

Supporting Information for:

Intrinsic White-Light Emission from Layered Perovskites

Emma R. Dohner,[†] Adam Jaffe,[†] Liam R. Bradshaw,[§] and Hemamala I. Karunadasa^{*,†}

[†]*Department of Chemistry, Stanford University, Stanford, California 94305, United States*

[§]*Department of Chemistry, University of Washington, Seattle, Washington 98195, United States*

Experimental details

Table S1–S3

Figures S1–S25

References

Experimental section

All manipulations were conducted in air unless otherwise noted. Solvents were of reagent grade or higher purity. All reagents were purchased from commercial vendors and used as received. Abbreviations used: EDBE = 2,2'-(ethylenedioxy)bis(ethylammonium).

(EDBE)[PbCl₄] (1-Cl)

A 20-mL solution of PbCl₂ (1.00 g, 3.60 mmol) in 12-M HCl was added dropwise to a cold (−70 °C), stirred, 5.5-mL solution of 2,2'-(ethylenedioxy)bis(ethylamine) (1.5 mL, 10.3 mmol) in 12-M HCl. After 10 minutes, the resulting colorless precipitate was filtered through a glass frit and washed with cold diethyl ether (5 × 5 mL). The colorless solid was held at reduced pressure for 12 h to afford 1.08 g (60.1% yield) of product. Crystals of **1-Cl** suitable for x-ray structure determination were obtained through diffusion of diethyl ether into a 4-mL solution of **1-Cl** (0.10 g, 0.20 mmol) in 12-M HCl. IR(neat): 3197 (w), 3143 (m), 3078 (m), 3001 (m), 2968 (m), 2898 (s), 2870 (s), 2802 (m), 2551 (w), 2443 (w), 1603 (m), 1479 (s), 1468 (s), 1414 (w), 1377 (m), 1329 (m), 1315 (w), 1265 (m), 1219 (w), 1171 (w), 1138 (s), 1101 (s), 1045 (s), 970 (s), 874 (w), 827 (m), 532 (w), 444 (m) cm^{−1}. Anal. Calcd. for C₆H₁₈O₂N₂PbCl₄: C, 14.44%; H, 3.63%; N, 5.61%. Found: C, 14.61%; H, 3.74%; N, 5.46%.

(EDBE)[PbBr₄] (2-Br)

A 4-mL solution of PbBr₂ (1.00 g, 2.72 mmol) in 9-M HBr was added dropwise to a cold (−70 °C), stirred, 5-mL solution of 2,2'-(ethylenedioxy)bis(ethylamine) (1.0 mL, 6.85 mmol) in 9-M HBr. After 10 minutes, the resulting colorless precipitate was filtered using a glass frit and washed with cold diethyl ether (5 × 5 mL). The colorless solid was held at reduced pressure for 12 h to afford 1.66 g (90.0% yield) of product. Crystals of **2-Br** suitable for x-ray structure determination were obtained through diffusion of diethyl ether into a 2-mL solution of **2-Br** (0.20 g, 0.29 mmol) in 9-M HBr. IR(neat): 3176 (w), 3030 (m), 2920 (m), 2871 (m), 2750 (w), 2663 (w), 1583 (s), 1466 (s), 1448 (s), 1387 (m), 1350 (m), 1317 (m), 1294 (m), 1269 (m), 1255 (m), 1176 (w), 1166 (w), 1124 (s), 1084 (s), 1049 (s), 1030 (m), 993 (s), 978 (s), 962 (s), 887 (s), 806 (m), 789 (m), 559 (m), 501 (m) cm^{−1}. Anal. Calcd. for C₆H₁₈O₂N₂PbBr₄: C, 10.64%; H, 2.68%; N, 4.14%. Found: C, 10.66%; H, 2.86%; N, 4.19%.

(EDBE)[PbI₄] (3-I)

A 6-mL solution of PbI₂ (1.00 g, 2.17 mmol) in 8-M HI was added dropwise to a cold (−70 °C), stirred, 5-mL solution of 2,2'-(ethylenedioxy)bis(ethylamine) (1.0 mL, 6.85 mmol) in 8-M HI. After 10 minutes, the resulting yellow precipitate was filtered using a glass frit and washed with cold diethyl ether (5 × 5 mL). The yellow solid was held at reduced pressure for 12 h to afford 1.70 g (90.6% yield) of product. Crystals of **3-I** suitable for x-ray structure determination were obtained through diffusion of diethyl ether into a 3-mL solution of **3-I** (0.20 g, 0.23 mmol) in 8-M HI. IR(neat): 3153 (w), 3028 (m), 2952 (m), 2902 (m), 2866 (m), 1570 (s), 1458 (s), 1444 (s), 1387 (m), 1348 (m), 1313 (m), 1290 (m), 1267 (m), 1253 (m), 1161 (w), 1120 (m), 1095 (m), 1078 (s), 1045 (s), 989 (s), 974 (s), 958 (s), 941 (s), 879 (s), 800 (s), 779 (s), 551 (m), 499 (m) cm^{−1}. Anal. Calcd. for C₆H₁₈O₂N₂PbI₄: C, 8.33%; H, 2.10%; N, 3.24%. Found: C, 8.53%; H, 2.17%; N, 3.24%.

(EDBE)[PbBr_{4-x}Cl_x] and (EDBE)[PbBr_{4-x}I_x]

Crystalline (EDBE)[PbBr₄] was synthesized as described above. The solid (0.05 g) was dissolved in a 1-mL aqueous solution containing the volumetric ratios of 9-M HBr:12-M HCl given below. The solution

was sonicated for 5 minutes to ensure complete dissolution of the solid. Then 4 mL of cold (0 °C) 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 mass spectrometry (ICP-MS). This technique was used to synthesize (EDBE)[PbBr_{4-x}Cl_x] with *x* of 0, 0.24, 0.41, 1.56, and 1.84 from solutions containing HBr:HCl volumetric ratios of 1:0, 1:1, 2:3, 3:5, and 1:4, respectively. A similar technique was used to synthesize (EDBE)[PbBr_{4-x}I_x] with *x* of 0, 0.36, 0.77, 1.46, 3.25, and 3.87 from solutions containing HBr:HI volumetric ratios of 1:0, 39:1, 9:1, 4:1, 3:2, 2:3, and 1:4, respectively.

Crystal structure determination

Crystals were coated with Paratone-N oil, mounted on a Kapton® loop, and transferred to a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector. Frames were collected using ω and ψ scans with Mo K α radiation ($\lambda = 0.71073$ Å). 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 V2012.¹ Space-group assignments were based upon systematic absences, *E*-statistics, agreement factors for equivalent reflections, and successful refinement of the structures. The structures were solved by direct methods, expanded through successive difference Fourier maps using SHELXS-97, and refined against all data using the SHELXTL-2013 software package.²⁻⁴ Weighted *R* factors, *R*_w, and all goodness-of-fit indicators are based on *F*². 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.

Calculation of polyhedral distortion

For each (EDBE)[PbX₄] (X = Cl, Br, or I) structure, Cartesian coordinates were obtained for a lead atom and the six halides that comprise its octahedral coordination environment. These values were supplied to *SHAPE*,⁵ a program that calculates continuous shape measures for atomic positions relative to an idealized polyhedron based on minimal distortion paths,⁶ generalized interconversion coordinates,⁷ and the following algorithm:⁸

$$S = \min \frac{\sum_{k=1}^N |Q_k - P_k|^2}{\sum_{k=1}^N |Q_k - Q_0|^2} \times 100$$

Here, *S* is a dimensionless continuous symmetry measure obtained by assessing the root-mean-square (rms) deviation of *N* vertices from their idealized positions. *Q_k* is a vector containing the coordinates of the *N* vertices and *P_k* is the vector for idealized positions. *Q₀* is the coordinate vector of the center of mass, and *S* is normalized by the rms distance from the center of mass to all vertices thus avoiding size effects.

Other physical measurements

Powder x-ray diffraction (powder XRD) measurements were performed on a PANalytical X'Pert powder diffractometer with a Cu anode (*Kα*₁ = 1.54060 Å, *Kα*₂ = 1.54443 Å, *Kα*₂/*Kα*₁ = 0.50000), a programmable divergence slit with a nickel filter, and a PIXcel^{1D} detector. The instrument was operated

in a Bragg-Brentano geometry with a step size of 0.02° (2 θ). Simulated powder patterns were calculated using the crystallographic information files (CIFs) from single-crystal x-ray experiments. C, H, and N analyses were performed by MHW Laboratories (Phoenix, AZ). Thermogravimetric analyses were performed with a Netzsch TG 209 F1 Libra Thermo-Microbalance with alumina pans at a heating rate of $5^\circ\text{C}/\text{min}$, using 5-mg samples. Infrared spectra were collected on a Thermo Nicolet 6700 FTIR spectrometer with a Smart Orbit attenuated total reflectance accessory. Raman measurements were taken on a Bruker Vertex 70 FTIR spectrometer with a RAM II Raman attachment, using a liquid nitrogen-cooled-MCT detector and a 1064 nm Nd:YAG laser as an excitation source. Inductively-coupled plasma mass spectrometry (ICP-MS) measurements to determine halide ratios in (EDBE)[PbBr_{4-x}Cl_x] and (EDBE)[PbBr_{4-x}I_x] 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. Room-temperature 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. Low-temperature photoluminescence was measured using a spectrograph (Acton Research SpectraPro 500i) equipped with a silicon CCD array detector (Hamamatsu), using excitation from the 351-nm line of an Ar laser. Samples were cooled to liquid helium temperatures using a cold finger Janus ST-500 cryostat. Excitation intensities were measured using a Newport 818-UV-L photodiode.

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, Wittmann, and Friend.⁹ 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 testing

To test for material 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 (with an intensity of $720 \mu\text{W}/\text{cm}^2$) for 3 months. PLQE measurements were taken at periodic intervals.

PL intensity dependence on excitation power density

Emission from permanent material defects typically show a sublinear dependence on excitation power density, with eventual saturation when all defects are filled.^{10,11} For such emission to show a linear power dependence: excitation rate $\ll$ relaxation rate.¹²

For (EDBE)[PbBr₄] (2-Br):

σ = absorption cross section, A = absorbance, ε_M = molar extinction coefficient, L = film thickness, C = concentration, N_A = Avogadro's number, q_p = laser photon flux, I = laser intensity, h = Planck's constant, c = velocity of light, λ = laser wavelength.

$$\text{Excitation rate} = \sigma q_p$$

$$A = \varepsilon_M \times C \times L$$

$$A/L = 5 \times 10^5 \text{ cm}^{-1} \text{ and } C = 0.0043 \text{ mol}/\text{cm}^3 \text{ (obtained from formula units per unit cell volume)}$$

$$\varepsilon_M = 1.16 \times 10^8 \text{ cm}^2/\text{mol}$$

$$\sigma = \ln(10) \times (\varepsilon_M / N_A) = 4.46 \times 10^{-16} \text{ cm}^2/\text{Pb}^{2+}$$

$$I = 300 \times 10^{-3} \text{ W}/\text{cm}^2$$

$$q_p = I\lambda/hc = 5.36 \times 10^{17} \text{ s}^{-1}\text{cm}^{-2}$$

$$\sigma q_p = (4.46 \times 10^{-16} \text{ cm}^2/\text{Pb}^{2+}) \times (5.36 \times 10^{17} \text{ s}^{-1}\text{cm}^{-2}) = 239 \text{ (s}^{-1}/\text{Pb}^{2+}) \sim 10^2 \text{ (s}^{-1}/\text{Pb}^{2+})$$

$$\text{Relaxation rate} = N/(\text{PL lifetime})$$

$$N = \text{number of emissive defects per Pb}^{2+}. \text{ PL lifetime at 300 K} = 14 \times 10^{-9} \text{ s} \sim 10^{-8} \text{ s}$$

If emission arises from permanent material defects, because we see no sign of PL saturation at a laser power density of $300 \text{ mW}/\text{cm}^2$:

Excitation rate $\ll$ relaxation rate

$$10^2 \text{ (s}^{-1}/\text{Pb}^{2+}) \ll N/(10^{-8})$$

So, $N \gg 10^{-6}$ defects per Pb^{2+} or $N' \gg 10^{15}$ defects/ cm^3 .

A defect concentration that is significantly greater than 10^{15} defects/ cm^3 would be unlikely to occur intrinsically in our materials. Because we observe white-light emission from single crystals and highly crystalline films, the observed linear power dependence suggests that the emissive defects are photogenerated.

Table S1. Crystallographic data^a for (EDBE)[PbCl₄] (**1-Cl**), (EDBE)[PbBr₄] (**2-Br**), and (EDBE)[PbI₄] (**3-I**)

	1-Cl	2-Br	3-I
Empirical Formula	C ₆ H ₁₈ O ₂ N ₂ PbCl ₄	C ₆ H ₁₈ O ₂ N ₂ PbBr ₄	C ₆ H ₁₈ O ₂ N ₂ PbI ₄
Formula Weight, g·mol ⁻¹	499.23	677.04	865.04
Temperature, K	100(2)	100(2)	100(2)
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> , Å	7.7316(10)	6.0917(3)	6.4940(5)
<i>b</i> , Å	7.5418(10)	28.7804(14)	29.461(2)
<i>c</i> , Å	13.2928(18)	8.8860(4)	9.2666(7)
β , °	102.481(4)	91.852(2)	91.777(2)
Volume, Å ³	756.79(17)	1557.09(13)	1772.0(2)
<i>Z</i>	2	4	4
Density (calculated), g·cm ⁻³	2.191	2.888	3.242
Absorption coefficient, mm ⁻¹	11.839	21.087	16.479
<i>F</i> (000)	468	1224	1512
Crystal size, mm ³	0.1 × 0.15 × 0.01	0.1 × 0.1 × 0.05	0.1 × 0.08 × 0.01
θ range, °	5.31 to 25.34	2.40 to 26.02	2.31 to 25.34
Index ranges	$-8 \leq h \leq 9$ $-9 \leq k \leq 9$ $-16 \leq l \leq 16$	$-7 \leq h \leq 7$ $-35 \leq k \leq 35$ $-10 \leq l \leq 10$	$-7 \leq h \leq 7$ $-35 \leq k \leq 35$ $-11 \leq l \leq 11$
Reflections collected/unique	10361/1381	39338/3067	44931/3209
Completeness to $\theta_{\max}$, %	98.3	100	99.0
Max. and min. transmission	0.332, 0.204	0.745, 0.258	0.745, 0.397
Data/restraints/parameters	1381/35/71	3067/0/138	3209/0/138
Goodness-of-fit on F^2	1.155	1.085	1.002
Final <i>R</i> indices [$I > 2\sigma(I)$] ^b	$R_1 = 0.0285$ $wR_2 = 0.0786$	$R_1 = 0.0234$ $wR_2 = 0.0623$	$R_1 = 0.0163$ $wR_2 = 0.0415$
<i>R</i> indices (all data) ^b	$R_1 = 0.0285$ $wR_2 = 0.0786$	$R_1 = 0.0246$ $wR_2 = 0.0638$	$R_1 = 0.0173$ $wR_2 = 0.0425$
Largest diff. peak and hole, e·Å ⁻³	2.022, -1.705	2.337, -1.826	1.112, -1.088

^aObtained with monochromated Mo K α ($\lambda = 0.71073$ Å) radiation^b $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)]^{1/2}$

Table S2. Continuous symmetry measures (S) associated with distortions in the lead-halide octahedra. Higher S values denote greater distortion from ideal octahedral geometry.

	S (dimensionless)
(EDBE)[PbCl ₄] (1-Cl)	4.52
(EDBE)[PbBr ₄] (2-Br)	0.57
(EDBE)[PbI ₄] (3-I)	0.31

Table S3. Selected bond lengths (Å) and angles (°). X(*ter*) and X(*br*) refer to terminal and bridging halides, respectively.

	1-Cl	2-Br	3-I
Pb–X(<i>ter</i>)	2.881(2)	2.9360(5) 2.8069(5)	2.9966(4) 3.1512(4)
Pb–X(<i>br</i>)	2.842(2) 2.835(2)	3.0920(5) 3.0096(4) 3.1291(5) 3.2780(5)	3.2375(4) 3.2674(4) 3.3005(4) 3.4590(4)
X(<i>ter</i>)–Pb–X(<i>br</i>)	100.17(2) 90.33(7) 70.76(7) 90.02(7)	95.197(13) 98.762(14) 87.790(14) 91.434(12) 85.337(13) 95.455(12) 173.448(19) 172.975(13)	96.742(10) 89.655(10) 87.459(9) 86.008(12) 94.717(9) 94.824(11) 175.850(10) 175.525(10)
X(<i>ter</i>)–Pb–X(<i>ter</i>)	158.29(10)	83.718(14)	86.008(12)

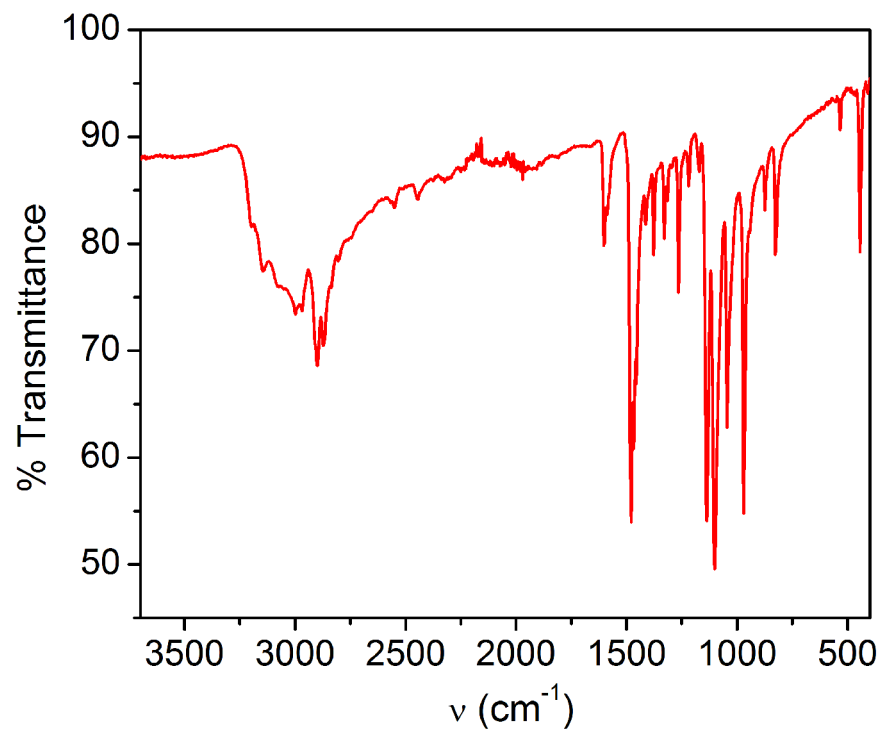


Figure S1. Solid-state vibrational spectrum of (EDBE)[PbCl₄] (**1-Cl**).

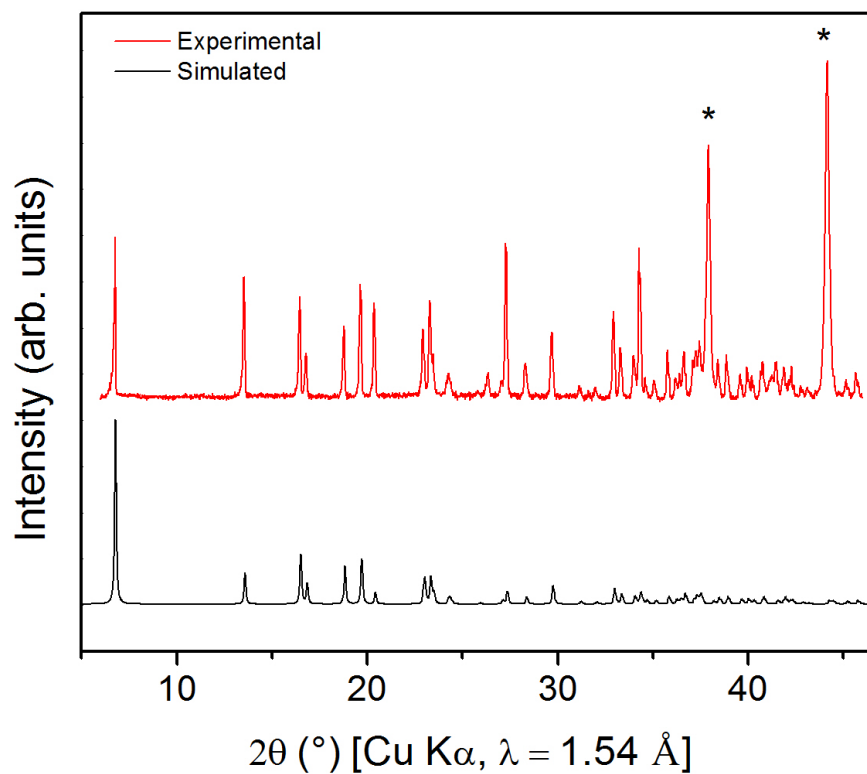


Figure S2. Powder XRD pattern of (EDBE)[PbCl₄] (**1-Cl**) and the simulated pattern from room-temperature single-crystal data of **1-Cl**. Asterisks denote peaks from the Al sample stage.

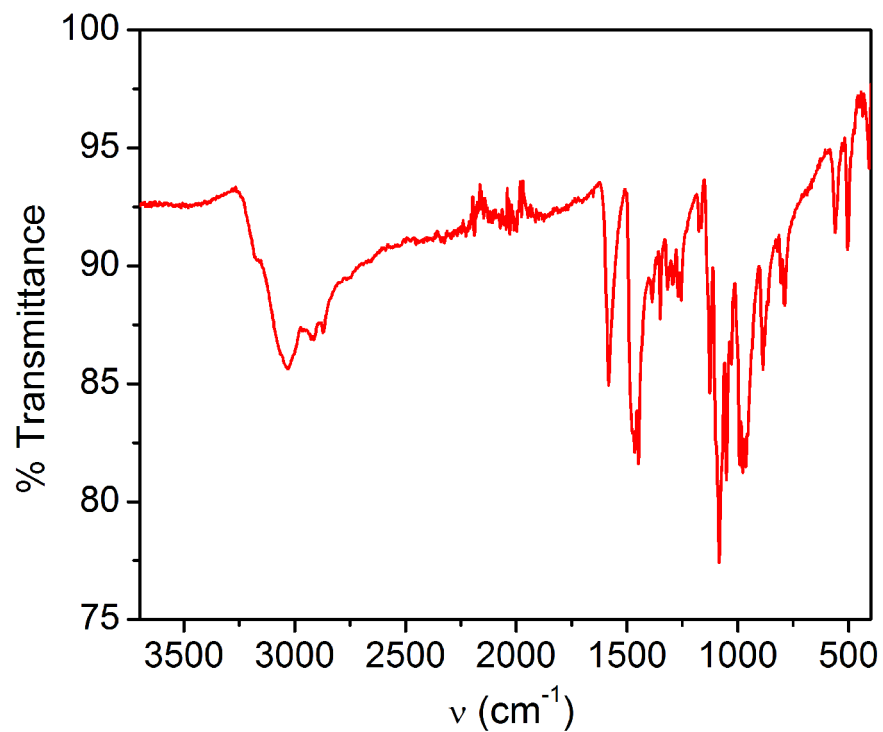


Figure S3. Solid-state vibrational spectrum of (EDBE)[PbBr₄] (2-Br).

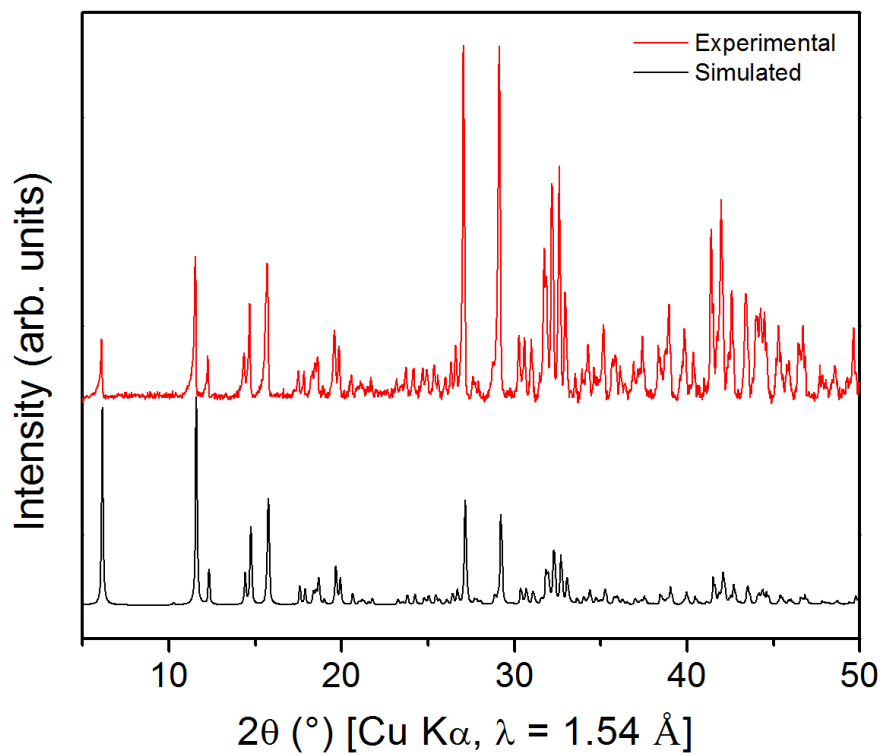


Figure S4. Powder XRD pattern of (EDBE)[PbBr₄] (2-Br) and the simulated pattern from room-temperature single-crystal data of 2-Br.

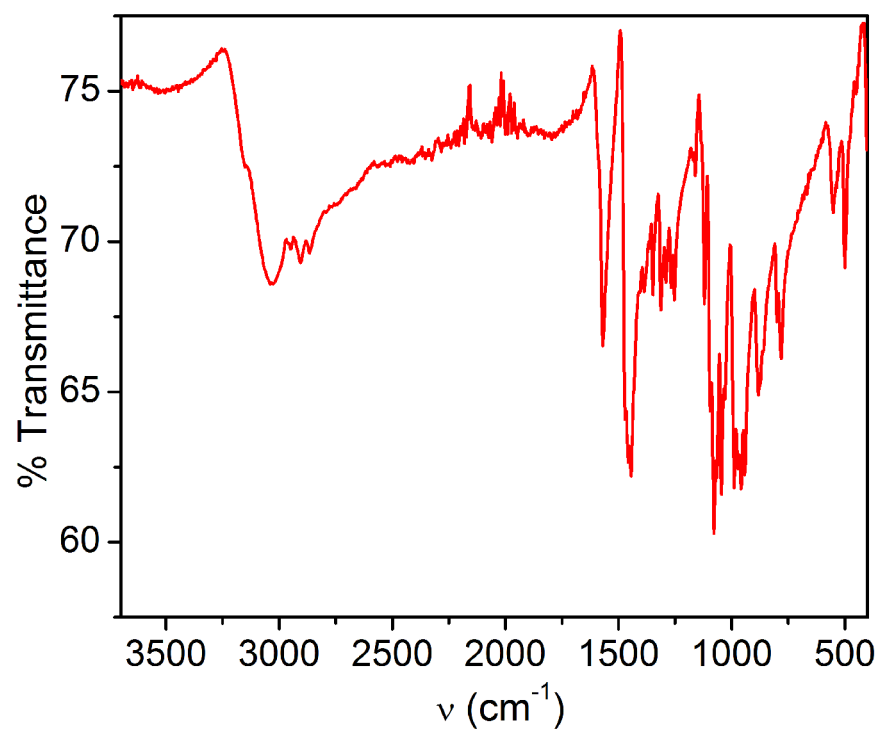


Figure S5. Solid-state vibrational spectrum of (EDBE)[PbI₄] (**3-I**).

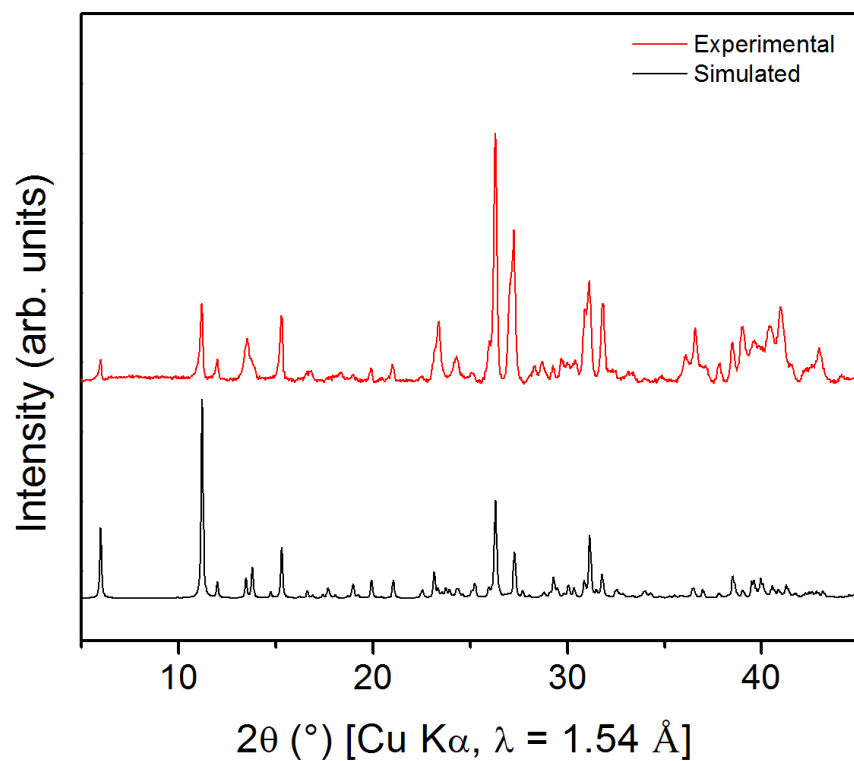


Figure S6. Powder XRD pattern of (EDBE)[PbI₄] (**3-I**) and the simulated pattern from room-temperature single-crystal data of **3-I**.

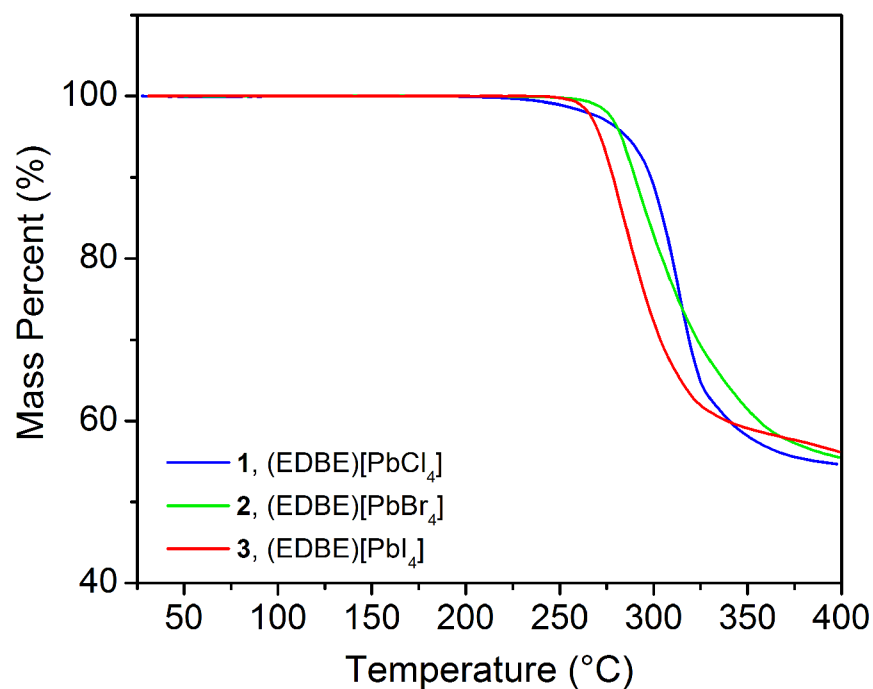


Figure S7. Thermogravimetric analysis of (EDBE)[PbCl₄] (**1-Cl**), (EDBE)[PbBr₄] (**2-Br**), and (EDBE)[PbI₄] (**3-I**). Mass-loss onsets occur at 210, 260, and 248 °C, respectively.

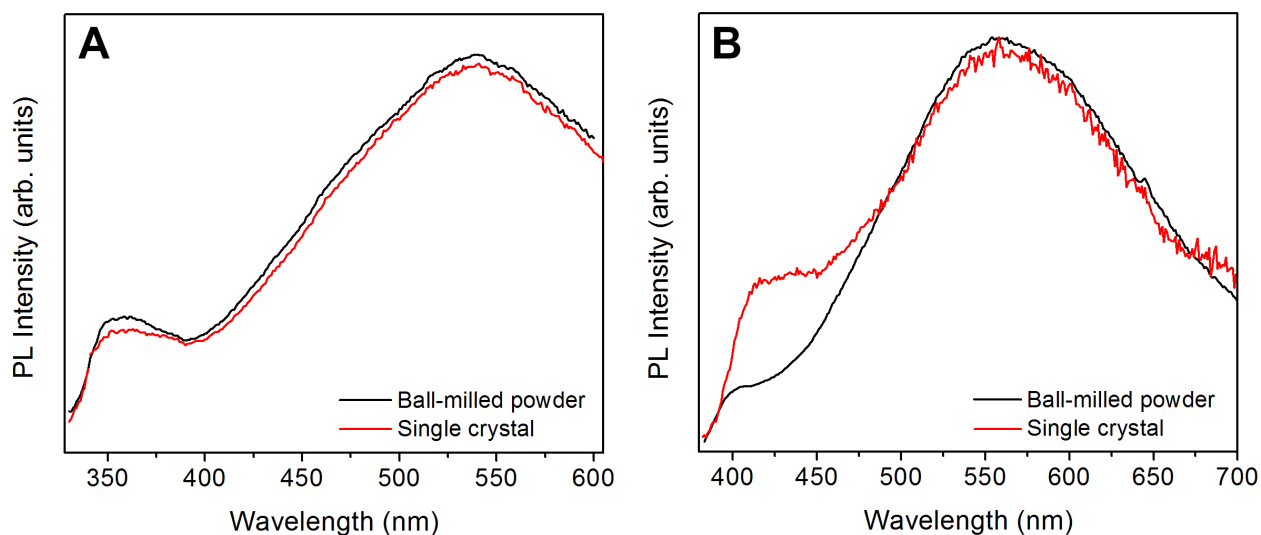


Figure S8. Photoluminescence from single crystals and ball-milled powders of (A) (EDBE)[PbCl₄] (**1-Cl**) and (B) (EDBE)[PbBr₄] (**2-Br**). Ball-milled powders have a particle size of ca. 1 μ m, while single crystals of **1-Cl** and **2-Br** have dimensions of 1 $\times$ 0.5 $\times$ 0.1 cm and 1 $\times$ 0.4 $\times$ 0.1 cm, respectively.

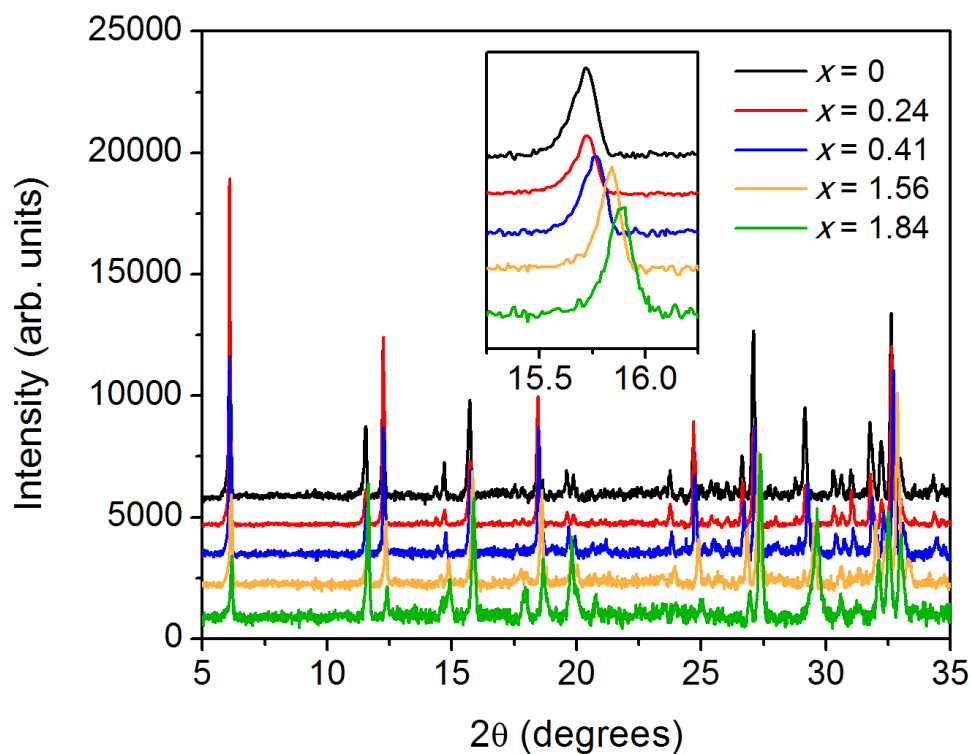


Figure S9. PXRD patterns of non-oriented powders of (EDBE)[PbBr_{4-x}Cl_x] indicating single-phase materials with a systematic change to smaller lattice spacings upon substitution of chloride for bromide.

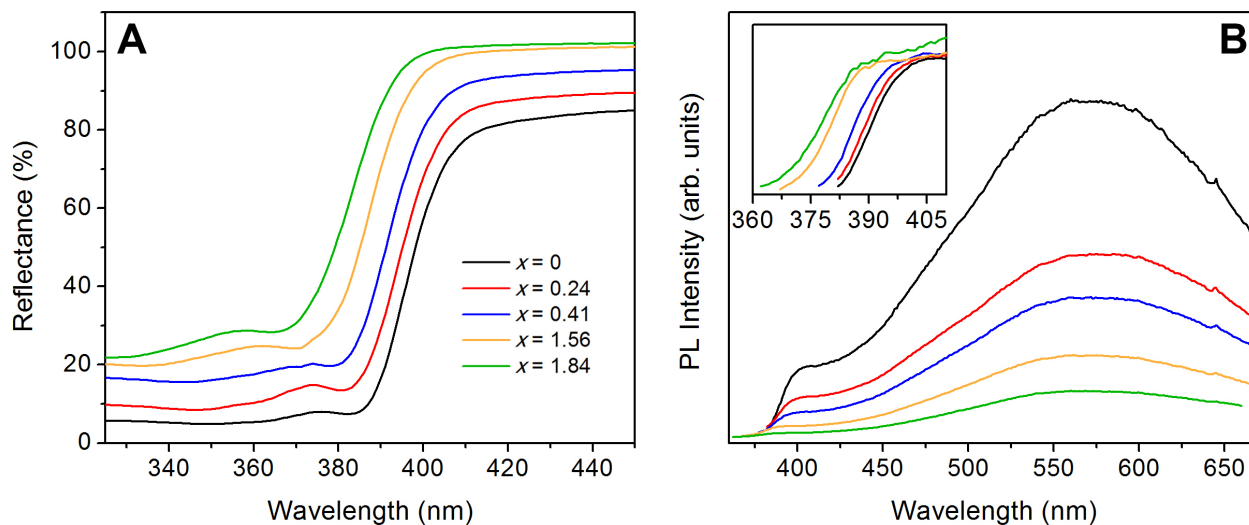


Figure S10. Diffuse reflectance (A) and photoluminescence (B) of (EDBE)[PbBr_{4-x}Cl_x]. Diffuse reflectance spectra are offset for clarity, and PL spectra are unscaled. Excitonic absorption, bandgap absorption, and higher-energy shoulder emission (inset of B) show a blueshift with increasing chloride content, while the position of the broad emission is unchanged.

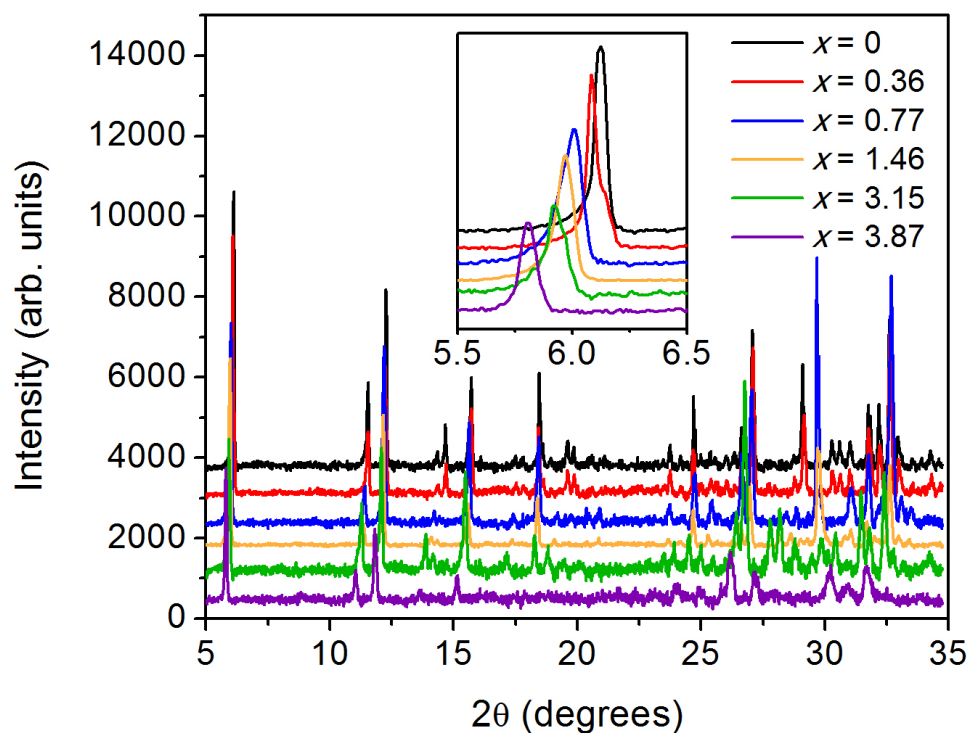


Figure S11. PXRD patterns of non-oriented powders of (EDBE)[PbBr_{4-x}I_x] indicating single-phase materials with a systematic change to larger lattice spacings upon substitution of iodide for bromide.

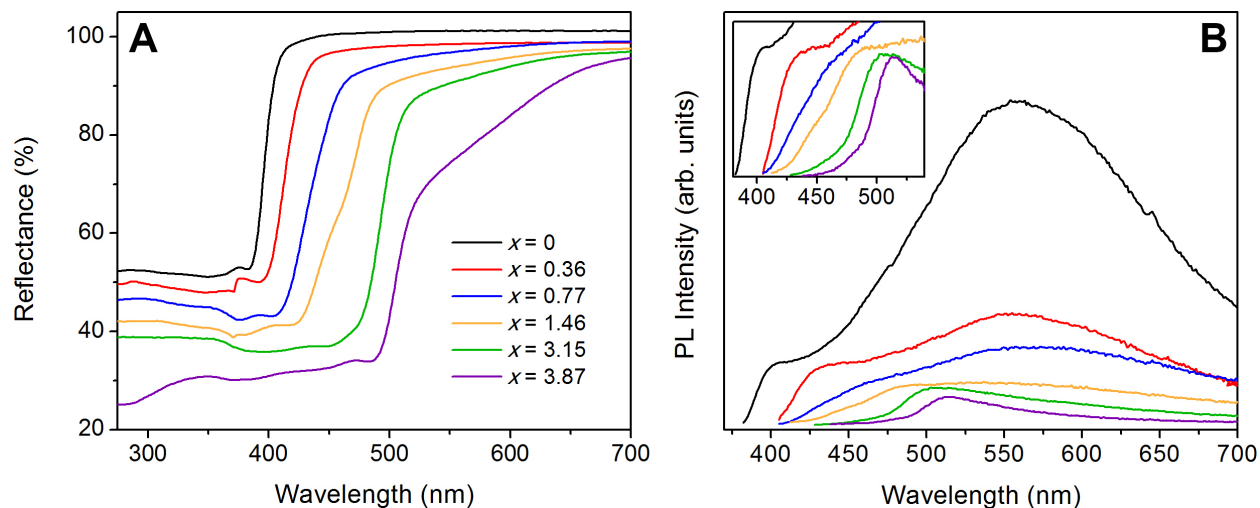


Figure S12. Diffuse reflectance (A) and photoluminescence (B) of (EDBE)[PbBr_{4-x}I_x]. Diffuse reflectance spectra are offset for clarity. PL spectrum of $x = 0$ is scaled by 1/20, while other PL spectra are unscaled. Excitonic absorption, bandgap absorption, and higher-energy shoulder emission (inset of B) show a redshift with increasing iodide content, while the position of the broad emission is unchanged.

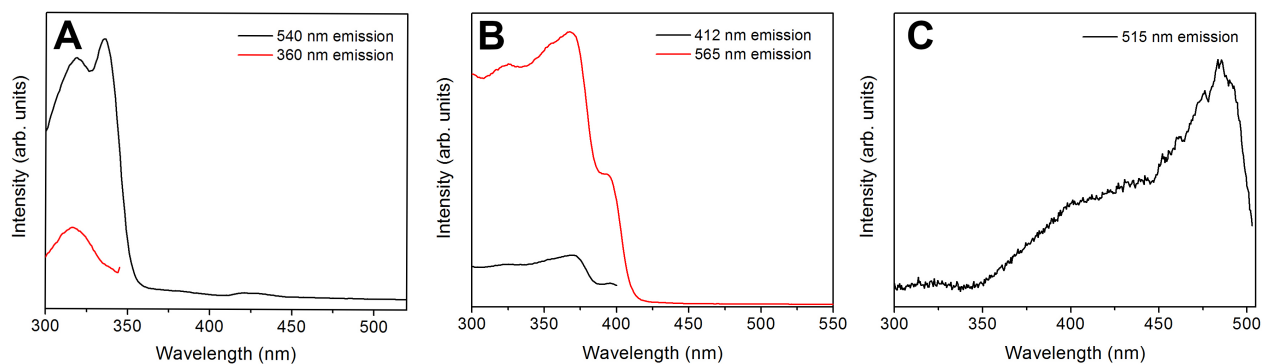


Figure S13. (A) Excitation spectra for the 360 and 540 nm emissions of (EDBE)[PbCl₄] (**1-Cl**). (B) Excitation spectra for the 412 and 565 nm emissions of (EDBE)[PbBr₄] (**2-Br**). (C) Excitation spectrum for the 505 nm emission in (EDBE)[PbI₄] (**3-I**).

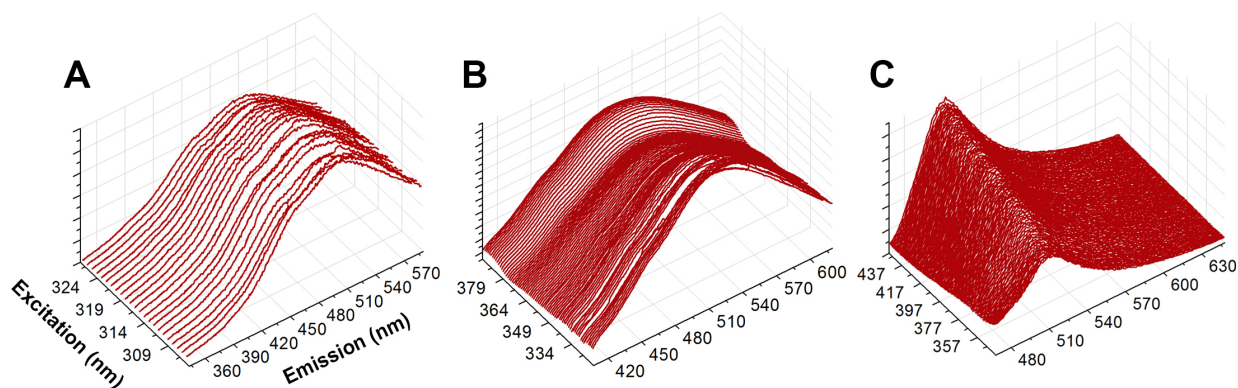


Figure S14. Emission-excitation spectra of (A) (EDBE)[PbCl₄] (**1-Cl**), (B) (EDBE)[PbBr₄] (**2-Br**), and (C) (EDBE)[PbI₄] (**3-I**).

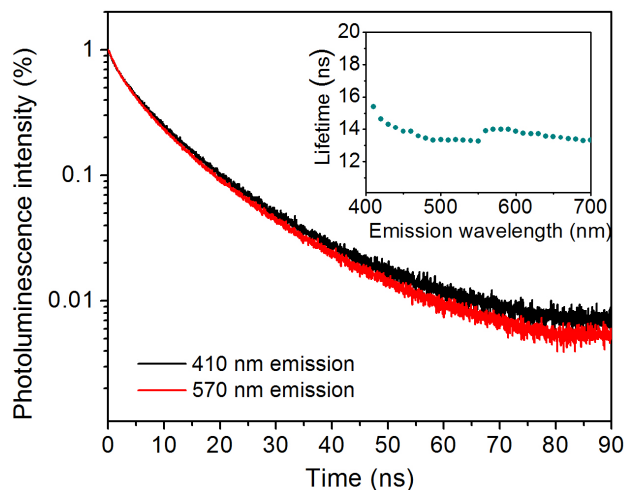


Figure S15. (A) Photoluminescence decay of the emission from (EDBE)[PbBr₄] (**2-Br**). Inset: Lifetime for the broad emission of **2** (400 – 700 nm) obtained by fits to the first 5 ns of data. $\lambda_{\text{ex}} = 375$ nm.

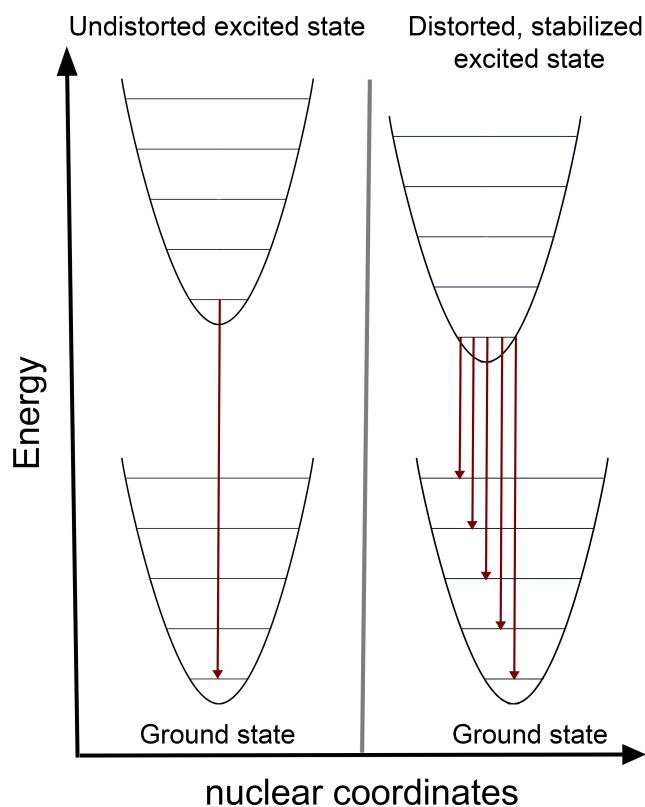


Figure S16. Schematic of transitions that can lead to emission broadening from an excited state that is distorted with respect to the ground state. Stabilization of the distorted excited state can lead to a Stokes-shifted emission.

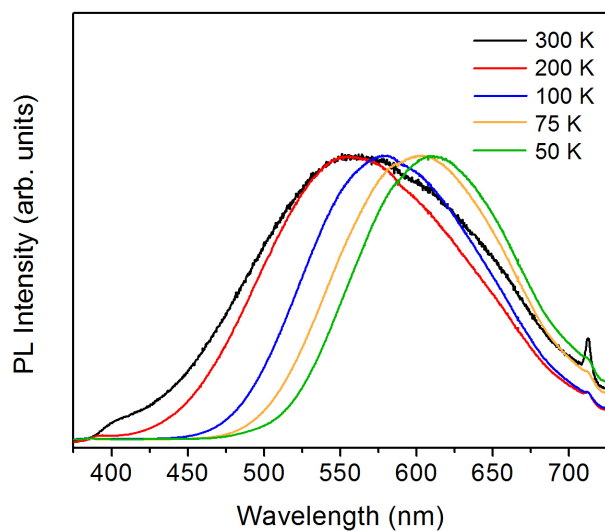


Figure S17. Photoluminescence spectra of (EDBE)[PbBr₄] (2-Br) from 50 to 300 K. Spectra are normalized to the broadband peak intensity. $\lambda_{\text{ex}} = 355$ nm.

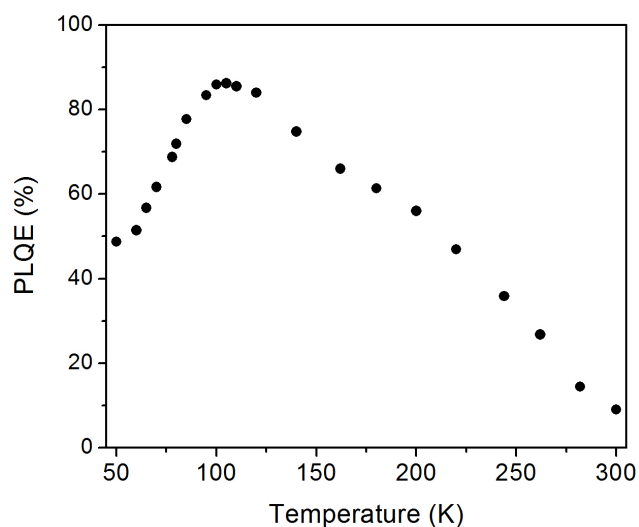


Figure S18. Photoluminescence quantum efficiency (400 – 700 nm) of (EDBE)[PbBr₄] (2-Br) as a function of temperature. $\lambda_{\text{ex}} = 355$ nm.

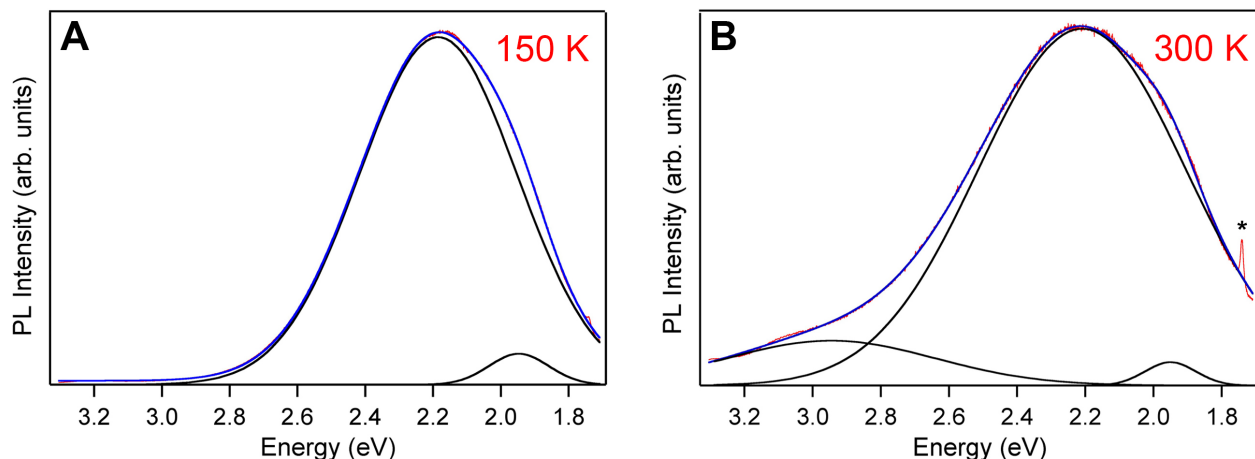


Figure S19. Multi-peak fitting analyses of photoluminescence spectra of (EDBE)[PbBr₄] (2-Br) at 150 (A) and 300 K (B). Red: experimental data; black: deconvoluted peaks; blue: peak convolution. All spectra in the 50 – 150 K range can be modeled with the two-peak model shown in (A), while all spectra in the 150 – 300 K range require a three-peak model due to the higher-energy shoulder (B). The feature at 1.75 eV marked with an asterisk in (B) corresponds to the second harmonic of the 355-nm laser.

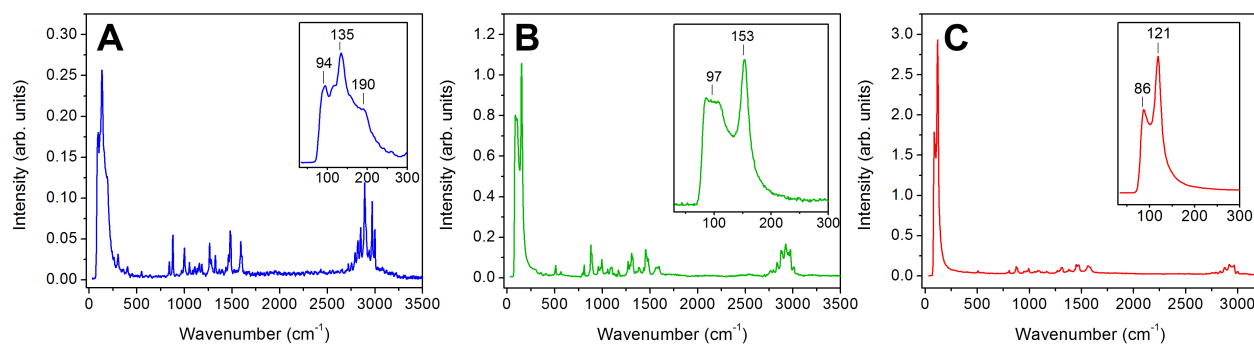


Figure S20. Raman vibrational spectra of (A) (EDBE)[PbCl₄] (1-Cl), (B) (EDBE)[PbBr₄] (2-Br), and (C) (EDBE)[PbI₄] (3-I). Measurements were conducted with a 1064-nm Nd:YAG laser. Insets show the Pb-halide stretching region of each spectrum.

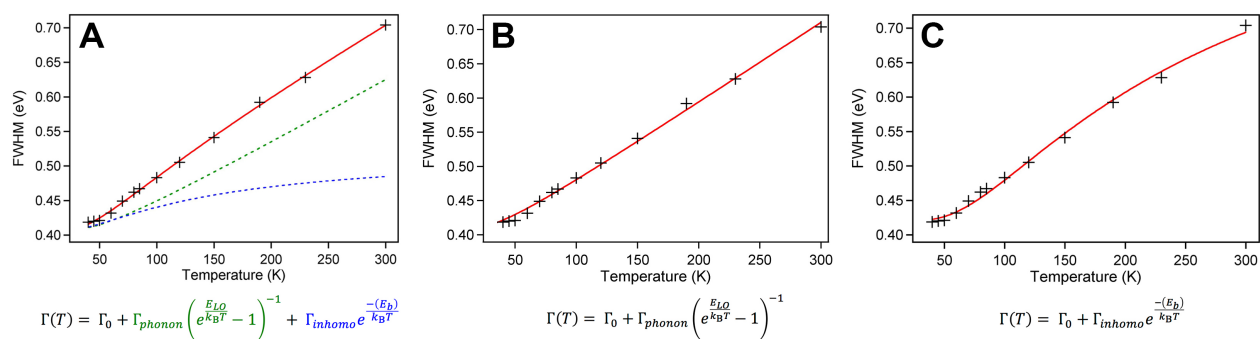


Figure S21. Relationship between the full width at half maximum (FWHM) of the broad emission in 2-Br and temperature. A) Electron-phonon coupling (green) and inhomogeneous (blue) contributions to the best fit (red) using the model in the manuscript text. Best fits to the data considering a purely phonon-coupled (B) or inhomogeneous (C) model.

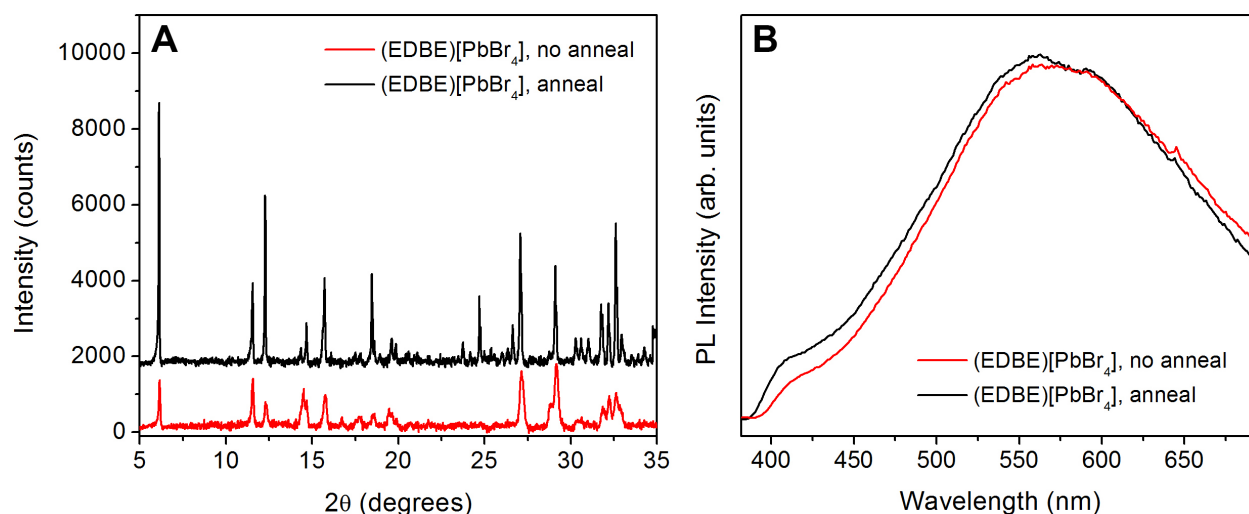


Figure S22. PXRD patterns (A) and photoluminescence (B) from a pressed pellet of (EDBE)[PbBr₄] (2-Br) before and after annealing for 24 h at 150 °C. PXRD patterns have been offset for clarity, but are otherwise unscaled. Photoluminescence spectra are unscaled. $\lambda_{ex} = 365$ nm.

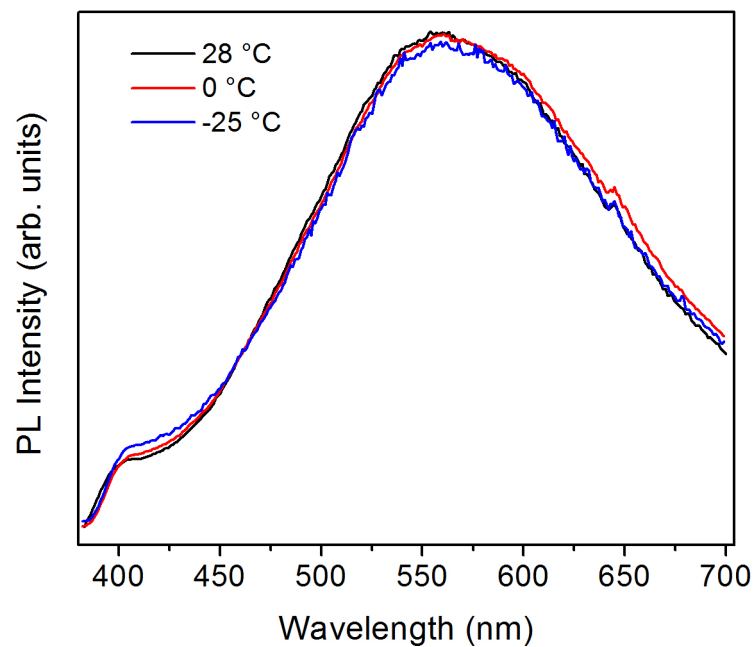


Figure S23. Photoluminescence from microcrystalline powders of (EDBE)[PbBr₄] (2-Br) crystallized at different temperatures.

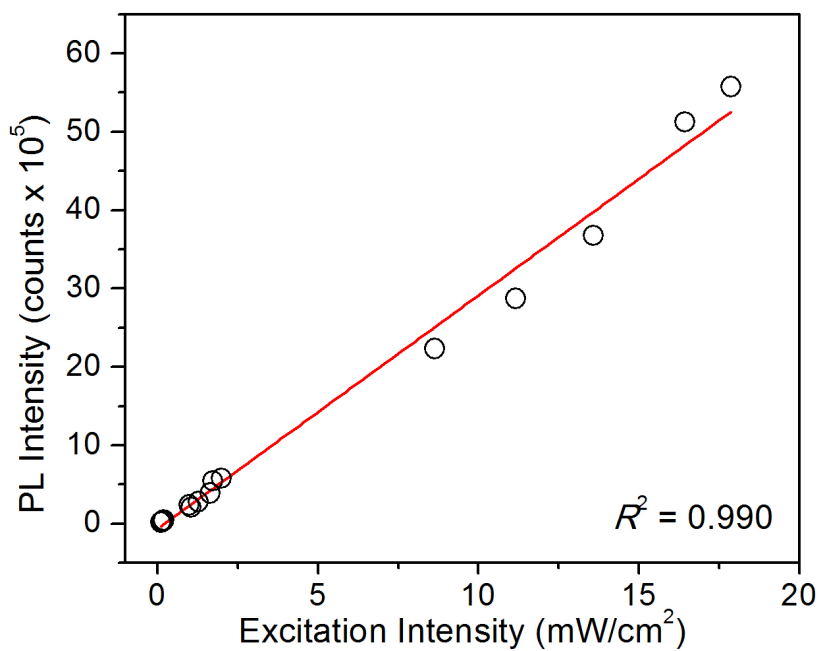


Figure S24. Dependence of emission intensity on excitation power density in 2-Br at 84 K. $\lambda_{\text{ex}} = 355$ nm.

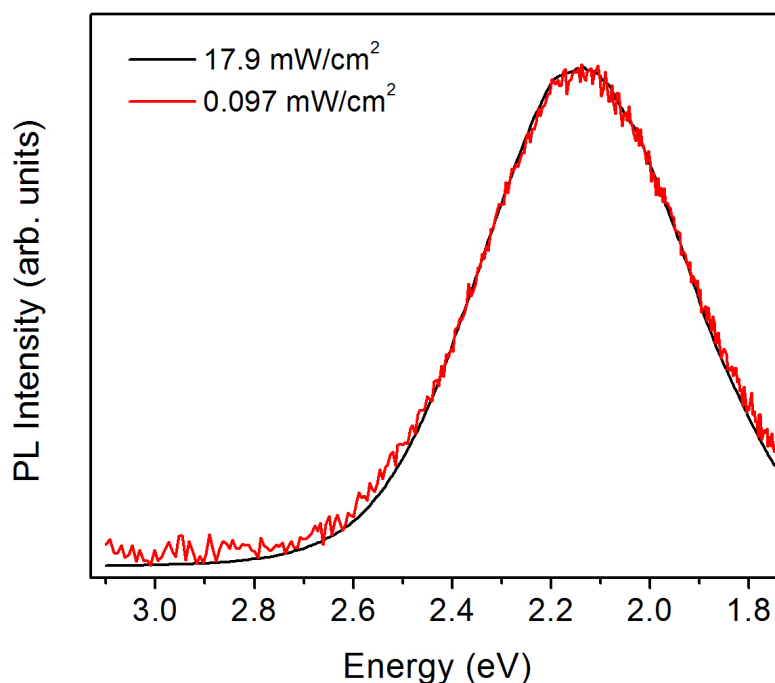


Figure S25. Overlay of photoluminescence spectra of **2-Br** taken at 84 K. Excitation intensities are given in the legend. $\lambda_{\text{ex}} = 355$ nm.

References

1. Bruker AXS Inc.: Madison, Wisconsin, 2007.
2. Sheldrick, G. M. *Acta. Cryst. Sect. A* **2008**, *64*, 112.
3. Muller, P., Herbst-Irmer, R., Spek, A. L., Schneider, T. R., Sawaya, M. R. *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*; Oxford University Press: New York, 2006.
4. Sheldrick, G. M. Göttingen, 1997.
5. Llunell, M.; Casanova, D.; Cirera, J.; Alemany, P.; Alvarez, S.; 2.0 ed. Universitat de Barcelona, 2010.
6. Casanova, D.; Cirera, J.; Llunell, M.; Alemany, P.; Avnir, D.; Alvarez, S. *J. Am. Chem. Soc.* **2004**, *126*, 1755.
7. Cirera, J.; Ruiz, E.; Alvarez, S. *Chem. Eur. J.* **2006**, *12*, 3162.
8. Pinsky, M.; Avnir, D. *Inorg. Chem.* **1998**, *37*, 5575.
9. de Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.
10. Tongay, S.; Suh, J.; Ataca, C.; Fan, W.; Luce, A.; Kang, J. S.; Liu, J.; Ko, C.; Raghunathanan, R.; Zhou, J.; Ogletree, F.; Li, J.; Grossman, J. C.; Wu, J. *Sci. Rep.* **2013**, *3*.
11. Schmidt, T.; Lischka, K.; Zulehner, W. *Phys. Rev. B* **1992**, *45*, 8989.
12. Reshchikov, M. A.; Korotkov, R. Y. *Phys. Rev. B* **2001**, *64*, 115205.