Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Highly efficient self-trapped exciton luminescence of Sb^{3+}-doped $(CH_6N_3)_3BiCl_6$ for ethanol detection

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Experimental methods

Chemicals

Guanidine Hydrochloride (CH_5N_3·HCl, 99%), bismuth chloride ($BiCl_3$), antimong trichlonde ($SbCl_3$), methanol (MeOH, 99.5%) was purchased from Macklin. Hydrochloric acid (HCl, 37 wt% in water) was purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol (EtOH, 99%) was purchased from Nanning Blue Sky Experimental Equipment Co., Ltd. All chemicals were used directly without further purification.

Synthesis

Synthesis of Sb-doped $(CH_6N_3)_3BiCl_6$ bulk single crystals

High quality Sb doped $(CH_6N_3)_3BiCl_6$ bulk single crystals were synthesized by natural room temperature evaporation crystallization. Clear precursor solutions were also obtained by heating and stirring a mixture of CH_6N_3·HCl: [$BiCl_3$+$SbCl_3$]: methanol: HCl = 3.00 mmol: 1.00 mmol: 2.00 mL: 0.1 mL was stirred at 50 ℃ for 20 min. And then the hot clear precursor solution was cooled to room temperature and evaporated in an undisturbed environment. After 24-72 hours, high-quality bulk single crystals slowly grow out without any disturbance.

The preparation of LED lamp base on 20%Sb-doped $(CH_6N_3)_3BiCl_6$ powder

The synthesized microcrystal powder was mixed with UV curable resin, then the mixture was coated on a commercial 365 nm UV GaN LED chip, and cured under UV light to make an LED lamp.

Experimental process of single-crystal resolution

The crystals are tested on a "CCD area detector" diffractometer at 296.15 K. The structure is solved using Olex2. The structural solution program utilizes charge flipping, and refinement is performed with the XL refinement package using least squares minimization.

Characterizations

The crystal structure was characterized by X-ray powder diffraction (XRD, Bruker D8 Discover). The elemental composition and chemical state were identified by X-ray

photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi). The scanning electron microscopy (SEM, Hitachi SU8020) was used to observe the morphology. The photoluminescence (PL), photoluminescence excitation (PLE) spectrum, time-resolved photoluminescence (TRPL), photoluminescence quantum yields (PLQYs), temperature-dependent PL spectra, and temperature-dependent PL decay curve were obtained on the Edinburgh FLS-1000 spectrofluorometer and Horiba Jobin Yvon Fluorolog-3 spectrometer. The Lambda 750 ultraviolet-visible spectrophotometer was used to measure the absorption spectrum. The photoelectric properties of the as-fabricated LED device, including the emission spectra, correlated color temperature (CCT), and Commission Internationale de L'Eclairage (CIE) chromaticity coordinate were obtained on an ATA-1000 (Everfine, China) optoelectronic analyzer.

Computational Methods

All calculations at density functional theory are carried out using the Vienna Ab initio simulation package (VASP)[1] The generalized gradient approximation of the Perdew–Burke–Ernzerhof (PBE)[2, 3] parameterization with projector-augmented wave[4] method are performed for the exchange and correlation functional. The kinetic-energy cutoff of 450 eV and a 2×1×2 Monkhorst–Pack k-mesh for the wavefunction basis set is employed. For the elements C, H, N, Bi, Sb and Cl, ultra-soft pseudopotentials are used. The energy convergence criterion is set as 1.0×10^{-5} eV for structural relaxations.

Table S1. Bond length and bond angles of $(CH_6N_3)_3BiCl_6$ Single-crystal.

Atom-atom	Bi-Cl1	Bi-Cl2	Bi-Cl3	Bi-Cl4	Bi-Cl5	Bi-Cl6
Length/Å	2.724	2.643	2.792	2.669	2.769	2.626
Atom-atom-atom	Cl1-Bi-Cl2	Cl1-Bi-Cl3	Cl1-Bi-Cl5	Cl1-Bi-Cl6	Cl2-Bi-Cl3	Cl2-Bi-Cl4
Angle/°	87.78	88.11	91.03	93.17	89.81	92.44
Atom-atom-atom	Cl2-Bi-Cl6	Cl3-Bi-Cl4	Cl3-Bi-Cl5	Cl4-Bi-Cl5	Cl6-Bi-Cl4	Cl5-Bi-Cl6
Angle/°	88.64	89.77	88.78	88.71	88.95	92.80

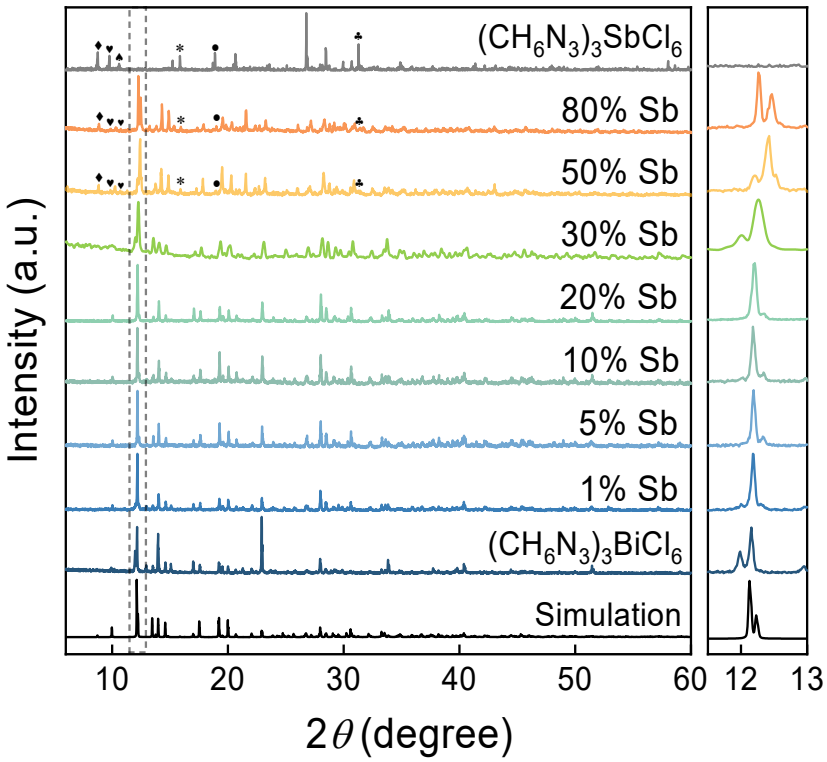

Fig. S1 PXRD patterns of Sb^{3+}:$(CH_6N_3)_3BiCl_6$ with different Sb-feeding concentration.

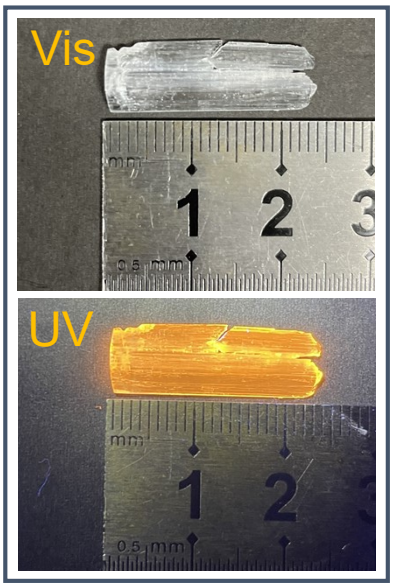

Fig. S2 Photograph of 5%Sb^{3+}: $(CH_6N_3)_3BiCl_6$ crystal under daylight and 365-nm UV lamp.

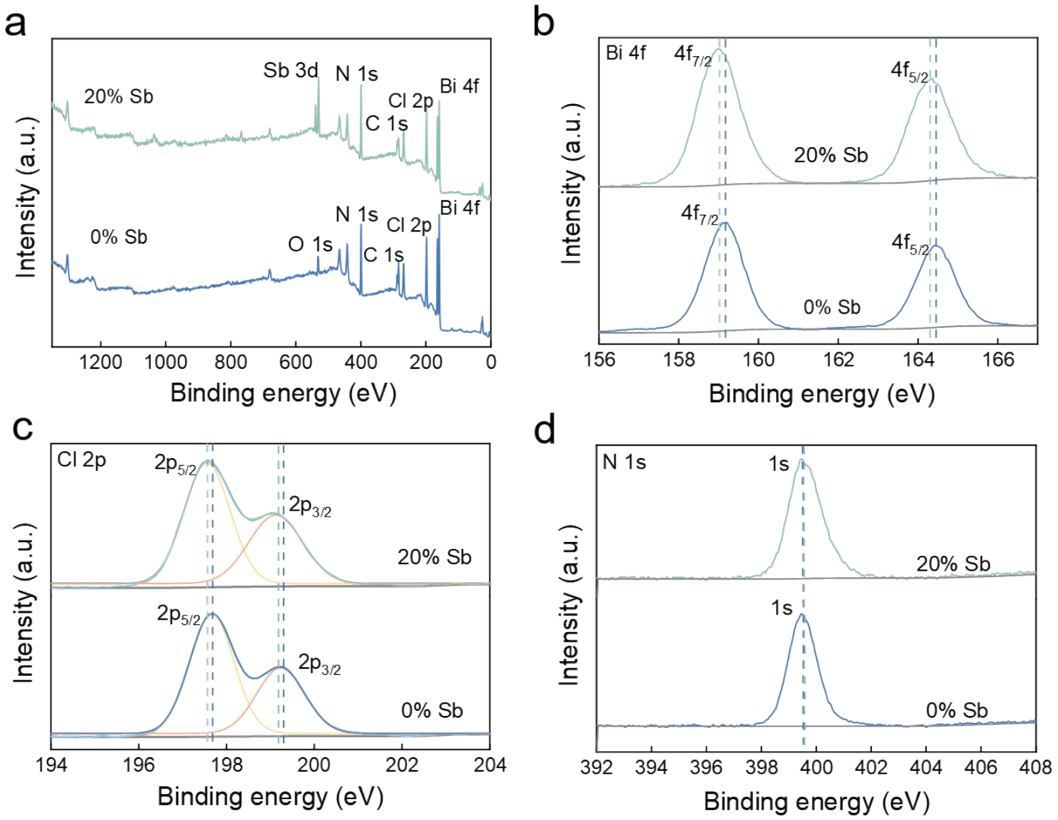

Fig. S3 (a)Total XPS spectra of pristine $(CH_6N_3)_3BiCl_6$ and 20%Sb^{3+}:$(CH_6N_3)_3BiCl_6$. High-resolution XPS spectra and peak fitting for (b) Bi, (c) Cl, and (d) N of pristine $(CH_6N_3)_3BiCl_6$ and 20%Sb^{3+}:$(CH_6N_3)_3BiCl_6$, respectively.

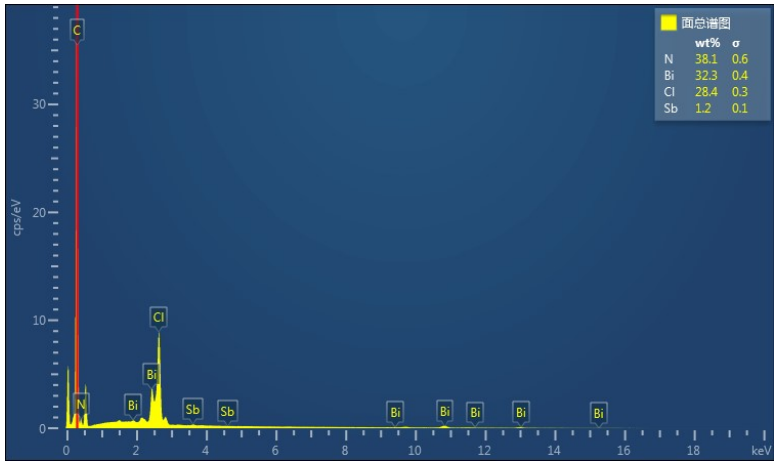

Fig.S4 The energy disperse spectra of 10%Sb^{3+}:$(CH_6N_3)_3BiCl_6$.

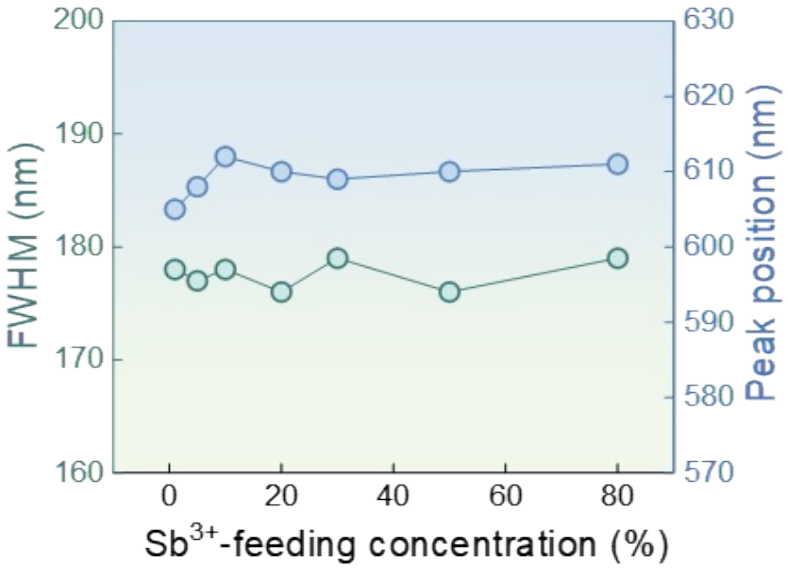

Fig. S5 FWHM and peak position of Sb^{3+}:$(CH_6N_3)_3BiCl_6$ with different Sb-feeding concentration.

Table S1. Summary of the space group, PLQY and bandgap of Bi-based HMHs.

Materials	PLQY	Space group	Ref.
Eu^{3+}: $Cs_3Bi_2Br_9$	42.4%	*P*3*m*1	5
Cs_3BiI_6	1.57%	$P6_3/mmc$	6
Mn^{2+}: $Cs_2NaBiCl_6$	15%	*Fm*3*m*	7
Al^{3+}: $Cs_2AgBiCl_6$	17.2%	*Fm*3*m*	8
$Rb_7Bi_3Cl_{16}$	28%	*P*-31*c*	9
$MA_3Bi_2Br_9$	12%	*P*3*m*1	10
$(PMA)_3BiBr_6$	<1%	$P2_1/c$	11
Sb^{3+}: $(C_8NH_{12})_4BiBr_7 \cdot H_2O$	0.45%	*P*1	12
Sb^{3+}: $(TMEDA)_3Bi_2Cl_{12} \cdot H_2O$	38%	$P2_1/n$	13
Sb^{3+}: $(CH_6N_3)_3BiCl_6$	53.27%	$P2_1/n$	this work

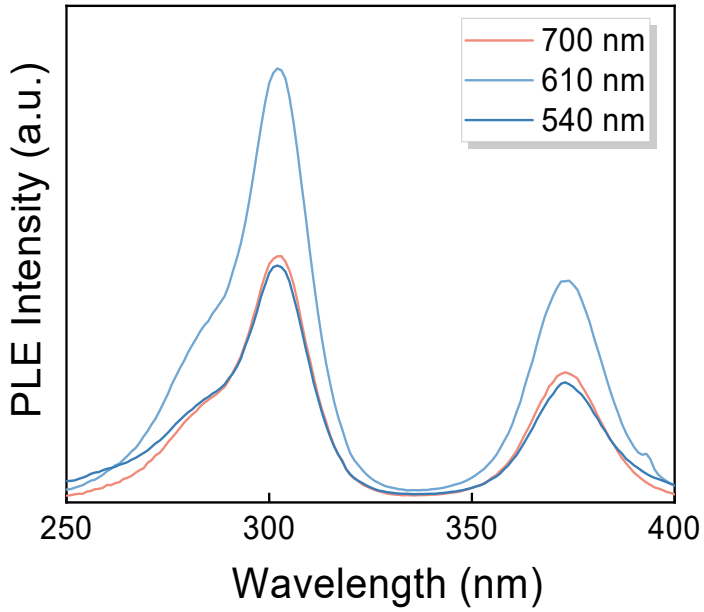

Fig. S6 PL excitation (PLE) (λ_{em}=540 nm, 610 nm, 700 nm) spectra of 20%Sb^{3+}:$(CH_6N_3)_3BiCl_6$.

Table S2. The PL lifetime fitting results of x%Sb^{3+}:$(CH_6N_3)_3BiCl_6$.

x%Sb	A1(%)	τ1(*μ*s)	A2(%)	τ2(*μ*s)	τ_{ave}(*μ*s)
1	96.11	3.76	3.89	15.95	5.54
5	97.29	3.37	2.71	21.31	5.72
10	97.25	3.96	2.75	20.38	6.05
20	95.48	3.34	4.52	20.51	7.23
30	93.17	3.42	6.83	11.57	5.03
50	92.96	2.77	7.04	11.91	5.02
80	85.82	2.35	14.18	8.72	4.78

Table S3. Temperature-dependent PL lifetime fitting results of Sb^{3+}:$(CH_6N_3)_3BiCl_6$.

Temperature (K)	A	τ(*μ*s)
100	0.28	4.26
140	0.35	4.02
180	0.46	3.69
220	0.49	3.26
260	0.41	2.99
300	0.35	2.57
320	0.25	1.77
380	0.15	0.97

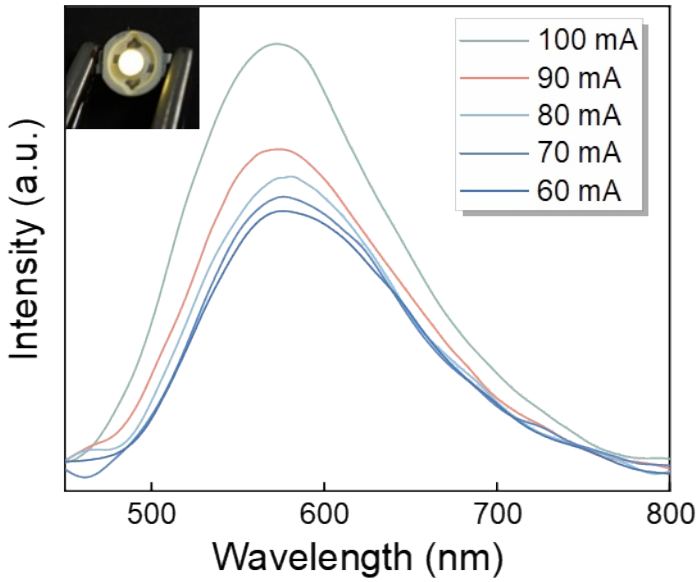

Fig. S7 The PL spectra of LED were driven at different currents. Inset: working photos of this device.

Notes and references

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