

Supporting information for:

## **Self-assembly of broadband white-light emitters**

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## Experimental details

All manipulations were conducted in air. Dimethylformamide (DMF) was dried using the JC Meyer solvent purification system. All reagents were purchased from commercial vendors and used as received. Abbreviations used: *N*-MPDA = *N*<sup>1</sup>-methylpropane-1,3-diammonium, *N*-MEDA = *N*<sup>1</sup>-methylethane-1,2-diammonium.

### (*N*-MPDA)[PbBr<sub>4</sub>] (**1**)

A 12-M solution of HBr (0.5 mL, 6.0 mmol) was added dropwise to a stirred 5-mL ethanol solution of *N*<sup>1</sup>-methylpropane-1,3-diamine (0.5 mL, 4.8 mmol) at 0 °C. The resulting solid was filtered, washed with cold acetone, and held at reduced pressure for 12 h to afford (*N*-MPDA)Br<sub>2</sub> as a colorless, crystalline solid. Solid PbBr<sub>2</sub> (0.10 g, 0.27 mmol) and (*N*-MPDA)Br<sub>2</sub> (0.067 g, 0.27 mmol) were combined in 5 mL of 12-M HBr and sonicated for 5 minutes to obtain a clear solution. Pale-yellow crystals of **1** were obtained by allowing diffusion of acetone into the 12-M HBr solution over a period of 12 h. The crystals were filtered through paper, washed with acetone, and dried under reduced pressure to afford 0.076 g (45.2% yield) of product. Anal. Calcd. for C<sub>4</sub>H<sub>14</sub>N<sub>2</sub>PbBr<sub>4</sub>: C, 7.79; N, 4.54; H, 2.29. Found: C, 8.00; N, 4.50; H, 2.51. IR (neat): 3004 (s), 2915 (w), 2765 (w), 1574 (s), 1482 (vs), 2460 (s), 1377 (m), 1302 (w), 1172 (m), 1119 (m), 991 (s), 766 (vs), 669 (m), and 472 (m) cm<sup>-1</sup>.

### (*N*-MEDA)[PbBr<sub>4</sub>] (**2**)

A 12-M solution of HBr (0.5 mL, 6.0 mmol) was added dropwise to a stirred 5-mL ethanol solution of *N*<sup>1</sup>-methylethane-1,2-diamine (0.5 mL, 5.7 mmol) at 0 °C. The solvent was removed under reduced pressure to afford (*N*-MEDA)Br<sub>2</sub> as a colorless, highly hygroscopic solid that was further dried for 12 h under vacuum and stored in a desiccator. Solid PbBr<sub>2</sub> (0.10 g, 0.27 mmol) and (*N*-MEDA)Br<sub>2</sub> (0.064 g, 0.27 mmol) were combined in 5 mL of 12-M HBr and sonicated for 5 minutes to obtain a clear solution. Colorless plate-like crystals of **2** were obtained through diffusion of acetone into this solution over a 12-h period. The crystals were filtered through paper, washed with acetone, and dried under reduced pressure to afford 0.098 g (59.7 % yield) of product. Anal. Calcd. for C<sub>3</sub>H<sub>12</sub>N<sub>2</sub>PbBr<sub>4</sub>: C, 5.97; N, 4.65; H, 2.01. Found: C, 6.23; N, 4.63; H, 2.00. IR (neat): 3026 (s), 2773 (w), 2695 (w), 2670 (w), 1560 (m), 1477 (vs), 1396 (m), 1327 (m), 1194 (m), 1105 (s), 1027 (s), 955 (s), 927 (s), 764 (vs), and 428 (m) cm<sup>-1</sup>.

### (*N*-MEDA)[PbBr<sub>4-x</sub>Cl<sub>x</sub>]

Crystalline (*N*-MEDA)[PbCl<sub>4</sub>] was synthesized in a similar manner to **2** using (*N*-MEDA)Cl<sub>2</sub> and PbCl<sub>2</sub>. The solid (0.01 g) was dissolved in 0.4 mL of an aqueous solution containing a specific volumetric ratio of 9-M HBr:12-M HCl. The solution was sonicated for 5 minutes to ensure complete dissolution of the solid. Then 4 mL of cold acetone was added and the vial was sonicated for 2 minutes to afford a colorless crystalline solid. The solid was filtered, washed with acetone, and dried under reduced pressure. The lead:bromide ratios of the materials were determined through inductively coupled plasma analysis (ICP-MS). This technique was used to synthesize (*N*-MEDA)[PbBr<sub>4-x</sub>Cl<sub>x</sub>] with *x* of 0, 0.5, 0.7, and 1.2 from solutions containing HBr:HCl volumetric ratios of 1:0, 7:1, 3:1, and 5:3, respectively.

## Other physical measurements

Infrared spectra were collected on a Thermo Nicolet 6700 spectrometer with a Smart Orbit attenuated total reflectance accessory. Carbon, hydrogen, and nitrogen analyses were obtained from MHW Laboratories (Phoenix, AZ). Thermogravimetric analyses were performed in a Netzsch F1 Libra

instrument using alumina pans and heating rates of 5 °C/min. Typical sample sizes were 1–5 mg. ICP-MS measurements to determine halide ratios in (N-MEDA)[PbBr<sub>4-x</sub>Cl<sub>x</sub>] were conducted in 0.5% nitric acid solutions using a Thermo XSeries II ICP-Mass Spectrometer.

### **Optical measurements**

Reflectance measurements were collected on a Shimadzu UV-2600 spectrometer equipped with an integrating sphere. Samples were packed as powders into sample holders with a reflective backing of compact barium sulfate. Absorption measurements were taken on spin-coated films using an Agilent Cary 6000i spectrometer in transmission mode. Emission and excitation spectra were collected on non-oriented powders mounted on quartz slides using a Horiba Jobin-Yvon Spex Fluorolog-3 fluorimeter equipped with a 450-W xenon lamp and a thermoelectrically-cooled R928P detector. Incident light was passed through a double-grating monochromator and data were collected using the FluorEssence 2.3.15 software.

### **Time-resolved photoluminescence**

Measurements were performed using a Time-Correlated Single Photon Counting (TCSPC) system from PicoQuant. Pulverized samples on glass slides were excited with a pulsed-laser diode, (model LDH-P-C-375: 375 nm, 150 ps FWHM 10 MHz) and detected with a single photon avalanche diode (PDM 100CT SPAD) attached to a monochromator and processed by a PicoHarp 300 correlating system.

### **Photoluminescence quantum efficiency (PLQE)**

Absolute PLQE measurements were performed on powders on glass slides placed in an integrating sphere to account for any directional dependence of the emission profile. Samples were excited using monochromatic light produced by a mercury-arc lamp and a monochromator fiber coupled to the sphere. The spectra of the emitted light and any unabsorbed excitation light were measured using a Princeton Instruments SpectraPro 500i spectrograph fiber-coupled to the sphere. A total of three spectra were taken with 1) the sample in the excitation beam, 2) the sample in the sphere but not directly in the excitation beam, and 3) no sample present, to account for light absorption due to scattering inside the sphere. The PLQE was then calculated using formulas derived by de Mello *et al.*<sup>1</sup> The combined responsivity of the sphere, collection fiber, and spectrometer were calibrated at each wavelength using a calibration photodiode from Newport. A PLQE of 80% was measured for a dilute solution of Rhodamine-101 in ethanol using this method, which is close to the accepted value of ca. 100%. The lower value we measure may be due to slight reabsorption of the photoluminescence.

### **Stability under continuous irradiation**

A pulverized sample was mounted on a quartz slide, placed in a quartz ampoule, and sealed under vacuum. The ampoule was then placed under a fan-cooled 4-W 365-nm UV lamp for seven days. During this period no material degradation or decrease in photoluminescence could be observed. Photoluminescence quantum efficiency (PLQE) measurements obtained before and after irradiation were within experimental error. PLQE before irradiation = 0.50, PLQE after the 7-day irradiation = 0.52.

### **Powder x-ray diffraction (PXRD)**

Experiments were conducted on a Panalytical X'Pert Pro diffractometer with a Bragg-Brentano geometry and PIXCEL detector equipped with a nickel filter. Experimental conditions are given in Table S1. The

simulated powder patterns were calculated using the crystallographic information files (CIF) from single-crystal x-ray experiments.

**Table S1.** Experimental details for powder x-ray diffraction experiments

Step size ( $^{\circ}$ 2Theta)	0.02
Divergence slit type	Automatic
Anode material	Cu
K $\alpha_1$ (Å)	1.54060
K $\alpha_2$ (Å)	1.54443
K $\alpha_2$ / K $\alpha_1$ ratio	0.50000

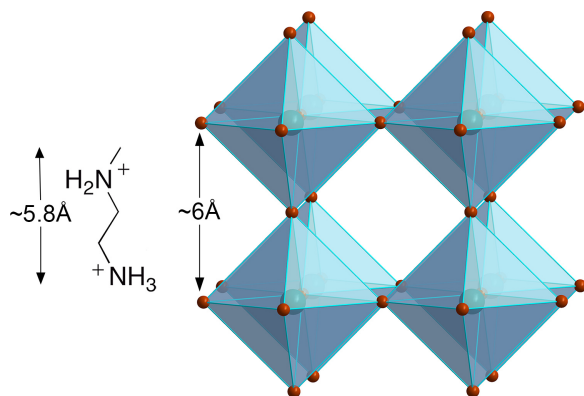
### X-ray crystallography

Crystals were coated with Paratone-N oil, attached to a Kapton loop, and transferred to a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector. Frames were collected using  $\omega$  and  $\phi$  scans and the unit-cell parameters were refined against all data. The crystals did not show significant decay during data collection. Data were integrated and corrected for Lorentz and polarization effects using SAINT 8.27b, and were corrected for absorption effects using SADABS V2012.<sup>2</sup> Space-group assignments were based upon systematic absences, *E*-statistics, agreement factors for equivalent reflections, and successful refinement of the structure. The structures were solved by direct methods and expanded through successive difference Fourier maps using SHELXS-97. They were refined against all data using the SHELXTL-2013 software package.<sup>3</sup> Hydrogen atoms were inserted at idealized positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom or 1.5 times that of the attached nitrogen. Thermal parameters for all non-hydrogen atoms were refined anisotropically. Disorder in the *N*-MPDA molecules was modeled by constraining C–C and C–N distances to values of 1.54 and 1.52 Å, respectively, and implementing rigid-bond restraints for anisotropic displacement parameters. The occupancies of disordered groups were allowed to refine freely, while constraining the sum of the occupancies to unity. Similar rigid-bond restraints were also applied to atoms not involved in the disorder to stabilize the refinement. Details regarding the data quality and a summary of the residual values of the refinements are listed in Table S2.

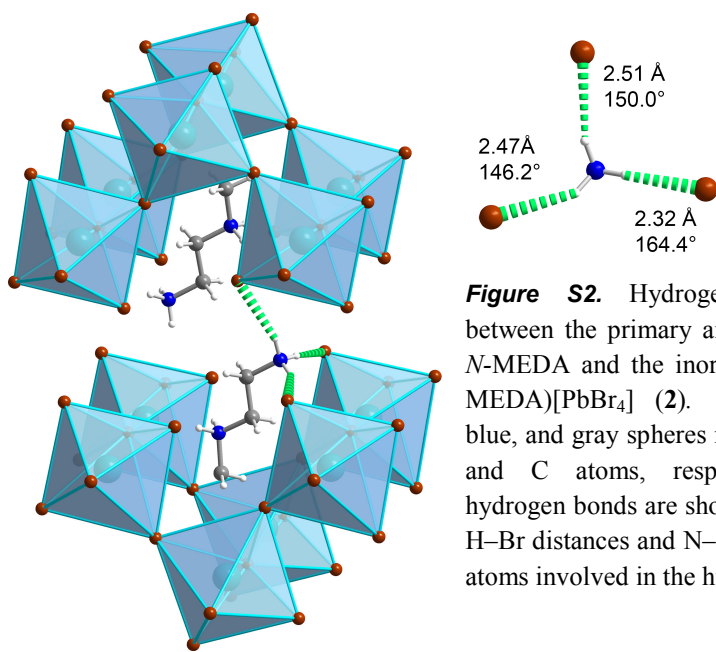
**Table S2.** Crystallographic data<sup>a</sup> for (*N*-MPDA)[PbBr<sub>4</sub>] (**1**) and (*N*-MEDA)[PbBr<sub>4</sub>] (**2**)

	<b>1</b>	<b>2</b>
Formula	C <sub>4</sub> N <sub>2</sub> H <sub>14</sub> PbBr <sub>4</sub>	C <sub>3</sub> N <sub>2</sub> H <sub>12</sub> PbBr <sub>4</sub>
FW	616.98	602.98
<i>T</i> , K	100(2)	100(2)
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> , Å	8.3162(4)	6.0761(3)
<i>b</i> , Å	8.3161(3)	8.3926(5)
<i>c</i> , Å	20.1181(9)	23.7433(16)
$\beta$ , deg	101.695 (2)	90
<i>V</i> , Å <sup>3</sup>	1362.45(10)	1210.77(12)
<i>Z</i> , Calculated density	4, 3.008	4, 3.308
$\mu$ , mm <sup>-1</sup>	24.072	27.084
<i>F</i> (000)	1096	1064
Crystal size, mm <sup>3</sup>	0.050 × 0.020 × 0.010	0.050 × 0.025 × 0.005
Theta range, deg	2.66 to 25.40	2.57 to 25.38
Index ranges	$-9 \leq h \leq 9$ $-9 \leq k \leq 9$ $-23 \leq l \leq 23$	$-7 \leq h \leq 7$ $-10 \leq k \leq 10$ $-28 \leq l \leq 28$
Reflections collected / unique	16003 / 2467	21733 / 2222
<i>R</i> <sub>int</sub>	0.0452	0.0892
Data / restraints/ parameters	2467 / 164 / 160	2222 / 41 / 94
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.161	1.431
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	<i>R</i> <sub>1</sub> = 0.0755, w <i>R</i> <sub>2</sub> = 0.1719	<i>R</i> <sub>1</sub> = 0.0340, w <i>R</i> <sub>2</sub> = 0.0444
Final <i>R</i> indices [all data]	<i>R</i> <sub>1</sub> = 0.0822, w <i>R</i> <sub>2</sub> = 0.1748	<i>R</i> <sub>1</sub> = 0.0512, w <i>R</i> <sub>2</sub> = 0.0460
Largest diff. peak and hole, eÅ <sup>-3</sup>	6.863 and −5.756	2.170 and −1.286

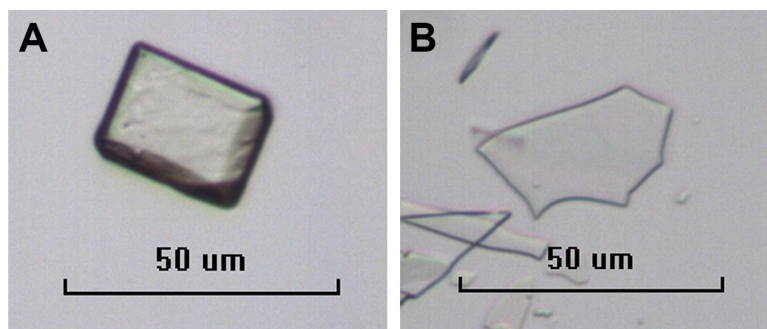
<sup>a</sup>Obtained with monochromated Mo Kα ( $\lambda = 0.71073$  Å) radiation<sup>b</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$



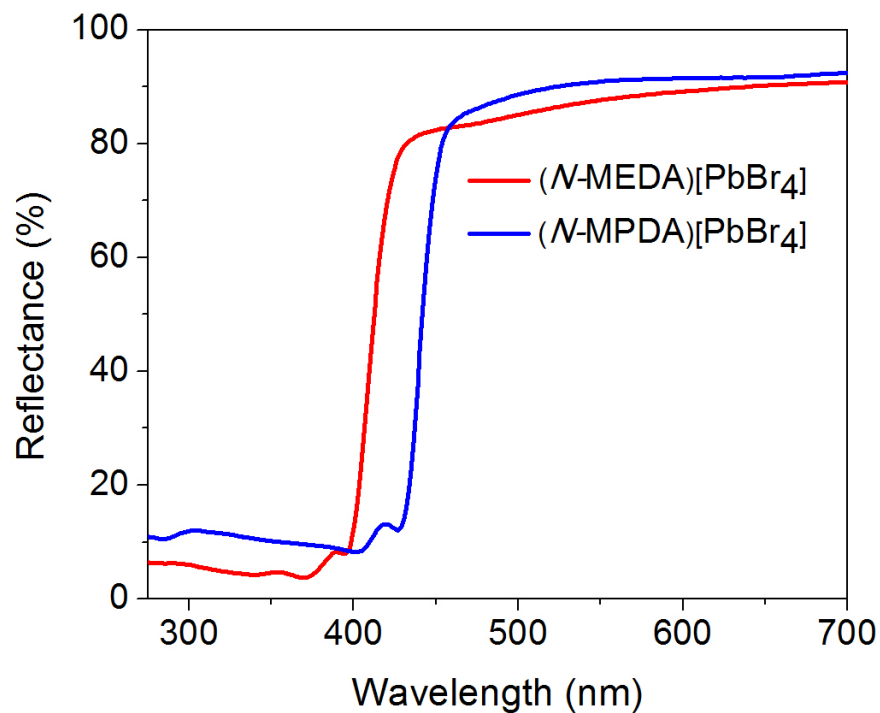
**Figure S1.** A geometric comparison between the length of *N*-MEDA (in a typical conformation) and the cavity of a three-dimensional perovskite. Turquoise and brown spheres represent Pb and Br atoms, respectively. Distances were obtained from the crystal structures of (*N*-MEDA)[PbBr<sub>4</sub>] (**2**) and (CH<sub>3</sub>NH<sub>3</sub>)[PbBr<sub>3</sub>].



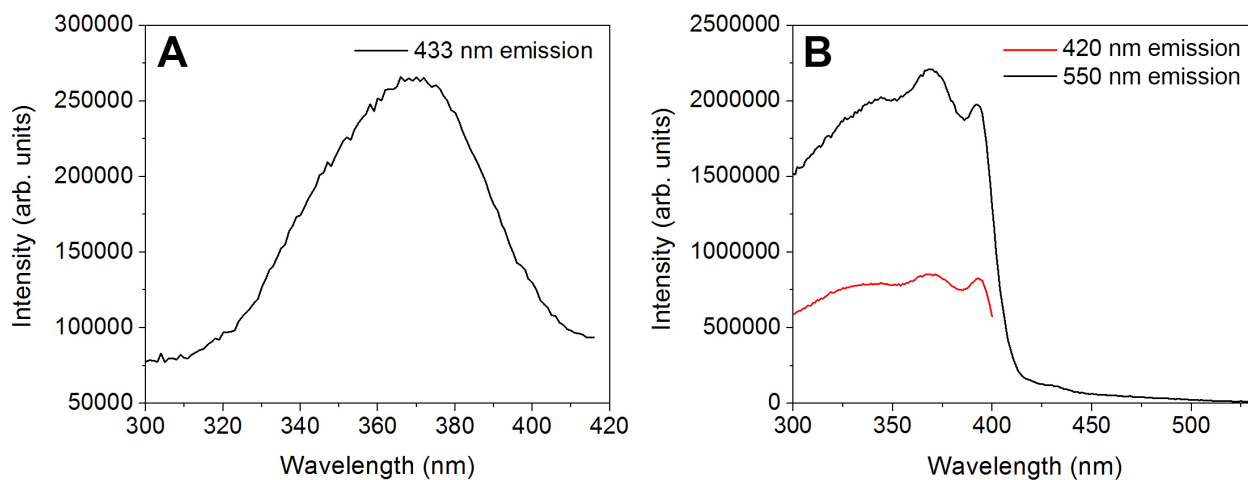
**Figure S2.** Hydrogen bonds (green) between the primary ammonium group of *N*-MEDA and the inorganic layers in (*N*-MEDA)[PbBr<sub>4</sub>] (**2**). Turquoise, brown, blue, and gray spheres represent Pb, Br, N, and C atoms, respectively. Not all hydrogen bonds are shown for clarity. Inset: H–Br distances and N–H–Br angles for the atoms involved in the hydrogen bonds.



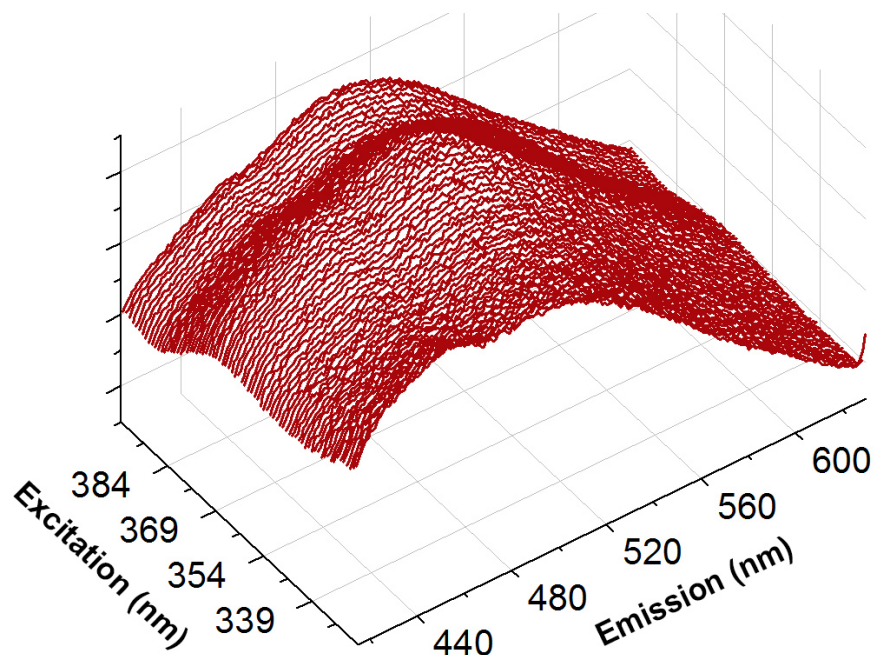
**Figure S3.** Optical micrographs of x-ray quality single crystals of (A) (*N*-MPDA)[PbBr<sub>4</sub>] (**1**) and (B) (*N*-MEDA)[PbBr<sub>4</sub>] (**2**).



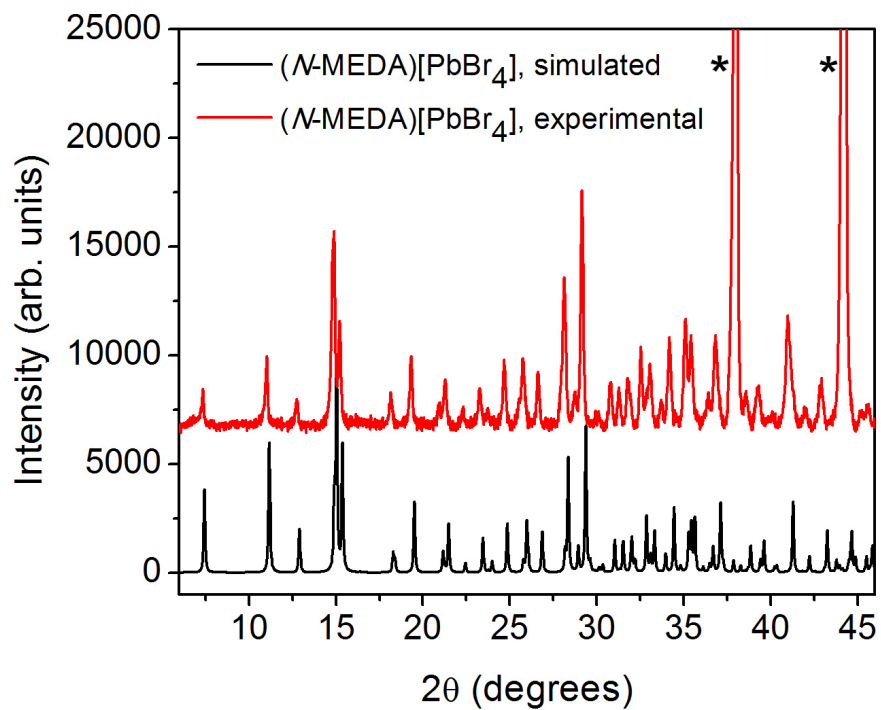
**Figure S4.** Diffuse reflectance spectra of perovskites. The exciton absorption for (N-MPDA)[PbBr<sub>4</sub>] (1) and (N-MEDA)[PbBr<sub>4</sub>] (2) is at 430 and 398 nm, respectively.



**Figure S5.** (A) Excitation spectrum for the 433-nm emission of (N-MPDA)[PbBr<sub>4</sub>] (1). (B) Excitation spectra for the 420- and 550-nm emissions in (N-MEDA)[PbBr<sub>4</sub>] (2).

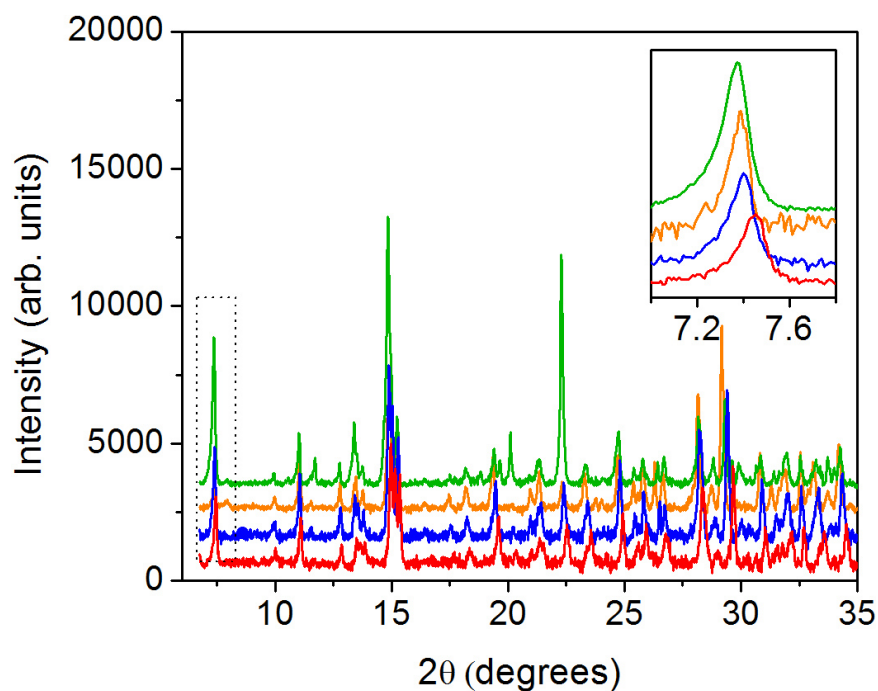


**Figure S6.** Simultaneous excitation/emission scans of (N-MEDA)[PbBr<sub>4</sub>] (**2**), showing similar photoluminescence over a wide range of excitation wavelengths (329 nm to 395 nm).

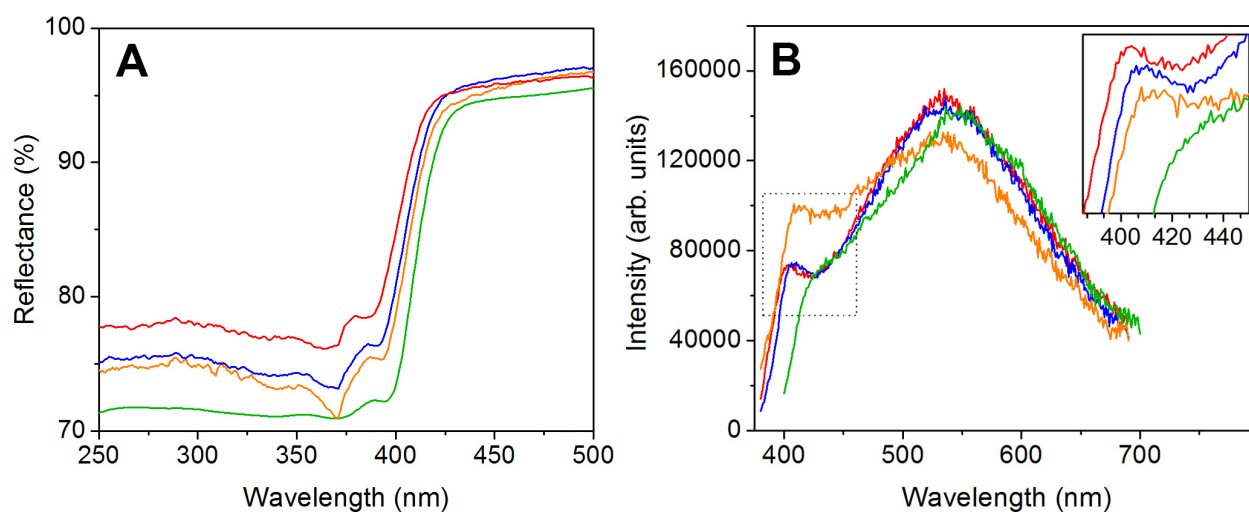


**Figure S7.** Experimental PXRD pattern of a pulverized sample of (N-MEDA)[PbBr<sub>4</sub>] (**2**, red line) and the simulated pattern (black line) obtained from the single crystal x-ray structure. Reflections marked by asterisks are due to the aluminum sample stage.

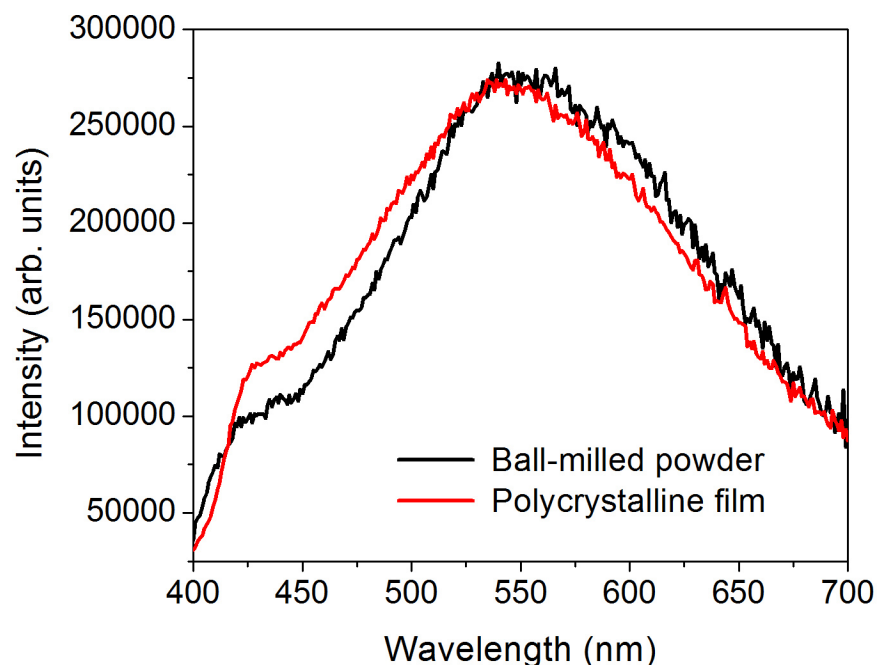




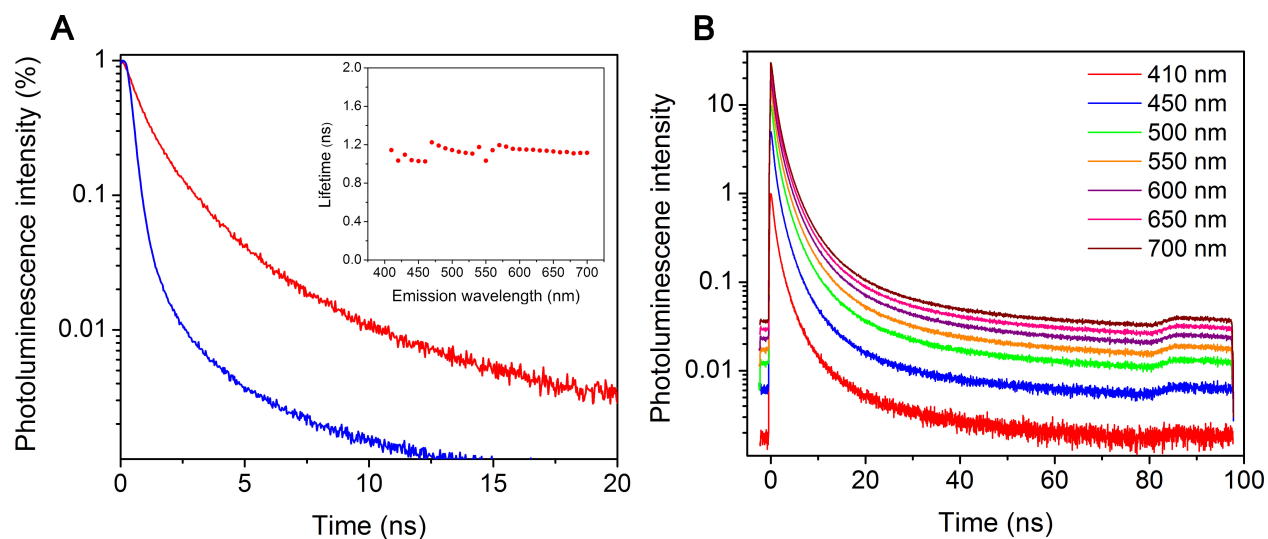
**Figure S8.** PXRD patterns of nonoriented powders of  $(N\text{-MEDA})[\text{PbBr}_{4-x}\text{Cl}_x]$  ( $x = 0$  (green), 0.5 (orange), 0.7 (blue), and 1.2 (red)) indicating single-phase materials with a systematic change to smaller lattice spacings upon substitution of chloride for bromide.



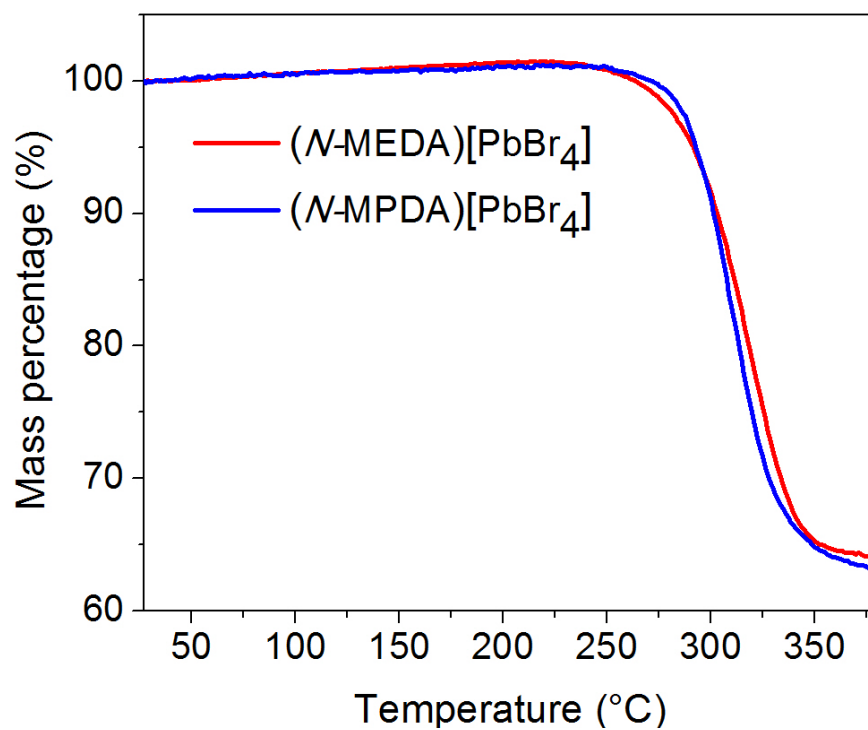
**Figure S9.** (A) Diffuse reflectance spectra of  $(N\text{-MEDA})[\text{PbBr}_{4-x}\text{Cl}_x]$  ( $x = 0$  (green), 0.5 (orange), 0.7 (blue), and 1.2 (red)) show a systematic change to higher band gaps upon substitution of chloride for bromide. (B) Emission spectra of the materials, with inset showing a systematic blueshift of the higher energy (ca. 420 nm) shoulder with increasing chloride content. Emission intensity of the spectra in the inset has been scaled for easier comparison between peak values.



**Figure S10.** Comparison between the emission spectra of a dropcast polycrystalline film (thickness ca. 0.5 mm) and a ball-milled powder (particle size ca. 10  $\mu\text{m}$ ) of  $(N\text{-MEDA})[\text{PbBr}_4]$  (**2**).



**Figure S11.** (A) Photoluminescence decay of  $(N\text{-MPDA})[\text{PbBr}_4]$  (**1**) at 433 nm (blue) and  $(N\text{-MEDA})[\text{PbBr}_4]$  (**2**) at 550 nm (red). Inset: Life time for the broad emission of **2** (from 400 to 700 nm) obtained by fits to the first 2 s of data. (B) Photoluminescence decay of **2**, showing the same profile at different emission wavelengths. Curves are offset for clarity. Excitation wavelength = 375 nm.



**Figure S12.** Thermogravimetric analyses of (N-MPDA)[PbBr<sub>4</sub>] (**1**) and (N-MEDA)[PbBr<sub>4</sub>] (**2**). Both show constant mass until 250 °C; subsequent mass loss corresponds to the mass of amine hydrobromide.

## References

1. de Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.
2. SAINT and SADABS; Bruker AXS Inc.: Madison, WI, (2007).
3. (a) Sheldrick, G. M. *SHELXL-97, Program for crystal structure refinement*; Göttingen, **1997**. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.