Supporting Information

Manipulating the inorganic motif by kinetic control of organic-inorganic antimony halide for larger Stokes shift and significantly enhanced quantum efficiency

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Materials.

SbCl$_3$ (99.9% metals basis)were purchased from Alfa Aesar,1-carboxymethyl-3-methylimidazolium chloride ([HO$_2$CMMIm]Cl, 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.

Experimental details.

Single crystalSynthesis of compound 1-2.
A mixtureof SbCl$_3$ (0.228 g, 1 mmol), 1-carboxymethyl-3-methylimidazolium chloride ([HO$_2$CMMIm]Cl,0.354 g, 2 mmol) in Acetonitrile (20mL) and Ethylacetate (20mL) was stirred and heated in 100mL round bottom flask fitted with a chilled-water cooled condenser allowing the liquid to condense during the experiment.A flask containing these ingredients was heated to 90°C for 6 hour and colorless crystals of compound **1** slowly precipitated out from the solution on the wall of the flask and the products were separated as soon as they formed. A few hours

later, compound **2** with green emission started to form quickly at the bottom of the flask.Stopped the reaction and cooled slowly to room temperature. To separate the two different phases, crystals **2** were firstly suck out. Crystal sample of **1** were collected by filtration from the reaction solution and washed with a small amount of acetonitrile for three times. These samples were then dried in a vacuum oven overnight before other measurements were made.

Single crystal X-ray diffraction (SXRD). Single crystalsof $H_3(L)_3SbCl_5 \cdot Cl$ were selected and diffraction data were collected at 200K on a Bruker D8 Venture CCDdiffractometer with the use of IµS 3.0 microfocus X-ray Mo Kαradiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ re-quest/cif. The CCDC number of compound **1** is 2190859.

Powder X-ray diffraction (PXRD). PXRD analyses were performed on Bruker D8 Powder X-ray Diffractometer with Advance automated diffraction system using Cu Kα radiation (λ=1.5406 Å) at 40 kV/40 mA. The sample pattern was collected at room temperature in a 2θ range of 5–50° with a step size of 0.01 and the simulated pattern was calculated by Mercury software using the crystallographic information from cif file.

Thermogravimetric (TG) analysis. TG analyse of the compound **1** was measured on a computer-controlled TG 550 system. The powder samplewas loaded into platinum pans andheated with a ramp rate of 10 °C/min from room temperature to 500 °C under a nitrogen flux of 40 mL/min.

Optical diffuse reflectance measurements. Optical diffuse reflectance spectra were carried out at room temperature on a Shimadzu UV-3600 spectrophotometer with $BaSO_4$power as the reflectance reference. Raw data were collected in the wavelength range of 200-800 nm and converted to absorptionvia the Kubelka-Munk function.

Microscope. The microscope images were obtained on Nikon Eclipse Ci-POL microscope with DS-Fi3 camera module under UV(360 nm) LED light source.

Excitation and photoluminescence spectrum measurements. Excitation and Steady-state photoluminescence spectra were obtained from 77K to room temperature using cryostat pattern (by liquid nitrogen) on a Edinburgh Instrument FLS1000 spectrofluorometer.

Internal quantum yield measurements. Internal quantum yields (IQYs) of powder sample was acquired on a FS5 fluorescence spectrometer with 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 FLS100 spectrofluorometer. The dynamics of emission decay were monitored by using the FLS1000's time-correlated single-photon counting capability (1024 channels; 100 µs window) using Xe flash lamp as the excitation source. The average lifetime was obtained by mono-exponential fitting as followed:

$$\tau_{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

where A_1, A_2, A_3 are the pre-exponential factor, and τ_1, τ_2, τ_3 are the lifetimes components, if necessary.

DFT calculation: First-principle calculations of the density of states (DOS) of compounds 1 were carried out using the CASTEP code implemented in the Material studio. Generalized gradient approximations (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional (xc) were used in all calculations. The plane-wave basis set energy cutoff was set at 10.0 eV, ultrasoft pseudopotentials were used for all chemical elements and the total energy tolerance was set to be $1×10^{-5}$ eV/atom.

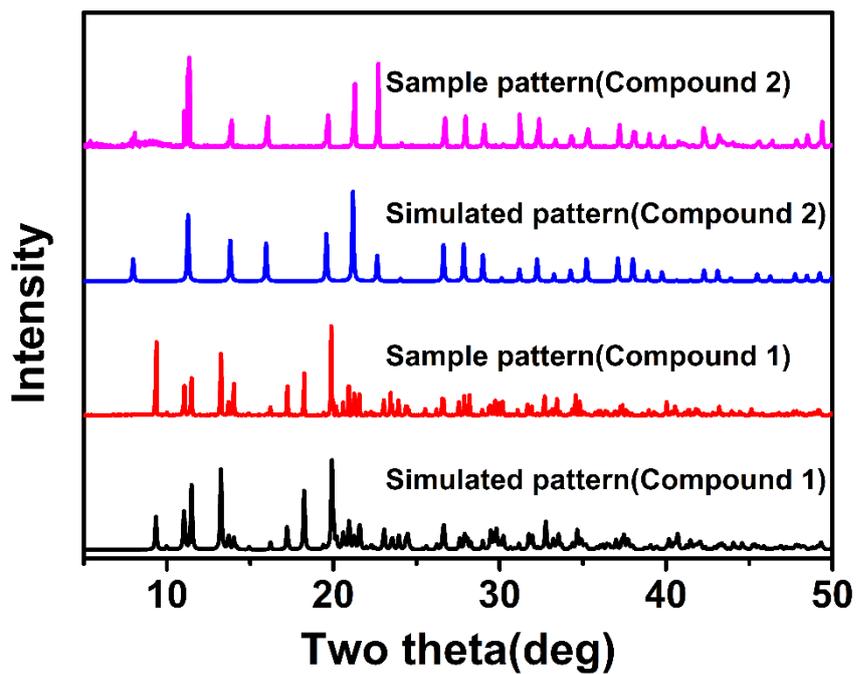**Figure S1.** PXRD patterns of simulated pattern of compound **1** compound **2**.
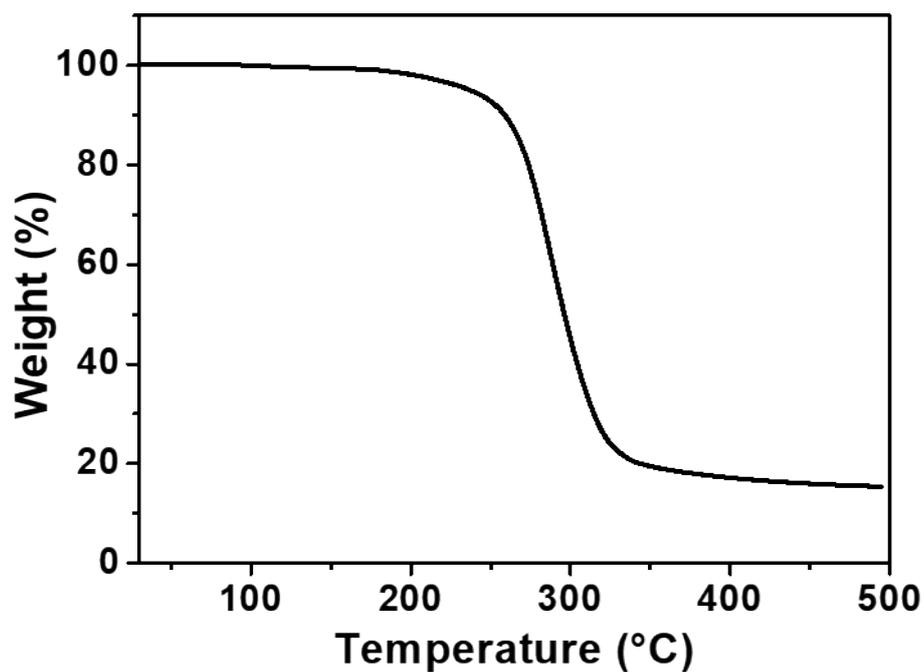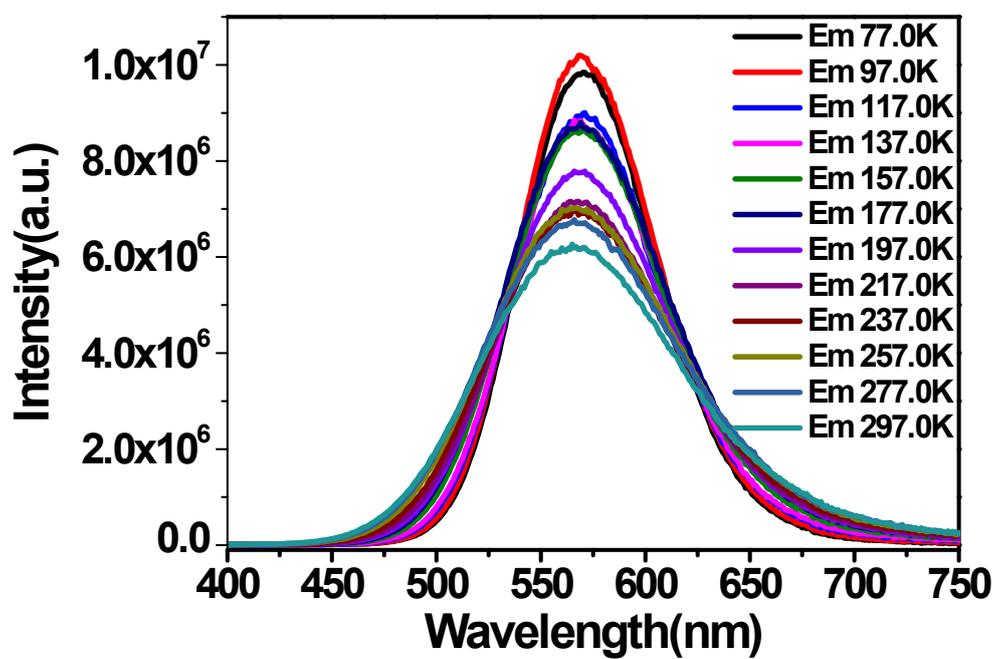

Figure S2. TG plot of compound **1**.

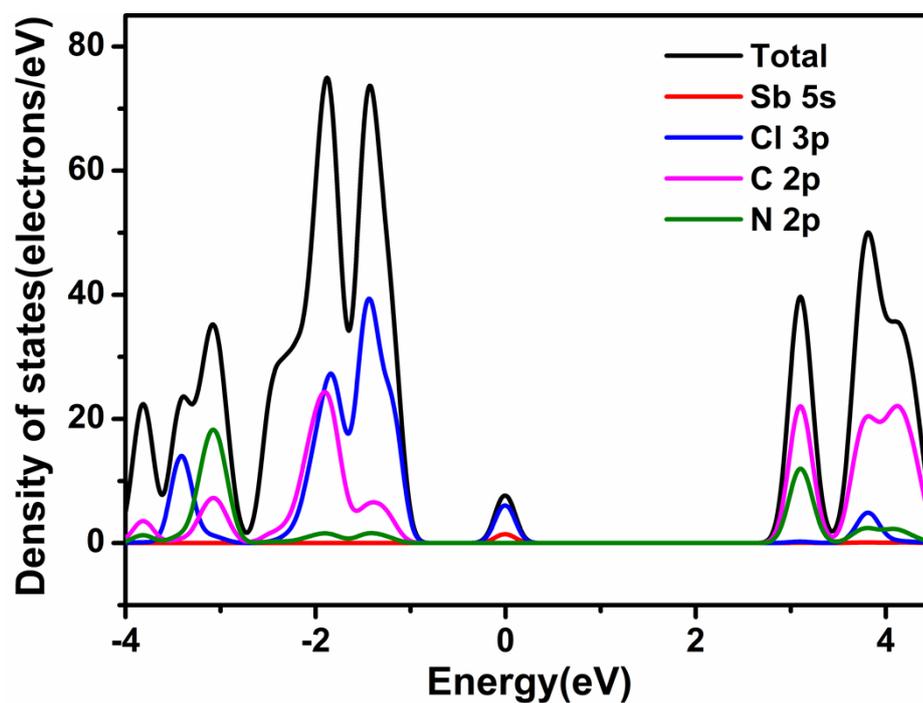**Figure S3.** Temperature-dependent photoluminescence spectra of compound **1** under 340 nm excitation.

Figure S4. Density of states plot of compound **2**.

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

Empirical formula	C18H27N6O6SbCl6
Formula mass	757.92
Space group	P21/c
a/Å	20.8758(6)
b/Å	8.7858(2)
c/Å	17.7065(4)
α/°	90
β/°	114.926(1)
γ/°	90
V/Å³	2945.06(13)
Z	4
λ	0.71073
T/K	200K
$R^{1[a]}$	0.0501
wR^2	0.0948

Table S2. Selected bond angles for compound **1** and **2**.

1				2			
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Sb	Cl2	97.25(3)	Cl1[i]	Sb	Cl1[v]	91.28(2)
Cl1	Sb	Cl3	173.06(3)	Cl1[v]	Sb	Cl1[iii]	88.02(2)
Cl3	Sb	Cl2	83.97(3)	Cl1[ii]	Sb	Cl1[iii]	91.98(2)
Cl4	Sb	Cl1	90.97(3)	Cl1[v]	Sb	Cl1[iv]	88.02(2)
Cl4	Sb	Cl2	171.75(3)	Cl1[i]	Sb	Cl1[iv]	88.02(2)
Cl4	Sb	Cl3	87.78(3)	Cl1[iv]	Sb	Cl1[iii]	91.98(2)
Cl5	Sb	Cl1	85.72(3)	Cl1[v]	Sb	Cl1	91.98(2)
Cl5	Sb	Cl2	89.10(3)	Cl1[iv]	Sb	Cl1[ii]	91.28(2)
Cl5	Sb	Cl5	87.48(3)	Cl1[i]	Sb	Cl1	91.28(2)
				Cl1[ii]	Sb	Cl1	88.02(2)
				Cl1[i]	Sb	Cl1[ii]	88.02(2)
				Cl1[iii]	Sb	Cl1[ii]	88.02(2)

Table S3. Bond lengths for compound **1** and **2**.

	1			2	
Atom	Atom	Length/º	Atom	Atom	Length/º
Sb	Cl1	2.5828(10)	Sb	Cl1	2.6470(6)
Sb	Cl2	2.7334(10)	Sb	Cl1#1	2.6470(6)
Sb	Cl3	2.6612(10)	Sb	Cl1#1	2.6470(5)
Sb	Cl4	2.5444(10)	Sb	Cl1#1	2.6470(6)
Sb	Cl5	2.4029(9)	Sb	Cl1#1	2.6470(6)
			Sb	Cl1#1	2.6470(5)

Symmetry transformations used to generate equivalent atoms: #1 (1-y, x-y, z) ,(1/3+x-y, -1/3+x, 2/3-z) ,(1/3+y, 2/3-x+y, 2/3-z) ,
(4/3-x, 2/3-y, 2/3-z) 2.6471(5) ,(1-x+y, 1-x, z) .

Table S4. Hydrogen bonds for compound **1**.

D–H…A	d(D–H)	d(H…A)	d(D…A)	Angle(DHA)
O(2)–H(2)…Cl(6)	0.84	2.30	3.097(3)	159.0
O(3)–H(3A)…Cl(6)	0.84	2.17	2.997(3)	168.0
C(2)–H(2B)…Cl(2)	0.99	2.09	3.444(4)	115.0
C(3)–H(3)…Cl(2)	0.95	2.73	3.574(4)	148.4
C(16)–H(16)…Cl(2)	0.95	2.85	3.622(4)	139.1
C(8)–H(8A)…Cl(3)	0.99	2.65	3.569(4)	154.0
C(8)–H(8A)…Cl(4)	0.99	2.95	3.620(4)	125.5
C(9)–H(9)…Cl(5)	0.95	2.73	3.544(4)	145.9

Table S5. Hydrogen bonds for compound **2**.

D–H…A	d(D–H)	d(H…A)	d(D…A)	‹(DHA)
C(2)–H(2A)…Cl(1)	0.97	2.85	3.539(2)	128.7
C(3)–H(3)…Cl(1)	0.93	2.98	3.433(2)	111.9
C(3)–H(3)…Cl(1)	0.93	2.78	3.624(2)	151.0