(C₁₆H₂₈N)₂SbCl₅: A new lead-free zero-dimensional metal-halide hybrid with bright orange emission

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ABSTRACT Zero-dimensional (0D) metal halides are in a blossoming status for their fascinating optoelectronic properties. Herein, an antimony-based metal halide of (C₁₆H₂₈N)₂SbCl₅ (C₁₆H₂₈N⁺ = benzyltripropylammonium cations), where the isolated [SbCl₅]²⁻ clusters are surrounded by C₁₆H₂₈N⁺ to form a 0D square-pyramidal structure, was synthesized and investigated. The (C₁₆H₂₈N)₂SbCl₅ exhibited a broadband orange emission at 633 nm upon the low-energy irradiation (400 nm) with a near-unity photoluminescence quantum efficiency (97.8%). Interestingly, (C₁₆H₂₈N)₂SbCl₅ showed an additional emission peak at 477 nm upon the higher-energy irradiation (300 nm), which is attributed to the transformation of the doublet of spin-orbit couplings into two independent self-trapped excitons (STEs). Temperature-dependent Raman spectra clearly revealed the characteristics of multi-phonon coupling, demonstrating a strong anharmonic electron-phonon interaction in (C₁₆H₂₈N)₂SbCl₅. Temperature-dependent emission spectra and density functional theory results illustrated that the observed dual-band emission originated from singlet and triplet STEs in [SbCl₅]²⁻ units. Combined with the efficient emission and excellent stability of (C₁₆H₂₈N)₂SbCl₅, a stable white-light-emitting diode with an ultra-high color rendering index of 96.6 was fabricated.

Keywords: lead-free, 0D metal halides, photophysical mechanism, antimony halide, white-light-emitting diode

INTRODUCTION

Lead halide perovskites (LHPs) have captured tremendous attention in photoelectric devices due to their fascinating properties [1–3]. It is well known that low-dimensional metal halides possess a strong quantum confinement effect and excellent photophysical properties (such as broadband emission and large Stokes shift), in comparison with three-dimensional (3D) LHPs of CsPbBr₃ and CH₃NH₃PbBr₃, thus showing unique advantages in the solid-state lighting (SSL) field [4–6]. Generally, low-dimensional metal halides can be classified into 2D, 1D, and 0D frameworks at the molecular level, on the basis of

the connection mode of BX₆⁴⁻ octahedron [7–9]. Among low-dimensional metal halides, 0D ones are unique and different, in which the independent metal-halide anion clusters are completely isolated by alkaline metal or large organic amine cations to form a typical single-crystalline “host-guest” structure [10,11]. Therefore, the 0D metal halides possess the lowest dimensionality, softest lattice, strongest local quantum confinement, and strongest electron-phonon interaction, enabling highly efficient emission [12].

Plenty of 0D lead-based metal halides have recently been developed, which show excellent photophysical properties. However, because lead is known to be toxic and environmentally unfriendly, 0D lead-free metal halides have become a hot material. Obviously, the main group elements of Sn²⁺, Ge²⁺, Bi³⁺, and Sb³⁺ with *ns*² lone pairs are excellent candidates to replace Pb²⁺ as new optically active centers [13,14]. Previous reports found that the metal ions of Sn²⁺ and Ge²⁺ are easily oxidized in the atmosphere, and the active center of Bi³⁺ has low luminous efficiency, while antimony-based metal halides exhibit high luminous efficiency and excellent air stability. Up to now, there have been some reports on 0D organic antimony chloride hybrids, including [Bzmim]₃SbCl₆ (photoluminescence quantum efficiency (PLQE) ~87.5%, green emission) [15], H₃SbBr₆(L)₆ (PLQE ~55%, green-yellow emission) [16], [DMPZ]₂SbCl₆·Cl·(H₂O)₂ (PLQE ~75.94%, yellow emission) [17], (TPA)₂SbCl₅ (PLQE ~95.3%, orange emission) [18], (Ph₄P)₂SbCl₅ (PLQE ~87.5%, red emission) [19]. Further, compared with Pb²⁺-based compounds, there are relatively few studies on organic antimony halide hybrids, and the relationship between their structures and properties is not fully understood, which greatly hinders the development of Sb³⁺-based metal halides in the future.

Here, we designed a new 0D structure of (C₁₆H₂₈N)₂SbCl₅ by inserting C₁₆H₂₈N⁺ cations into the SbCl₃ lattice. Surprisingly, the as-synthesized (C₁₆H₂₈N)₂SbCl₅ system gave bright orange dual-emission bands at 477 and 633 nm with a near-unity PLQE (97.8%). Based on our experimental data and density functional theory (DFT) computations, the observed dual-emission bands can be ascribed to the radiative transitions from both singlet and triplet self-trapped excitons (STEs). More importantly, this compound possessed excellent chemical and thermal stabilities,

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which are desirable properties for down-conversion phosphors in the SSL.

EXPERIMENTAL SECTION

Materials

Benzyltripropylammonium chloride ($C_{16}H_{28}NCl$, 96%, Inno-Chem), ethyl ether (99.5%, Macklin), antimonous chloride ($SbCl_3$, 99%, Aladdin), and N,N -dimethylformamide (DMF, 99.5%, Aladdin) were purchased and used without further purification.

Synthesis of $(C_{16}H_{28}N)_2SbCl_5$ single crystals (SCs)

$SbCl_3$ (0.2281 g) and $C_{16}H_{28}NCl$ (0.5397 g) were fully dissolved in DMF at room temperature (RT) to form a transparent solution. $(C_{16}H_{28}N)_2SbCl_5$ SCs were prepared by diffusing ethyl ether into DMF solution at RT overnight, and then the obtained SCs were washed with ethyl ether and dried under reduced pressure.

Characterization

The crystal structure information of the sample was investigated on SMART APEX II X-ray single-crystal diffractometer. The powder X-ray diffraction (PXRD) pattern was recorded by the Bruker Advance D8 diffractometer. The emission and excitation spectra were collected by the FLS980 instrument. The absorption spectrum was acquired using the LAMBDA 1050 spectrophotometer. Decay lifetimes and PLQE were obtained by Edinburgh Instruments of FLS980. Time-resolved PL data were collected by the FLS980 instrument, excited by a 300-nm laser. Temperature-dependent PL spectra were obtained by Horiba, with the excitation wavelength at 300 nm. The Raman spectra were measured by the LabRAM HR Evolution instrument. The morphology was obtained and studied *via* scanning electron microscopy (Zeiss SUPRA 40VP device). The element composition and distribution were clarified by energy-dispersive spectrometry (EDS, Oxford). Thermal stability was evaluated by the STA449F3 instrument at a heating rate of 20 K min^{-1} .

Calculation methods

The first-principles electronic structure of $(C_{16}H_{28}N)_2SbCl_5$ was examined at the level of DFT with 500 eV basis set using the VASP code. To reach the equilibrium structure, the fractional atomic coordinates were totally relaxed until Hellman-Feynman force was <0.01 eV $\text{\AA}^{-1}$. The band structure and density of states (DOS) results were obtained by Perdew-Burke-Ernzerhof (PBE) function with Grimme D3 correction. The kinetic energy cutoff was 600 eV, and the Monkhorst-Pack grid of $4 \times 4 \times 3$ in the Brillouin zone was selected.

RESULTS AND DISCUSSION

The crystal structure of $(C_{16}H_{28}N)_2SbCl_5$ was characterized by single-crystal XRD (SCXRD), and the results are depicted in Fig. 1a, b. Each Sb atom was coordinated with five Cl atoms to form a $[SbCl_5]^{2-}$ square-pyramidal structure. Moreover, all $[SbCl_5]^{2-}$ units were encircled by the insulating $C_{16}H_{28}N^+$ cations (Fig. 1c), constituting a typical ionic 0D framework. $(C_{16}H_{28}N)_2SbCl_5$ was crystallized in the triclinic space group of $P\bar{1}$, and the corresponding cell parameters are $a = 9.1202$ $\text{\AA}$, $b = 11.9498$ $\text{\AA}$, $c = 17.9040$ $\text{\AA}$, and $V = 1817.66$ $\text{\AA}^3$. The shortest distance between two adjacent Sb atoms in this compound is

Figure 1 (a) Crystal structure of $(C_{16}H_{28}N)_2SbCl_5$ (orange sphere: antimony; green sphere: chlorine; gray sphere, nitrogen; wine sphere, carbon). (b) Ball-and-stick model of $[SbCl_5]^{2-}$ cluster. (c) Organic cation of $C_{16}H_{28}N^+$.

9.12 $\text{\AA}$, which denotes the absence of interaction between adjacent $[SbCl_5]^{2-}$ anions. The distance of Sb–Cl ranges from 2.3721(3) to 2.6223(3) $\text{\AA}$, and the angle around the Sb changes from 84.679(12) $^\circ$ to 175.928(11) $^\circ$; more crystallographic data are listed in Tables S1–S4. Then, we quantitatively evaluated the size of asymmetric coordination environment (σ^2) of the Sb^{3+} center using the following equation:

$$\sigma^2 = \frac{1}{7} \sum_{i=1}^8 (\alpha_i - 90^\circ)^2, \quad (1)$$

where α_i represents the angle of Cl–Sb–Cl in $(C_{16}H_{28}N)_2SbCl_5$. The calculated value of σ^2 is 6.45, which is larger than those of $(TTA)_2SbCl_5$ ($\sigma^2 = 4.98$, TTA = tetraethylammonium) [20] and $(TMA)_2SbCl_5 \cdot DMF$ ($\sigma^2 = 5.3$, TMA = trimethylamine) [21] in previous reports, illustrating that the lone pair in $(C_{16}H_{28}N)_2SbCl_5$ has higher chemical activity, and further ensures that this compound has strong exciton radiation recombination and high PLQE. Subsequently, the phase purity of $(C_{16}H_{28}N)_2SbCl_5$ was verified by PXRD patterns (Fig. S1), which showed similar characteristics as the calculated SCXRD results. The chemical compositions of this compound were characterized by EDS, and the results are given in Fig. S2b. The molar ratio of Cl:Sb is 82.9:17.1, which is consistent with the stoichiometry from the SCXRD result. The element mapping result indicates that the distribution of Sb and Cl elements is relatively uniform in $(C_{16}H_{28}N)_2SbCl_5$ SC.

The optical properties of $(C_{16}H_{28}N)_2SbCl_5$ SCs were characterized at RT, and the results are presented in Fig. 2. In Fig. 2a, this compound exhibits a broad low-energy (LE) emission band at 633 nm with the wide full width at half maxima (FWHM) of 143 nm upon the 400 nm irradiation. In addition, a large Stokes shift (268 nm, 1.44 eV) was observed, which reveals a negligible self-absorption in $(C_{16}H_{28}N)_2SbCl_5$. Interestingly, $(C_{16}H_{28}N)_2$

Figure 2 (a) Excitation and emission spectra of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ SCs at RT. Inset: a photograph of this compound under 365 nm UV light. (b) Absorption spectrum of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ at RT, and corresponding Tauc plot of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$. PL decay lifetimes of the HE (c) and LE (d) emission bands of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$.

SbCl_5 exhibited a dual-emission band; an additional high-energy (HE) emission at 477 nm under the 300 nm irradiation. The inset shows the optical image of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ SCs under the 365 nm ultraviolet (UV) light. The $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ SCs emitted intense orange light with PLQE of 97.8% (Fig. S3). Such a high PLQE and the negligible self-absorption illustrate that this compound is suitable for SSL. The PLE spectra of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ SCs are also depicted in Fig. 2a, in which the broad PLE band probed at 633 nm, and a sharp PLE band probed at 477 nm can be observed. The distinct difference of the PLE profile suggests that the dual-emission bands for this compound originate from different excited states. Fig. S4a demonstrates the normalized wavelength-dependent emission profiles, indicating the obvious excitation-dependent emission characteristic. The Commission Internationale de l'Eclairage (CIE) color coordinates of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ were calculated according to the emission spectra, which changed from (0.45, 0.35) to (0.58, 0.41) under excitation from 300 to 400 nm (Fig. S5). Moreover, we also measured the emission spectrum of $\text{C}_{16}\text{H}_{28}\text{NCl}$. As illustrated in Fig. S6, no PL signal was detected, which excludes the effect of organic ligands on the emission performance of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$. The absorption spectrum of powdered $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ is given in Fig. 2b, from which one can see two consecutive absorption bands peaked at 324 and 356 nm, respectively. Further, the band-gap was also calculated to be 3.31 eV by the Tauc's function (Fig. 2b, inset). The decay lifetime of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ was assessed at RT under 300 nm laser excitation. As depicted in Fig. 2c, d, the decay curves can be fitted by a monoexponential function, which illustrates that the observed HE and LE emission bands possessed a single-exciton radiation characteristic without non-radiative recombination defects [22]. The lifetime of the HE emission band is 7.44 ns, while that of the LE emission band is 4.71 μs . The obvious

contrast between these two lifetimes suggests their different emission natures. Generally, the Sb^{3+} -based metal halide with ns^2 electronic configuration has a lone pair, which plays an important role in the stereochemical activity, and the observed broadband emission stems from the STE emission caused by excited-state structural reorganization [20]. According to previous reports of Sb-based metal halides or Sb-doped lead-free metal halides, the recombination time of singlet STE is faster than that of the triplet STE for their transition rules [20,23]. Thus, the observed fast decay time of the HE band and the slow decay time of the broad LE band can be ascribed to the radiative recombination from singlet and triplet STEs, respectively. Subsequently, we measured the power-dependent emission spectra of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$, excited by a 405-nm laser (Fig. S7). The LE emission intensity showed a linear dependence on the excitation powers, which illustrates that the observed LE emission is intrinsic emission [24,25]. The PLE spectra of this compound were also measured in the emission wavelength region of 590–650 nm (Fig. S4b), which had similar characteristics, indicating that the LE emission is derived from the same excited state. Therefore, the broad LE band at 633 nm should be attributed to the triplet STE emission.

The electronic properties of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ were examined, and the band structures and DOS were calculated through DFT calculations. As represented in Fig. 3a, $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ possesses a direct band-gap of 3.19 eV, lower than the experimental value of 3.31 eV. Such a difference between DFT-derived and experimental band-gap values can be attributed to the fact that the DFT calculations may underestimate the band-gap of semiconductors [26]. The calculated DOS of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ is given in Fig. 3b. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are dominated by flat bands, which indicates a strong quantum

Figure 3 (a) Band structures and (b) DOS of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$.

confinement effect. This result also illustrates exceedingly weak electronic interactions among $[\text{SbCl}_5]^{2-}$ clusters, which coincides with the large Sb–Sb distance (9.12 Å) [27]. Thus, the near-unity PLQE of this compound can be ascribed to the negligible self-absorption, free of non-radiative recombination defect and a strong exciton confinement effect in the 0D framework [28]. In addition, the LUMO of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ mainly consists of Sb-p and Cl-p states, while the HOMO is mostly composed of Sb-s and Cl-p contributions. These results confirm that the organic ligand in the lattice plays a negligible role in the HOMO and LUMO, and the organic cations have a minor contribution to the photophysical properties of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$. Consequently, the observed dual-emission band is mainly derived from isolated inorganic $[\text{SbCl}_5]^{2-}$ clusters.

To get a deeper insight into the dual-emission mechanism of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ SCs, the temperature-dependent PL spectra (80–360 K) were measured from 80 to 360 K under the 300 nm irradiation. As shown in Fig. 4a, there are always two emission bands at each temperature, and the emission intensity increases gradually from 360 to 80 K because of the prohibition of non-radiative recombination [5]. Fig. 4b depicts the PL/temperature correlation maps of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ SCs, whereas the PL peak position *versus* temperature is shown in Fig. 4c. The HE emission band position is insensitive to temperature, and its emission peak position is maintained at 541 nm at any temperatures, which indicates its definite composition. However, the LE emission band position showed a consecutive blue shift at higher temperatures. Generally, in band-to-band radiative transition semiconductors, the band-gap shrinkage due to the enhancement of electron-phonon interaction occurs at higher temperatures, and hence the PL peak position will shift to a long wavelength direction with the increase of temperature [29,30]. For the hot-materials of 3D LHPs, the PL peak position undergoes a distinct blue shift with the rise of temperature, which can be assigned to the acoustic phonon-exciton interaction and lattice expansion [31]. Therefore, the un-shifted HE peak position in the temperature window studied here means that the above two interactions are balanced or counteracted [6]. For the LE peak position, the blue-shifted emission band position at higher temperature can be dominantly due to the latter reason discussed above, and a similar phenomenon was observed in $(\text{MA})_4\text{Cu}_2\text{Br}_6$ (MA = methylamine) SCs [32]. The FWHM of the two emission bands became narrower as temperature decreases (Fig. S8), which illustrates that the electronic interactions with phonons were reduced. Moreover, the maximum PL intensity of the HE (I_{HE}) emission band increased faster than that of the LE (I_{LE}) emission band as temperature

decreases, whereas the $I_{\text{HE}}/I_{\text{LE}}$ ratio increases gradually as temperature decreases (Fig. S9).

It is well known that the Huang-Rhys factor (S) is closely related to the electron-phonon coupling strength and can be calculated using the following formula [33]:

$$\text{FWHM} = 2.36\sqrt{S}\hbar\omega_{\text{phonon}}\sqrt{\coth\frac{\hbar\omega_{\text{phonon}}}{2k_{\text{B}}T}}, \quad (2)$$

where $\hbar\omega_{\text{phonon}}$ is the frequency of the longitudinal optical phonon, k_{B} is the Boltzmann constant, and T is the temperature. Based on the fitting results in Fig. 4d, the S is 26.1. Obviously, the obtained value of S is far greater than those of many common emitters and is comparable to some lead-free metal halides reported previously (Table S5). This indicates a strong electron-phonon interaction in this compound that is conducive to the formation of STEs in $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ [34].

Raman spectra were measured at 80 and 300 K to understand the effect of electron-phonon coupling on the formation mechanism of the STEs in $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$. In Fig. 4e, the whole vibration intensity of phonon modes of Cl–Sb–Cl exhibited a significant increase at high temperatures, indicating a stronger electron-phonon interaction at high temperatures. Furthermore, the Raman wavenumber shifted to a lower energy direction when the temperature increased from 80 to 300 K, which can be attributed to the lattice expansion, as has been observed similarly in CsPbBr_3 [35] and other lead-free metal halides [9,11]. Moreover, the profiles of all Raman spectra are similar to each other as temperature varies, illustrating unchanged structure and symmetry of $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ at these two temperatures. The Raman mode with wavenumber lower than 100 cm^{-1} is intramolecular liberation, and that at 102 cm^{-1} is the intramolecular translation, while those at 163 and 336 cm^{-1} are the $\nu_2(\text{A}_g)$ and $\nu_1(\text{A}_g)$ modes that are related to the intramolecular bending of the SbCl_3 lattice [36]. As temperature varies, the 51 cm^{-1} Raman mode is always the strongest one, which is the typical profile of big polaron state [37], and suggests that the polaron can be easily formed in this system. Particularly, the Raman bands at 102, 250, 336, and 480 cm^{-1} can be approximately viewed as the overtones of the bands at 51, 124, and 163 cm^{-1} , which illustrates a strong anharmonic electron-phonon interaction [18]. Moreover, several different multi-phonon coupling characteristics demonstrate that multiple STEs existed in the $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$.

For Sb^{3+} with $5s^2$ electron configuration, the ground state (GS) is denoted as $^1\text{S}_0$, while the excited state splits into four energy levels, namely, $^1\text{P}_1$ and $^3\text{P}_n$ ($n = 0, 1, 2$). The $^1\text{S}_0 \rightarrow ^3\text{P}_0$ and $^1\text{S}_0 \rightarrow ^3\text{P}_2$ transitions are forbidden, whereas the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ and $^1\text{S}_0 \rightarrow ^1\text{P}_1$ transitions are parity-allowed, owing to spin-orbit

Figure 4 Temperature-dependent spectra and photophysical processes of $(C_{16}H_{28}N)_2SbCl_5$. (a) Emission spectra at different temperatures (80–360 K). (b) PL/temperature correlation maps. (c) PL peak position *versus* temperature. (d) FWHM *versus* temperature. (e) Raman spectra measured at 80 and 300 K (inset) under laser excitation at 532 nm. (f) An illustration of the photophysical processes.

coupling [38–40]. Due to the large separation, 3P_1 and 1P_1 can be coupled with different multiple phonons, thus forming different STEs, i.e., singlet and triplet STEs in $[SbCl_5]^{2-}$ units (Fig. 4f). Therefore, one can conclude that the observed dual-emission mechanism has the following mechanism: under the HE irradiation (e.g., 300 nm), electrons are excited from 1S_0 to HE-excited states (3P_1 and 1P_1). Subsequently, the excited electrons are rapidly transferred onto LE-excited states, which are ES1 (HE singlet STEs) and ES2 (LE triplet STEs), *via* the intersystem crossing (ISC), and then return to the GS. Eventually, the narrower HE emission band (477 nm) and broader LE emission band (633 nm) can be observed *via* the radiative recombination from the singlet and triplet STEs in $[SbCl_5]^{2-}$ units. As a matter of fact, only a single broadband emission at 633 nm with a large Stokes shift was observed under the LE irradiation (e.g., 400 nm), which is related to the triplet STEs emission. Moreover, the photophysical mechanism was also confirmed by decay lifetime measurements, where the singlet state is on the vibrational energy level of the triplet state (Fig. 4f), and most singlet STEs are quickly transformed into the triplet STEs, resulting in a singlet STEs emission with a short decay lifetime, while the LE emission band exhibits a triplet STEs emission with a long decay lifetime.

Remarkably, $(C_{16}H_{28}N)_2SbCl_5$ SCs show excellent stability, which forms a solid basis for lighting applications. First, an outstanding stability of this system against humidity is shown in atmosphere. When $(C_{16}H_{28}N)_2SbCl_5$ was stored in air for three months (55% relative humidity), its luminous intensity remained almost unchanged (Fig. S10), so does its PXRD pattern (Fig. S11). Second, the initial decomposition temperature of $(C_{16}H_{28}N)_2SbCl_5$ is found to be as high as 190°C, indicating a good thermal stability of such material (Fig. S12). Also as shown in Fig. S13, $(C_{16}H_{28}N)_2SbCl_5$ exhibited praiseworthy photo-stability; the PL intensity was still greater than 95.9% of the initial point after 240-min irradiation time. Moreover, when the

$(C_{16}H_{28}N)_2SbCl_5$ was subjected to repeated heating and cooling cycles for 8 times within the temperature range of 300–380 K (Fig. S14), a commendable emission intensity is observed. Taken together, these results illustrate that the as-synthesized compound possessed excellent PL output under the 365 nm UV light illumination and thermal treatment. The superior stability of $(C_{16}H_{28}N)_2SbCl_5$ can be attributed to the fact that the local excitons in the emission center of $[SbCl_5]^{2-}$ units are well protected by organic cations $C_{16}H_{28}N^+$.

To demonstrate the above properties, we fabricated a white-light-emitting diode (WLED) device by mixing $(C_{16}H_{28}N)_2SbCl_5$ with a commercial phosphor of blue $BaMgAl_{10}O_{17}:Eu^{2+}$ and green $Ba_2SiO_4:Eu^{2+}$ and then excited the mixture by the 365 nm UV chip. The WLED showed efficient warm white light, and the relevant color coordinate was (0.36, 0.37) and the correlated color temperature (CCT) was 4726 K (Fig. 5a, b), corresponding to a color rendering index of up to 96.6, which is far greater than other lead-free metal halide-based WLEDs, such as $Cs_2ZrCl_6:Bi^{3+}$ (81.9) [41], $(OCTAm)_2SnBr_4$ (81) [42], and $[DMPZ]_2SbCl_6 \cdot Cl \cdot (H_2O)_2$ (92) [17]. Furthermore, the as-fabricated device showed remarkable color stability under different driving currents (Fig. 5c). The luminous efficiency and electroluminescent spectral profile remained basically unchanged after running the device for 240 min (Fig. 5d and Fig. S15), illustrating that the as-fabricated device had good optical stability. Therefore, we believe $(C_{16}H_{28}N)_2SbCl_5$ can serve as an ideal down-conversion phosphor for the UV-pumped WLEDs.

CONCLUSIONS

In summary, we reported a new lead-free luminescent material, $(C_{16}H_{28}N)_2SbCl_5$, in which the isolated $[SbCl_5]^{2-}$ clusters were surrounded by $C_{16}H_{28}N^+$ cations to form an independent 0D framework. Interestingly, $(C_{16}H_{28}N)_2SbCl_5$ exhibited a dual-emission band at 477 and 633 nm, stemming from singlet and triplet STE emissions, respectively. Also noteworthy, this

Figure 5 (a) Electroluminescent spectrum of WLED from $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$. (b) CIE chromaticity diagram of fabricated WLED. The inset exhibits the operating WLED. (c) Driving current dependence of the EL spectra. (d) Long-term stability of the as-fabricated WLED.

compound possessed outstanding stability and intense orange emission with PLQE of 97.8%, allowing it to be an ideal candidate material for photoelectric applications. At last, using $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ as an orange down-conversion phosphor, a stable WLED with the CIE of (0.36, 0.37), CCT of 4726 K, and an ultra-high color rendering index of 96.6 was demonstrated. Our results in this work demonstrate that the lead-free metal halides based on $(\text{C}_{16}\text{H}_{28}\text{N})_2\text{SbCl}_5$ have great potential in solid-state displays.

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Author contributions Peng H, Wang J, and Zou B designed and carried out the experiments. Peng H and Tian Y performed the material preparation and analyzed the data. Yu Z and Ke B measured the temperature-dependent emission spectra. Wang X performed the theoretical calculation. Zhao Y and Dong T helped to fabricate the LED device. All authors participated in discussing the data and writing the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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(C₁₆H₂₈N)₂SbCl₅: 一种具有亮橙色发射的新型无铅零维金属卤化物杂化物

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摘要 零维金属卤化物因其迷人的光电特性而处于蓬勃发展的状态。本文报道了一种(C₁₆H₂₈N)₂SbCl₅ (C₁₆H₂₈N⁺ = 苄基三丙基铵阳离子)的碲基金属卤化物, 其中孤立的[SbCl₅]²⁻团簇被C₁₆H₂₈N⁺包围, 形成零维方形金字塔结构。(C₁₆H₂₈N)₂SbCl₅在低能辐照(400 nm)时在633 nm处呈现宽带橙色发射, 具有97.8%的近单位光致发光量子效率。有趣的是, (C₁₆H₂₈N)₂SbCl₅在高能辐照(300 nm)时在477 nm处显示出一个额外的发射峰, 这是由自旋-轨道耦合的二重态转变为两个独立的自束缚激子形成的。变温拉曼光谱显示了多声子耦合的特征, 这证明(C₁₆H₂₈N)₂SbCl₅中存在强烈的非谐性电子-声子相互作用。变温发射光谱和密度泛函理论计算表明, 所观察到的双峰发射源于[SbCl₅]²⁻单元中的单重态和三重态自束缚激子。结合(C₁₆H₂₈N)₂SbCl₅的高效发光和优异的稳定性, 我们还制备了超高显色指数为96.6的稳定白光发光二极管。