

## Electronic Supplementary Information

### Thermal Conductivity of Perovskite-type Metal-Organic Framework Crystal

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## Materials and measurement

Reagent grade chemicals were used for all syntheses and sample washing. Powder X-ray diffraction measurements was done on an as-synthesized sample of the polycrystalline bulk material using a Bruker D8 Advance theta-2theta diffractometer with Cu radiation (Cu K $\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ ). A TA instruments TGA Q50 set up was used to record the thermo gravimetric analysis results from room temperature to 753K at a heating rate of 10°C/min.

### Synthesis of perovskite MOF [NH<sub>2</sub>NH<sub>3</sub>][Co(HCOO)<sub>3</sub>] (1)

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.0 mmol, 0.291 g) in 5.0 mL methanol solution was layered onto 5.0 mL of methanol with formic acid, 95% (78 mmol, 3.2 mL) and hydrazine monohydrate, 98% (6.2 mmol, 0.6 mL) to facilitate solvent diffusion. Magenta colored big rectangular crystals appeared after 24 hours. Mother solvent was removed and the rectangular crystals were separated from the bulk phase and washed with reagent grade ethanol. Perovskite structure was confirmed with single crystal X-ray diffraction measurements.

### Synthesis of perovskite MOF [NH<sub>2</sub>NH<sub>3</sub>][Co(HCOO)<sub>3</sub>] (2)

Perovskite MOF **1** was heated under Nitrogen up to 353 K to obtain **2**. Phase transformation from **1** to **2** was determined by X-ray crystallography.

### Sample preparation for thermal conductivity measurement of 1

As synthesized mm sized cuboid shaped crystals were picked from the bulk phase. Reagent grade ethanol was used to clean the crystal surfaces and the washed crystals were kept under a vacuum for 3 hours. Defect free crystals were picked under a microscope. Tip of a pair of tweezers was placed on the each crystal to check their ability to withstand physical pressure. A crystal with good ruggedness was selected for the measurement of thermal conductivity

## Crystallographic studies and refinement of the crystal structures

The X-ray diffraction data for one crystal of **Co\_formate** were measured at different temperatures on Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K $\alpha$  INCOATEC ImuS micro-focus source ( $\lambda = 1.54178 \text{ \AA}$ ) and Oxford 700 Cryostream Cooler (Temperature range: 80K to 400K). The diffraction data integration and reduction were performed using SaintPlus<sup>1</sup>. Absorption correction was performed by multi-scan method implemented in SADABS<sup>2</sup>. Space groups were determined using XPREP implemented in APEX3<sup>3</sup>. Structures were solved using SHELXT and refined using SHELXL-2016<sup>4-7</sup> (full-matrix least-squares on F<sup>2</sup>) through OLEX2 interface program<sup>8</sup>. All non-hydrogen atoms were refined anisotropically. (C-)H hydrogen atoms were placed in geometrically calculated positions and were included in the refinement process using riding model. Crystal data and refinement conditions for the same crystal collected at different temperatures are shown in Tables 1-4.

**Notes:** The crystal undergoes phase transition at 343.15K (determined by DSC measurement). Above transition point (data measured at 353.15K and 393.15K) the structure has higher symmetry and framework seems to be less “distorted”. Due to the fact that the cavity becomes more symmetric, as compared to low temperature phase, the cation can now occupy two symmetrically equivalent positions and therefore is disordered (through the mirror symmetry plane).

**Co\_formate\_100K and Co\_formate\_298K:** Hydrogen atoms of NH<sub>2</sub> and NH<sub>3</sub> groups were found from difference Fourier map and were refined with restraints or as riding with AFIX 137. The structure was refined as twin with 2<sub>[100]</sub> rotation as twinning operator.

**Co\_formate\_353K and Co\_formate\_393K:** Cation was modeled as disordered over two positions through the mirror plane. Hydrogen atoms of NH<sub>2</sub> and NH<sub>3</sub> groups were found from difference Fourier map and were refined with restraints (NH<sub>2</sub>, assignment of hydrogen atoms is tentative to some extent) or as riding with AFIX 137 (NH<sub>3</sub>).

**Table S1 Crystal data and structure refinement for Co\_formate\_100K.**

Identification code	Co_formate_100K
CCDC number	1565711
Empirical formula	C <sub>3</sub> H <sub>8</sub> CoN <sub>2</sub> O <sub>6</sub>
Formula weight	227.04
Temperature/K	100
Crystal system	orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub>
a/Å	8.6505(2)
b/Å	7.7272(2)
c/Å	11.4884(3)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	767.93(3)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.964
μ/mm <sup>-1</sup>	17.629
F(000)	460.0
Crystal size/mm <sup>3</sup>	0.114 × 0.097 × 0.058
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.696 to 154.676
Index ranges	-10 ≤ h ≤ 10, -9 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	11215
Independent reflections	1597 [R <sub>int</sub> = 0.0794, R <sub>sigma</sub> = 0.0472]
Data/restraints/parameters	1597/6/131
Goodness-of-fit on F <sup>2</sup>	1.041
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0321, wR <sub>2</sub> = 0.0684
Final R indexes [all data]	R <sub>1</sub> = 0.0423, wR <sub>2</sub> = 0.0730
Largest diff. peak/hole / e Å <sup>-3</sup>	0.54/-0.33
Flack parameter	0.002(5)

**Table S2 Crystal data and structure refinement for Co\_formate\_298K.**

Identification code	Co_formate_298K
CCDC number	1565714
Empirical formula	C <sub>3</sub> H <sub>8</sub> CoN <sub>2</sub> O <sub>6</sub>
Formula weight	227.04
Temperature/K	298
Crystal system	orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub>
a/Å	8.6592(3)
b/Å	7.7641(2)
c/Å	11.5528(4)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	776.71(4)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.942
μ/mm <sup>-1</sup>	17.430
F(000)	460.0
Crystal size/mm <sup>3</sup>	0.114 × 0.097 × 0.058
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.652 to 154.234
Index ranges	-10 ≤ h ≤ 10, -9 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	11359
Independent reflections	1620 [R <sub>int</sub> = 0.0993, R <sub>sigma</sub> = 0.0595]
Data/restraints/parameters	1620/6/119
Goodness-of-fit on F <sup>2</sup>	1.046
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0388, wR <sub>2</sub> = 0.0858
Final R indexes [all data]	R <sub>1</sub> = 0.0563, wR <sub>2</sub> = 0.0951
Largest diff. peak/hole / e Å <sup>-3</sup>	0.56/-0.42
Flack parameter	-0.001(7)

**Table S3 Crystal data and structure refinement for Co\_formate\_353K.**

Identification code	Co_formate_353K
CCDC number	1565712
Empirical formula	C <sub>3</sub> H <sub>8</sub> CoN <sub>2</sub> O <sub>6</sub>
Formula weight	227.04
Temperature/K	353
Crystal system	orthorhombic
Space group	<i>Pnma</i>
a/Å	8.5725(2)
b/Å	11.6308(3)
c/Å	7.8437(2)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
Volume/Å <sup>3</sup>	782.06(3)
Z	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.928
$\mu$ /mm <sup>-1</sup>	17.311
F(000)	460.0
Crystal size/mm <sup>3</sup>	0.114 × 0.097 × 0.058
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54178)
2 $\theta$ range for data collection/°	13.616 to 153.856
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -9 ≤ l ≤ 9
Reflections collected	11448
Independent reflections	864 [R <sub>int</sub> = 0.0527, R <sub>sigma</sub> = 0.0198]
Data/restraints/parameters	864/6/74
Goodness-of-fit on F <sup>2</sup>	1.132
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0278, wR <sub>2</sub> = 0.0639
Final R indexes [all data]	R <sub>1</sub> = 0.0346, wR <sub>2</sub> = 0.0676
Largest diff. peak/hole / e Å <sup>-3</sup>	0.18/-0.49

**Table SS4 Crystal data and structure refinement for Co\_formate\_393K.**

Identification code	Co_formate_393K
CCDC number	1565713
Empirical formula	C <sub>3</sub> H <sub>8</sub> CoN <sub>2</sub> O <sub>6</sub>
Formula weight	227.04
Temperature/K	393
Crystal system	orthorhombic
Space group	<i>Pnma</i>
<i>a</i> /Å	8.5650(9)
<i>b</i> /Å	11.6420(12)
<i>c</i> /Å	7.8673(8)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
Volume/Å <sup>3</sup>	784.48(14)
Z	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.922
$\mu$ /mm <sup>-1</sup>	17.257
F(000)	460.0
Crystal size/mm <sup>3</sup>	0.114 × 0.097 × 0.058
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54178)
2 $\theta$ range for data collection/°	13.584 to 144.888
Index ranges	-10 ≤ <i>h</i> ≤ 10, -14 ≤ <i>k</i> ≤ 14, -9 ≤ <i>l</i> ≤ 9
Reflections collected	11333
Independent reflections	823 [ <i>R</i> <sub>int</sub> = 0.0561, <i>R</i> <sub>sigma</sub> = 0.0200]
Data/restraints/parameters	823/7/74
Goodness-of-fit on F <sup>2</sup>	1.114
Final R indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0263, <i>wR</i> <sub>2</sub> = 0.0601
Final R indexes [all data]	<i>R</i> <sub>1</sub> = 0.0353, <i>wR</i> <sub>2</sub> = 0.0655
Largest diff. peak/hole / e Å <sup>-3</sup>	0.18/-0.44

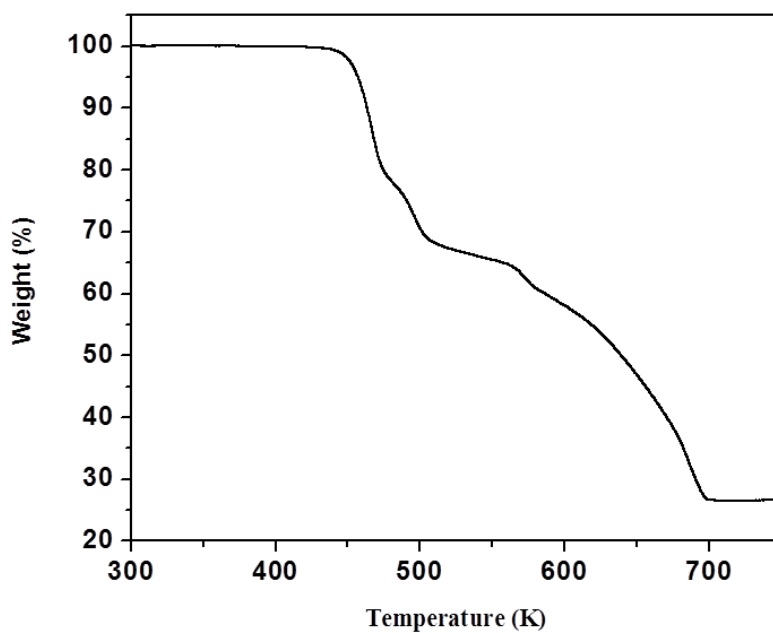
**Table S5. Cell parameters of single crystal 1 at different temperatures**

Temperature(K)	100	200	300	353	393
a(Å)	8.651	8.670	8.659	8.573	8.565
b(Å)	11.727	7.736	7.764	11.631	11.642
c(Å)	7.488	11.515	11.553	7.844	7.867
$\alpha = \beta = \gamma$ (deg)	90	90	90	90	90
V(Å <sup>3</sup> )	767.93	772.28	776.71	782.06	784.48

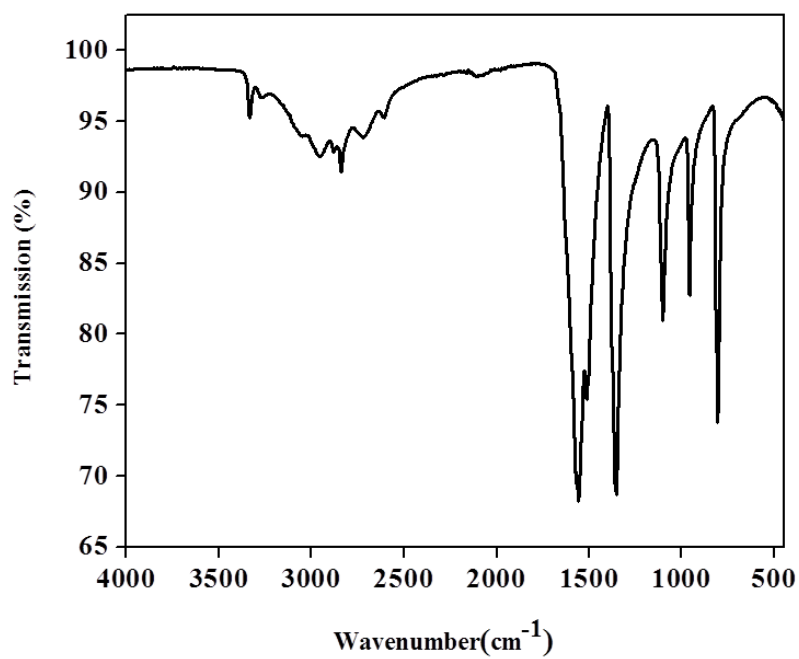
**Table S6. Comparison between the reported values for bulk crystal compounds and this work**

	Thermal Conductivity at 300K (W/m-K)
Co <sub>0.9</sub> Fe <sub>0.1</sub> Sb <sub>3</sub> (Lattice thermal conductivity) <sup>9</sup>	~ 3.5
Co <sub>0.995</sub> Ni <sub>0.005</sub> Sb <sub>3</sub> (Lattice thermal conductivity) <sup>9</sup>	~ 5.5
Yb <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.5</sub> Sn <sub>0.5</sub> (Lattice thermal conductivity) <sup>10</sup>	~ 2.5
Zr <sub>0.5</sub> Hf <sub>0.5</sub> NiSn(Annealed for 2 days) <sup>11</sup>	~ 4.0
<b>This work</b>	1.3
Bi <sub>2</sub> Te <sub>3</sub> (Lattice thermal conductivity in the plane of the a axes) <sup>12</sup>	~ 1.4
CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> <sup>13</sup>	0.5

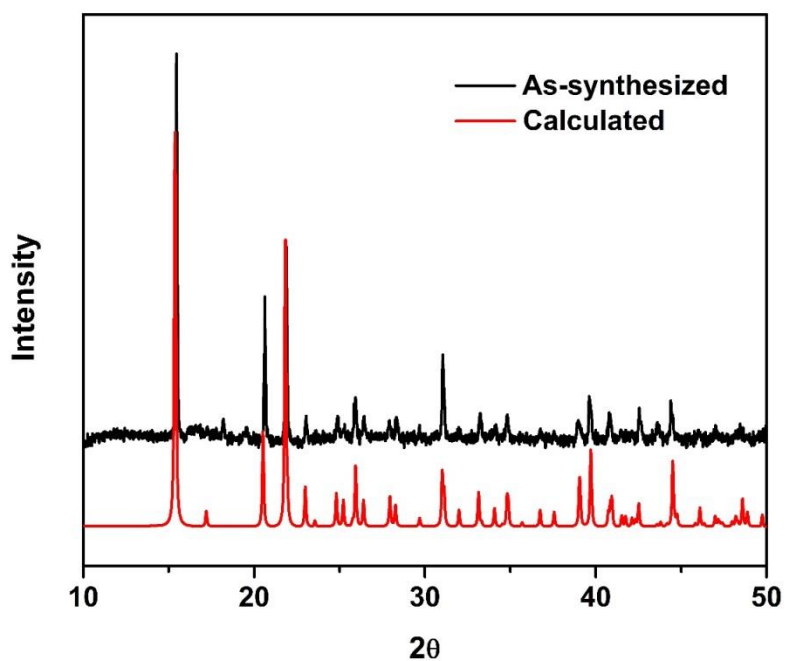




**Fig. S1** Thermo gravimetric analysis of the perovskite polymorph  $[\text{NH}_2\text{NH}_3][\text{Co}(\text{HCOO})_3]\mathbf{1}$ . 34.3% weight loss that occurs in two sub steps by 544 K corresponds to the loss of  $\text{NH}_2\text{NH}_3 \cdot \text{HCOO}$  from the structure. Stability of the structure through 433K confirms the phase transition phenomenon of the polymorph.



**Fig. S2** IR spectra plot of 1.



**Fig. S3** Background reduced PXRD of an as-synthesized polycrystalline bulk sample of 1.

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