

Supplementary Information of

“New family of Hofmann-like coordination polymers constructed by imidazole ligands, associated with spin crossover and anisotropic thermal expansions “

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Experimental Section

Synthesis

All complexes were prepared and crystallized by slow diffusion of two solutions in a glass tube. For **1**, one of which contained a solution of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (39.2 mg, 1.00×10^{-4} mol) and HIm (13.6 mg, 2.00×10^{-4} mol) in 2 mL of N_2 bubbling water (1 mL) / ethanol (1 mL) mixed solvent with N_2 gas. The other contained a solution of $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ (25.8 mg, 1.00×10^{-4} mol) in 1 mL of degassing water. The two solutions were filling the glass tube. Yellow single crystals suitable for single crystal X-ray diffraction were formed over 4 days. For **2**, one of which contained a solution of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (39.2 mg, 1.00×10^{-4} mol), ascorbic acid (8.8 mg, 0.50×10^{-4} mol) and 1-MeIm (16.4 mg, 2.00×10^{-4} mol) in 2 mL of bubbling water (1 mL) / ethanol (1 mL) mixed solvent with N_2 gas. The other contained a solution of $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ (25.8 mg, 1.00×10^{-4} mol) in 0.5 mL of degassing water. The two solutions were filling the glass tube. Yellow single crystals suitable for single crystal X-ray diffraction were formed over 7 days. Elemental analysis confirmed the organic content (**1**: Elemental Analysis: Found: C, 33.30; H, 2.40; N, 31.16 %. Calculated for: $\text{C}_{10}\text{H}_8\text{FeNiN}_8$ C, 33.85; H, 2.27; N, 31.60 %. IR (nujol method, cm^{-1}): 2152 ($\nu(\text{C}\equiv\text{N})$). **2**: Elemental Analysis: Found: C, 37.18; H, 3.18; N, 28.96 %. Calculated for $\text{C}_{12}\text{H}_{12}\text{FeNiN}_8$: C, 37.65; H, 3.16; N, 29.28 %; IR (nujol method, cm^{-1}): 2151 ($\nu(\text{C}\equiv\text{N})$). The solid state IR spectra of **1** and **2** had $\text{C}\equiv\text{N}$ bands at 2150 cm^{-1} for **1** and 2158 cm^{-1} for **2**, which are both at higher wavenumbers than that of free $[\text{Ni}(\text{CN})_4]^{2-}$ (2121 cm^{-1}), at room temperature. This suggests that both of the CN groups of $[\text{Ni}(\text{CN})_4]^{2-}$ act as tetradentate bridging ligands. The thermogravimetric analysis (TGA) of **1-3** show the decomposition of coordinated axial ligands (Figure. S8). The samples were also checked by XRPD data (Figure S9). No impurity and isomers were observed.

Structure analysis

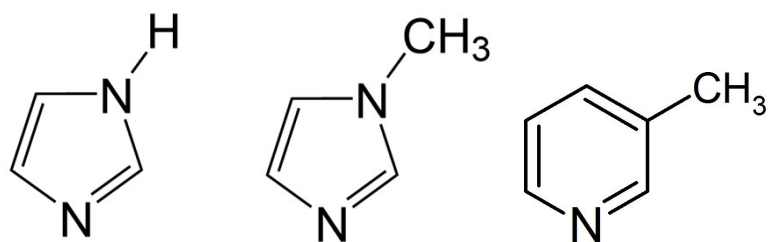
Data collection of single crystal X-ray diffraction was performed on a BRUKER APEX SMART CCD area-detector diffractometer for **1** and **2** with Monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) (Bruker, Billerica, MA, USA). A selected single crystal was carefully mounted on a thin glass capillary and immediately placed under a liquid cooled N_2 stream. The diffraction data were treated using SMART and SAINT, and absorption correction was performed using SADABS [Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction for Area Detector Data; University of Göttingen: Göttingen, Germany, 1996.]. The structures were solved using direct methods with SHELXTL [Sheldrick, G. M. SHELXL, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically. The crystal structure of **2** at LS state could not be determined due to loss of crystallinity. It might be related to ill-defined two-step phase transition in cooling mode, which partially causes the some trapping the intermediate phase inducing incomplete structural transition. We described here the only HS state. Crystallographic data and parameters for **1** and **2** are displayed in Table S1 and S2. Crystallographic data were deposited with Cambridge Crystallographic Data Centre (CCDC): Deposition numbers CCDC-2145131 for compound **1** (296 K), CCDC-2145130 for **2** (296 K). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

XRPD measurement and

The powder X-ray diffraction patterns for **1** and **2** were collected on a Rigaku Smart lab diffractometer with using Johansson type crystal-monochromated $\text{CuK}\alpha$ radiation. Variable temperature data for **2** was performed using an Anton Paar TTK 600 Chamber. Diffraction patterns at 20 K intervals in the ranges 300 to 85 K with a cooling rate of $0.7 \text{ K} \cdot \text{min}^{-1}$ were collected. The acquisition time of all the data from 10.0° to 45° in 2θ was set to $0.5^\circ/\text{min}$ to obtain exploitable intensities. The cell parameters at variable temperatures 300-150 K were determined by Rietveld analysis using Rigaku software (SmartLab Studio II). In order to determine the only lattice constant, the lattice parameters, scale factor and profile function were refined (see Fig. S7 and Table S3).

Magnetic measurement

We measured the temperature dependence of the magnetic susceptibility of complexes for **1** and **2** in the temperature range of 2–300 K with a cooling and heating rate of $0.7 \text{ K} \cdot \text{min}^{-1}$ in a 1 kOe field on a Quantum Design MPMS-XL SQUID magnetometer (Quantum Design, Inc., Pacific Center Court San Diego, CA, USA). The diamagnetism of the samples and sample holders were considered.



Scheme S1. Molecular structure of the using ligands Him, 1-MeIm and 3-Mepy.

Table S1. Crystal data for **1** and **2**.

	1	2
Empirical formula	C ₁₀ H ₈ FeN ₈ Ni	C ₁₂ H ₁₂ FeN ₈ Ni
Formula weight	354.8	382.9
Crystal size (mm ³)	0.20 × 0.20 × 0.10	0.15 × 0.15 × 0.05
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Imma</i>	<i>C2/m</i>
<i>a</i> (Å)	14.5159(16)	16.4065(17)
<i>b</i> (Å)	7.2602(8)	7.3671(8)
<i>c</i> (Å)	13.1876(14)	7.2016(7)
<i>V</i> (Å ³)	1389.8(3)	823.96(15)
<i>β</i> (°)	90	108.810(2)
<i>Z</i> value	4	2
Final <i>R</i> ₁ , <i>R</i> _w (<i>I</i> > 2σ)	0.0541, 0.1472	0.0281, 0.0847
Final <i>R</i> ₁ , <i>R</i> _w (all data)	0.0595, 0.1489	0.0359, 0.0880

Table S2. Selected Fe-N bond lengths and angles for **1** and **2**.

1		2	
Bond lengths (Å)	Bond angles (degree)	Bond lengths (Å)	Bond angles (degree)
Fe(1)-N(1):2.186(4)	N(1)-Fe(1)-N(1):180.0	Fe(1)-N(1):2.173(2)	N(1)-Fe(1)-N(1):180.0
Fe(1)-N(2):2.145(5)	N(2)-Fe(1)-N(1):89.47(14)	Fe(1)-N(2):2.173(3)	N(2)-Fe(1)-N(1):89.17(8)
Ni(1)-C(1):1.859(4)	N(2)-Fe(1)-N(2):180.0	Ni(1)-C(1):1.866(2)	N(2)-Fe(1)-N(2):180.0
	C(1)-N(1)-Fe(1):173.1(3)		C(1)-N(1)-Fe(1):169.8(2)
	C(2)-N(2)-Fe(1):125.1(5)		C(2)-N(2)-Fe(1):127.3(3)
	C(4)-N(2)-Fe(1):129.6(5)		C(4)-N(2)-Fe(1):127.0(3)
	N(1)-C(1)-Ni(1):175.1(4)		N(1)-C(1)-Ni(1):177.3(2)
	C(1)-Ni(1)-C(1):174.9(3)		C(1)-Ni(1)-C(1):180.00(9)

Table S3. Closest centroid/atomic distances between adjacent ligands.

	1	2	3
centroid-centroid distance (Å)	3.65815 (1)	4.11724 (81)	3.68390 (195)
centroid-atomic distance (Å)	centroid-N(3): 3.7039 (13)	centroid-N(3): 3.7475 (10)	centroid-C(4): 3.6235(94)
atomic-atomic distance (Å)	C(4)-C(3): 3.6316 (2)	N(3)-N(3): 3.7126 (1)	C(5)-C(5): 3.6514 (267)

Table S4. Cell parameters for **1**, **2** and **3** at 300-150 K.

<i>a</i> axis	300 K	280 K	260 K	240 K	220 K	200 K	180 K	160 K	150 K
1 (Å)	14.510(3)	14.512(3)	14.520(4)	14.518(4)	14.527(4)	14.534(4)	14.528(3)	14.534(3)	14.528(4)
2 (Å)	16.392(2)	16.385(2)	16.373(2)	16.362(2)	16.3530(13)	16.3670(11)	16.328(2)	16.316(2)	
3 (Å)	7.205(3)	7.201(2)	7.202(2)	7.198(2)	7.199(2)	7.197(2)	7.194(2)	7.193(2)	7.196(4)
									□
<i>b</i> axis	300 K	280 K	260 K	240 K	220 K	200 K	180 K	160 K	150 K
1 (Å)	7.3081(15)	7.3029(16)	7.3009(15)	7.2944(15)	7.2936(17)	7.2898(12)	7.2854(10)	7.2813(11)	7.2780(12)
2 (Å)	7.3604(9)	7.3573(9)	7.3511(9)	7.3457(9)	7.3408(7)	7.3420(6)	7.3276(9)	7.3228(9)	
3 (Å)	16.106(7)	16.096(5)	16.084(5)	16.068(5)	16.068(4)	16.046(6)	16.024(5)	16.009(5)	16.005(8)
									□
<i>c</i> axis □	300 K	280 K	260 K	240 K	220 K	200 K	180 K	160 K	150 K
1 (Å)	13.403(3)	13.381(3)	13.365(3)	13.340(3)	13.329(3)	13.307(3)	13.293(2)	13.277(2)	13.264(3)
2 (Å)	7.1925(12)	7.2000(11)	7.2064(11)	7.2141(12)	7.2234(7)	7.2416(7)	7.2409(12)	7.2514(11)	
3 (Å)	7.426(4)	7.430(3)	7.429(3)	7.429(3)	7.433(3)	7.427(4)	7.423(4)	7.423(4)	7.420(5)
β □	300 K	280 K	260 K	240 K	220 K	200 K	180 K	160 K	150 K
2 (°)	108.838(5)	108.789(5)	108.736(5)	108.675(5)	108.606(4)	108.564(3)	108.440(6)	108.308(6)	

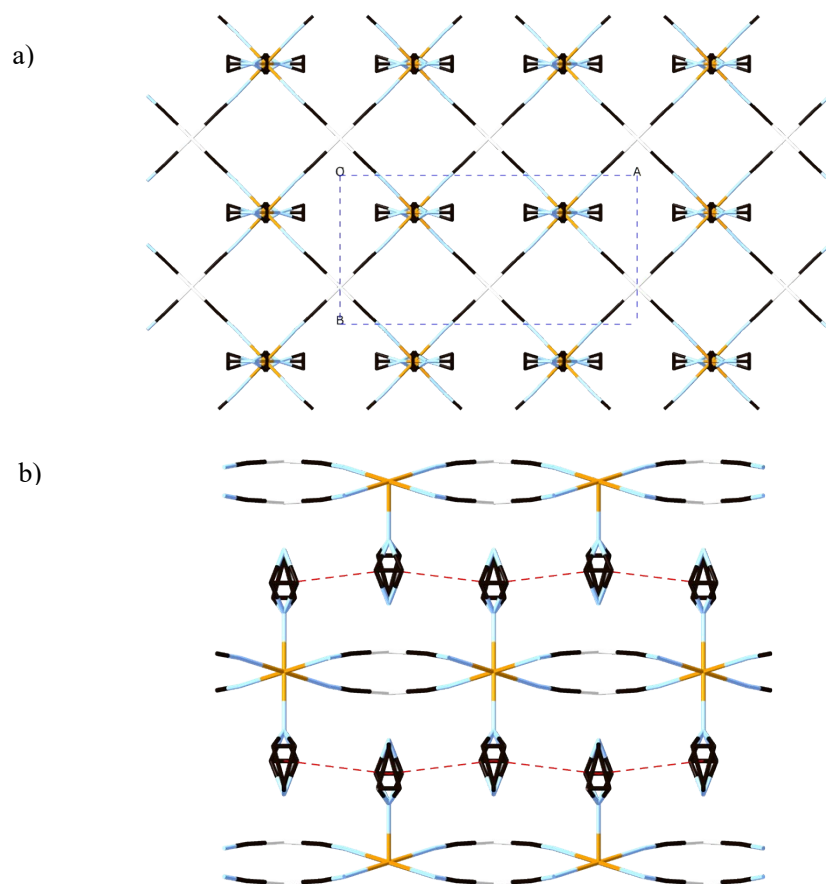


Fig. S1 View of the layer of **1** (a). Representation of intermolecular short contact of **1** (b) (close centroid-centroid as showing red dashed line). In this picture, substituents of the ligands are omitted for clarity.

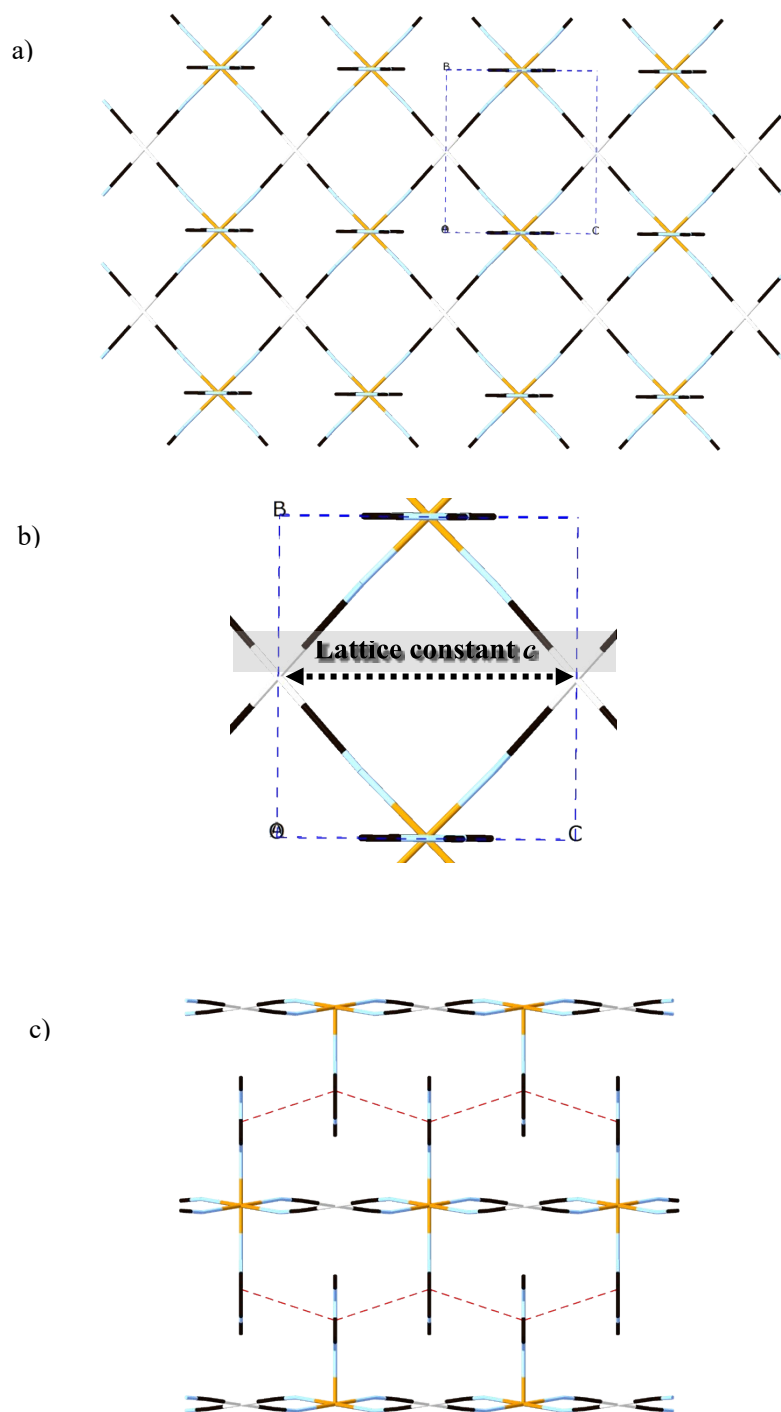


Fig. S2 View of the layer (a) and its one rectangle (b) of **2**. Representation of intermolecular short contacts of **2** (c) (close centroid-centroid as showing red dashed line). In this picture, substituents of the ligands are omitted for clarity.

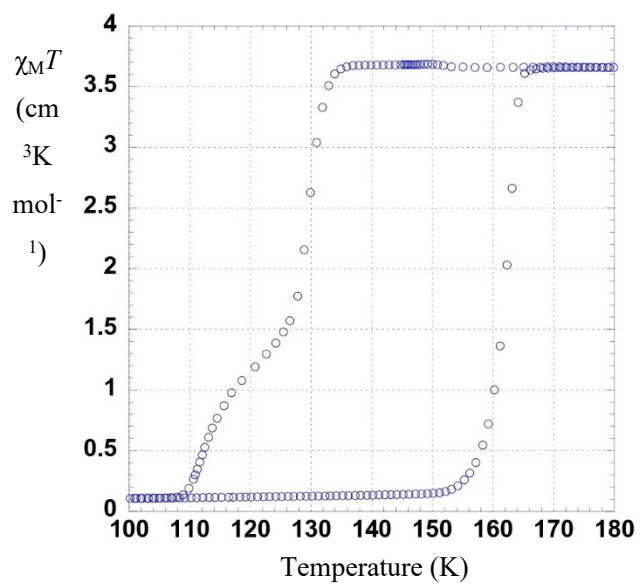


Fig. S3 Enlargement of the magnetic behavior for 2.

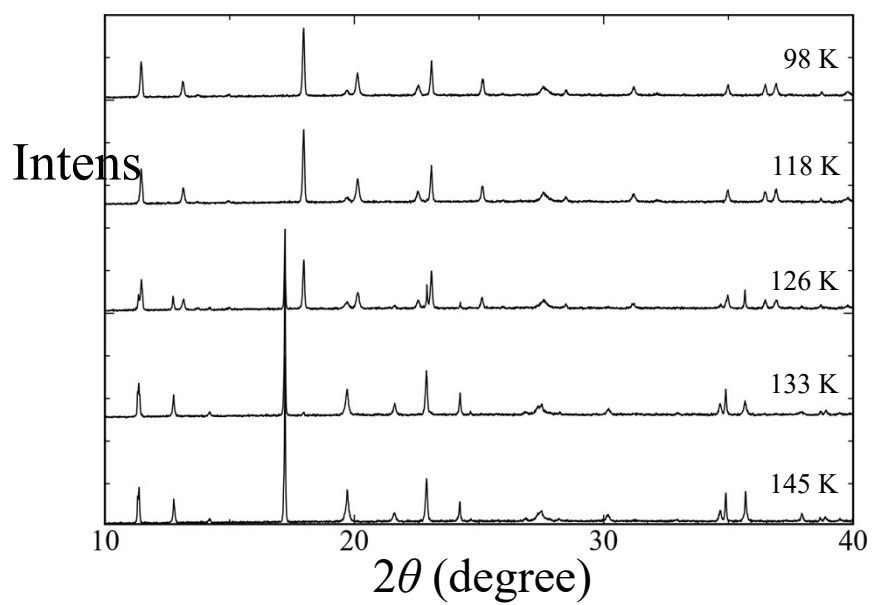


Fig. S4 Short interval variable temperature XRPD profiles of **2** in the temperature range around T_c .

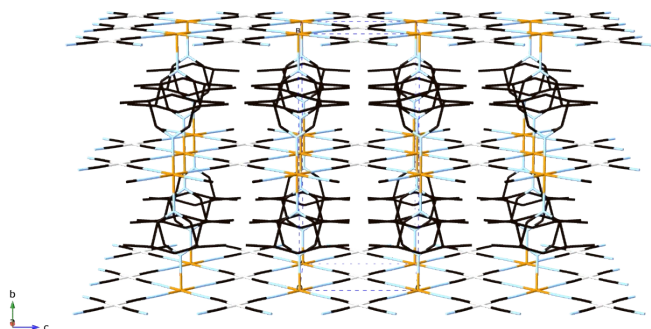


Fig. S5 View of the stacking layers of **3** [ref:13]. In these pictures, hydrogen atoms are omitted for clarity.

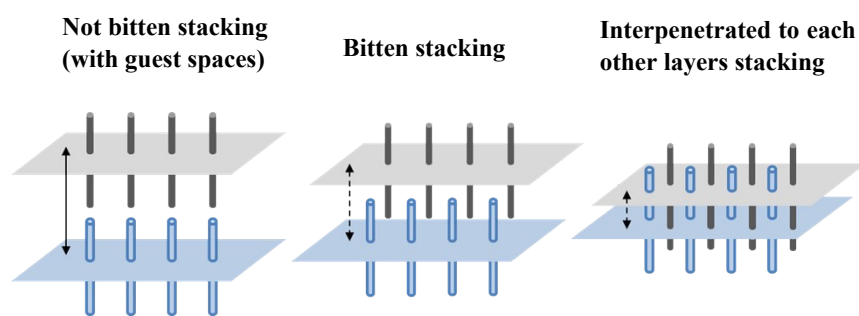


Fig. S6 Schematic representation of the 2D stacking types.

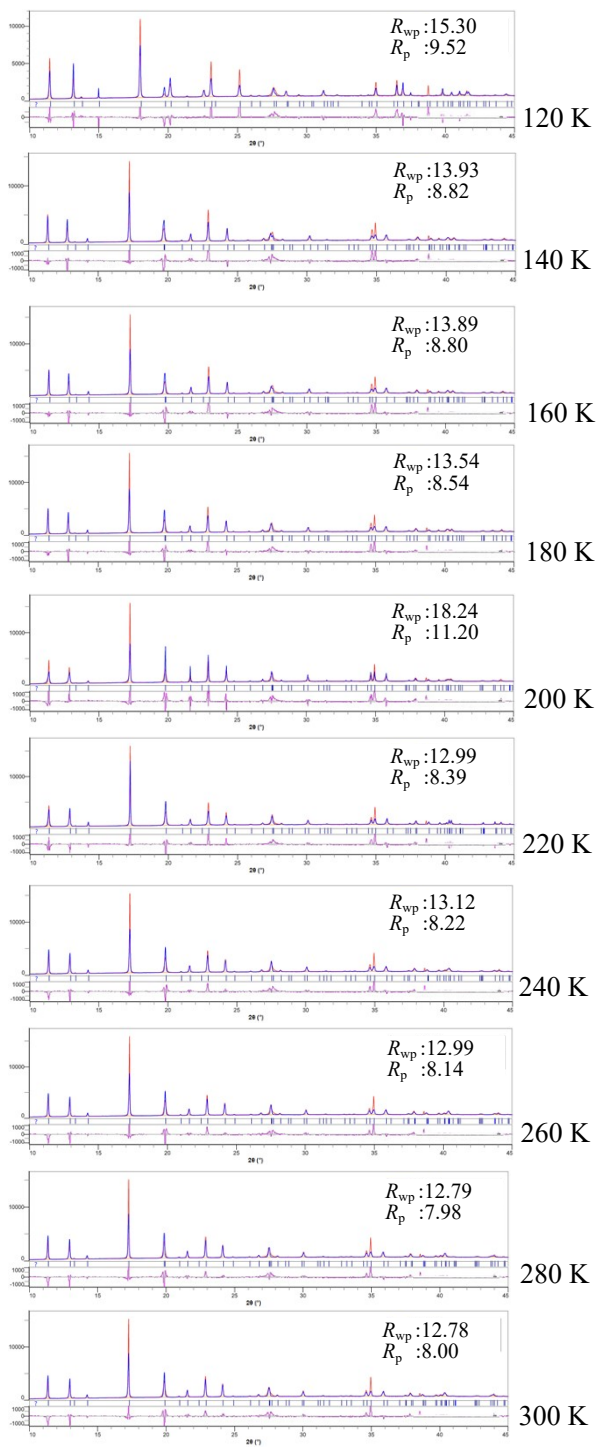


Fig. S7. The fitting results of Rietveld analysis for 2.

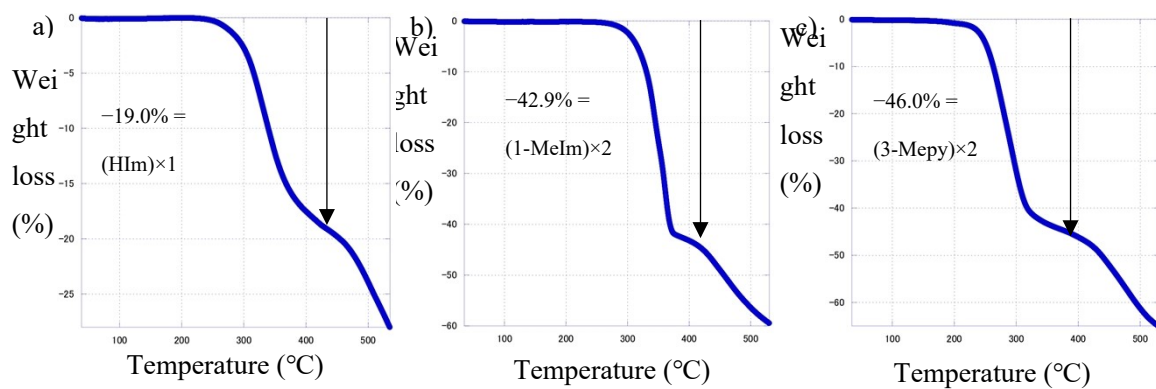


Fig. S8. Thermogravimetric analysis for **1** (a), **2** (b) and **3** (c) was carried under nitrogen atmosphere at a heating rate of 10 K/min.

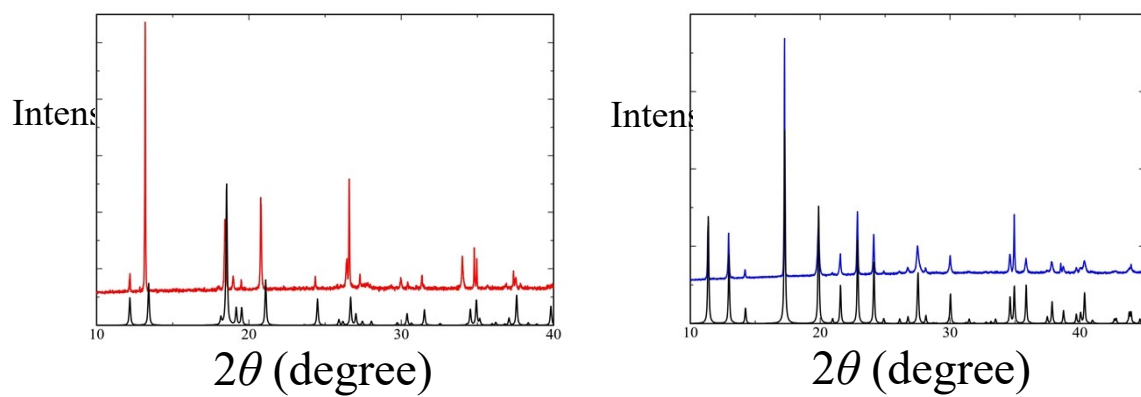


Fig. S9. X-ray Powder diffraction for **1** (a) and **2** (b) at room temperature (experimental data: red line (**1**) and blue line (**2**), simulation data: black line)