

Supporting Information Impact of Two Diammonium Cations on the Structure and Photophysics of Layered Sn-based Perovskites

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Synthesis of materials

EDBEI₂ 1 mL of 1,2-bis(2-aminoethoxy)ethane (TCI Chemicals, 98%) was dissolved in 5 mL of ethanol. Then, 2 mL of hydriodic acid (Sigma-Aldrich, 57%) was added drop-wise under vigorous magnetic stirring and ice-bath cooling. After 4h of stirring and cooling, the solvent was removed by a rotary evaporator. The resulting pale yellow precipitate was washed by re-dissolving it in hot ethanol and precipitating with diethyl ether 6 times until white crystals were obtained. The remaining solvent was roto-evaporated and the final product was further dried in a vacuum for 48 hours and stored under N₂ atmosphere.

OBEI₂ 1 mL of 2,2'-oxybis(ethylamine) (TCI Chemicals, 98%) was dissolved in 3 mL of ethanol. The rest of the procedure is the same as for EDBEI₂.

OBESnI₄ and EDBESnI₄ The single crystal synthesis involved an antisolvent vapour crystallisation method inside a N₂-filled glovebox. In this method, 1 mL of anhydrous N,N-dimethylformamide (Sigma-Aldrich, anhydrous, 99.8%) was added to a 1:1 molar ratio of

SnI₂ (Alfa Aesar, ultra-dry, 99.999%) and the synthesized organic salt (OBEI₂ or EDBEI₂) to obtain 1 M solutions. The solutions were stirred for half an hour until well-dissolved. Subsequently, the solutions were filtered using 0.2 μm PTFE membrane filters and were placed in a small vial closed with parafilm. The small vial was placed in a bigger vial with 3.5 mL of anhydrous dichloromethane (Sigma-Aldrich, anhydrous, 99.8%). A small puncture was made in the parafilm and the big vial was closed with a PTFE cap; over the course of several days to a week, millimetre-sized black-brown crystals were formed for OBESnI₄ and red crystals for EDBESnI₄.

Thin film preparation

15 by 15 mm glass substrates were ultrasonically cleaned using a soapy solution and rinsed with deionized water, followed by acetone and isopropanol for 10 min each. The substrates were dried in an oven at 100 °C and then exposed to a UV-Ozone treatment for 20 min. 0.5 M solutions of SnI₂ (Sigma-Aldrich, 99.99%) and the organic salt (OBEI₂ or EDBEI₂) were dissolved together with 0.05 M SnF₂ (Sigma-Aldrich, 99%) in anhydrous dimethyl formamide (Sigma-Aldrich, 99.8%) and anhydrous dimethyl sulfoxide (Alfa Aesar, 99.8%) in a 4:1 volume ratio and stirred overnight. The resultant solution was filtered using a 0.2 μm PTFE filter. The thin films were blade coated by pipetting 20 μL solution with the blade height at 1200 μm, the blade speed at 20 mm/s, and the temperature-controlled stage was set at 70 ° or at 100 °C, depending on the sample. All films underwent additional annealing on a hotplate at 70 °C or 100 °C for 10 minutes. All films were prepared and stored inside a nitrogen-filled glovebox.

X-ray diffraction

Single crystals were selected and cut to an appropriate size and mounted on nylon loops using cryo oil in a N₂-filled glovebox. A Bruker D8 Venture diffractometer with a Mo K_α source (0.71073 Å) in conjunction with a Photon100 area detector was used to acquire the diffraction pattern. A nitrogen flow (Oxford Cryosystems, Cryostream Plus) was used

to maintain temperature control. Bruker Apex III software with the Bruker SHELXTL Software Package (SHELXL-2018/3¹) was used to obtain the structural solution. All non-hydrogen atoms were refined anisotropically, where the hydrogen atoms were placed in idealised positions. The crystallographic parameters of both materials are displayed in Table S1. The structures are deposited in the Cambridge Crystallographic Data Centre with numbers CCDC 2204974-2204975.

Powder X-ray diffraction on thin films was performed in a Bruker D8 Advance diffractometer equipped with a Cu K α source. Bragg-Brentano geometry was used to collect the diffraction patterns.

Absorbance spectroscopy

Samples were prepared by grinding single crystals to a fine powder using a mortar and pestle and placing it on top of a sample holder filled with barium sulphate. Diffuse reflectance spectra were taken in a UV-VIS spectrophotometer (Shimadzu, UV 3600) using an integrating sphere attachment (ISR - 3100). The Kubelka-Munk transformation was performed using the supplied measurement software. The absorbance of thin films was performed in transmission mode.

Photoluminescence spectroscopy

An optically pumped Ti:sapphire crystal (Coherent, Mira 900) was used to create ultra-fast laser pulses (150 fs). These pulses were used to generate the second harmonic (400 nm) using a Coherent Harmonic Generator. An iris spatially limited the excitation beam to 2 mm and neutral density filters were used to adjust the excitation fluence. The beam was focused on the sample with a lens (150 mm focal length) at a 20° angle in reflection geometry. The excitation fluence per pulse was estimated assuming the diameter of the focused beam d_{focus} is equal to $1.27 \times f_{lens} M^2 / D$, where f_{lens} is the focal length, M the quality factor (assumed to be 1), and D the incident diameter of the excitation beam. The samples were mounted either in a N₂-filled sample chamber or a vacuum sample chamber of a cryostat (Oxford Instruments, MicrostatHiRes). The photoluminescence was collected using an achromatic doublet,

where a 425 nm and a 435 nm long pass filter were used to block the scattered laser light. A spectrograph equipped with a 501/mm grating or a 1501/mm grating was used for the steady-state and time-resolved spectra. Steady-state spectra were taken using a spectral-calibrated EM-CCD camera (Hamamatsu) and time-resolved spectra were taken with a streak camera (Hamamatsu, S20) either in synchroscan or in single sweep mode. In single sweep mode, an optical pulse picker was used to reduce the 76 MHz repetition rate of the excitation beam.

Confocal laser scanning microscopy

Mapping of the photoluminescence of the thin films was performed with a home-built confocal laser scanning microscope. An inverted microscope (Nikon, Eclipse Ti) was combined with a continuous wave laser (Melles Griot, 488 nm) to excite the thin films in reflection mode. A set of photomultiplier tubes was used for detecting the photoluminescence, enabling simultaneous detection in the spectral ranges of 590 ± 50 nm and >650 nm. Samples were mounted in a cryostat to prevent air exposure (Oxford Instruments, MicrostatHiRes).

Table S1: Structural and refinement parameters of single crystal X-ray diffraction

Formula	C ₄ H ₁₄ I ₄ N ₂ OSn	C ₆ H ₁₈ I ₄ N ₂ O ₂ Sn
Crystal system	monoclinic	monoclinic
Space Group	P 1 2 ₁ /c 1	P 1 2 ₁ /c 1
<i>a</i> (Å)	8.6827(7)	6.5320(4)
<i>b</i> (Å)	9.0135(9)	29.3042(18)
<i>c</i> (Å)	19.7936(18)	9.2159(6)
α (°)	90	90
β (°)	98.697(3)	92.267(2)
γ (°)	90	90
<i>V</i> (Å ³)	1531.3(2)	1762.68(19)
Z	4	4
Crystal dimensions (mm ³)	0.25 x 0.18 x 0.16	0.12 x 0.11 x 0.03
θ range (°)	2.49 to 33.21	2.61 to 30.50
Density (calculated) (g/cm ³)	3.177	2.926
μ (mm ⁻¹)	9.706	8.445
Temperature (K)	100(2)	100(2)
Measured Reflections	94289	79904
Independent Reflections	5863	5381
Reflections with $I > 2\sigma(I)$	5016	4553
R_{int}	0.0544	0.0602
$R_1 [I > 2\sigma(I)]^a$	0.0267	0.0317
R_1 [all data] ^a	0.0377	0.0435
$wR_2 [I > 2\sigma(I)]^b$	0.0528	0.0704
wR_2 [all data] ^b	0.0562	0.0730
Data / restraints / parameters	5863 / 0 / 111	5381 / 0 / 138
Goodness-of-fit on F^2	1.228	1.146
largest diff. peak and hole (eÅ ⁻³)	0.754 and -2.061	1.432 and -1.608

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}, \text{ where } w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 5.3148P] \text{ for } C_4H_{14}I_4N_2OSn \text{ and } w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 3.7526P] \text{ for } C_6H_{18}I_4N_2O_2Sn$$

with $P = (F_o^2 + 2F_c^2)/3$

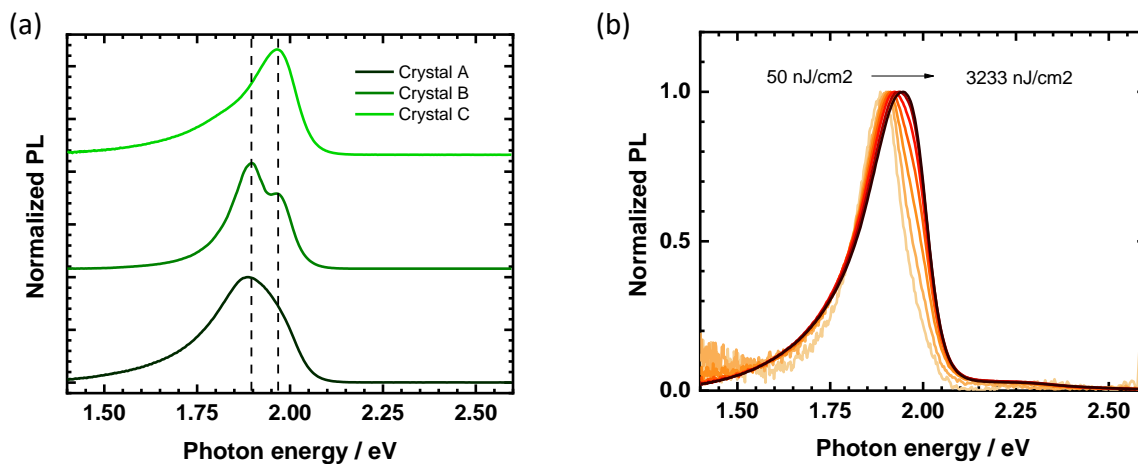


Figure S1: (a) Photoluminescence spectra showing the crystal to crystal variation of OBESnI_4 out of the same batch. (b) Photoluminescence spectra as a function of excitation fluence.

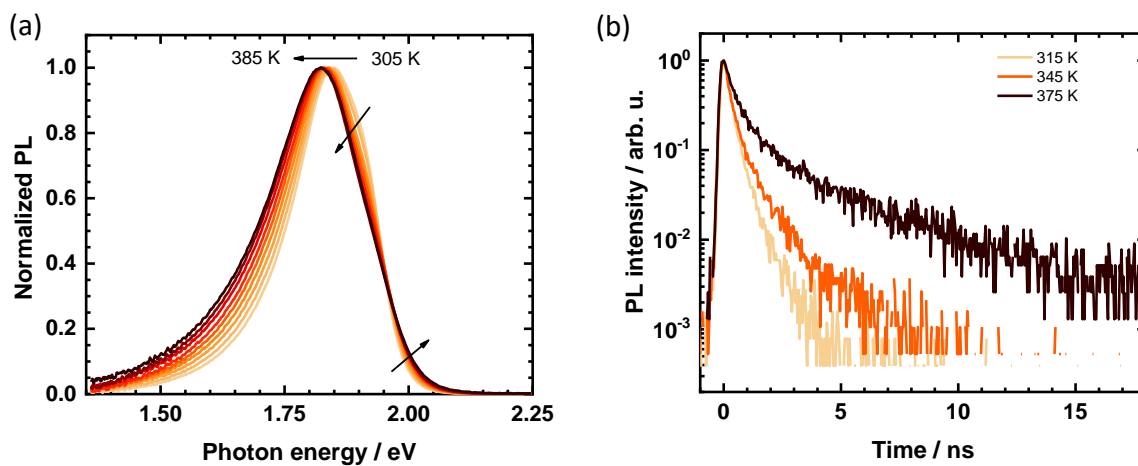


Figure S2: High-temperature steady-state photoluminescence spectra (a) and time-resolved decays (b) of OBESnI_4

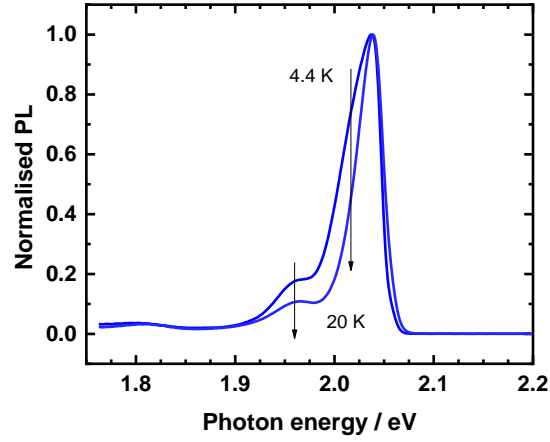


Figure S3: Low-temperature steady-state photoluminescence spectra of OBESnI_4

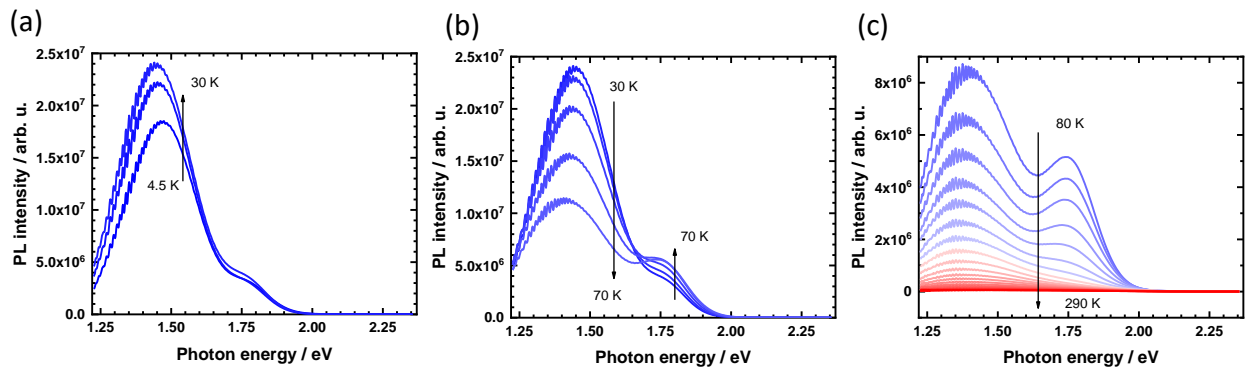


Figure S4: Temperature-dependent steady-state photoluminescence spectra of EDBESnI_4 from 4.5 K to 30 K (a), 30 K to 70 K (b), and 80 K to 290 K (c).

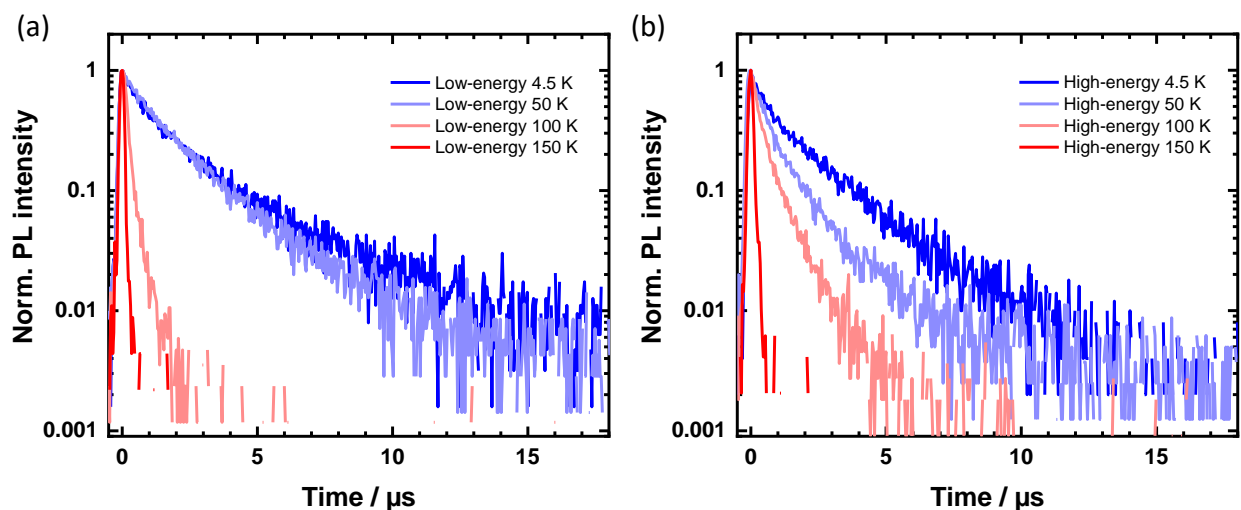


Figure S5: Temperature-dependent time-resolved photoluminescence decays of EDBESnI₄ for the low-energy peak at 1.4 eV (a) and the high-energy peak at 1.8 eV (b).

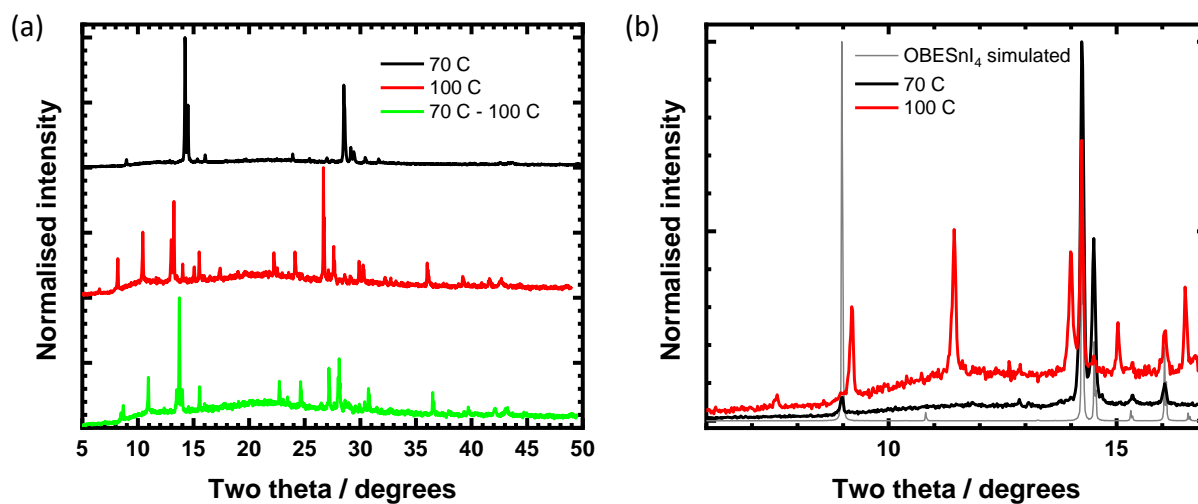


Figure S6: Powder X-ray diffraction patterns of OBESnI₄ thin films (a) and zoom-in with simulated diffraction pattern calculated using the structural model obtained from single crystals (b).

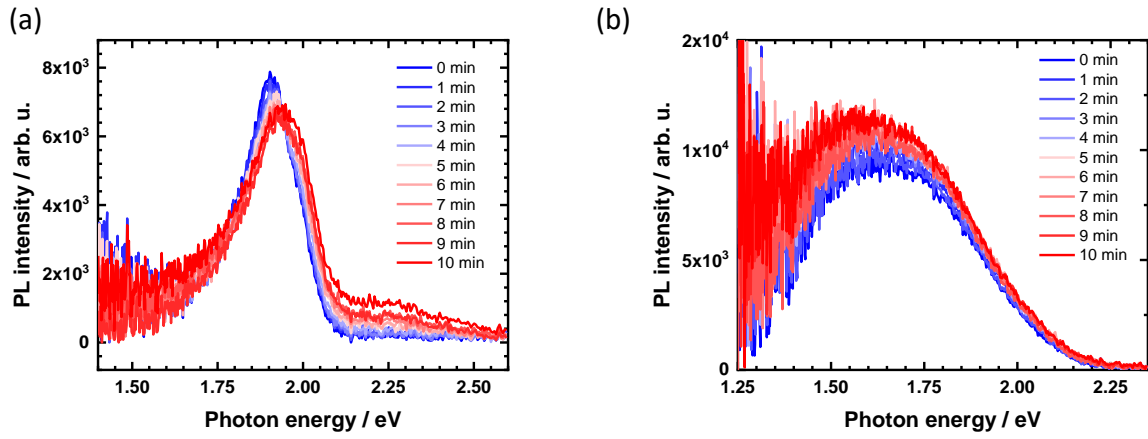


Figure S7: Photoluminescence spectra of OBESnI₄ (a) and EDBESnI₄ (b) single crystals upon continuous laser illumination in nitrogen environment.

References

- (1) Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallographica Section C* **2015**, *71*, 3–8.