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# **Supplementary Information:**

# Materials discovery and design limits in MDABCO halide perovskites

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# S1. Synthesis

**Warning:** The synthesis of all compounds involves the use of strong acids, which are corrosive, cause severe burns and, in the case of HI, are toxic to aquatic life. Reactions with HI and iodide salts may generate iodine, which causes serious irritation and damage to organs and is harmful if swallowed, and triiodide, which causes irritation, sensitisation and is toxic.

**Synthesis.** All reagents were used as received from suppliers: 1,4diazabicyclo[2.2.2]octane (DABCO) (>98%, Tokyo Chemical Industry), HI (57 wt%, Alfa Aesar), HBr (48 wt%, Fisher Chemical), HCl (37 wt%, Fisher Chemical), Mel (>99%, Sigma Aldrich), AgNO<sub>3</sub> (≥99%, Sigma-Aldrich), H<sub>3</sub>PO<sub>3</sub> (50 wt%, >98%, Alfa Aesar), Csl (99%, Sigma-Aldrich), RbBr (99.8%, Alfa Aesar), NH<sub>4</sub>Cl (>99%, Acros), ethyl acetate (Fisher Chemical), and petroleum ether (40-60 °C, ≥90%, Sigma Aldrich).

**[MDABCO]I**. *DABCO* (5.609 g, 50 mmol) was dissolved in ethyl acetate (50 mL) and cooled to 273 K. Mel (3.1 mL, 50 mmol) was added dropwise, and the reaction mixture was left to stir for *ca.* 10 minutes. The resultant precipitate was filtered under vacuum, washed with petroleum ether (3 × 5 mL), and dried at 373 K for 1 day to yield a white powder (11.85 g, 46.7 mmol, 93%). <sup>1</sup>H NMR (DMSO-d6, 400 MHz, 25 °C):  $\delta$  [ppm] = 3.32 (s, 1.5H, H<sub>2</sub>O), 3.27 (dd, *J* = 8.0, 7.1 Hz, 6H), 3.02 (dd, *J* = 9.0, 6.2 Hz, 6H), 2.97 (s, 3H). IR ( $\bar{\nu}_{max}$ , cm<sup>-1</sup>): (solid) 3441, 3322, 3158, 2999, 2956, 2879, 1650, 1614, 1465, 1423, 1347, 1322, 1196, 1115, 1054, 1000, 987, 911, 841, 794, 730, 682.

**[MDABCO]Br**<sub>2</sub>. *MDABCO*-I (3.000 g, 11.81 mmol) was dissolved in water (15 mL) and the vessel was enclosed in foil. AgNO<sub>3</sub> (2.005 g, 11.81 mmol) was added, resulting in the formation of a yellow precipitate. The precipitate was filtered and washed with water (4 × 5 mL). HBr (48 wt%, 9.0 mL, 80 mmol) was added to the resulting filtrate and left to crystallise for 17 hours. The product was filtered and dried at 373 K for 47 hours to yield a pale orange powder (2.441 g, 8.475 mmol, 72%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, 25 °C):  $\delta$ 

[ppm] = 3.67 (dd, J = 9.2, 6.1, 6H), 3.53 (dd, J = 9.3, 5.9, 6H), 3.18 (s, 3H). IR ( $\bar{\nu}_{max}$ , cm<sup>-1</sup>): (solid) 3003, 2901, 2807, 2756, 2666, 2536, 2456, 1471, 1440, 1399, 1246, 1189, 1118, 1057, 967, 910, 845, 514, 430.

**[MDABCO]Cl<sub>2</sub>**. *MDABCO*-I (4.00 g, 17.7 mmol) was dissolved in water (15 mL) and the vessel was enclosed in foil. AgNO<sub>3</sub> (2.674 g, 15.74 mmol) was added, resulting in the formation of a yellow precipitate. The precipitate was filtered and washed with water (3 × 5 mL). HCl (37 wt%, 8.71 mL, 106.1 mmol) was added to the resulting filtrate and left to crystallise for 5 days. The resulting solid was dried at 373 K for 23 hours to yield a yellow solid (2.974 g, 14.94 mmol, 95%). <sup>1</sup>H NMR (DMSO-d6, 400 MHz, 25 °C):  $\delta$  [ppm] = 3.87 (dd, *J* = 9.4, 5.9, 6H), 3.26 (s, 3H). IR ( $\bar{\nu}_{max}$ , cm<sup>-1</sup>): (solid) 3007, 2348, 1471, 1344, 1253, 1189, 1115, 1057, 969, 913, 847, 695, 612, 516, 432.

**[MDABCO]CsI<sub>3</sub>.** MDABCO-I (0.254 g, 1 mmol) and CsI (0.26 g, 1 mmol) were dissolved fully in a mix of water and excess HI (48 wt%). The solution was heated to evaporate all liquid and the resulting solid was dried in a vacuum oven for 12 hours. The solid was redissolved in water and droplets of the solution were left to crystallise on a glass slide under a nitrogen atmosphere. Crystals of the pseudo-cubic perovskite formed amongst other impurity phases. Elemental analysis of the impure sample: C 13.3 %, H 2.5 %, N 6.3 % (calculated: C 13.1 %, H 2.5 %, N 4.4 %). We have not yet been able to synthesis a pure sample for bulk analysis and we have observed that crystals turn orange over time when exposed to X-ray radiation and elevated temperature.

**[MDABCO]RbBr**<sub>3</sub>. MDABCO-Br<sub>2</sub> (0.250 g, 0.87 mmol) and RbBr (0.143 g, 0.87 mmol) were added to a vial and dissolved in water (3 mL). HBr (48 wt%, 0.6 mL, 5.29 mmol) was added dropwise, and the solution was left to evaporate until crystallisation was observed. The bulk sample was found to be stable for several weeks under ambient conditions but is mildly hygroscopic. Elemental analysis: C 18.3 %, H 3.3 %, N 6.4 % (calculated: C 18.5 %, H 3.5 %, N 6.2 %).

**[MDABCO]NH<sub>4</sub>Cl<sub>3</sub>**. MDABCO-Cl<sub>2</sub> (0.500 g, 2.51 mmol and NH<sub>4</sub>Cl (0.134 g, 2.51 mmol) were added to a vial and dissolved in water (3 mL). HCl (37 wt%, 1.26 mL, 15.3 mmol) was added and the solution left to evaporate until crystallisation was observed. The bulk sample was found to be stable for several weeks under ambient conditions but is mildly hygroscopic. Elemental analysis: C 33.4 %, H 7.4 %, N 16.1 % (calculated: C 33.3 %, H 7.9 %, N 16.6 %).

#### S2. X-ray diffraction

**[MDABCO]CsI<sub>3</sub>.** A suitable crystal was selected and mounted on a Newport 4-circle diffractometer with a Dectris Pilatus 300 K detector at beamline I19-2 at Diamond Light Source (see Fig. S1 for a representative crystal). Data were collected with X-rays at the Rh K edge using the in-house GDA software.<sup>1</sup> The crystal was kept at  $\Box$  298.15 K during data collection. Data were processed using Xia2<sup>2</sup> within Dials,<sup>3,4</sup> and Olex2,<sup>5</sup> in which the structure was solved with the SHELXT<sup>6</sup> structure solution program using Intrinsic Phasing and refined by a full-matrix least-squares procedure on F<sup>2</sup> in SHELXL.<sup>7</sup>

**Crystal Data** for **[MDABCO]CsI<sub>3</sub>**:  $C_7H_{16}Br_3N_2Rb$  (*M* =453.42 g/mol): orthorhombic, space group Pna2<sub>1</sub> (no. 33), a = 14.1838(10) Å, b = 9.9322(6) Å, c = 9.6159(6) Å, V = 1354.65(15) Å<sup>3</sup>, Z = 4, T = 291.15 K,  $\mu$ (CuK $\alpha$ ) = 15.114 mm<sup>-1</sup>, *Dcalc* = 2.223 g/cm<sup>3</sup>, 11848 reflections measured (10.874°  $\leq 2\Theta \leq 146.728°$ ), 2594 unique ( $R_{int} = 0.0563$ ,  $R_{sigma} = 0.0357$ ) which were used in all calculations. The final  $R_1$  was 0.0318 (I > 2 $\sigma$ (I)) and  $wR_2$  was 0.0817 (all data).

**[MDABCO]RbBr<sub>3</sub> and [MDABCO]NH<sub>4</sub>Cl<sub>3</sub>**. Suitable crystals were selected and mounted on a Rigaku SuperNova diffractometer using an Atlas diffractometer (Fig. S1). Data were collected using Cu Kα radiation. The crystals were kept at 292(2) K and 290.3(2) K respectively during data collection. The data collections were driven and processed and absorption corrections were applied using CrysAlisPro.<sup>12</sup> Using Olex2,<sup>5</sup> the structure was solved with the SHELXT<sup>6</sup> structure solution program using Intrinsic Phasing and refined by a full-matrix least-squares procedure on F<sup>2</sup> in SHELXL.<sup>7</sup> In **[MDABCO]NH<sub>4</sub>Cl<sub>3</sub>** the hydrogen atoms bonded to N(1) and N(101) were located in the electron density and refined freely. All remaining hydrogen atoms in both structures were fixed as riding models and the isotropic thermal parameters (U<sub>iso</sub>) were based on the U<sub>eq</sub> of the parent atoms.

**Crystal Data** for **[MDABCO]RbBr**<sub>3</sub>: C<sub>7</sub>H<sub>16</sub>Br<sub>3</sub>N<sub>2</sub>Rb (M =453.42 g/mol): orthorhombic, space group Pna2<sub>1</sub> (no. 33), a = 14.1838(10) Å, b = 9.9322(6) Å, c = 9.6159(6) Å, V = 1354.65(15) Å<sup>3</sup>, Z = 4, T = 291.15 K,  $\mu$ (CuK $\alpha$ ) = 15.114 mm<sup>-1</sup>, *Dcalc* = 2.223 g/cm<sup>3</sup>, 11848 reflections measured (10.874° ≤ 2 $\Theta$  ≤ 146.728°), 2594 unique ( $R_{int}$  = 0.0563,  $R_{sigma}$  = 0.0357) which were used in all calculations. The final  $R_1$  was 0.0318 (I > 2 $\sigma$ (I)) and  $wR_2$  was 0.0817 (all data).

**Crystal Data** for **[MDABCO]NH<sub>4</sub>Cl<sub>3</sub>**:  $C_7H_{20}Cl_3N_3$  (M = 252.61 g/mol): monoclinic, space group P2<sub>1</sub>/n (no. 14), a = 14.8238(4) Å, b = 10.1333(3) Å, c = 16.4441(4) Å,  $b = 90.577(2)^\circ$ , V = 2470.01(12) Å<sup>3</sup>, Z = 8, T = 290.3(2) K,  $\mu$ (Cu K $\alpha$ ) = 6.439 mm<sup>-1</sup>, *Dcalc* = 1.359 g/cm<sup>3</sup>, 9853 reflections measured (7.99°  $\leq 2\Theta \leq 145.694^\circ$ ), 4788 unique ( $R_{int} = 0.0250$ ,  $R_{sigma} = 0.0295$ ) which were used in all calculations. The final  $R_1$  was 0.0417 (I > 2 $\sigma$ (I)) and  $wR_2$  was 0.1102 (all data).



Figure S1. Representative camera images of crystals mounted for diffraction experiments: (a) [MDABCO]CsI<sub>3</sub>, (b) [MDABCO]RbBr<sub>3</sub>, and (c) [MDABCO]NH<sub>4</sub>Cl<sub>3</sub>. Note that the image of [MDABCO]CsI<sub>3</sub> shown is a different crystal to the one used to generate structural data reported here.

#### S3. Tolerance factor

 $\mathsf{TF} = (r_{\mathsf{A}} + r_{\mathsf{X}}) / (\sqrt{2} \times (r_{\mathsf{B}} + r_{\mathsf{X}}))$ 

TF	r <sub>x</sub> / Å	Cl-	Br <sup>_</sup>	<b>I</b> -	$BF_4^-$	$PF_6^-$
r <sub>B</sub> / Å		1.81	1.96	2.2	2.32	2.56
K <sup>+</sup>	1.38	1.00	0.99	0.97	0.96	0.94
$NH_4^+$	1.46	0.98	0.96	0.95	0.94	0.93
Rb⁺	1.52	0.96	0.95	0.93	0.92	0.91
Cs⁺	1.67	0.92	0.91	0.90	0.89	0.88

MDABCO  $r_A = 2.7$  Å. (Effective) ionic radii taken from Shannon,<sup>8</sup> Zhang,<sup>9</sup> Sun<sup>10</sup> and Choi.<sup>11</sup>

## S4. Octahedral factor

 $OF = r_B / r_X$ 

OF	r <sub>x</sub> / Å	CI-	Br-	I-	$BF_4^-$	$PF_6^-$
r <sub>B</sub> / Å		1.81	1.96	2.2	2.32	2.56
K+	1.38	0.76	0.70	0.63	0.59	0.54
$NH_4^+$	1.46	0.81	0.74	0.66	0.63	0.57
Rb⁺	1.52	0.84	0.78	0.69	0.66	0.59
Cs⁺	1.67	0.92	0.85	0.76	0.72	0.65

## **S5.** Volume per formula unit.

V' = V / Z'

V'	CI-	Br <sup>_</sup>	I-	BF <sub>4</sub> <sup>-</sup>	$PF_6^-$
K+			369.57		
NH4 <sup>+</sup>	308.75	368.20	377.90	390.83	477.13
Rb⁺		338.66	380.00		
Cs <sup>+</sup>		322.53	387.45		

## S6. Bond valence sum.

BVS =  $\Sigma(\exp((R-d)/b))$ .

BVS	Cl <sup>_</sup>	Br <sup>_</sup>	I-	BF <sub>4</sub> <sup>-</sup>	$PF_6^-$
K+			0.82 (2.88)		
NH <sub>4</sub> <sup>+</sup>	0.93 (2.619)	0.60 (2.769)	1.05 (3.009)	1.01 (2.129)	1.02 (2.129)
Rb+		0.81 (2.78)	1.04 (3.01)		
Cs <sup>+</sup>			1.52 (3.18)		

b = 0.37 Å (K, Rb, Cs) or 0.372 Å (NH<sub>4</sub>). Values in parentheses correspond to R.

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