

Electronic Supplementary Information (ESI)

Synthesis, optical and electronic properties of one-dimensional sulfoxonium-based hybrid metal halide, (CH₃)₃SOPbI₃

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Experimental Methods

Materials. Trimethylsulfoxonium iodide (98%) and *N,N*-dimethylformamide (99.8%) were obtained from Sigma-Aldrich. Lead (II) iodide (99.99%) was purchased from TCI.

Synthesis and growth of trimethylsulfoxonium lead triiodide, (CH₃)₃SOPbI₃ crystals. Briefly, trimethylsulfoxonium iodide and lead iodide were equimolarly added into 7.5 mL dimethylformamide and then dissolved upon ultrasonication for 10 min. The resulting precursor solution at 0.05 M was stirred for an hour and left to evaporate at room temperature without disturbance for two weeks until yellow needle-like crystals appeared. The crystals were left in the precursor solution prior to X-ray diffraction, optical microscopic, scanning electron microscopic and electrical characterization of single crystals. The crystals were filtered, washed with dimethylformamide and stored in a glovebox prior to Raman spectroscopic characterization.

Characterization. For single-crystal X-ray diffraction measurement, a specimen of C₃H₉I₃OPbS, approximate dimensions 0.186 mm × 0.203 mm × 0.394 mm, was used for the single crystal X-ray crystallographic analysis. The X-ray intensity data were measured. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.400. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2984 and 0.7461. The structure was solved and refined using the Bruker SHELXTL Software Package. The final anisotropic full-matrix least-squares refinement on F² with 58 variables converged at R1 = 0.0225, for the observed data and wR2 = 0.0471 for all data. The goodness-of-fit was 1.155. On the basis of the final model, the calculated density was 3.702 g/cm³. The single crystal data was submitted to the Cambridge Crystallographic Data Centre (CCDC) with reference number CCDC 1910346.

The optical images of (CH₃)₃SOPbI₃ crystals on a glass slide was examined by using an Olympus BX51 microscope. The morphology of (CH₃)₃SOPbI₃ crystals was examined on a glass slide by using field-emission scanning electron microscope (FEGSEM, JSM 7600F). The Raman spectra of (CH₃)₃SOPbI₃ crystals and (CH₃)₃SOI precursor were obtained by using a micro Raman system (JYT64000) with a 488 nm excitation laser source. The steady-state photoluminescence spectrum of (CH₃)₃SOPbI₃ crystal was obtained using a PerkinElmer LS55 spectrophotometer while the time-resolved PL spectra was acquired by using a time-correlated single photon counting system (PicoHarp 300, PicoQuant) with an excitation wavelength of 405 nm. The 2D X-ray diffraction pattern of a single (CH₃)₃SOPbI₃ crystal was acquired at room temperature using a Bruker X-ray diffraction system (2D GADDS XRD) with a two-dimensional general area diffraction detector. The powder X-ray diffraction pattern of grounded (CH₃)₃SOPbI₃ crystals were measured by using a Bruker D8 Advance X-ray Diffractometer. The UV-vis diffuse reflectance spectrum and the Fourier-transform infrared spectroscopy (FTIR) spectrum of grounded (CH₃)₃SOPbI₃ crystals in KBr pellet were collected with a Shimadzu UV-Vis 3600 equipped with an integrating sphere and a FTIR spectrometer (Perkin Elmer 2000), respectively. Dynamic light scattering of the mixed trimethylsulfoxonium lead iodide and lead iodide was measured immediately after dissolved upon ultrasonication for 10 min by using a Malvern ZetaSizer 3000HSA. For electrical characterization, a pair of 10-mm wide gold electrodes of 80 nm in thickness with a 2-mm spacing were thermally evaporated on a glass substrate. A single crystal was carefully withdrawn from the precursor solution and placed on the gold electrodes and left to dry at room temperature for 10 min. The probes were either directly connected to the two gold electrodes or connected to one gold electrode and the surface of the crystal for measuring their current-voltage (*I-V*) curves using a Keithley 2400 source meter.

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (CH₃)₃SOPbI₃. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pb(1)	10646(1)	7500	7501(1)	9(1)
I(1)	8180(1)	5569(1)	8499(1)	12(1)
I(2)	8213(1)	7500	5717(1)	14(1)
S(1)	2655(2)	7500	3489(1)	10(1)
O(1)	3069(5)	7500	2499(3)	17(1)
C(1)	4472(7)	7500	4198(4)	14(1)
C(2)	1442(5)	6239(4)	3830(3)	15(1)

Table S2. Bond lengths [Å] and angles [°] for (CH₃)₃SOPbI₃.

Pb(1)-I(2)	3.1572(4)
Pb(1)-I(1)	3.2035(3)
Pb(1)-I(1)#1	3.2035(3)
Pb(1)-I(2)#2	3.2175(4)
Pb(1)-I(1)#3	3.2363(3)
Pb(1)-I(1)#2	3.2363(3)
S(1)-O(1)	1.441(4)
S(1)-C(1)	1.732(5)
S(1)-C(2)#1	1.755(4)
S(1)-C(2)	1.755(4)
C(1)-H(1A)	0.99(7)
C(1)-H(1B)	0.94(5)
C(1)-H(1B)#1	0.94(5)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
I(2)-Pb(1)-I(1)	89.814(8)
I(2)-Pb(1)-I(1)#1	89.814(8)
I(1)-Pb(1)-I(1)#1	84.031(9)
I(2)-Pb(1)-I(2)#2	178.481(11)
I(1)-Pb(1)-I(2)#2	91.315(8)
I(1)#1-Pb(1)-I(2)#2	91.314(8)
I(2)-Pb(1)-I(1)#3	90.683(8)
I(1)-Pb(1)-I(1)#3	179.282(8)
I(1)#1-Pb(1)-I(1)#3	96.489(7)
I(2)#2-Pb(1)-I(1)#3	88.179(7)
I(2)-Pb(1)-I(1)#2	90.683(8)
I(1)-Pb(1)-I(1)#2	96.489(7)
I(1)#1-Pb(1)-I(1)#2	179.281(8)
I(2)#2-Pb(1)-I(1)#2	88.179(8)
I(1)#3-Pb(1)-I(1)#2	82.987(9)
Pb(1)-I(1)-Pb(1)#4	74.089(6)
Pb(1)-I(2)-Pb(1)#4	74.970(8)
O(1)-S(1)-C(1)	112.6(3)
O(1)-S(1)-C(2)#1	112.86(17)
C(1)-S(1)-C(2)#1	106.05(18)
O(1)-S(1)-C(2)	112.86(17)
C(1)-S(1)-C(2)	106.04(18)
C(2)#1-S(1)-C(2)	105.8(3)
S(1)-C(1)-H(1A)	112(4)
S(1)-C(1)-H(1B)	105(3)
H(1A)-C(1)-H(1B)	110(4)
S(1)-C(1)-H(1B)#1	105(3)
H(1A)-C(1)-H(1B)#1	110(4)
H(1B)-C(1)-H(1B)#1	114(6)
S(1)-C(2)-H(2A)	109.5
S(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
S(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 $x, -y+3/2, z$ #2 $x+1/2, y, -z+3/2$ #3 $x+1/2, -y+3/2, -z+3/2$ #4 $x-1/2, y, -z+3/2$

Table S3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{CH}_3)_3\text{SOPbI}_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb(1)	7(1)	13(1)	8(1)	0	-1(1)	0
I(1)	15(1)	10(1)	10(1)	1(1)	0(1)	0(1)
I(2)	9(1)	28(1)	6(1)	0	0(1)	0
S(1)	11(1)	12(1)	8(1)	0	1(1)	0
O(1)	25(2)	19(2)	7(2)	0	4(2)	0
C(1)	12(2)	17(3)	15(3)	0	-3(2)	0
C(2)	21(2)	17(2)	8(2)	-1(2)	1(1)	-8(2)

Table S4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{CH}_3)_3\text{SOPbI}_3$.

	x	y	z	U(eq)
H(1A)	4170(80)	7500	4870(50)	21(17)
H(1B)	5060(60)	6790(40)	4040(40)	29(14)
H(2A)	1250	6263	4513	23
H(2B)	2070	5503	3666	23
H(2C)	330	6249	3503	23

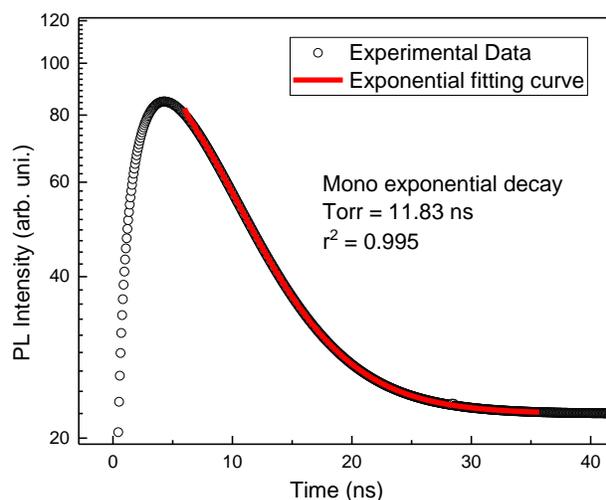


Figure S1. Time-resolved photoluminescence (TRPL) spectra of $(\text{CH}_3)_3\text{SOPbI}_3$. Its PL lifetime of 11.83 ns is comparable to other 1D hybrid organic-inorganic metal halides such as (4-(aminomethyl)pyridinium) PbBr_4 ¹ and $(\text{C}_7\text{H}_{16}\text{N})\text{PbBr}_3$ ² with lifetime of 16.50¹ and 4.3 ns², respectively. Their single crystal nature with less defects leads to a fast decay process for the radiative recombination of excitons.¹

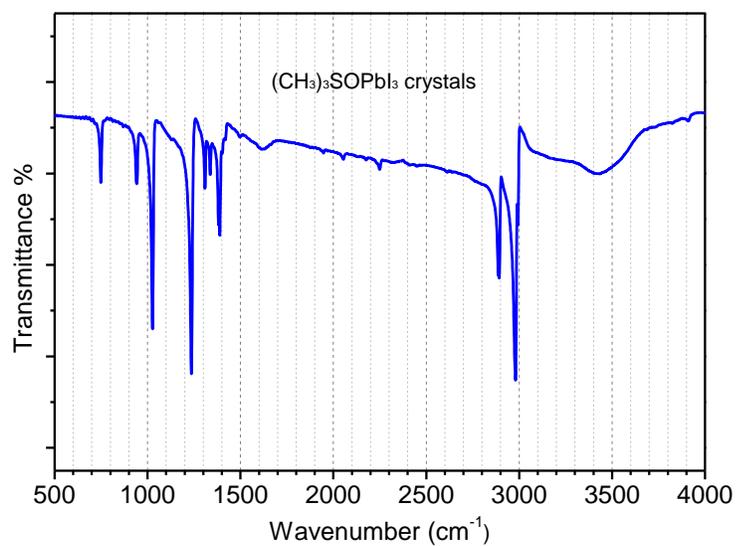


Figure S2. Fourier transform infrared (FTIR) spectrum of the grounded $(\text{CH}_3)_3\text{SOPbI}_3$ crystals in KBr pellet.

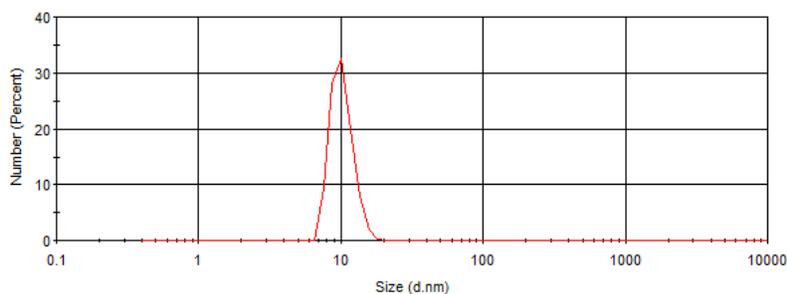


Figure S3. Dynamic light scattering (DLS) measurements of $(\text{CH}_3)_3\text{SOPbI}_3$ crystals.

References

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