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# Compositional Nanodomain Formation in Hybrid Formate Perovskites

## SUPPLEMENTARY INFORMATION

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## 1 Methods

#### Synthesis

Polycrystalline samples of general formula  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$ , where M = Mg, Mn, Zn and x = 0.0, 0.1, 0.2, ..., 1.0, were prepared by a method analogous to that published for the M = Cd series.<sup>S1–3</sup> Two 10 ml methanolic solutions were mixed in a glass vial, sealed, and stirred overnight at room temperature. The first of these contained 563 mg of  $[C(NH_2)_3]_2CO_3$ (3.13 mmol) and 0.365 ml of HCOOH (9.68 mmol). The other contained the appropriate metal nitrate(s) in the relevant ratios: 10x mL of 0.1 M Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O solution and 10(1 - x) mL of 0.1 M M(NO<sub>3</sub>)<sub>2</sub>.*x*H<sub>2</sub>O solution. It was imperative that methanol was used as the solvent as the presence of water could result in the formation of metal-formate dihydrates, M(HCOO)<sub>2</sub>.2H<sub>2</sub>O.<sup>S4</sup> After 16 hours of stirring, the polycrystalline powders were filtered, washed with methanol, dried and ground. The compounds were obtained in high yield (Table S1) and all compositions were confirmed by atomic absorption spectroscopy (AAS).

$\overline{x}$	$Cu_xMg_{1-x}$	$Cu_xMn_{1-x}$	$Cu_xZn_{1-x}$
0.0	85	88	93
0.1	87	80	73
0.2	90	97	93
0.3	90	87	89
0.4	90	86	92
0.5	90	84	89
0.6	88	86	81
0.7	89	87	86
0.8	82	88	86
0.9	86	89	92
1.0	82	77	80

**Table S1:** Percentage yields of series:  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$ , where M = Mg, Mn, Zn and x = 0.0, 0.1, 0.2..., 1.0.

#### Atomic absorption spectroscopy

Atomic absorption spectroscopy was used to confirm Cu:M ratios in  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$  samples for x = 0.1, 0.2, ..., 0.9. The measurements were carried out in-house, on a Varian AA240FS spectrometer, using Perkin Elmer ATOMAX hollow cathode lamps. The lamp current was 10 mA, the slit width was 0.1 nm, and the fuel was an acetylene/air mix.

Reference solutions were prepared for Cu, Mg, Mn, and Zn from Acros Organics  $1 \text{ g L}^{-1}$  stock solutions. The concentrations of the reference solutions were chosen such that they fell in the optimum working range for a given flame emission wavelength.

- (i) For Cu, at 327.4 nm the optimum working range is 0.03–10  $\mu$ L and the chosen concentrations were: 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 mg L<sup>-1</sup>.
- (ii) For Mg, at 285.2 nm the optimum working range is 0.003–1  $\mu$ L and the chosen concentrations were: 0.05, 0.10, 0.15, 0.25 and 0.30 mg L<sup>-1</sup>.
- (iii) For Mn, at 279.5 nm the optimum working range is 0.02–5  $\mu$ L and the chosen concentrations were: 0.5, 1.0, 1.5, 2.0 and 2.5 mg L<sup>-1</sup>.
- (iv) For Zn, at 213.9 nm the optimum working range is 0.01–2  $\mu$ L and the chosen concentrations were: 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mg L<sup>-1</sup>.

For each of the metal formate samples, a known mass was initially dissolved in concentrated nitric acid. These solutions were then successively diluted with water until the concentrations of the metal ions fell within the optimum working range. The reference solutions were likewise prepared by dilution with water.

Prior to measurement, the lamp and flame positions were optimised. Each measurement was repeated five times and an average calculated to ensure accuracy. By comparison with the relevant calibration curve, the concentrations of the metal ions were deducted from the absorption data. These concentrations were then converted to moles so that the ratio of Cu to M could be calculated. Due to the close agreement between the nominal and actual compositions, the nominal compositions have been referred to throughout the main text.

$x_{\rm nominal,M}$	$x_{\rm AAS,Mg}$	$x_{\rm AAS,Mn}$	$x_{\rm AAS,Zn}$
0.9	0.947(9)	0.903(35)	0.877(15)
0.8	0.897(20)	0.847(46)	0.769(18)
0.7	0.819(11)	0.688(34)	0.625(10)
0.6	0.739(8)	0.590(18)	0.526(11)
0.5	0.655(19)	0.507(61)	0.407(10)
0.4	0.672(69)	0.411(12)	0.347(11)
0.3	0.459(9)	0.304(14)	0.271(7)
0.2	0.340(12)	0.248(34)	0.168(11)
0.1	0.191(6)	0.119(5)	0.097(4)

**Table S2:** Experimental value of x determined by AAS for  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$  for x = 0.1, 0.2, ..., 0.9. Since phase separation occurs in the Mg systems, AAS cannot give the composition of the individual phases, but rather the total Cu content in a given sample.

#### **Powder X-ray Diffraction**

Powder diffraction measurements were collected on the I11 beamline at Diamond Light Source, located at the Harwell Science and Innovation campus in Oxfordshire. Finely ground samples were loaded into 0.5 mm borosilicate capillaries and placed in brass holders. Room temperature data were collected using the Mythen2 PSD detector across the range  $2^{\circ} < 2\theta < 92^{\circ}$ . Short exposure times ( $2 \times 4$  s, 0.25° offset) were used to prevent significant beam damage to the samples. The wavelength of radiation was refined as 0.82598 Å using a Si NIST 640c standard.

The data were analysed by Rietveld refinement<sup>S5</sup> implemented in TOPAS software (academic version 4.1).<sup>S6</sup> A silicon standard was measured to obtain accurate instrument parameters (*i.e.* intrinsic peak shape and zero point). Additional strain terms were added to the refinement to adjust the model peak shape to fit the data. The starting lattice parameters for the refinements were taken from published structures (for the endmembers) or calculated by refinement against endmember CIFs (for the mixed-metal samples). Chemically informed restraints were applied to the formate linkers so that the positions of these atoms could be refined. These restraints restricted the C–O and C–H bond lengths, and and the O–C–O and O–C–H angles. The lattice parameters, polynomial background function coefficients and axial divergence parameter were also refined.

#### Infrared Spectroscopy

Infrared spectroscopy measurements were carried out using a Bruker Tensor 27 FT-IR spectrometer, fitted with a diamond attenuated total reflection (ATR) module. After ensuring the instrument was clean, an initial background scan was taken. A small amount of polycrystalline powder was then applied to the diamond module and secured by the high pressure tower. The instrument was operated with OPUS data collection programme and data was collected in the range  $600-4000 \text{ cm}^{-1}$  at room temperature. The spectra were assigned by comparison with previously published data.<sup>S4</sup>

## 2 Powder X-ray Diffraction Refinements

#### Mg structure and Rietveld refinement

To the best of our knowledge, the structure of  $[C(NH_2)_3]Mg(HCOO)_3$  has not previously been reported. However, according to the tolerance factor,  $\alpha = 0.9907$ , <sup>S7</sup> it should form as a stable perovskite system. Powder synthesis, analogous to that of the Mn and Zn counterparts, produced a white polycrystalline sample. Rietveld refinement was subsequently used to determine the structure: the diffraction pattern indexed well in *Pnna* and therefore the Mn system was used as a starting model (Fig. S1). The refined parameters, alongside other crystallographic details, are outlined in Table S3 and Table S4.



*Figure S1:* Rietveld fit to the X-ray powder diffraction pattern ( $\lambda = 0.82598$  Å) for  $[C(NH_2)_3]Mg(HCOO)_3$  obtained using the structural model of Table S3 ( $R_{wp} = 3.105\%$ ). The inset shows the crystal structure of  $[C(NH_2)_3]Mg(HCOO)_3$ .

Empirical Formula	$MgO_6N_3C_4H_9$
Formula weight (g mol $^{-1}$ )	219.36
Crystal system	Orthorhombic
Space group	Pnna (No. 52)
Ζ	4
Sample colour	white
a/Å	8.40635(9)
b/Å	11.8045(1)
$c/{ m \AA}$	8.8505(1)
$V/{ m \AA}^3$	878.25(2)
$R_{\sf wp}$	3.105%

**Table S3:** Crystallographic details for  $[C(NH_2)_3]Mg(HCOO)_3$ .

Atom	x	y	z
Mg	0.2509(4)	0.25	0.5
01	0.2533(4)	0.4062(1)	0.3611(2)
O2	0.4005(3)	0.1905(2)	0.4097(3)
O3	0.5628(3)	0.1919(2)	0.6048(3)
C1	0.25	0.5	0.3003(3)
C2	0.5226(3)	0.2215(3)	0.4803(3)
C3	0.25	0.5	0.7565 (3)
N1	0.3356(3)	0.4258(2)	0.6846(4)
N2	0.25	0.5	0.9108(4)
H1	0.25	0.5	0.1975
H2	0.5833	0.2778	0.4367
H3	0.3399	0.4272	0.5861
H4	0.3988	0.3794	0.7308
H5	0.3089	0.4523	0.9523

**Table S4:** Crystallographic data for  $[C(NH_2)_3]Mg(HCOO)_3$ . The  $U_{iso}$  values were set to 0.025 Å<sup>2</sup>.

#### Phase analysis of Mg series

From the diffraction patterns it is apparent that the Mg-rich samples (x = 0.1-0.5) contain two distinct phases. For instance, in the region  $7.90^{\circ} < 2\theta < 8.25^{\circ}$  two reflections can be seen, but only one—(002)—is anticipated (Fig. S2). One of these reflections appears in all five samples at a constant value of  $2\theta = 8.0053^{\circ}$ . This corresponds to the (002) reflection of the Mg endmember, and its intensity increases with Mg concentration. The other reflection occurs at a higher angle and shifts incrementally with composition. This indicates the presence of two phases: the Mg endmember and a mixed-metal phase.

The fractions of each phase were determined by Rietveld refinement: all parameters for the Mg endmember were fixed, whilst the B-site occupancies, lattice parameters, strain and axial terms were refined for the mixed phase. The B-site occupancies were restrained to add to one, and could be refined owing to the significantly different electron counts of Mg<sup>2+</sup> and Cu<sup>2+</sup>. It was thus possible to ascertain the fraction of the mixed phase present and the proportion of Cu<sup>2+</sup> ions in this phase.



*Figure S2:* The Rietveld refinements of  $Cu_xMg_{1-x}$  where  $x_{nominal} = 0.1-0.5$ , in the region  $7.90^{\circ} < 2\theta < 8.25^{\circ}$ . The (002) reflection of the Mg endmember phase is highlighted in orange.

Nominal Mg composition	f(mixed-phase)	Cu composition of mixed-phase, $x$
1.0	0.00	0.00
0.9	0.44	0.30
0.8	0.58	0.50
0.7	0.68	0.51
0.6	0.76	0.56
0.5	0.85	0.66
0.4	1.00	0.69
0.3	1.00	0.79
0.2	1.00	0.86
0.1	1.00	0.91
0.0	1.00	1.00

*Table S5:* The mixed-phase fraction f and the ratio of Cu:Mn in this phase, as determined by Rietveld refinement.

#### $Pna2_1$ superlattice peak intensity and variation with composition

The endmember space groups— $Pna2_1$  and Pnan—share a group–subgroup relationship (note here the shift to the non-standard Pnan setting of Pnna). As a result, they can only be differentiated by a few reflections that are allowed in  $Pna2_1$  and forbidden in Pnan: (120), (210), (230), (320), (140) and (410), *i.e.* (hk0) with h + k odd and  $h, k \neq 0$ . Observed through PXRD, these reflections are very weak as their intensities are linked to the asymmetry of the M–O bond lengths, which in the case of Cu and Mn/Zn is very small. High-resolution PXRD data collected at a synchrotron are therefore necessary to distinguish these peaks from the background. The (210) reflection occurs in an isolated region of reciprocal space and has sufficient intensity to be used as the marker for  $Pna2_1$  symmetry.

The Rietveld refinements show that the (210) reflection is only present in the samples where  $x \ge 0.9$  for Cu<sub>x</sub>Mn<sub>1-x</sub> and Cu<sub>x</sub>Zn<sub>1-x</sub>, and x = 1.0 for Cu<sub>x</sub>Mg<sub>1-x</sub>. The area of this reflection, relative to the sharp (110) reflection, was tracked across the Cu<sub>x</sub>Mn<sub>1-x</sub> and Cu<sub>x</sub>Zn<sub>1-x</sub> series and compared to that calculated for the known structure (Fig. S3). The large uncertainties (Table S6) are due to the low intensity of the (210) reflection with respect to the background. Nevertheless, it is clear that the area of the peak decreases with Cu concentration, indicative of the approaching phase transition.

Compound	<i>I</i> (210)/ <i>I</i> (110) (%)
Cu <sub>1.0</sub> Mn <sub>0.0</sub> (expt.)	1.4(4)
Cu <sub>0.9</sub> Mn <sub>0.1</sub> (expt.)	0.78(3)
Cu <sub>1.0</sub> Zn <sub>0.0</sub> (expt.)	1.0(2)
Cu <sub>0.9</sub> Zn <sub>0.1</sub> (expt.)	0.58(2)

*Table S6:* Relative area of the (210) superlattice reflection in experimentally observed diffraction patterns.



*Figure S3:* The (110) reflection (red) and the (210) superlattice reflection (blue) fitted with Gaussian functions for compounds: (a)  $Cu_{1.0}Zn_{0.0}$ , (b)  $Cu_{0.9}Zn_{0.1}$ , (c)  $Cu_{1.0}Mn_{0.0}$  and (d)  $Cu_{0.9}Mn_{0.1}$ .

## **Rietveld refinements**

Figures S4–S6 show the powder X-ray diffraction refinements of synchrotron data for the series:  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$  where M = Mn, Zn, Mg and x = 0.0, 0.1, 0.2, ..., 1.0.



*Figure S4:* Synchrotron X-ray diffraction patterns (black lines) and Rietveld refinements (coloured lines) for  $[C(NH_2)_3]Cu_xMn_{1-x}(HCOO)_3$ . Blue indicates  $Pna2_1$  and pink indicates Pnna symmetry. The inset shows the presence/ absence of the (210) reflection used to distinguish  $Pna2_1$  and Pnna symmetry.



*Figure S5:* Synchrotron X-ray diffraction patterns (black lines) and Rietveld refinements (grey and blue lines) for  $[C(NH_2)_3]Cu_xZn_{1-x}(HCOO)_3$ . Blue indicates  $Pna2_1$  and grey indicates Pnna symmetry. The inset shows the presence/ absence of the (210) reflection used to distinguish  $Pna2_1$  and Pnna symmetry.



*Figure S6:* Synchrotron X-ray diffraction patterns (black lines) and Rietveld refinements (coloured lines) for  $[C(NH_2)_3]Cu_xMg_{1-x}(HCOO)_3$ . Blue indicates  $Pna2_1$  and orange indicates Pnna symmetry. The inset shows the presence/ absence of the (210) reflection used to distinguish  $Pna2_1$  and Pnna symmetry.

## **Refinement parameters**

Tables S7–S9 list of the lattice parameter values, determined by Rietveld refinement of the X-ray powder diffraction data in the previous section. The data correspond to the family of compounds  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$  where M = Mn (Table S7), Zn (Table S8), and Mg (Table S9).

x	Space group	a/Å	b/Å	c/Å	$V/{ m \AA}^3$
0.0	Pnna	8.5258(2)	11.9996(2)	9.0528(2)	926.16(3)
0.1	Pnna	8.5150(2)	11.9498(2)	9.0427(3)	920.11(4)
0.2	Pnna	8.5023(2)	11.8904(2)	9.0322(2)	913.11(4)
0.3	Pnna	8.5023(2)	11.8503(2)	9.0316(2)	909.98(3)
0.4	Pnna	8.4968(2)	11.7981(2)	9.0261(2)	904.83(3)
0.5	Pnna	8.4894(2)	11.7443(2)	9.0216(2)	899.47(4)
0.6	Pnna	8.4894(2)	11.6919(2)	9.0189(2)	895.18(4)
0.7	Pnna	8.4959(2)	11.6071(3)	9.0217(3)	889.65(4)
0.8	Pnna	8.5079(2)	11.5242(2)	9.0253(2)	884.90(3)
0.9	$Pna2_1$	8.5244(1)	9.0308(2)	11.4416(2)	880.80(2)
1.0	$Pna2_1$	8.5287(1)	9.0347(1)	11.3594(1)	875.29(1)

*Table S7:* Crystal symmetries and lattice parameters for  $[C(NH_2)_3]Cu_xMn_{1-x}(HCOO)_3$ .

x	Space group	a/Å	b/Å	c/Å	$V/{ m \AA}^3$
0.0	Pnna	8.3497(1)	11.7391(1)	8.9236(1)	874.67(2)
0.1	Pnna	8.3633(1)	11.7053(1)	8.9330(1)	874.50(2)
0.2	Pnna	8.3747(1)	11.6758(1)	8.9409(1)	874.24(2)
0.3	Pnna	8.3882(1)	11.6413(1)	8.9492(1)	873.89(2)
0.4	Pnna	8.4028(1)	11.6052(1)	8.9587(1)	873.61(2)
0.5	Pnna	8.4191(1)	11.5699(1)	8.9701(2)	873.76(2)
0.6	Pnna	8.4386(1)	11.5295(1)	8.9820(1)	873.88(2)
0.7	Pnna	8.4607(1)	11.4871(1)	8.9951(1)	874.23(2)
0.8	Pnna	8.4832(1)	11.4430(1)	9.0080(1)	874.44(2)
0.9	$Pna2_1$	8.5149(1)	9.0185(1)	11.4070(1)	875.97(2)
1.0	$Pna2_1$	8.5289(1)	9.0348(1)	11.3589(1)	875.28(1)

*Table S8:* Crystal symmetries and lattice parameters for  $[C(NH_2)_3]Cu_xZn_{1-x}(HCOO)_3$ .

x	Space group	a/Å	b/Å	c/Å	$V/{ m \AA}^3$
0.0	Pnna	8.4063(1)	11.8045(1)	8.85059(1)	878.25(2)
0.1	Pnna	8.4112(3)	11.7398(4)	8.8705(4)	875.92(6)
0.2	Pnna	8.4224(4)	11.6800(4)	8.8863(5)	874.18(7)
0.3	Pnna	8.4289(3)	11.6415(3)	8.9040(4)	873.71(6)
0.4	Pnna	8.4379(4)	11.6029(4)	8.9252(4)	873.81(6)
0.5	Pnna	8.4480(3)	11.5664(3)	8.9419(4)	873.74(6)
0.6	Pnna	8.4617(3)	11.5344(3)	8.9609(3)	874.58(5)
0.7	Pnna	8.4755(2)	11.4962(2)	8.9781(3)	874.79(4)
0.8	Pnna	8.4945(2)	11.4465(2)	8.9975(2)	874.85(3)
0.9	Pnna	8.5169(1)	11.4079(1)	9.0194(1)	876.32(2)
1.0	$Pna2_1$	8.5235(1)	9.0294(1)	11.3523(1)	873.69(2)

*Table S9:* Refinement parameters for  $[C(NH_2)_3]Cu_xMg_{1-x}(HCOO)_3$ , where x = 0.1 - 0.5 are two-phase, and the lattice parameters given represent the mixed Cu/Mg phase.

### **Strain Discussion**

The relative order of enthalpy of cation order  $\Delta H_{mix}(Zn,Cu) > \Delta H_{mix}(Mn,Cu)$  is difficult to rationalise in terms of differences in ionic radii: Ref. S8 gives divalent radii of 0.83, 0.74, and 0.73 Å for Mn<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup>, respectively. Instead we find the crystallographic strains act as a more physically relevant metric in this case. We define a total absolute strain

$$\epsilon = \left| \frac{a(\mathsf{M}) - a(\mathsf{Cu})}{a(\mathsf{Cu})} \right| + \left| \frac{b(\mathsf{M}) - b(\mathsf{Cu})}{b(\mathsf{Cu})} \right| + \left| \frac{c(\mathsf{M}) - c(\mathsf{Cu})}{c(\mathsf{Cu})} \right|$$
(1)

in terms of the lattice parameters of the endmember structures. Our experimental lattice parameters then give  $\epsilon = 5.9\%$  and 6.7% for M = Mn and Zn, respectively.

## 3 Semaphore Diagrams

These diagrams illustrate the behaviour of two distinct phases, A and B, when dissolved in each other. The *x*-axis represents composition, such that the end points correspond to pure A and B. A bold black line divides the diagram according to the relative fractions of two phases, if phase separation occurs. Thus, in the case of a complete solid solution (*i.e.* only one phase for all compositions), the black line is located at the top of the diagram [Fig. S7(a)]. Conversely, if A and B are mutually insoluble, the black line follows the diagonal of the diagram [Fig. S7(b)] For each phase, the colours indicate the relative fractions of A and B in each phase. Thus, the presence of two colours above/below the bold line indicates miscibility of the phases, as in the main paper.

In Fig. 2b in the main paper, both the orange and blue phase are present below the bold line, indicating this phase being a solution of the two endmembers. Above the bold line, only one colour (dashed) is seen. Thus the orange phase is soluble in the blue phase, whereas the blue phase is not soluble in the orange phase.



*Figure S7:* Examples of the diagrams for miscibility of two phases, A (shown in blue) and B (shown in red). (a) A and B are completely soluble in each other and only one phase is formed. (b) A and B are completely immiscible.

## 4 Infrared Spectroscopy

Figures S8–S10 show the infrared spectroscopy data for the series:  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$  where M = Mn, Zn, Mg and x = 0.0, 0.1, 0.2, ..., 1.0.



*Figure S8:* The IR spectra of  $[C(NH_2)_3]Mn_{1-x}Cu_x(HCOO)_3$  where (b) highlights the region 1280–1400 cm<sup>-1</sup> that contains the carboxylate stretches of the bridging formate.



*Figure S9:* The IR spectra of  $[C(NH_2)_3]Zn_{1-x}Cu_x(HCOO)_3$  where (b) highlights the region 1280–1400 cm<sup>-1</sup> that contains the carboxylate stretches of the bridging formate.



*Figure S10:* The IR spectra of  $[C(NH_2)_3]Mg_{1-x}Cu_x(HCOO)_3$  where (b) highlights the region 1280–1400 cm<sup>-1</sup> that contains the carboxylate stretches of the bridging formate.

## 5 Non-Negative Matrix Factorisation

In order to determine the experimental distribution of neighbouring cation pairs as a function of composition, we carried out non-negative matrix factorisation (NMF) analysis of infrared (IR) data using a custom implementation of the NMF algorithm. S9, S10 First, to transform the data for use in NMF, a baseline was defined and subtracted for each IR absorption spectrum in the 1250-1400 cm<sup>-1</sup> region. The resulting absorbances were then inverted (to ensure the nonnegative constraint of NMF is satisfied) and normalised. Focus is put on the 1250–1400 cm<sup>-1</sup> region because it contains the carboxylate stretches of the bridging formate. We rationalised that formate stretching frequencies should be sensitive to the nature of the two cations to which a formate anion is bound, and hence allow characterisation of the distribution of Cu-Cu, Cu-M and M–M neighbours in our samples. Second, each IR absorption profile is deconvolved into three components: two are constrained to each of the endmembers (*i.e.* M–M and Cu–Cu) and the third is initialised with random values in the range 0-1. This ensures the features of each endmember are preserved and we can also account for mixed-metal linkages (M-Cu) via the third component. The third component is then varied using a Monte Carlo (MC) algorithm. Finally, the relative weighting that each of the three components contributes to each IR profile is initialised to the expected values for a simple two-phase system. The weightings are then altered using a MC algorithm, while satisfying the constraint that the sum of the three weighting terms for each IR profile sums to unity. Initialisation of the relative contributions increases the speed of convergence to a solution and lowers the risk of converging on a local minimum.

NMF of IR data was carried out for each of the mixed-metal perovskite families  $[C(NH_2)_3]M_{1-x}Cu_x(HCOO)_3$  (M=Mn, Zn, Mg) and the relative fraction of M–M, M–Cu and Cu–Cu linkages were obtained. The results for M=Mn, Zn, Mg are entirely similar and indicate cation segregation at the atomic scale. The normalised IR absorption spectra of  $[C(NH_2)_3]M_{1-x}Cu_x(HCOO)_3$  with NMF fits and the NMF linker distributions are shown below [Figs. S11–S43].



*Figure S11:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S12:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.9}Mn_{0.1}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S13:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.8}Mn_{0.2}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S14:*  $[C(NH_2)_3]Cu_{0.7}Mn_{0.3}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S15:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.6}Mn_{0.4}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S16:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.5}Mn_{0.5}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S17:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.4}Mn_{0.6}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S18:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.3}Mn_{0.7}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S19:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.2}Mn_{0.8}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S20:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.1}Mn_{0.9}(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S21:* Normalised IR absorption spectra of  $[C(NH_2)_3]Mn(HCOO)_3$  in the formate C–O stretching region (coloured line) with NMF fit in black.



*Figure S22:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S23:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.9}Zn_{0.1}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S24:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.8}Zn_{0.2}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S25:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.7}Zn_{0.3}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S26:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.6}Zn_{0.4}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S27:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.5}Zn_{0.5}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S28:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.4}Zn_{0.6}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S29:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.3}Zn_{0.7}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S30:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.2}Zn_{0.8}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S31:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.1}Zn_{0.9}(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S32:* Normalised IR absorption spectra of  $[C(NH_2)_3]Zn(HCOO)_3$  in the formate C–O stretching region (grey line) with NMF fit in black.



*Figure S33:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S34:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.9}Mg_{0.1}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S35:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.8}Mg_{0.2}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S36:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.7}Mg_{0.3}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S37:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.6}Mg_{0.4}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S38:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.5}Mg_{0.5}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S39:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.4}Mg_{0.6}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S40:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.3}Mg_{0.7}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S41:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.2}Mg_{0.8}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S42:* Normalised IR absorption spectra of  $[C(NH_2)_3]Cu_{0.1}Mg_{0.9}(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S43:* Normalised IR absorption spectra of  $[C(NH_2)_3]Mg(HCOO)_3$  in the formate C–O stretching region (orange line) with NMF fit in black.



*Figure S44:* NMF linker distributions (data points) with equilibrium fit as a solid line  $(\Delta H_{\text{mix}} = 7.2 \text{ kJ mol}^{-1})$  in [C(NH<sub>2</sub>)<sub>3</sub>]Zn<sub>1-x</sub>Cu<sub>x</sub>(HCOO)<sub>3</sub>.



*Figure S45:* NMF linker distributions (data points) with equilibrium fit as a solid line  $(\Delta H_{\text{mix}} = 4.8 \text{ kJ mol}^{-1}) [C(NH_2)_3]Mg_{1-x}Cu_x(HCOO)_3.$ 

## 6 Equilibrium Calculations

We consider cation mixing in the context of the position of the equilibrium

$$\frac{1}{2}$$
M–M +  $\frac{1}{2}$ Cu–Cu  $\Rightarrow$  M–Cu,

where M–M denotes a M–(OCHO)–M linkage, *etc.* At equilibrium, the relative fractions f of the three linkage types will be related by an effective equilibrium constant

$$K = \frac{f(\mathsf{M}-\mathsf{Cu})}{\sqrt{f(\mathsf{M}-\mathsf{M})f(\mathsf{Cu}-\mathsf{Cu})}},$$
(2)

with the free energy of mixing given (as usual) by

$$\Delta G_{\rm mix} = -RT \ln K. \tag{3}$$

Here R is the gas constant and T is the temperature.

Note that it is possible to calculate the expected f values for a given total composition of Cu (and hence M) if the value of K is known. Denoting the total fractional Cu composition by x we have, by mass balance,

$$f(\mathsf{Cu-Cu}) + \frac{1}{2}f(\mathsf{M-Cu}) = x, \tag{4}$$

$$f(\mathbf{M}-\mathbf{M}) + \frac{1}{2}f(\mathbf{M}-\mathbf{C}\mathbf{u}) = 1 - x.$$
 (5)

Inverting Eqs. (2), (4), (5) we obtain f = f(Cu-Cu) as the (only) physical root of the quadratic

$$(K^{2} - 4)f^{2} + (K^{2} - 2K^{2}x + 8x)f - 4x^{2} = 0,$$
(6)

and then

$$f(\mathsf{M}-\mathsf{M}) = f(\mathsf{Cu}-\mathsf{Cu}) - 2x + 1, \tag{7}$$

$$f(\mathsf{M}-\mathsf{Cu}) = K\sqrt{f(\mathsf{M}-\mathsf{M})f(\mathsf{Cu}-\mathsf{Cu})}.$$
(8)

For a given set of observed linkage fractions  $f_{obs}(x)$ , and a given value of K, we can determine a goodness-of-fit

$$\chi(K) = \sum_{x=0,\dots,1} [f_{\text{obs}}(x) - f_{\text{calc}}(x, K)]^2,$$
(9)

which represents the extent to which K accounts for the observed f values. Hence, least-squares minimisation of  $\chi$  with respect to K gives an effective equilibrium constant driven by the experimentally-measured f values.

In the main text we make reference to enthalpies of mixing  $\Delta H_{mix}$ , which are calculated from K as follows. First, we make the assumption that the entropy of mixing  $\Delta S_{mix}$  is dominated by statistical rather than vibrational contributions (which we justify by the minimal change in masses and vibrational frequencies for M–M *vs* M–Cu *vs* Cu–Cu) and hence

$$\Delta S_{\rm mix} \simeq R \ln 2. \tag{10}$$

As such, we obtain

$$\Delta H_{\rm mix} = -RT\ln(K/2). \tag{11}$$

The best-fit values of *K* obtained using our IR/NMF-derived *f* values for each of the  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$  (M = Mg, Mn, Zn) families, together with the corresponding values of  $\Delta H_{mix}$  are listed in Table S10.

*Table S10:* Equilibrium constants and corresponding enthalpies of mixing for  $[C(NH_2)_3]Cu_xM_{1-x}(HCOO)_3$  (M = Mg, Mn, Zn).

М	K	$\Delta H_{mix}$ (kJ mol $^{-1}$ )
Mg	0.755	2.41
Mn	0.577	3.08
Zn	0.470	3.59

## 7 Reverse Monte Carlo Refinements

Representative RMC configurations for each combination of M and *x* are illustrated in Fig. S46, where they are compared against statistical distributions ( $\Delta H_{\text{mix}} = 0 \text{ kJ mol}^{-1}$ ). These configurations were generated as described in the main text and made use of the experimental linker distributions obtained from IR/NMF analysis.



*Figure S46:* Representative RMC cation distributions, obtained as a function of Cu fraction x(Cu) and M. Configurations for experimentally inaccessible compositions for M = Mg are represented by transparent images.

## 8 References

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