Thermal decomposition of formate perovskites

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Table S 1. Quality of reagents used in the synthesis of [AH][M(HCOO)$_3$] materials.

Starting reagent	Purity
Metallic salts	
$MgCl_2$	Sigma-Aldrich ≥98%
$MnCl_2{\cdot}4H_2O$	Sigma-Aldrich ≥98%
$CoCl_2{\cdot}6H_2O$	Sigma-Aldrich 98%
$NiCl_2$	Sigma-Aldrich 98%
$Cu(ClO_4)_2$	Sigma-Aldrich 98%
$ZnCl_2$	Fluka ≥98%
$Cd(ClO_4)_2{\cdot}xH_2O$	Sigma-Aldrich 98%
Organic reagents	
NaHCOO	Sigma-Aldrich ≥99%
NH_4HCOO	Panreac 99.995%
HCOOH	Fluka 98%
CH_3NH_3Cl	Sigma-Aldrich ≥99%
$(CH_3)_2NH$	Sigma-Aldrich ≥99%
$HCONHCH_3$	Sigma-Aldrich 99%

XRPD: $[CH_3NH_3][Mg(HCOO)_3]$

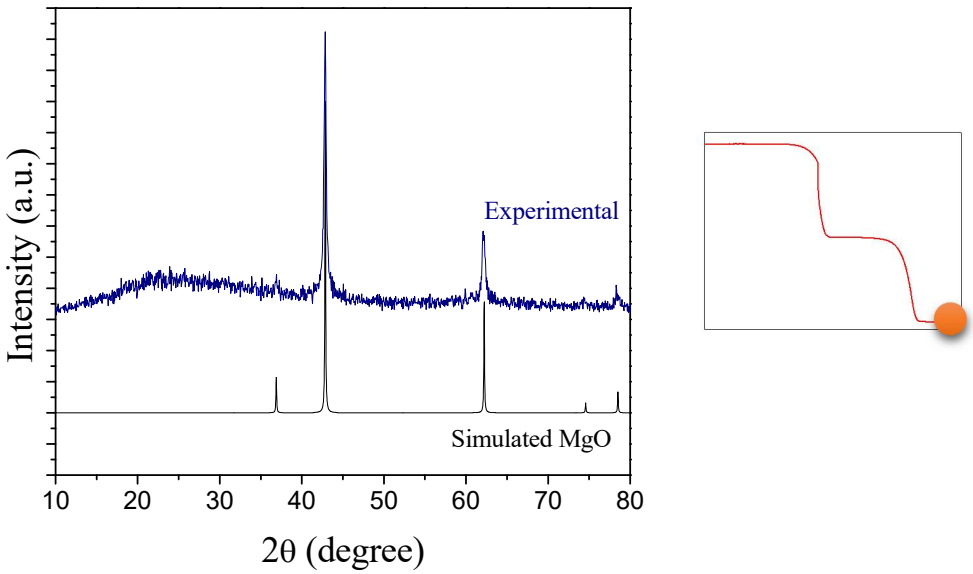

Figure S 1. XRPD pattern obtained after heating the $[CH_3NH_3][Mg(HCOO)_3]$ sample to 600°C. Comparison against the trace reported in the literature for MgO [1].

XRPD: $[CH_3NH_3][Mn(HCOO)_3]$

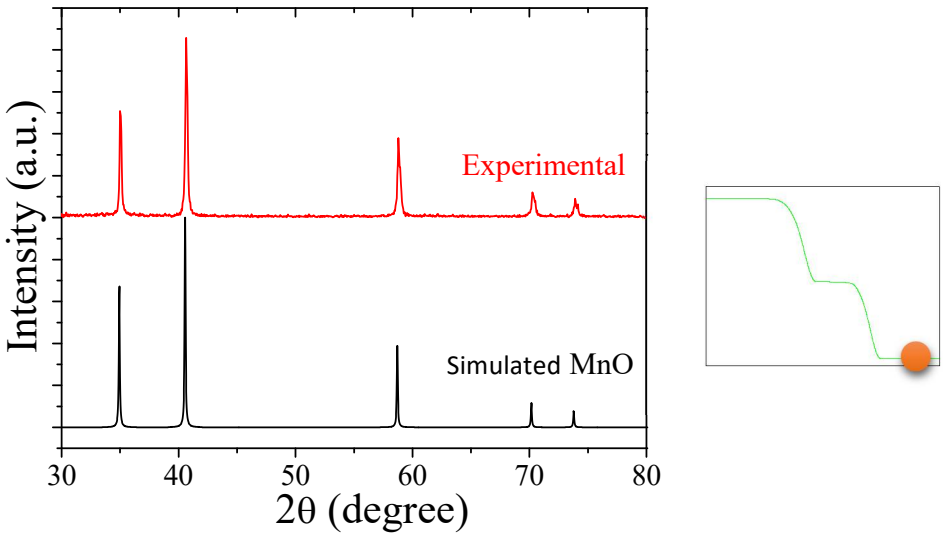

Figure S 2. XRPD pattern obtained after heating the $[CH_3NH_3][Mn(HCOO)_3]$ sample to 600°C. Comparison against the trace reported in the literature for MnO [1].

XRPD: $[CH_3NH_3][Zn(HCOO)_3]$

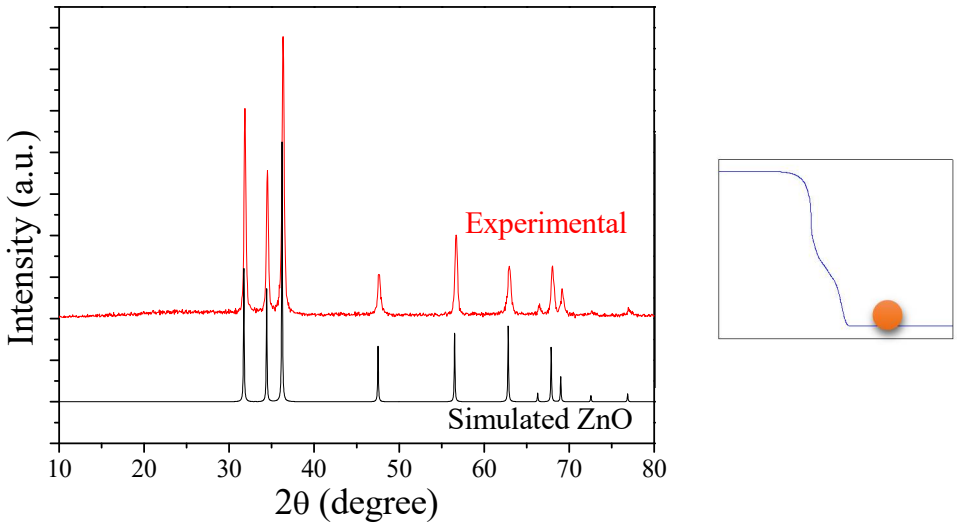

Figure S 3. XRPD pattern obtained after heating the $[CH_3NH_3][Zn(HCOO)_3]$ sample to 600°C. Comparison against the trace reported in the literature for ZnO [2].

XRPD: $[CH_3NH_3][Ni(HCOO)_3]$

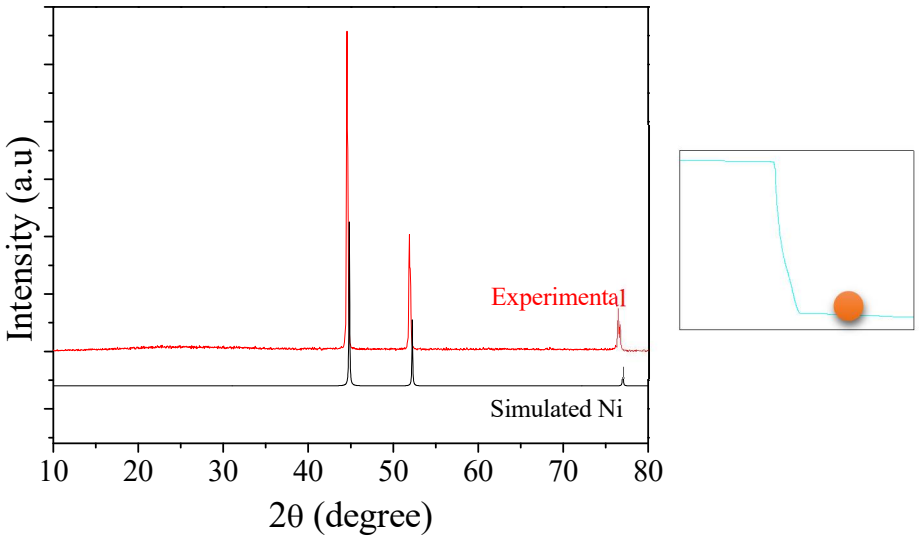

Figure S 4. XRPD pattern obtained after heating the $[CH_3NH_3][Ni(HCOO)_3]$ sample to 600°C. Comparison against the trace reported in the literature for Ni [3].

XRPD: $[CH_3NH_3][Cu(HCOO)_3]$

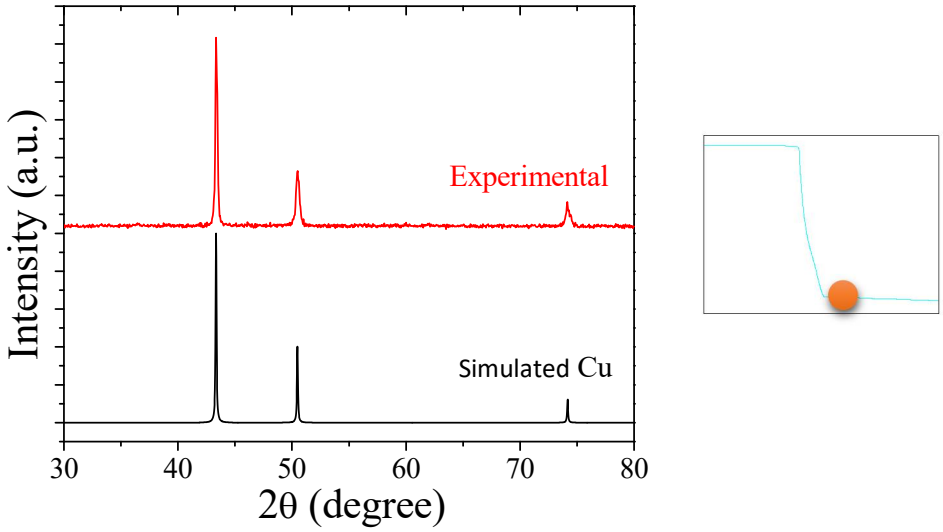

Figure S 5. XRPD pattern obtained after heating the $[CH_3NH_3][Cu(HCOO)_3]$ sample to 600 °C. Comparison against the trace reported in the literature for Cu [4].

XRPD: $[CH_3NH_3][Co(HCOO)_3]$

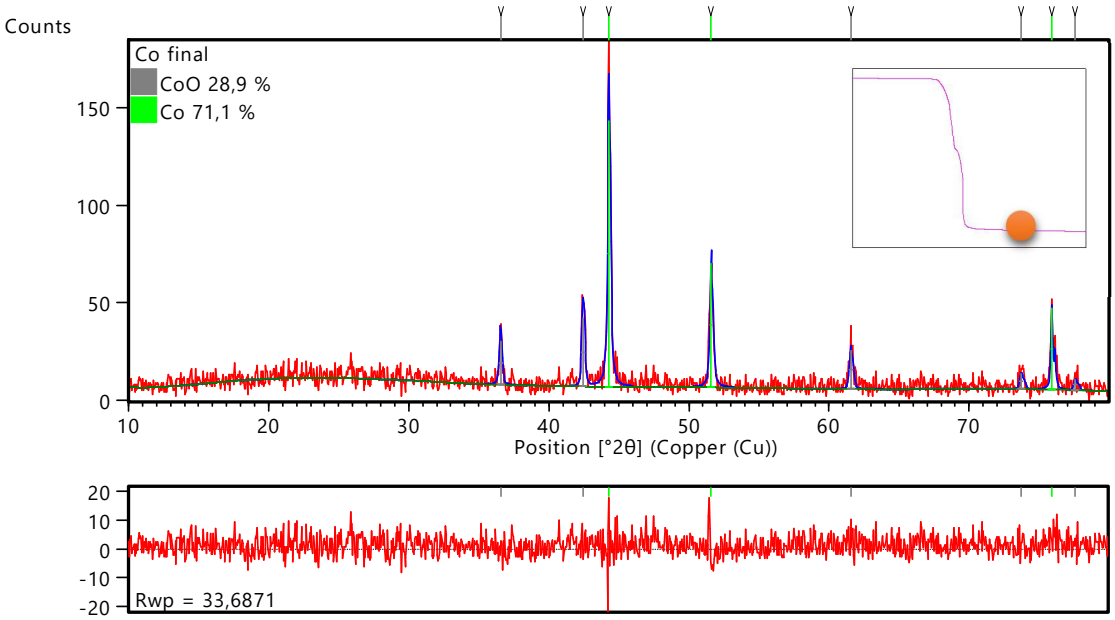

Figure S 6. Rietveld refinement of the XRPD pattern obtained after heating the $[CH_3NH_3][Co(HCOO)_3]$ sample to 600°C. Literature source for CoO [1] and Co [5].

XRPD: $[CH_3NH_3][Mg(HCOO)_3]$

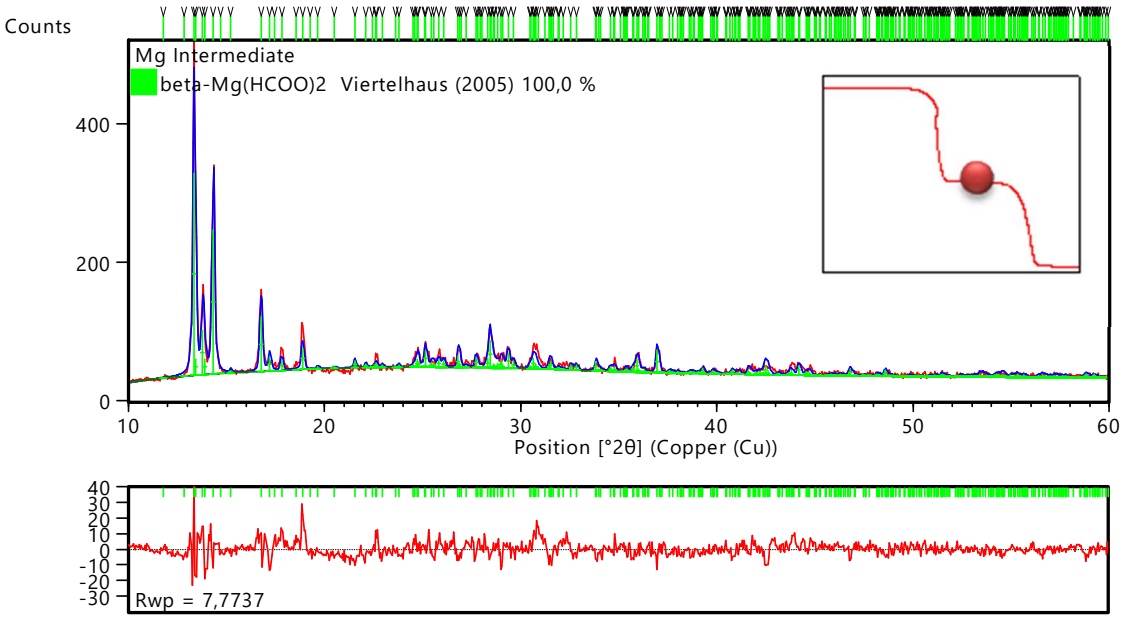

Figure S 7. Rietveld refinement of the XRPD pattern obtained after heating the $[CH_3NH_3][Mg(HCOO)_3]$ sample to 350°C. Literature source for β-$Mg(HCOO)_2$ [6].

XRPD: $[CH_3NH_3][Mn(HCOO)_3]$

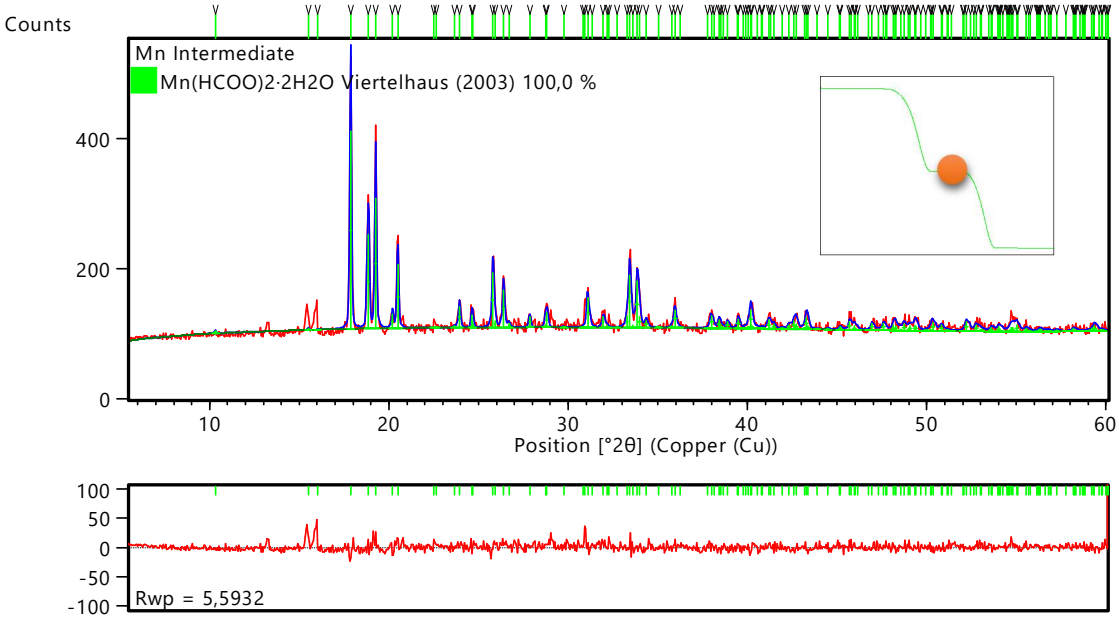

Figure S 8. Rietveld refinement of the XRPD pattern obtained after heating the $[CH_3NH_3][Mn(HCOO)_3]$ sample to 300 °C. Literature source for $Mn(HCOO)_2{\cdot}2H_2O$ [7].

IR of the gases released by TGA for $[CH_3NH_3][M(HCOO)_3]$ (M = Mg, Mn, Zn, Co, Ni, and Cu)

$[CH_3NH_3][Mg(HCOO)_3]$

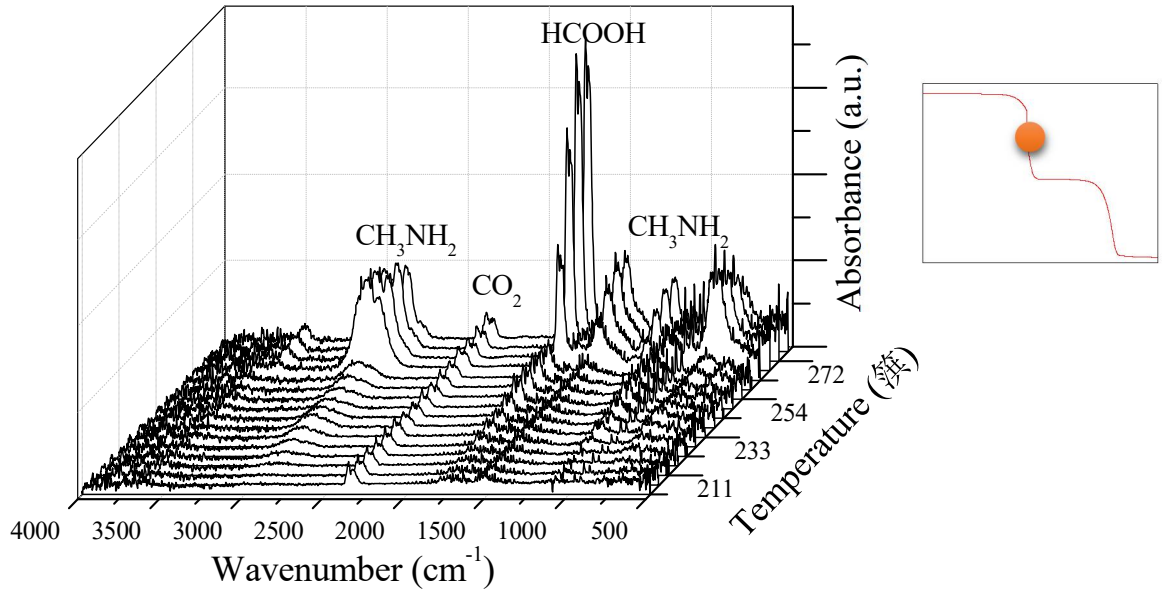

Figure S 9. IR spectra of released gases from $[CH_3NH_3][Mg(HCOO)_3]$ between 200-280 °C.

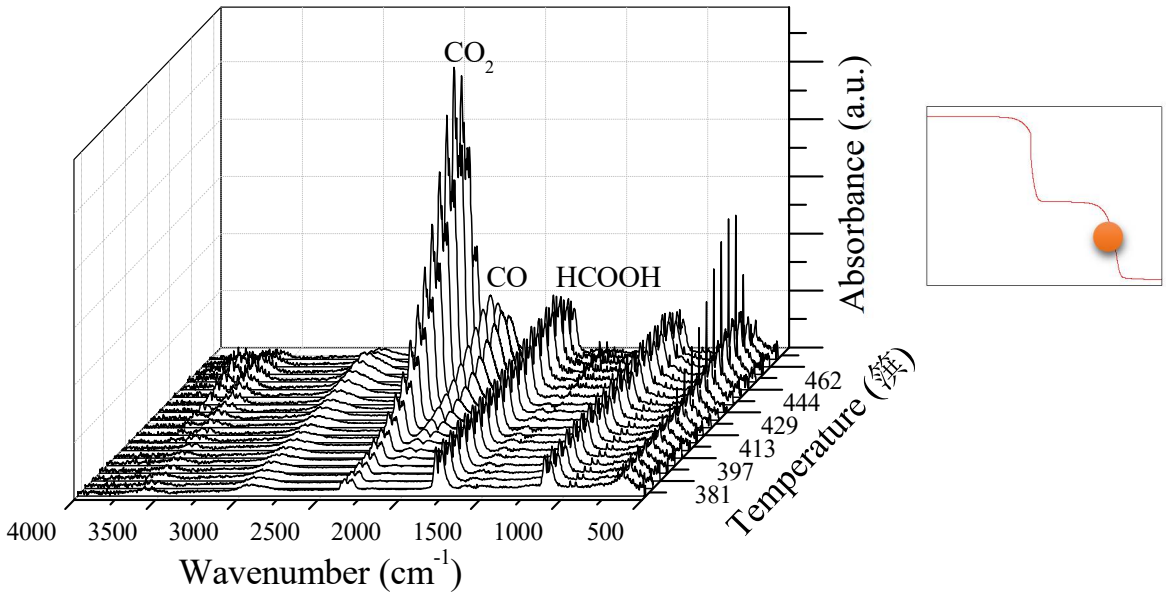

Figure S 10. IR spectra of released gases from $[CH_3NH_3][Mg(HCOO)_3]$ between 370-470 °C.

[CH_3NH_3][Mn(HCOO)$_3$]

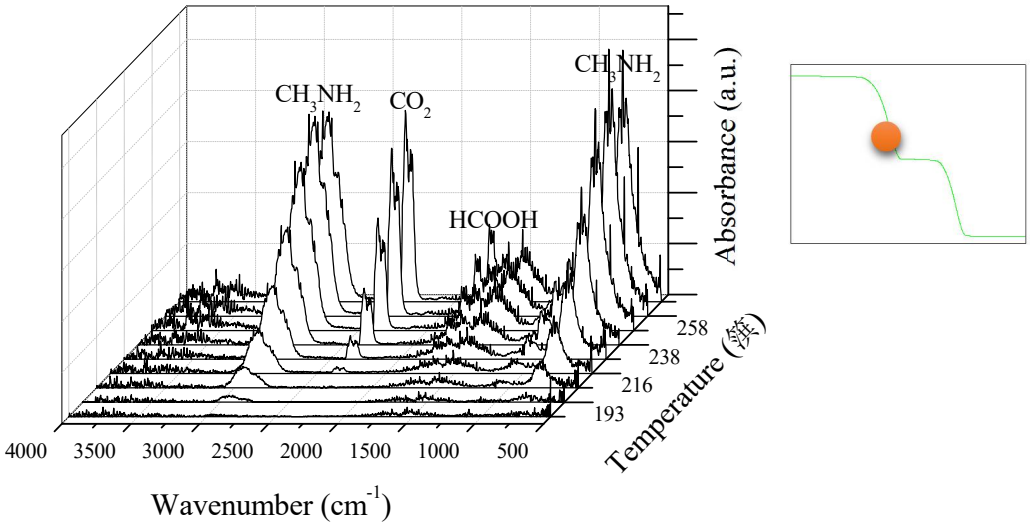

Figure S 11. IR spectra of released gases from [CH_3NH_3][Mn(HCOO)$_3$] between 180-280 °C.

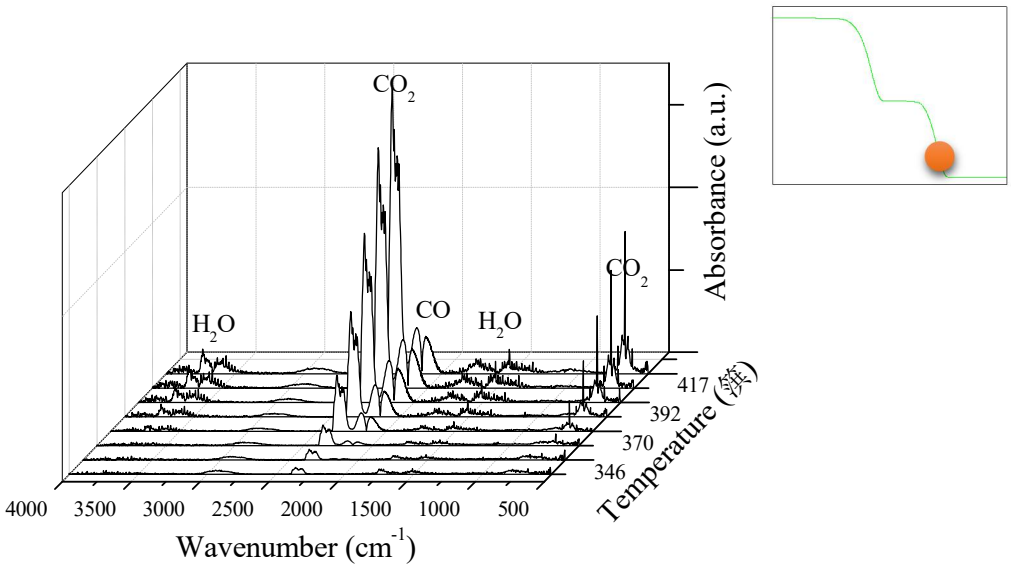

Figure S 12. IR spectra of released gases from [CH_3NH_3][Mn(HCOO)$_3$] between 340-423 °C.

[CH_3NH_3][$Zn(HCOO)_3$]

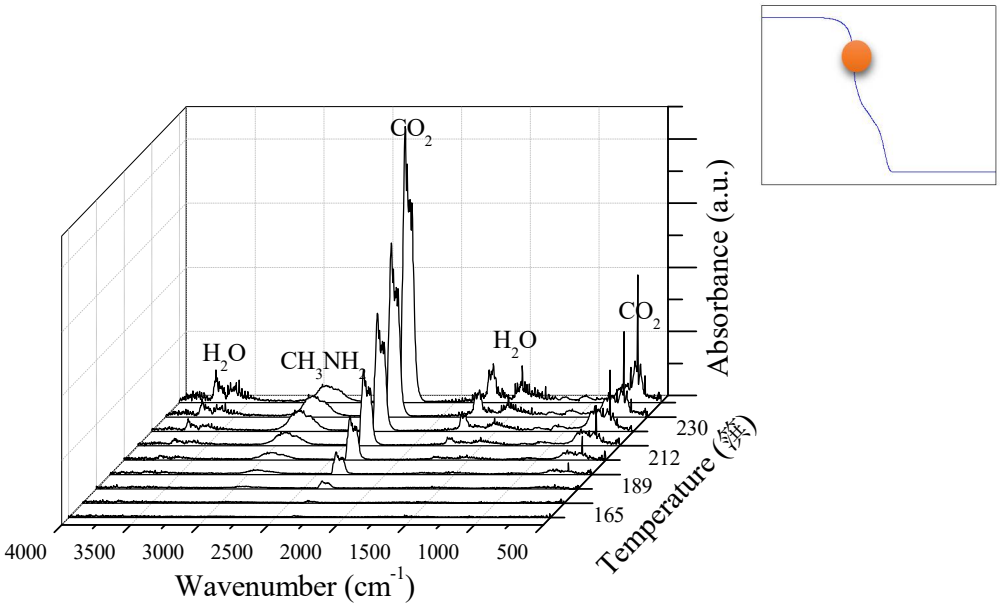

Figure S 13. IR spectra of released gases from [CH_3NH_3][$Zn(HCOO)_3$] between 160-240 °C.

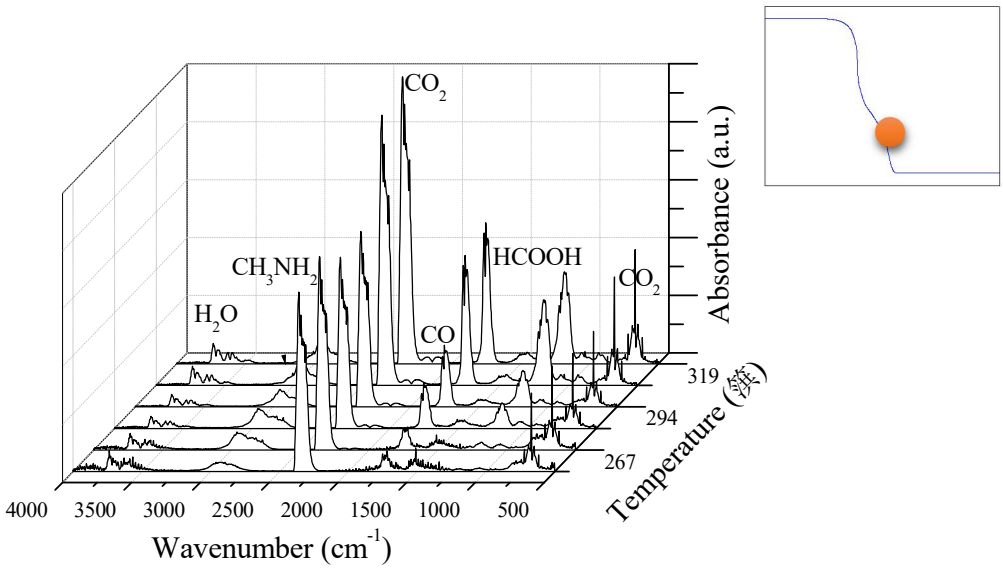

Figure S 14. IR spectra of released gases from [CH_3NH_3][$Zn(HCOO)_3$] between 240-320 °C.

[CH_3NH_3][$Co(HCOO)_3$]

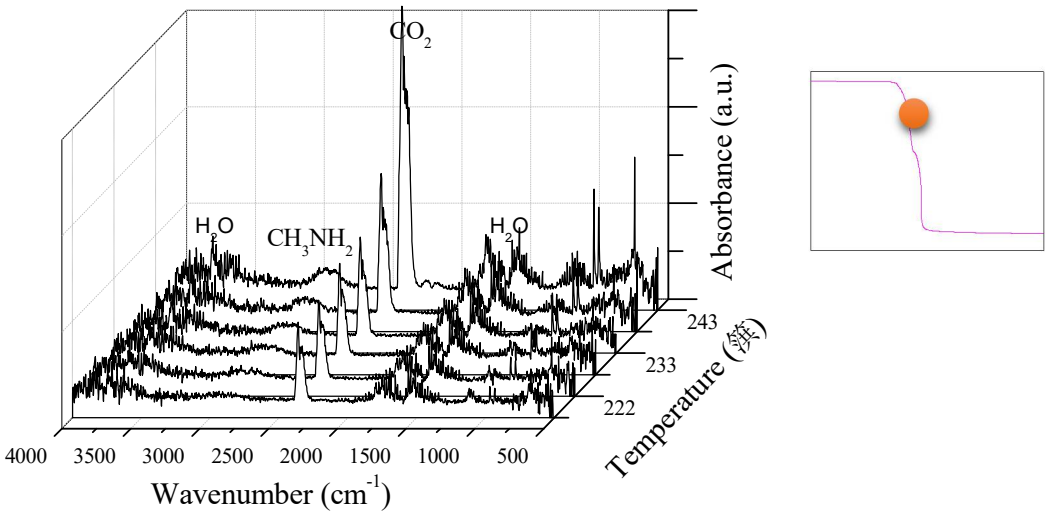

Figure S 15. IR spectra of released gases from [CH_3NH_3][$Co(HCOO)_3$] between 215-254 °C.

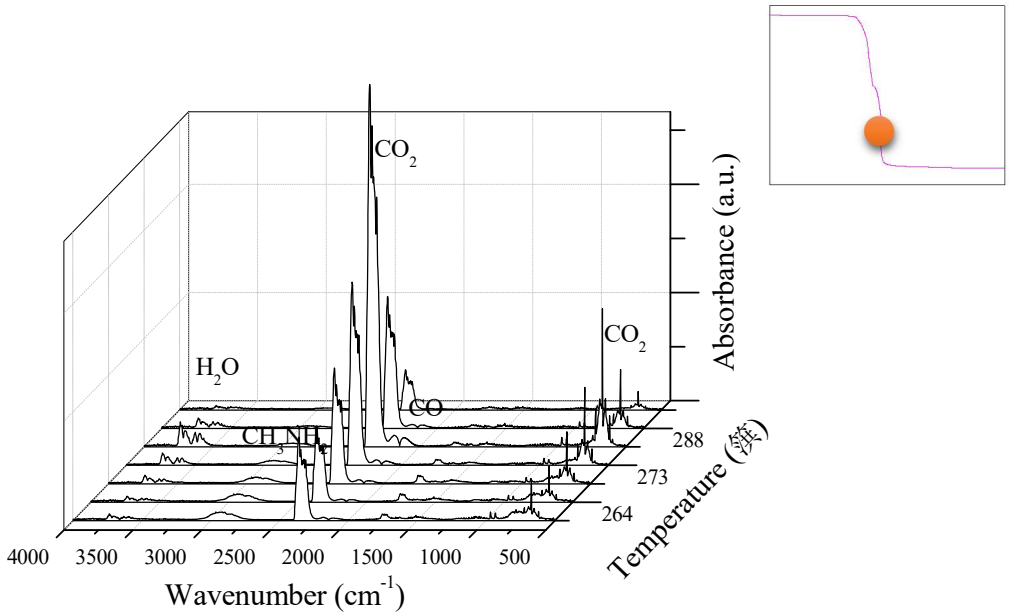

Figure S 16. IR spectra of released gases from [CH_3NH_3][$Co(HCOO)_3$] between 254-290 °C.

[CH_3NH_3][$Ni(HCOO)_3$]

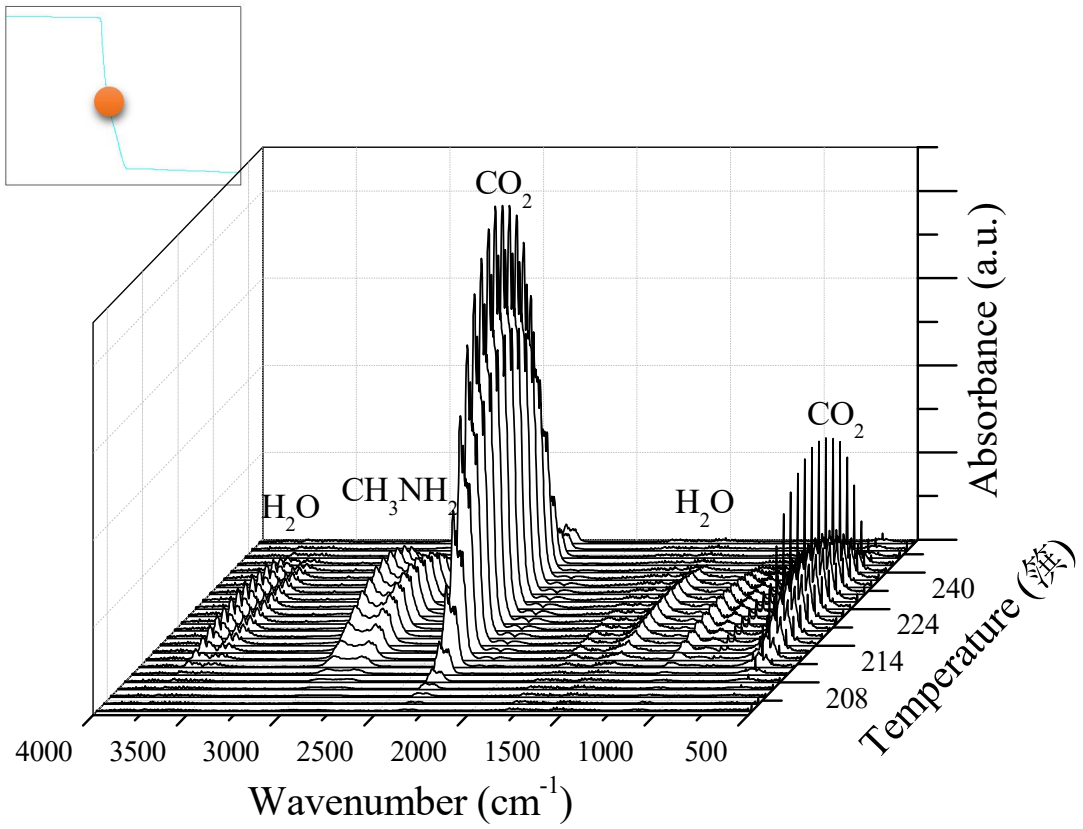

Figure S 17. IR spectra of released gases from [CH_3NH_3][$Ni(HCOO)_3$] between 200-280 °C, recorded at 2 K/min[1]

[CH_3NH_3][$Cu(HCOO)_3$]

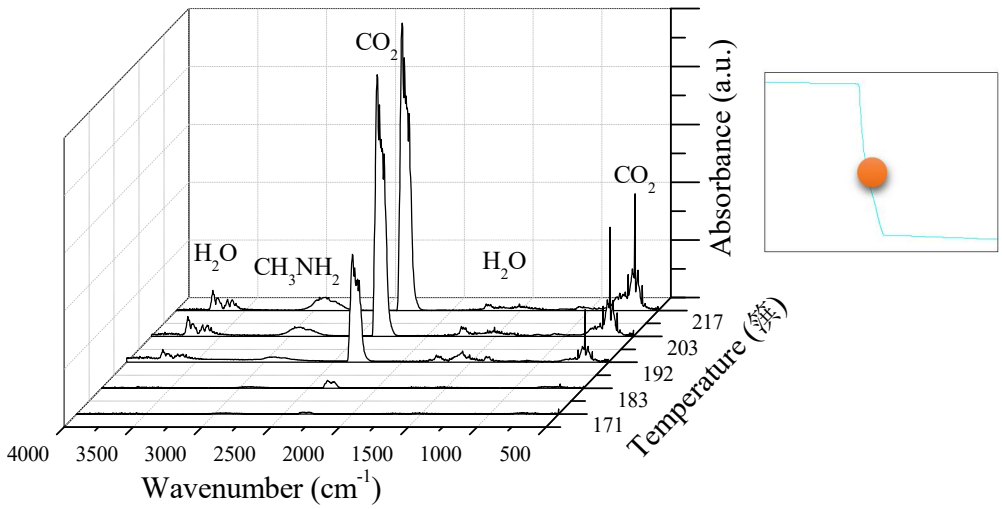

Figure S 18. IR spectra of released gases from [CH_3NH_3][$Cu(HCOO)_3$] between 170-220 °C.

[1] [CH_3NH_3][$Ni(HCOO)_3$] was heated at two different rates. At 5 K/min (Figure 2b-iii), as the rest of the formates, and at 2 K/min (Figure S17).

[AH][Cd(HCOO)$_3$] where [AH]$^+$= NH_4^+, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$

Table S2. Summary of the thermal decomposition of [AH][Cd(HCOO)$_3$] compounds.

[AH]$^+$	**Step nº**	**Decomposition range (ºC)**	**Weight loss**		**Decomposition product**
			Found (%)	**Calculated (%)**	
NH_4^+	1	100-166	23.4	23.4	$Cd(HCOO)_2$
	2	210-305	16.6	28.9	$Cd(CO_3)$ + Cd
	3	305-350	4.9	3.4	CdO + Cd
	4	350-510	29.6	27.7	CdO
$CH_3NH_3^+$	1	130-215	27.59	27.22	$Cd(HCOO)_2$
	2	230-304	28.56	28.50	$Cd(CO_3)$ + Cd
	3	304-350	2.78	2.68	CdO + Cd
	4	420-527	29.44	32.57	CdO
$(CH_3)_2NH_2^+$	1	100-180	30.16	31.04	$Cd(HCOO)_2$
	2	180-296	25.89	24.54	$Cd(CO_3)$ + Cd
	3	296-329	3.1	4.5	CdO + Cd
	4	329-470	22.08	26.80	CdO

XRPD: $[CH_3NH_3][Cd(HCOO)_3]$

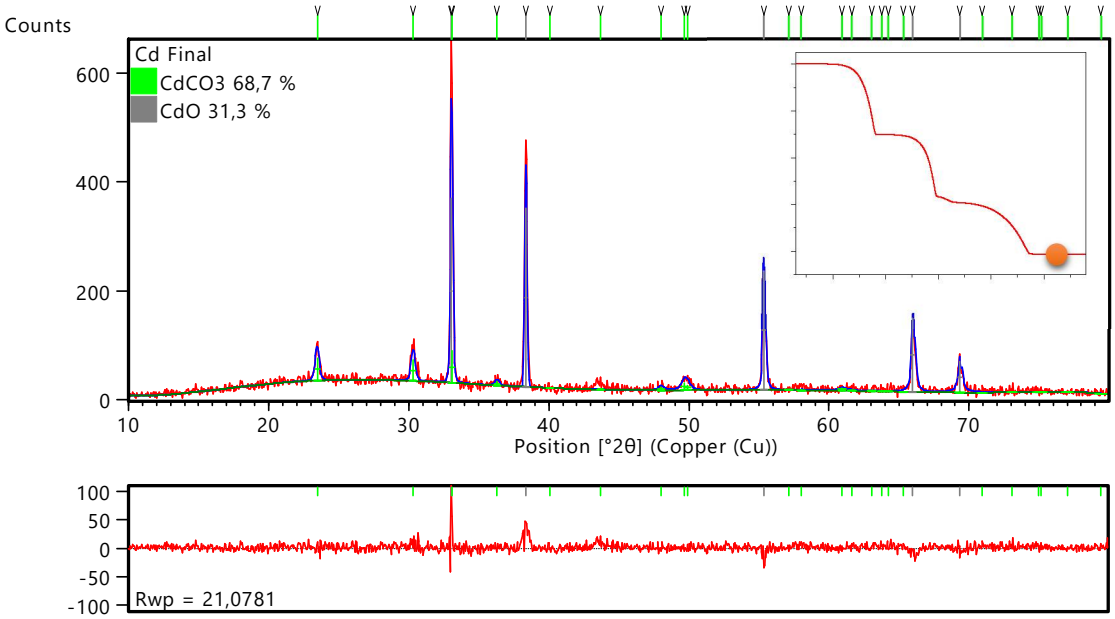

Figure S 19. Rietveld refinement of the XRPD pattern obtained after heating the $[CH_3NH_3][Cd(HCOO)_3]$ sample to 600°C. Literature source for $CdCO_3$ [8] and CdO [9].

IR of TGA gases for [AH][Cd(HCOO)$_3$]

[NH$_4$][Cd(HCOO)$_3$]

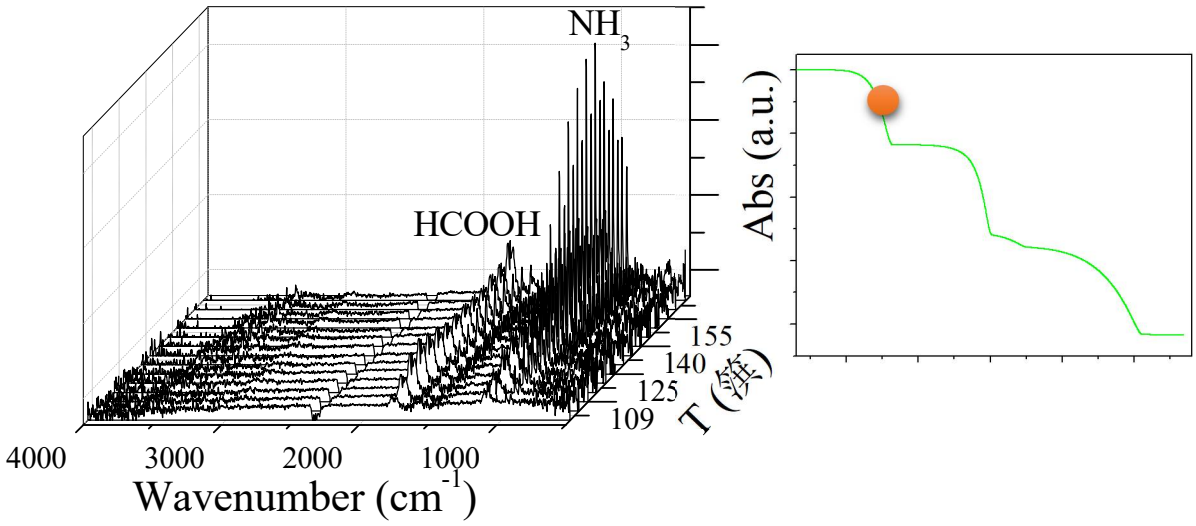

Figure S 20. IR spectra of released gases from [NH$_4$][Cd(HCOO)$_3$] between 100-166 °C.

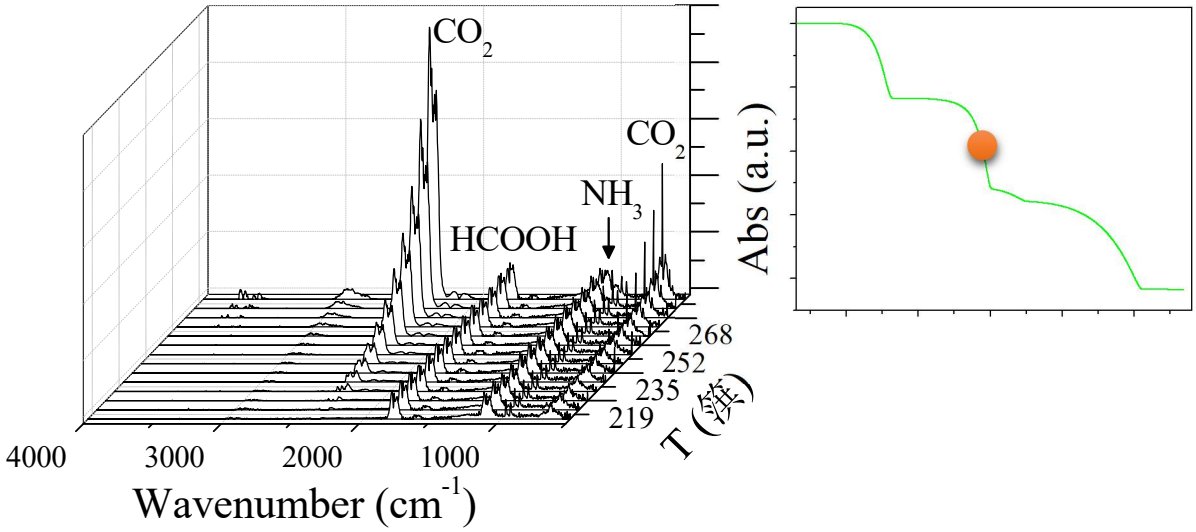

Figure S 21. IR spectra of released gases from [NH$_4$][Cd(HCOO)$_3$] between 210-290 °C.

$[(CH_3)_2NH_2]Cd(HCOO)_3$

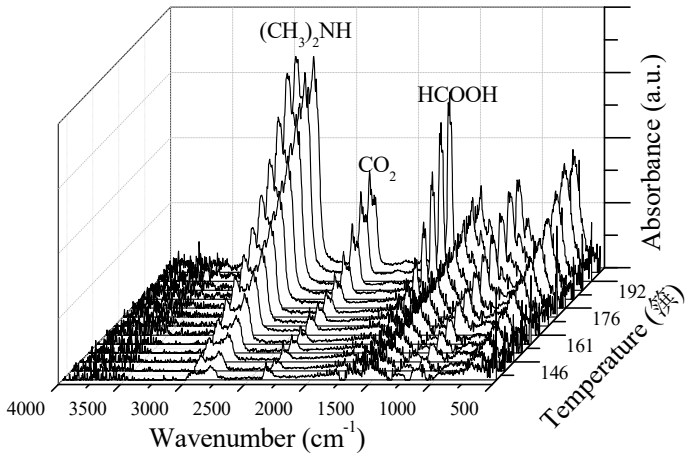

Figure S 22. IR spectra of released gases from $[(CH_3)_2NH_2][Cd(HCOO)_3]$ between 120-200 °C.

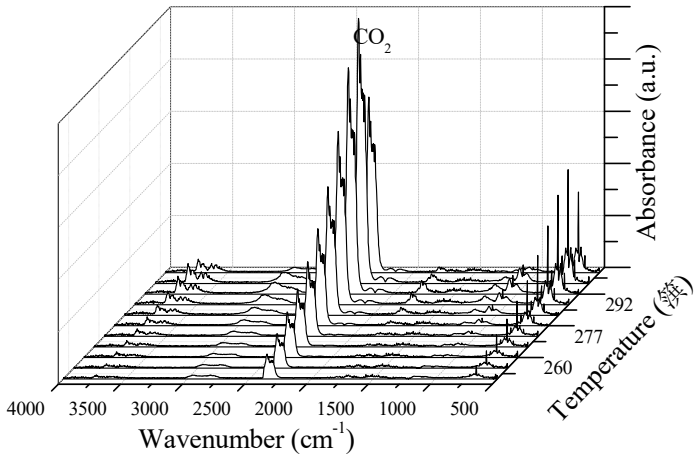

Figure S 23. IR spectra of released gases from $[(CH_3)_2NH_2][Cd(HCOO)_3]$ between 250-296 °C.

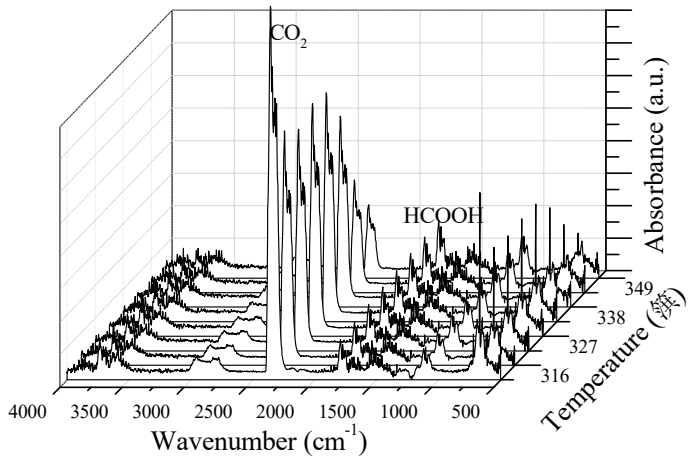

Figure S 24. IR spectra of released gases from $[(CH_3)_2NH_2][Cd(HCOO)_3]$ between 306-352 °C.

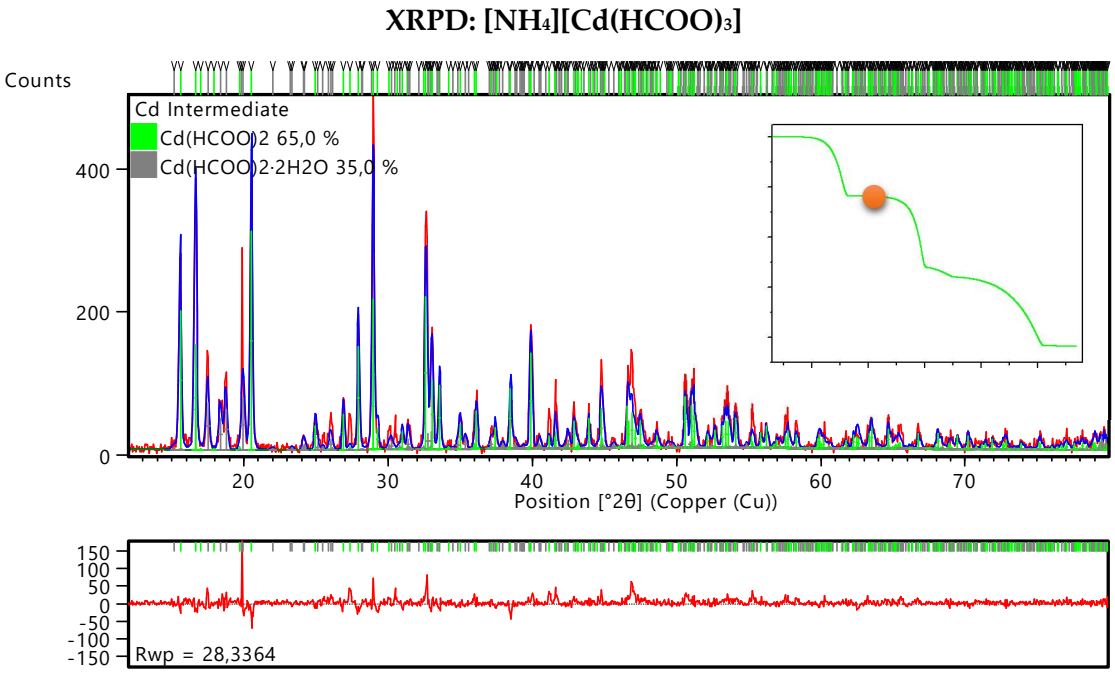

Figure S 25. Rietveld refinement of the XRPD pattern obtained after heating the $[NH_4][Cd(HCOO)_3]$ sample to 200°C. Literature source for $Cd(HCOO)_3 \cdot 2H_2O$ [10] and $Cd(HCOO)_2$ [11].

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