Electronic Supplementary Information

Metal-organic frameworks with rare topologies: lonsdaleite-typed metal formates and their magnetic properties

Hyunuk Kim,[a] Yinyong Sun,[a] Yonghwi Kim,[a] Takashi Kajiwara,[b] Masahiro Yamashita,*[b] and Kimoon Kim*[a]

[a]National Creative Research Initiative Center for Smart Supramolecules (CSS), Department of Chemistry and Division of Advanced Materials Science (WCU project), Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea. [b]Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan

E-mail: kkim@postech.ac.kr or yamasita@agnus.chem.tohoku.ac.jp

General Methods

All the reagents and solvents were purchased from commercial sources and used without further purification. Solvothermal reactions were carried out in sealed glass tubes. The single-crystal X-ray diffraction data of $[M_6(HCOO)_{12}]\cdot DEF$ (M = Mg^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Zn^{2+} (**4**)) were collected on a Siemens SMART CCD diffractometer equipped with a graphite-monochromated MoKa (λ = 0.71073 Å) radiation source. The magnetic susceptibilities of **2** and **3** were measured with a SQUID magnetometer (Quantum Design MPMS-7) in the temperature range of 2-300 K.

Synthesis

$[Mg_6(HCOO)_{12}]\cdot DEF$, 1: A solution of $Mg(ClO_4)_2\cdot 6H_2O$ (0.663 g, 2.0 mmol) and HCOOH (184 mg, 4.0 mmol) in DEF solution (12 mL) was heated at 110°C in a sealed glass tube. After 48 h colorless crystals were collected to give **1** (0.156 g, 50%). Anal. Calcd. for **1**: C, 25.94; H, 2.94; N, 1.78, Found: C, 25.76; H, 2.96; N, 1.79.

$[Fe_6(HCOO)_{12}]\cdot DEF$, 2: A solution of $FeCl_2\cdot 6H_2O$ (0.740 g, 3.2 mmol) and HCOOH (184 mg, 4.0 mmol) in DEF solution (18 mL) was heated in a teflon-lined steel bomb at 110°C for 2 days. After 2 days pale brown colorless crystals were collected to give **2** (0.247 g, 72%). Anal. Calcd. for **2**: C, 20.91; H, 2.37; N, 1.43, Found: C, 21.06; H, 2.52; N, 1.64.

$[Co_6(HCOO)_{12}]\cdot DEF$, 3: A solution of $Co(ClO_4)_2\cdot 6H_2O$ (0.732 g, 2.0 mmol) and HCOOH (184 mg, 4.0 mmol) in DEF solution (12 mL) was heated at 100°C in a sealed glass tube. After 36 h pink crystals were collected to give **3** (0.153 g, 46 %). Anal. Calcd. for **3**: C, 20.52; H, 2.33; N, 1.41 Found: C, 20.40; H, 2.48; N, 1.47.

$[Zn_6(HCOO)_{12}]\cdot DEF$, 4: A solution of $Zn(ClO_4)_2\cdot 6H_2O$ (0.745 g, 2.0 mmol) and HCOOH (184 mg, 4.0 mmol) in DEF solution (12 mL) was heated at 100°C for 24 h in a sealed glass tube and then was naturally cooled down to room temperature. After 24 h colorless crystals were collected to give **4** (0.247 g, 72%). Anal. Calcd. for **4**: C, 19.75; H, 2.24; N, 1.36, Found: C, 19.36; H, 2.42; N, 1.43.

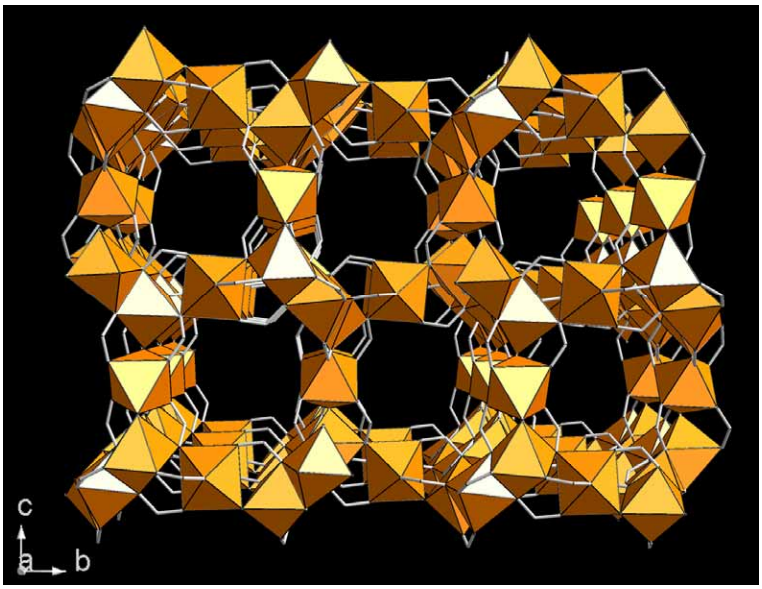

Figure S1. X-ray crystal structures of the metal-formates **1**–**4** with the **lon** net showing channels along the *a* axis. Guest molecules and hydrogen atoms are omitted for clarity.

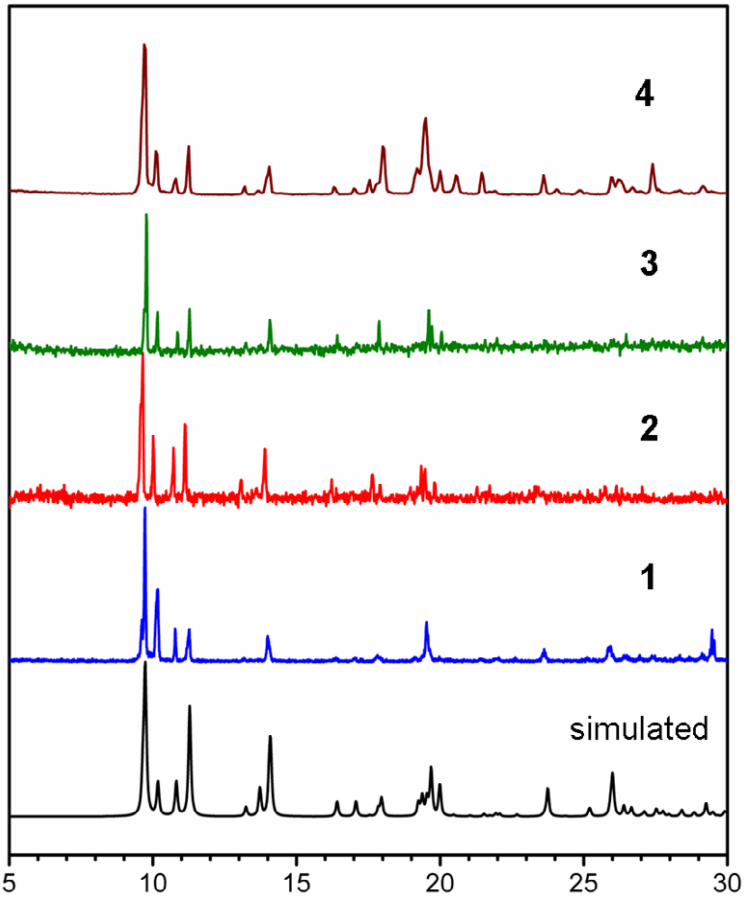

Figure S2. Powder XRD profiles for $[M_6(HCOO)_{12}]\cdot DEF$ (M = Mg^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Zn^{2+} (**4**)).

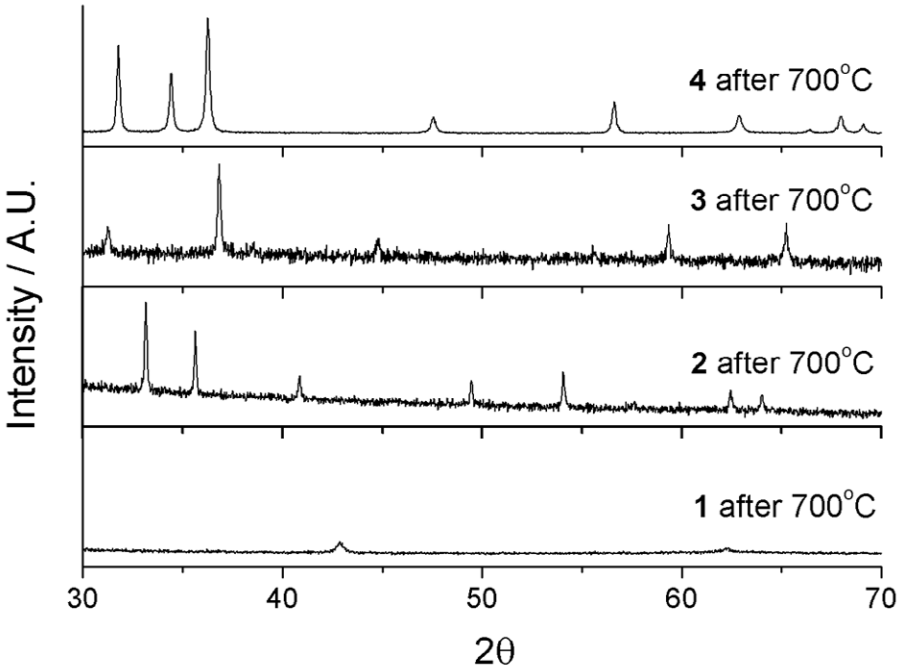

Figure S3. Powder XRD profiles for metal oxides after heating of $[M_6(HCOO)_{12}]\cdot DEF$ (M = Mg^{2+} (**1**), Fe^{2+} (**2**), Co^{2+} (**3**), Zn^{2+} (**4**)).

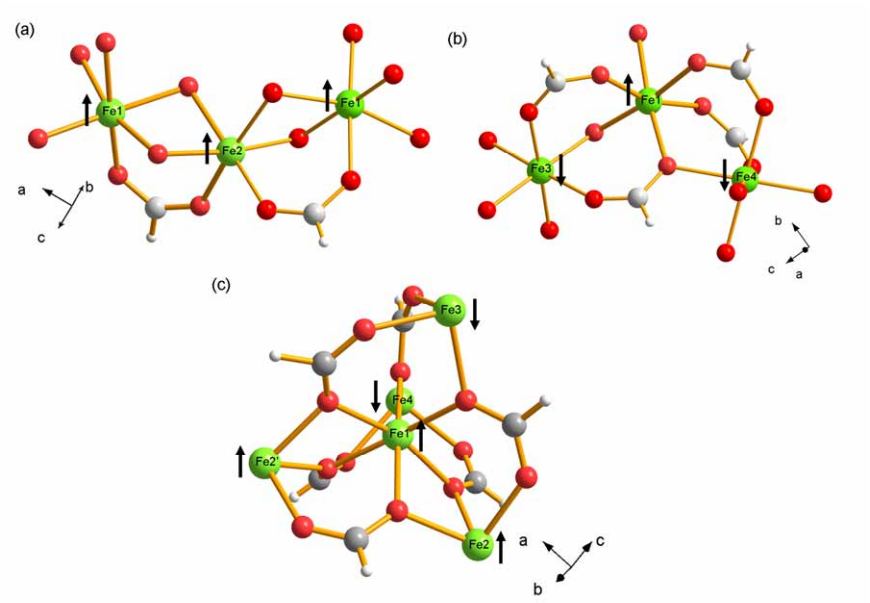

Figure S4. A fragment of **2** showing magnetic ordering. (a) ferromagnetic interactions; Fe1–O–Fe2, (b) antiferromagnetic interactions; Fe3–O–Fe1, Fe1–O–Fe4, (c) magnetic ordering in Fe-centered $FeFe_4$ tetrahedron.

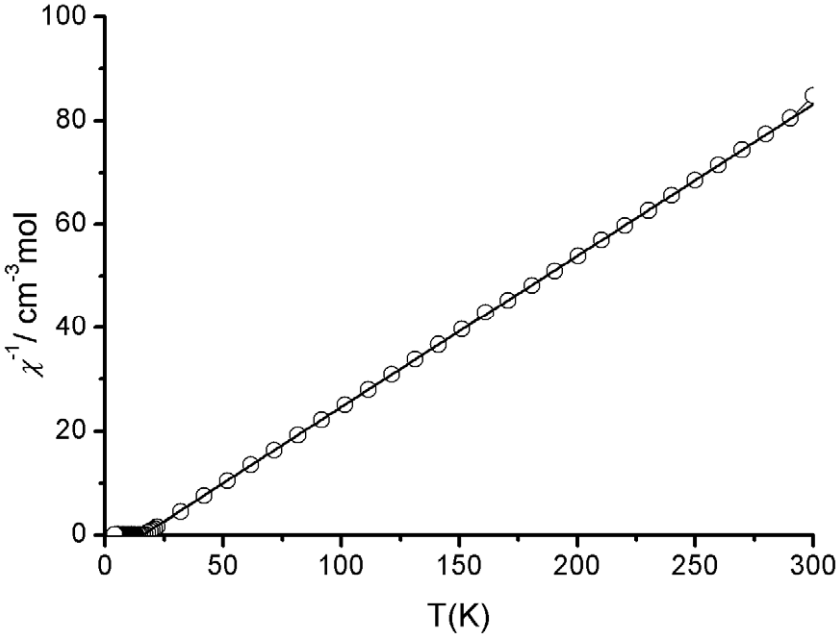

Figure S5. A plot of χ^{-1} vs *T* for **2**; the solid line is the best fit based on the Curie-Weiss Law with C = 3.417 and 3.460 cm^3Kmol^{-1}, Θ = 15.79.