

Supporting information

Zero-dimensional ionic antimony halide inorganic-organic hybrid with strong greenish yellow emission

Fang Lin,^a Hao Wang,^a Wei Liu^{*a} and Jing Li^{*b,a}

^a Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, 7098 Liuxian Blvd, Nanshan District, Shenzhen, 518055, China

^b Department of Chemistry and Chemical Biology, Rutgers University, 123 Bevier Road, Piscataway, NJ, 08854, USA

Materials and Characterization

Materials. SbBr₃ (99.9% metals basis) were purchased from Alfa Aesar, 1-carboxymethyl-3-methylimidazolium chloride (98%) were purchased from Merck, acetonitrile (>99%), ethylacetate (EA, AR,99%) were purchased from Aladdin. All reagents and solvents were used without further purification unless otherwise stated.

Synthesis of 1. A mixture of SbBr₃ (0.0361 g, 0.1 mmol), 1-carboxymethyl-3-methylimidazolium chloride (0.0354 g, 0.2 mmol) in acetonitrile (6mL) and ethylacetate (2 mL) was stirred in 20mL glass bottle for 1 hour to form a white precipitate, and then sealed in a Teflon-lined bomb and heated to a temperature of 120°C for 3 days, then cooled slowly to room temperature. Colorless crystals and white polycrystalline powder were slowly precipitated out from the solution.

Sample Washing and Drying. Upon completion of reactions, powder sample of **1** was collected by filtration from the reaction solution and washed with a small amount of acetonitrile for three times. The sample was then dried in a vacuum oven overnight before other measurements were made.

Single crystal X-ray diffraction (SXRD). Single crystal X-ray diffraction data were collected at 225K on a Bruker D8 Venture diffractometer with graphite-monochromated Ga K α radiation ($\lambda = 1.34139 \text{ \AA}$) The structures were solved by direct methods and refined by full-matrix least-squares on F₂ using the Bruker SHELXTL package.¹ These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The structures were deposited in Cambridge Structural Database (CSD) and the number is 1998894.

Powder X-ray diffraction (PXRD). PXRD analyses were carried out on a Bruker D8 Advance automated diffraction system using Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). The data were collected at room temperature in a 2 θ range of 3–50° with a scan speed of 1°/min.

The operating power was 40 kV/40 mA.

Optical diffuse reflectance measurements. Optical diffuse reflectance spectra were measured at room temperature on a Shimadzu UV-3600 spectrophotometer. Data were collected in the wavelength range of 300-1200 nm. BaSO₄ powder was used as a standard (100% reflectance). A similar procedure as previously described was used to collect and convert the data using the Kubelka-Munk function. The scattering coefficient (S) was treated as a constant since the average particle size of the samples used in the measurements was significantly larger than 5 μm.

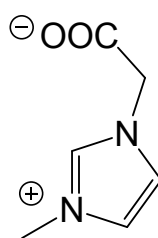
Thermogravimetric (TG) analysis. TG analyses of the title compounds were performed on a computer-controlled TG 550 (TA Instrument). Pure powder samples were loaded into platinum pans and heated with a ramp rate of 10 °C/min from room temperature to 700 °C.

Excitation spectrum measurements. Excitation spectra were measured at room temperature on a FLS1000 spectrofluorometer (Edinburgh Instruments) monitored at maximum of emission spectra.

Photoluminescence measurements. Steady-state photoluminescence spectra were obtained at room temperature and 77 K (liquid nitrogen was used to cool the samples) on a FLS1000 spectrofluorometer.

Internal quantum yield measurements. Internal quantum yield (QY) of samples in powder form was measured on a C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics) with a 150 W xenon monochromatic light source and 3.3 inch integrating sphere.

Time-resolved photoluminescence. Time-Resolved Emission data were collected at room temperature using the FLS1000 spectrofluorometer. The dynamics of emission decay were monitored by using the FLS1000's time-correlated single-photon counting capability (1024 channels; 10 μs window) with data collection for 10,000 counts. Excitation was provided by an Edinburgh EPL-360 picosecond pulsed diode laser. Long lifetime measurements at 77K (1024 channels; 800 μs window) were collected using Xe flash lamp as the excitation source. The lifetime was obtained by mono-exponential fitting.



2-(3-methyl-1*H*-imidazol-3-ium-1-yl)acetate

Figure S1. Structural plot of the organic ligand.

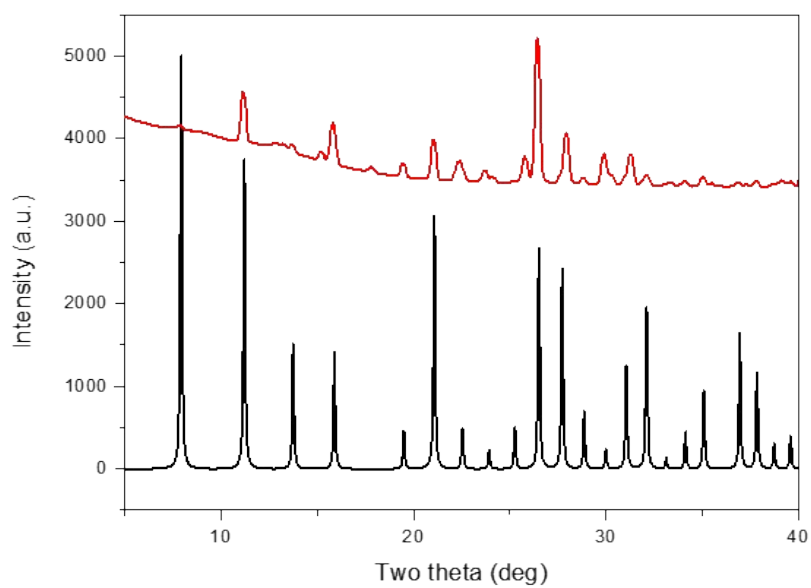


Figure S2. PXRD patterns of as-made (top) and simulated pattern of compound 1 (bottom).

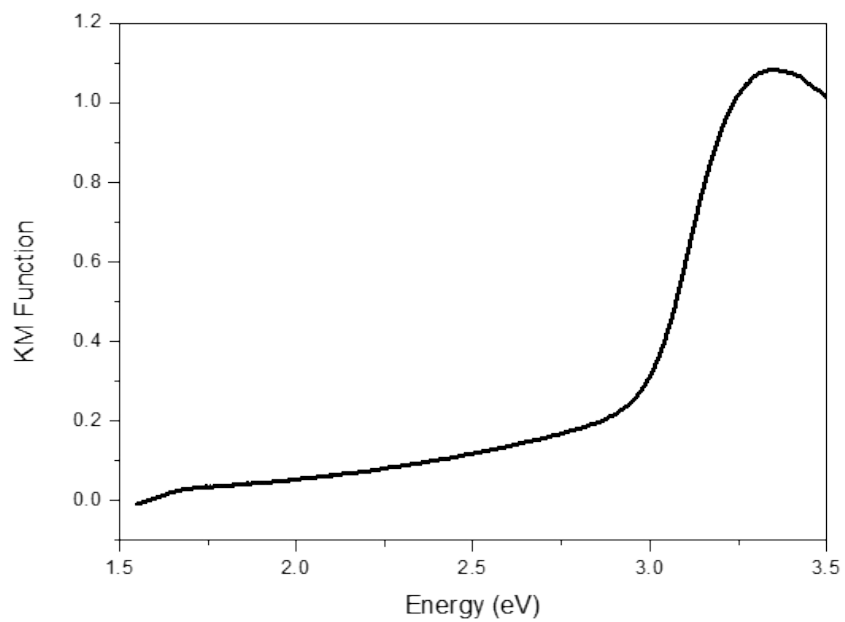


Figure S3. UV plot of compound 1.

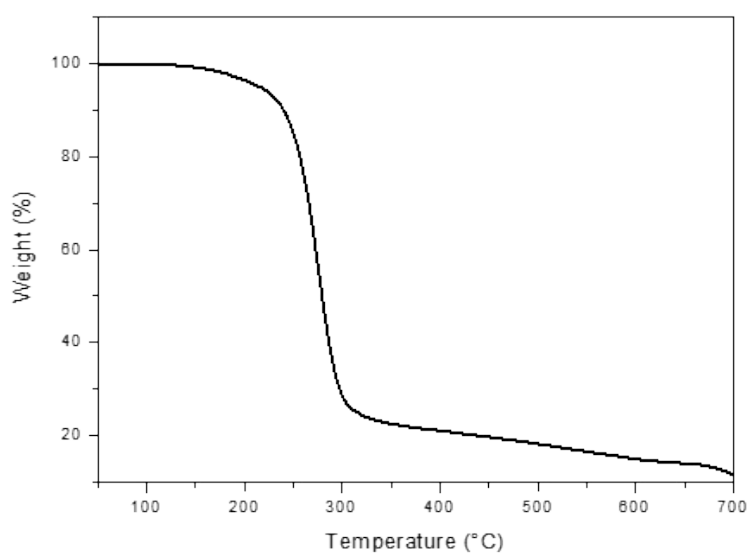


Figure S4. TGA plot of compound **1**.

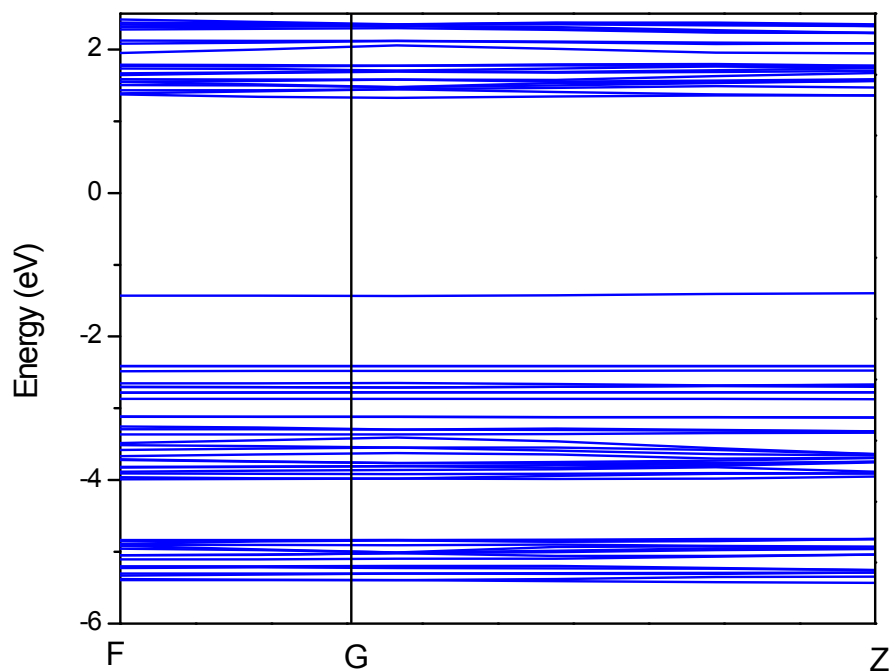


Figure S5. Calculated band structure for **1**.

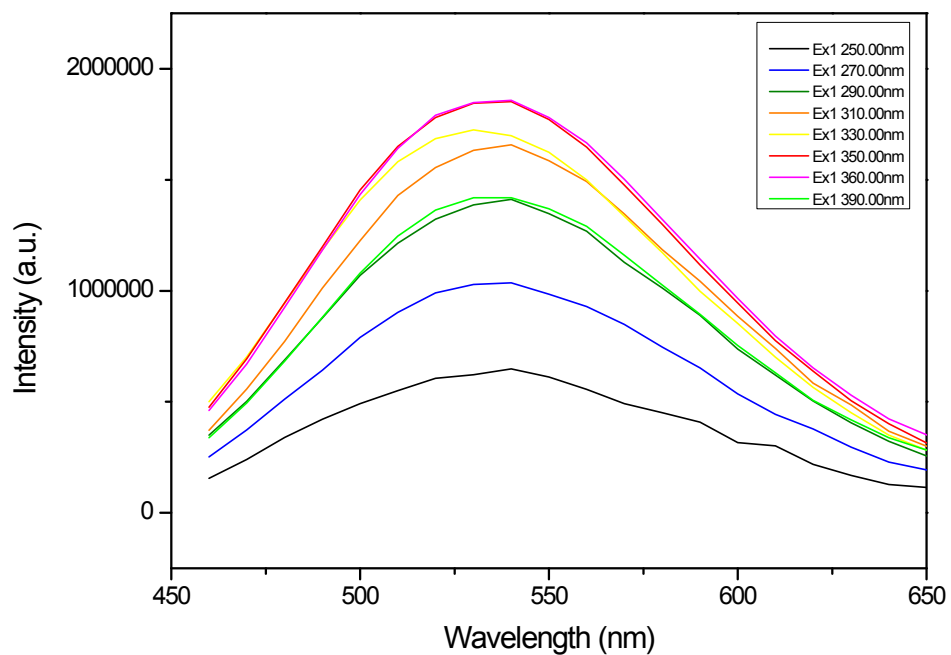


Figure S6. Emission spectra of **1** under various excitation energies.

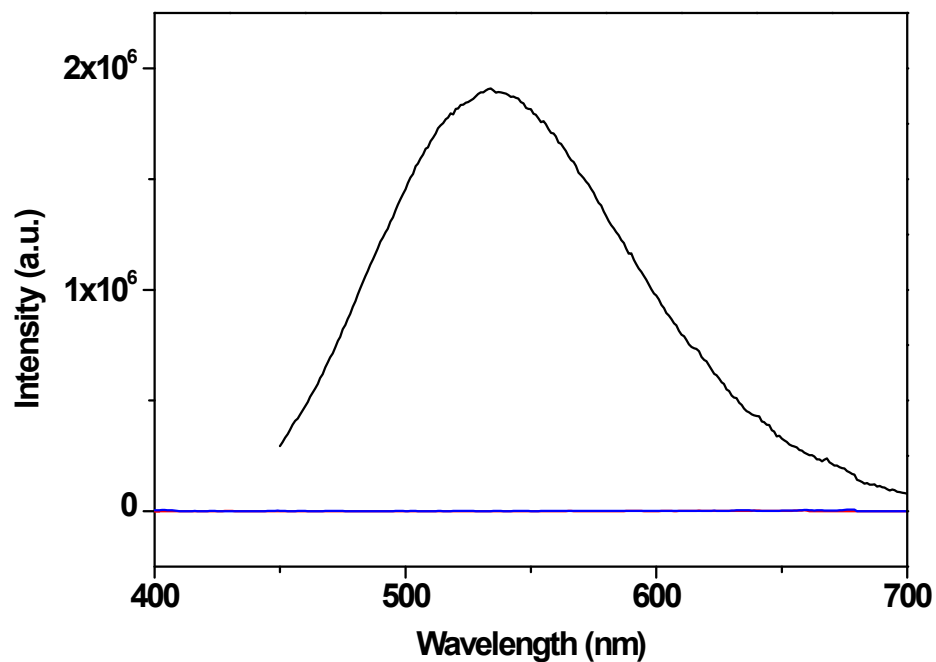


Figure S7. Emission spectra of **1** (black), SbBr_3 (blue), and the organic ligand (red).
 $\lambda_{\text{ex}}=360\text{nm}$.

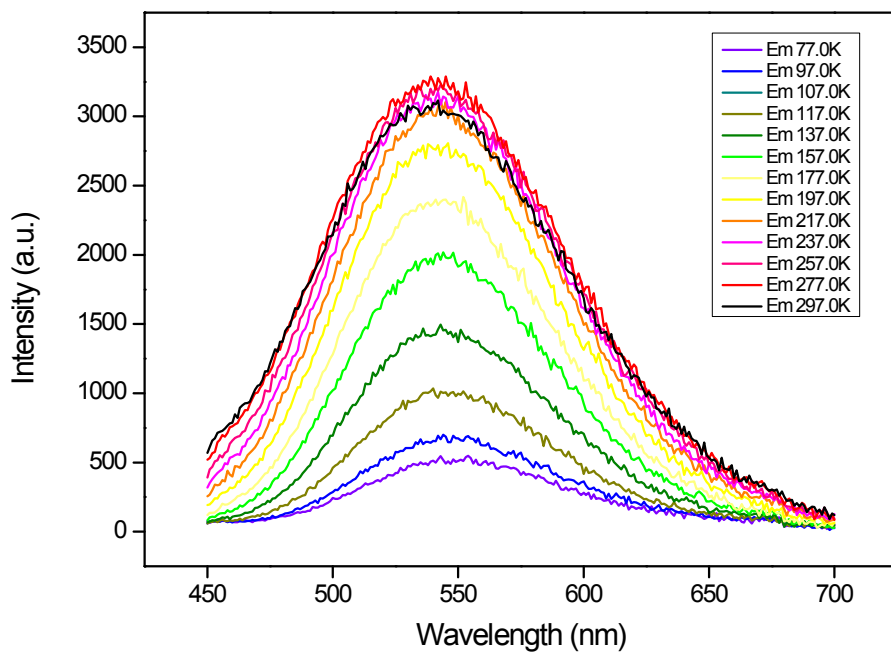


Figure S8. Emission spectra of **1** under various temperatures. $\lambda_{\text{ex}}=360\text{nm}$.

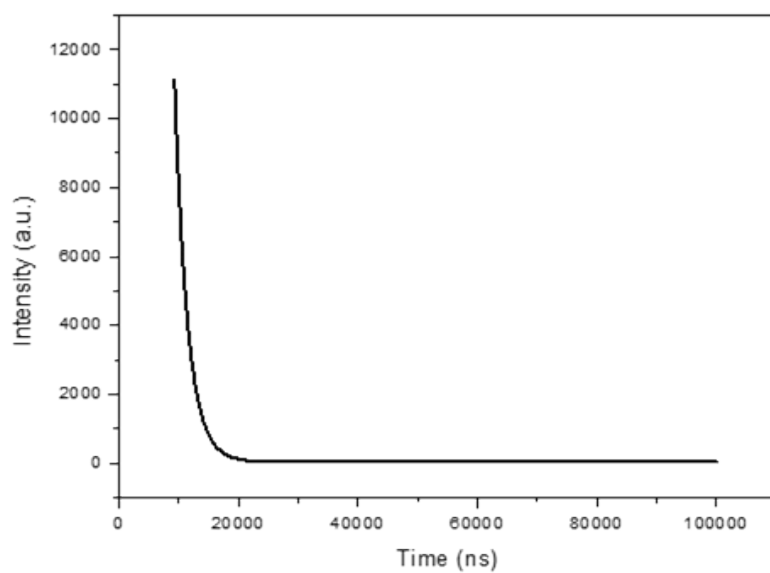


Figure S9. Luminescence decay curve at room temperature of compound **1**.

Table S1. Single crystal X-ray diffraction data of compound **1**

Compound	H ₃ SbBr ₆ (L) ₆
Formula	Br ₆ C ₃₆ H ₅₁ N ₁₂ O ₁₂ Sb
Fw	1445.10
Space Group	<i>R</i> -3
<i>a</i> (Å)	22.2753(9)
<i>b</i> (Å)	22.2753(9)
<i>c</i> (Å)	8.6405(4)
α (°)	90
β (°)	90
γ (°)	120
<i>V</i> (Å ³)	3712.9(3)
<i>Z</i>	3
<i>T</i> (K)	225(2)
λ (Å)	1.34139
ρ (g·cm ⁻³)	1.939
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0540
<i>wR</i> ₂ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.1649
<i>R</i> ₁ ^a (all data)	0.0542
<i>wR</i> ₂ ^a (all data)	0.1650

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

Table S2. Elemental analysis of compound **1**.

Compound		C %	H %	N %
1	Calculated	29.9	3.5	11.6
	Experimental	29.5	3.3	11.5

Table S3. A summary of recent reported luminescent Sb based hybrid structures

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Emission color	IQY(%)
[Bmim] ₂ SbCl ₅ ²	370	583	Yellow	86.5
(C ₉ NH ₂₀) ₂ SbCl ₅ ³	380	590	Orange	98
[4-methylpiperidinium] ₂ SbCl ₅ ⁴	373	--	White	1
(Ph ₄ P) ₂ SbCl ₅ ⁵	365	648	Red	87
[Bzmim] ₃ SbCl ₆ ⁶	365	525	Green	87.5
[Bzmim] ₂ SbCl ₅ ⁶	310	483	Blue	--
	375	600	Red	22.3
(TTA) ₂ SbCl ₅ ⁷	370	625	Red	86
	300	465, 625	White	68
(TEBA) ₂ SbCl ₅ ⁷	360	590	Yellow	98
	300	450, 590	Yellow	72
1	360	530	Greenish yellow	55

References:

1. G. M. Sheldrick, *Acta Crystallogr. C Struct. Chem.*, 2015, **71**, 3-8.
2. Z.-P. Wang, J.-Y. Wang, J.-R. Li, M.-L. Feng, G.-D. Zou and X.-Y. Huang, *Chem. Commun.*, 2015, **51**, 3094-3097.
3. C. Xi, Q. Chengjun, D. Wei, L. Jingwen, M. Xiaoming, Z. Yulu, L. Tao, T. Xiaoma, C. Hongmei and O. Yifang, *J. Phys. D: Appl. Phys.*, 2018, **51**, 405103.
4. A. Khan, A. Zeb, L. Li, W. Zhang, Z. Sun, Y. Wang and J. Luo, *J. Mater. Chem. C*, 2018, **6**, 2801-2805.
5. C. Zhou, M. Worku, J. Neu, H. Lin, Y. Tian, S. Lee, Y. Zhou, D. Han, S. Chen, A. Hao, P. I. Djurovich, T. Siegrist, M.-H. Du and B. Ma, *Chem. Mater.*, 2018, **30**, 2374-2378.
6. Z. Wang, Z. Zhang, L. Tao, N. Shen, B. Hu, L. Gong, J. Li, X. Chen and X. Huang, 2019, **58**, 9974-

9978.

7. Z. Li, Y. Li, P. Liang, T. Zhou, L. Wang and R.-J. Xie, *Chem. Mater.*, 2019, **31**, 9363-9371.