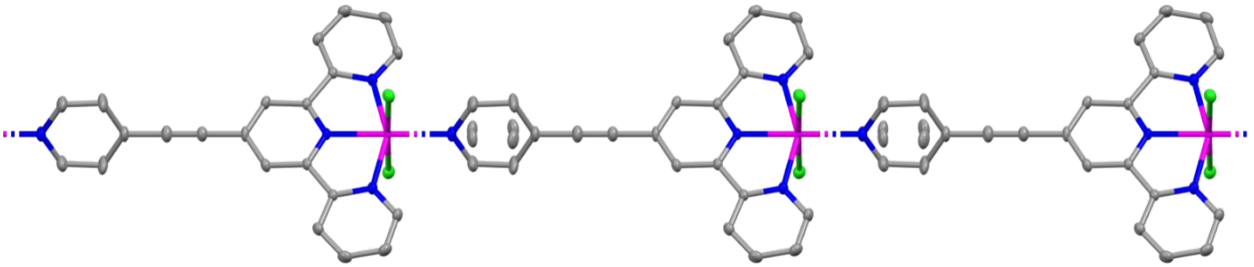

Figure S3 Single crystal structure of **2** at 173 K. The ligand hydrogen atoms are omitted for clarity. Color code: C, gray; N, blue; O, red; Cl, green; Co, Magenta.

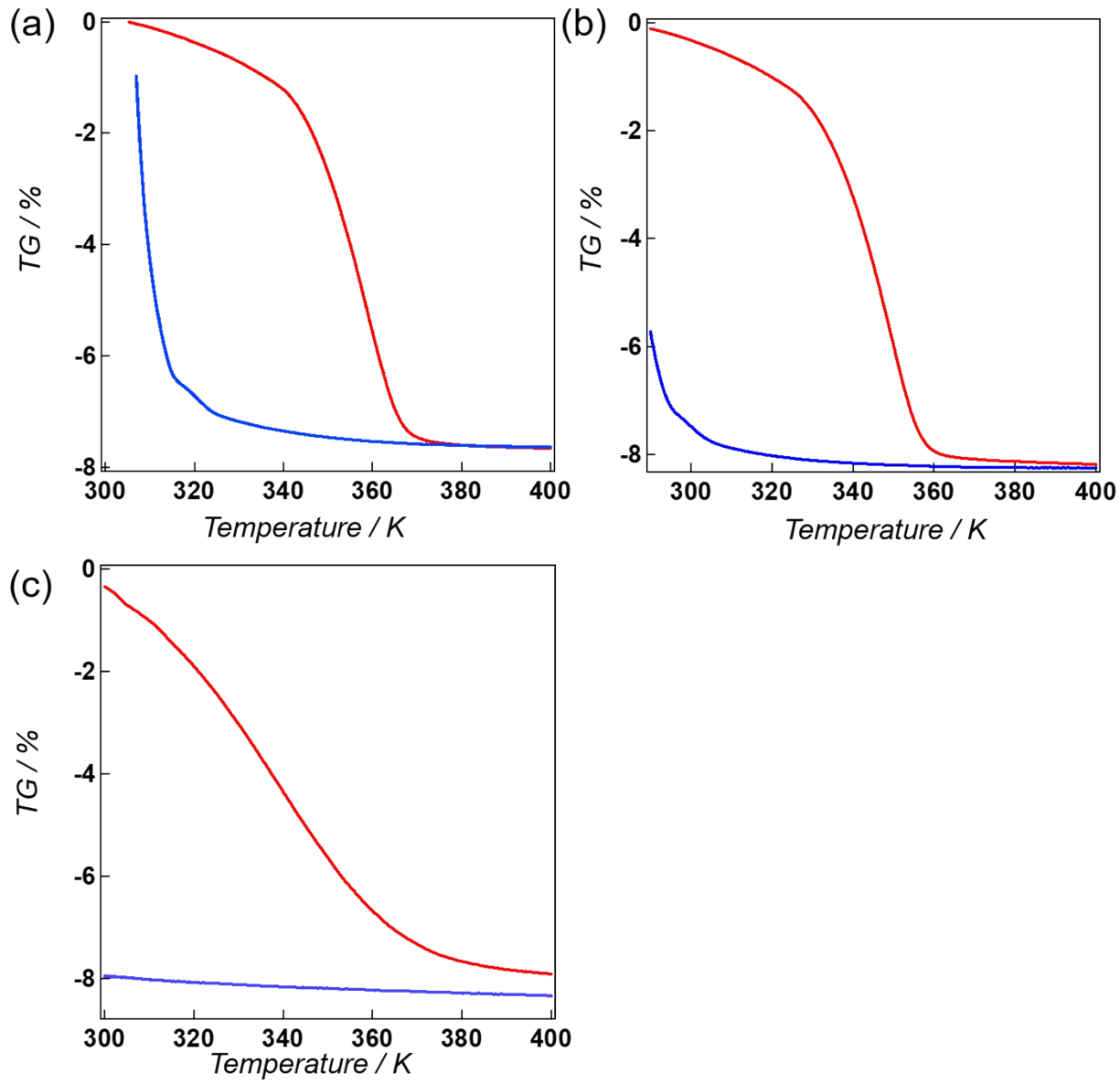

Figure S4. Thermogravimetric analysis (TGA) for (a)**1**·2H_2O, (b)re**1**·2H_2O and (c)**2**·2H_2O. These were obtained by heating the sample at 10 K min^{-1}, then maintaining it at 400 K for 10 min. followed by allowing it to cool in the atmosphere. The red line corresponds to heating while the blue line corresponds to cooling.

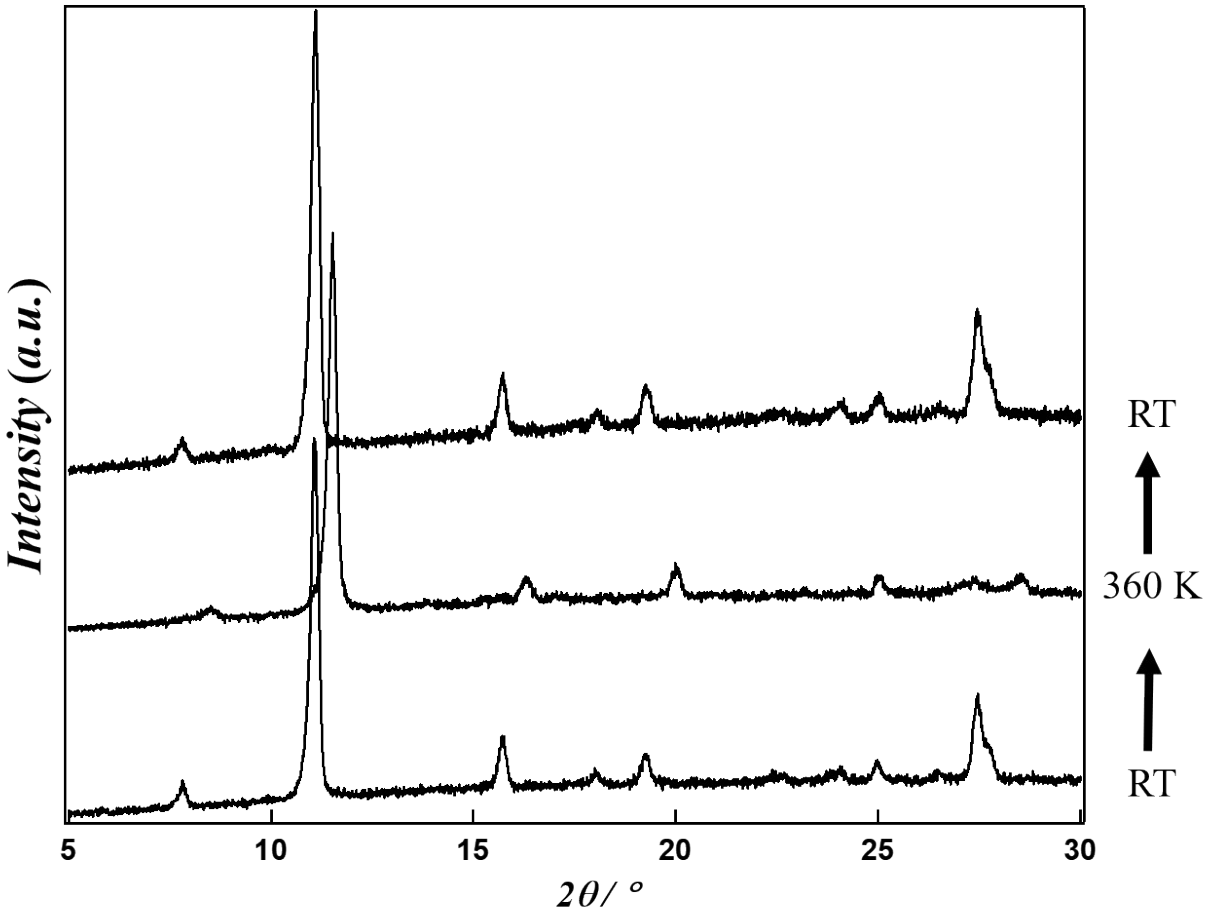

Figure S5. Temperature-dependent PXRD patterns of **1**·$2H_2O$ at 300 K, after heating at 360 K for 1h and after cooling at 300 K for 1 h.

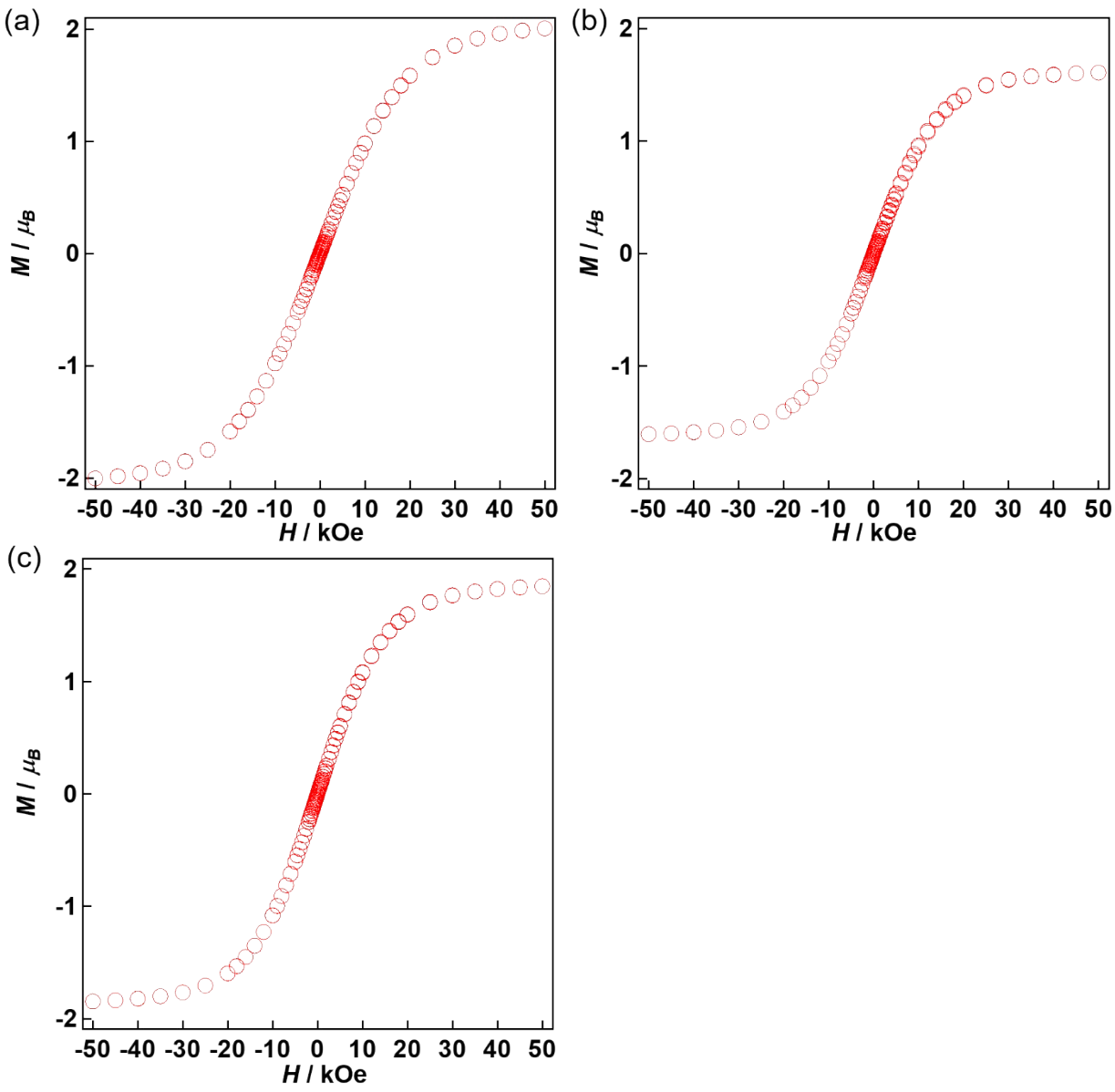

Figure S6. *M* versus *H* plots at 2 K for (a)**1**, (b)**2** and (c)**2**·2H_2O.

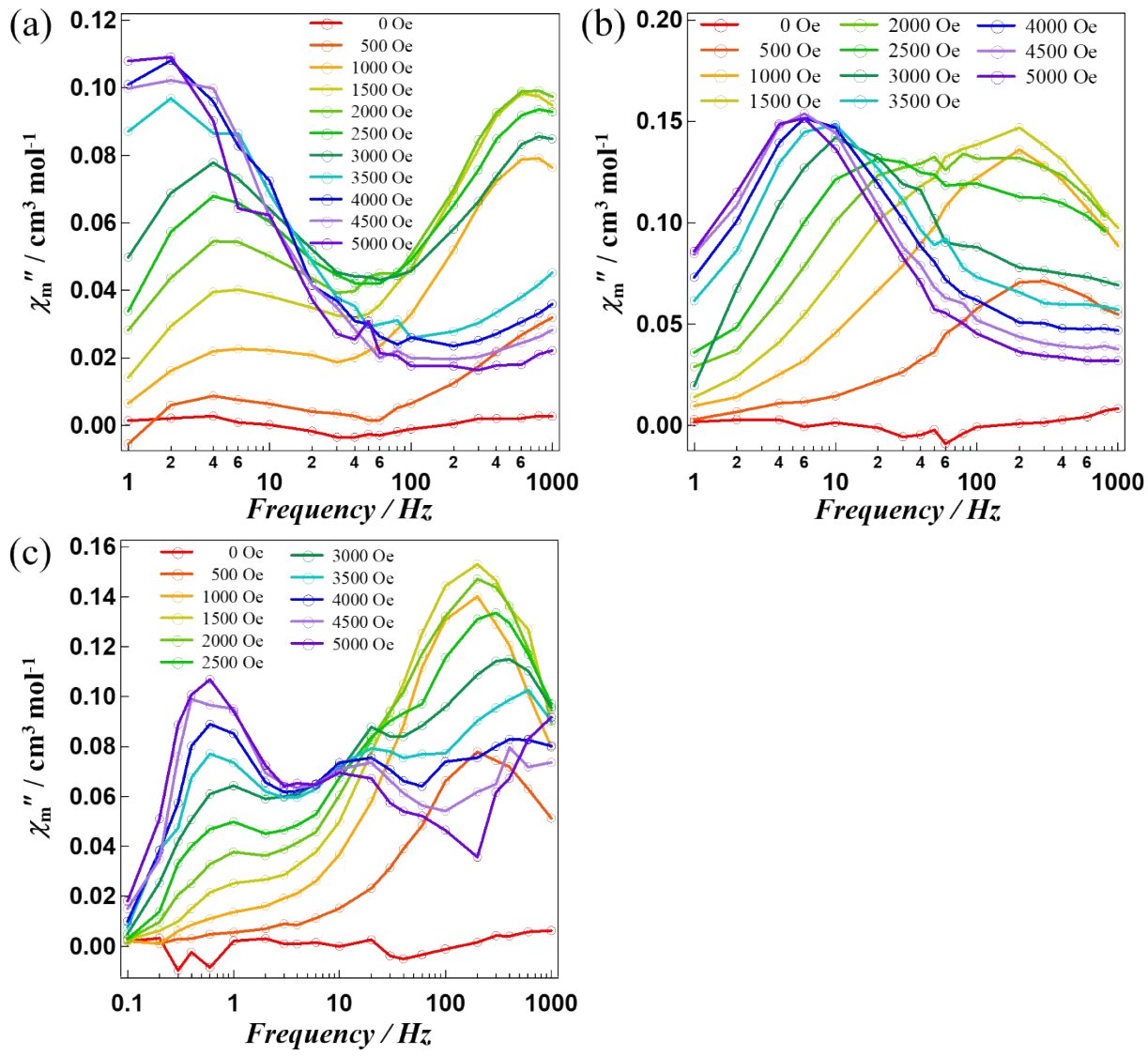

Figure S7. The variable frequency alternating current (ac) magnetic susceptibility data for (a) **1**, (b) **2** and (c) **2**·2H_2O collected under an applied filed bias between zero and 5000 Oe range.

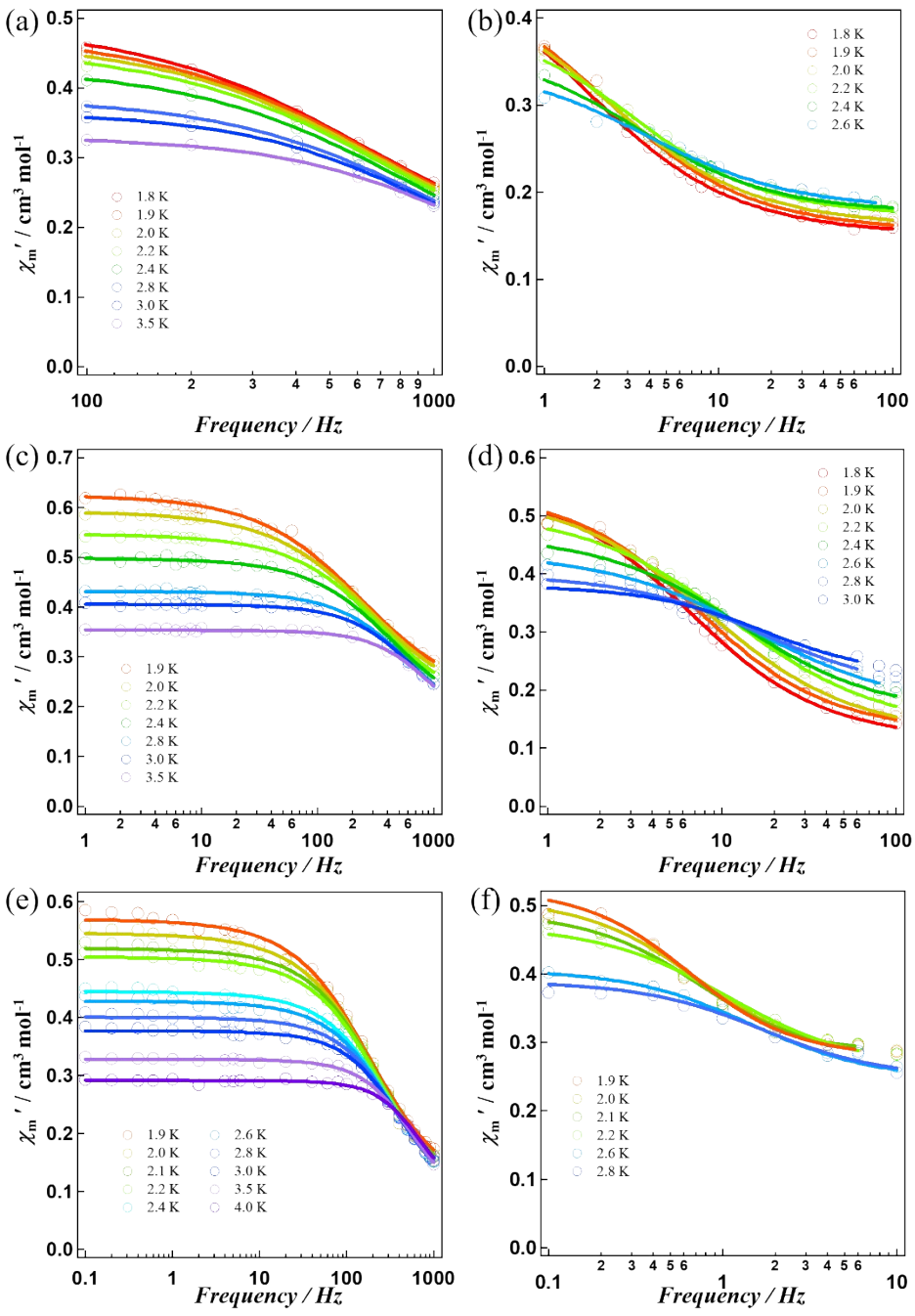

Figure S8. Variable-temperature in-phase (χ_m') components of the ac susceptibilities for **1** under an applied dc field of (a) 2000 Oe and (b) 4000 Oe, for **2** under an dc field of (c) 1000 Oe and (d) 4500 Oe, for **2**·2H_2O under an dc field of (e) 1500 Oe and (f) 5000 Oe. Solid lines represent the best fits for the Debye model.

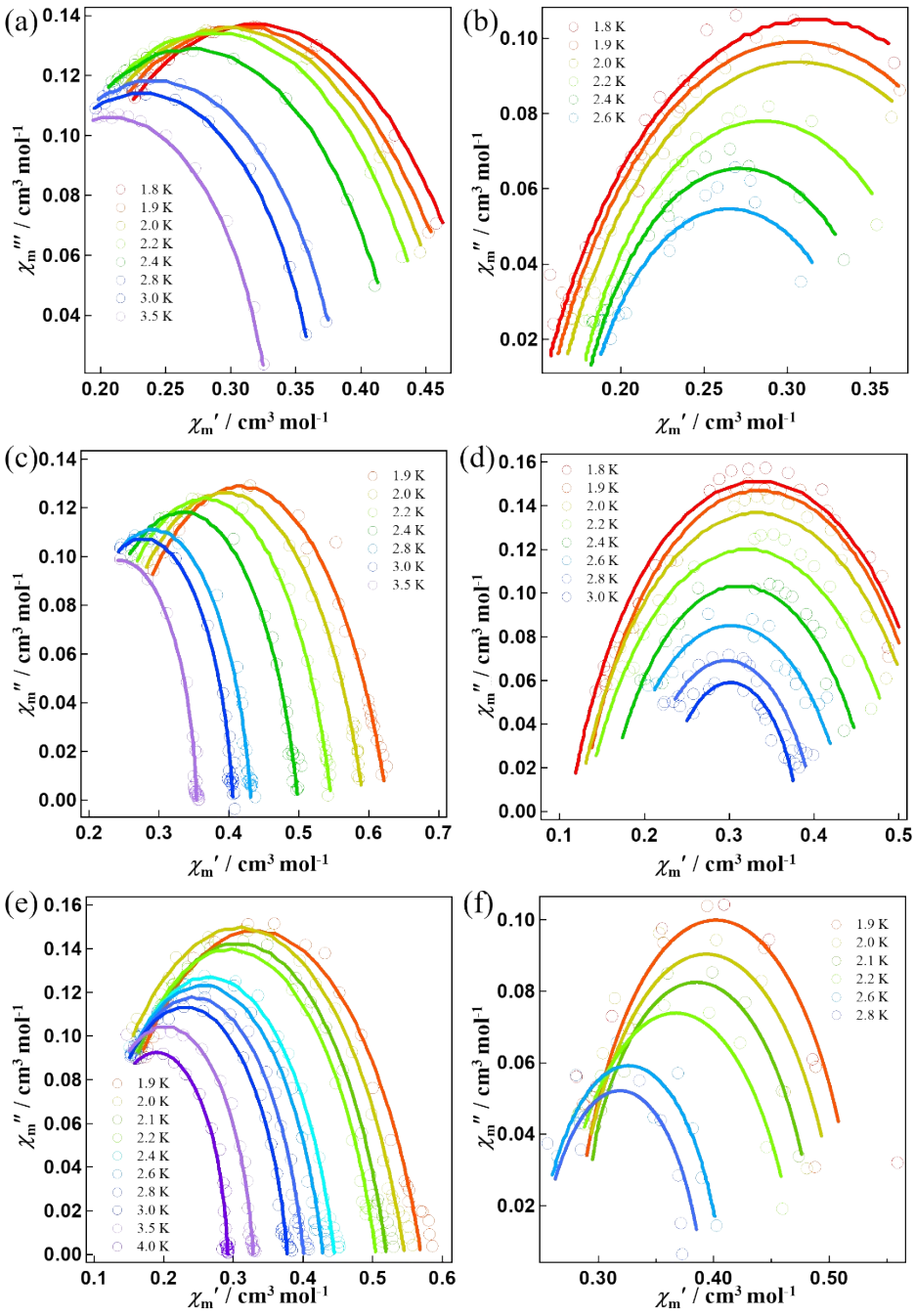

Figure S9. Cole-Cole plots for **1** under an applied dc field of (a) 2000 Oe and (b) 4000 Oe, for **2** under an dc field of (c) 1000 Oe and (d) 4500 Oe, for **2**·2H_2O under an dc field of (e) 1500 Oe and (f) 5000 Oe. Solid lines represent the best fits for the Debye model.

Table S5. Fitted parameters for the Cole-Cole plots for **1** under applied field of 2000 and 4000 Oe as determined within the generated Debye model (τ: magnetic relaxation time, α: distribution of relaxation times).

	2000 Oe		4000 Oe	
	High Frequency		Low Frequency	
T (K)	τ (s)	α	τ (s)	α
1.8	2.52×10^{-4}	0.157	8.87×10^{-2}	0.278
1.9	2.33×10^{-4}	0.144	6.99×10^{-2}	0.263
2.0	2.26×10^{-4}	0.152	7.07×10^{-2}	0.276
2.2	2.12×10^{-4}	0.163	4.85×10^{-2}	0.232
2.4	1.95×10^{-4}	0.148	4.52×10^{-2}	0.237
2.6	——	——	4.12×10^{-2}	0.283
2.8	1.63×10^{-4}	0.132	——	——
3.0	1.55×10^{-4}	0.109	——	——
3.5	1.22×10^{-4}	0.0976	——	——

Table S6. Fitted parameters for the Cole-Cole plots for **2** under applied field of 1000 and 4500 Oe as determined within the generated Debye model (τ: magnetic relaxation time, α: distribution of relaxation times).

	1000 Oe		4500 Oe	
	High Frequency		Low Frequency	
T (K)	τ (s)	α	τ (s)	α
1.8	——	——	2.42×10^{-2}	0.241
1.9	6.79×10^{-4}	0.299	2.16×10^{-2}	0.228
2.0	5.75×10^{-4}	0.280	1.90×10^{-2}	0.273
2.2	4.68×10^{-4}	0.237	1.40×10^{-2}	0.291
2.4	3.70×10^{-4}	0.207	1.24×10^{-2}	0.261
2.6	——	——	1.04×10^{-2}	0.293
2.8	2.61×10^{-4}	0.153	9.34×10^{-3}	0.254
3.0	2.32×10^{-4}	0.115	9.12×10^{-3}	0.188
3.5	1.64×10^{-4}	0.0701	——	——

Table S7. Fitted parameters for the Cole-Cole plots for **2**·$2H_2O$ under applied field of 1500 and 5000 Oe as determined within the generated Debye model (τ : magnetic relaxation time, α : distribution of relaxation times).

	1500 Oe		5000 Oe	
	High Frequency		Low Frequency	
T (K)	τ (s)	α	τ (s)	α
1.9	8.82×10^{-4}	0.291	0.247	0.140
2.0	7.63×10^{-4}	0.283	0.223	0.173
2.1	7.48×10^{-4}	0.251	0.216	0.162
2.2	6.98×10^{-4}	0.249	0.149	0.228
2.4	5.52×10^{-4}	0.222	——	——
2.6	5.16×10^{-4}	0.214	0.109	0.206
2.8	4.53×10^{-4}	0.188	0.934	0.202
3.0	4.04×10^{-4}	0.164	——	——
3.5	2.91×10^{-4}	0.121	——	——
4.0	2.33×10^{-4}	0.0628	——	——

Table S8. Parameters used to fit the Arrhenius plots given in Figure 6 using the approximations $\tau^{-1} = CT^n + AT$.

	B_{DC} (kOe)	Raman		Direct
		C (s^{-1} K^{-1})	n	A (s^{-1} K^{-1})
HF in **1**	2.0	2060	0.983	169
HF in **2**	1.5	196	2.41	240
HF in **2**·$2H_2O$	1.5	81.4	2.55	387

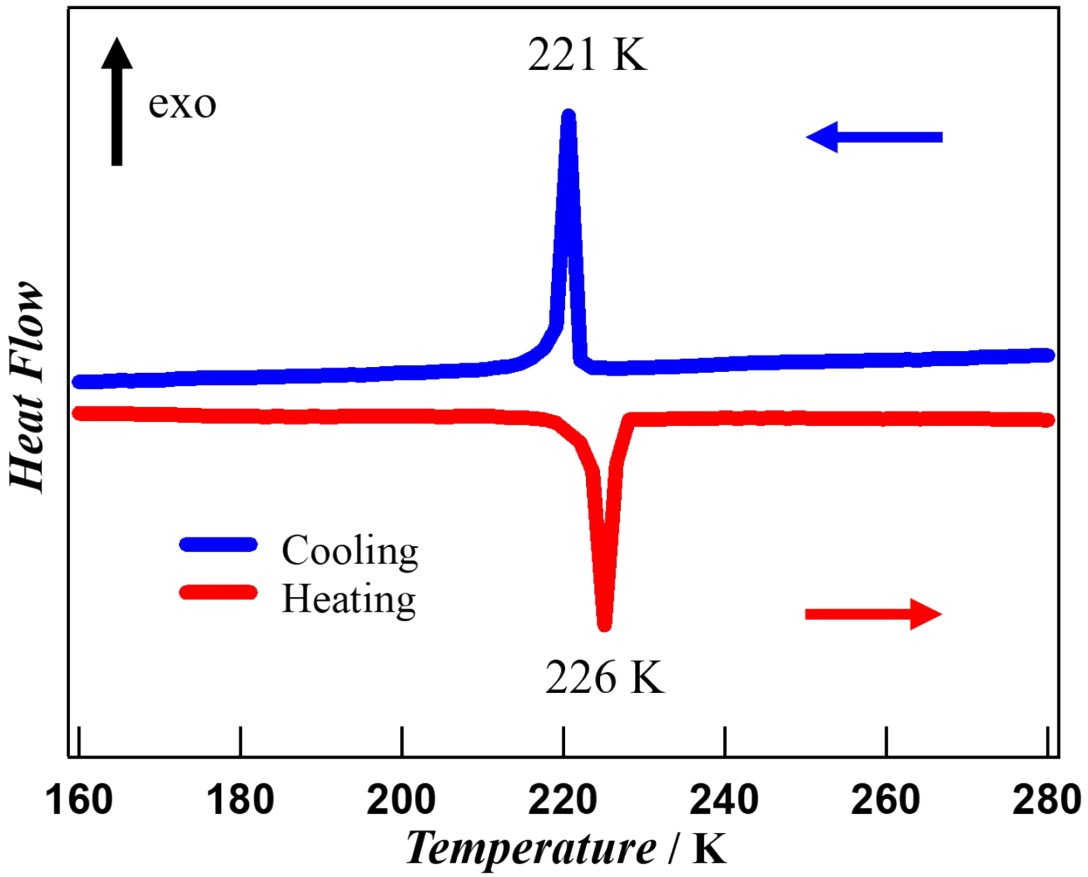

Figure S10. DSC curves for **1**·2H_2O in the range 160–280 K at 2 K min^{-1} (red: heating mode, blue: cooling mode).

Table S9. Enthalpy change ($|\Delta H|$) and entropy change $|\Delta S|$) for phase transition.

Phase transition temperature (K)	221	226
$\|\Delta H\|$ (J mol^{-1})	4.57×10^3	5.33×10^3
$\|\Delta S\|$ (J K^{-1} mol^{-1})	20.7	23.6

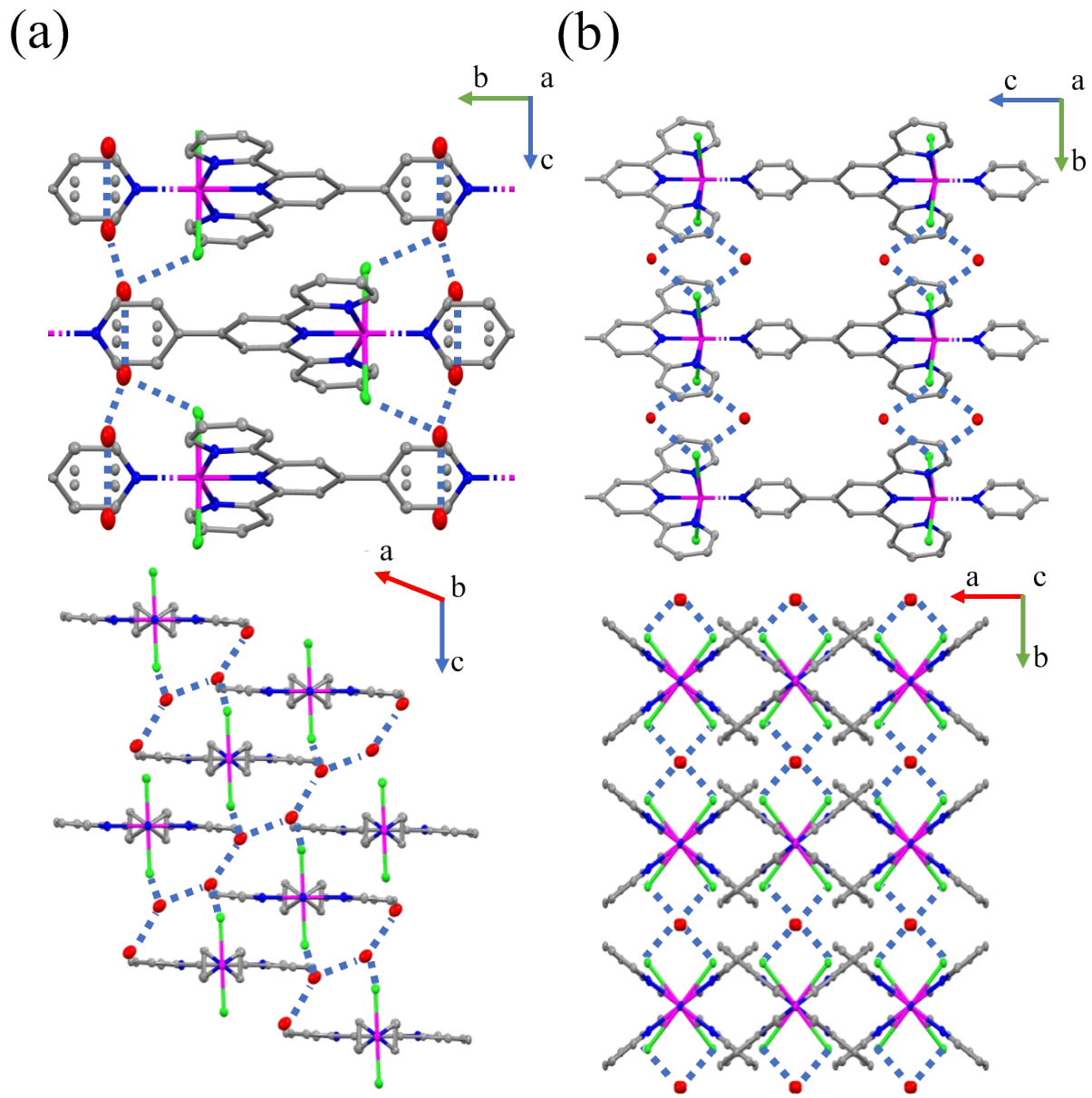

Figure S11. Differences in the packing structures and hydrogen bond networks for (a) *P*2/*n*-**1**·2H_2O and (b) **1**·2H_2O. The blue dash lines represent hydrogen bonds between the chloride ligands and water molecules. While each of the water molecules in *P*2/*n*-**1**·2H_2O has one hydrogen bond, each water molecules in **1**·2H_2O has two hydrogen bonds.