Modulation of the optical bandgap and photoluminescence quantum yield in pnictogen (Sb\(^{3+}/\)Bi\(^{3+}\))-doped organic–inorganic tin(IV) perovskite single crystals and nanocrystals

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**Highlights**

- 0D pnictogen-doped Sn(IV) perovskite SCs and NCs were synthesized.
- Water-stable Sb\(^{3+}/\)Bi\(^{3+}\)-doped Sn(IV) perovskite show tunable emission.
- Sn(IV) perovskite NCs show bright orange emission with PL QY of 41%.

**Abstract**

Water-stable, lead-free zero-dimensional (0D) organic–inorganic hybrid colloidal tin(IV) perovskite, A\(_2\)SnX\(_6\) (A is a monocationic organic ion and X is a halide) nanocrystals (NCs) with high photoluminescence (PL) quantum yield (QY) have rarely been explored. Herein, we report solution-processed colloidal NCs of blue light-emitting T\(_2\)SnCl\(_6\) and orange light-emitting T\(_2\)Sn\(_{1-x}\)Sb\(_x\)Cl\(_6\) [T\(^+\) = tetramethylammonium cation] from their corresponding single crystals (SCs). These colloidal NCs are well-dispersible in non-polar solvents, thereby maintaining their bright emission. This paves the way for fabricating homogeneous thin films of these NCs. Due to organic cation (T\(^+\))-controlled large spin–orbit coupling (SOC), the T\(_2\)Sn\(_{1-x}\)Sb\(_x\)Cl\(_6\) NCs exhibit bright orange emission with an enhancement in PL QY of 41% compared to their bulk counterpart. Furthermore, we explore T\(_2\)Sn\(_{1-x}\)Bi\(_x\)Cl\(_6\) and T\(_2\)Sn\(_{1-x}\)Sb\(_x\)Bi\(_x\)Cl\(_6\) SCs, which show blue and green emission, respectively; the latter is attributed to the newly formed Sb 5p and Sb 5s orbital-driven band structures confirmed by applying density functional theory (DFT) calculations. The SCs and NCs exhibit excellent stability in water under ambient conditions because of the in-situ generation of a hydrophobic and oxygen-resistant passivating layer of oxychloride in the presence of water. Our findings open a pathway for designing lead-free perovskites materials for thin-film-based optoelectronic devices.

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1. Introduction

Lead-free perovskites with the general formulas \( A_2C(B^{III})X_6 \), \( A_2B^{IV}X_6 \), and \( A_BX_6 \) have been widely studied for various practical applications such as solar cells, light-emitting diodes, and many others [1–4]. Among these, zero-dimensional (0D) metal-doped R\(_2\)-B\(_{IV}\)Cl\(_6\) perovskites and chloride vacancies and interstitial tin [14].

Research into organic–inorganic lead halide perovskite NCs was first reported in 2014 and it was followed with great interest due to their bright PL, easily tunable optical properties and, especially, defect tolerance during the fabrication of semiconductor devices [20–23]. However, its toxicity has impeded its application in consumer electronic devices despite its outstanding chemical and physical properties. Therefore, developing of lead-free perovskite NCs with excellent optical properties seems to be of great fundamental and practical significance. Much effort has been applied to the optical tuning of metal hybrid halides [2,19,24–28], albeit that their intrinsic indirect bandgap has impeded optimization and improvement of their PL properties. Although octahedral Sn exhibits similar photochemical properties to octahedral Pb-based perovskites, the ease of oxidation of Sn\(^{2+}\) becomes the bottleneck for its further development, and the poor stability of Sn\(^{2+}\) based perovskites has driven the demand for alternatives [19]. Sn\(^{4+}\) could be an excellent alternative since it shows outstanding stability compared to Sn\(^{2+}\) with high-energy 5 s\(^2\) electrons. The excellent stability of Sn\(^{4+}\)-based 0D perovskite in water and oxygen environments and the tunable direct bandgap make it the perfect option for next-generation semiconductor materials. More insight into the PL of these materials is required for producing better light-emitting device performance from 0D Sn-based perovskites. Thus, we choose SnCl\(_6\) containing Sn\(^{4+}\). To tune the band gap of Sn\(^{4+}\)-based 0D compounds, we choose different atomic number elements with stable oxidation states such as Sb\(^{3+}\) and Bi\(^{3+}\). We find that these compounds not only show bright PL but also excellent stability in water.

Herein, we report the synthesis of pure T\(_2\)SnCl\(_6\) (1), T\(_2\)Sn\(_{1-x}\)xBi\(_x\)Cl\(_6\) (2), T\(_2\)Sn\(_{1-x}\)xBi\(_x\)Cl\(_6\) (3), and T\(_2\)Sn\(_{1-x}\)xBi\(_x\)Cl\(_6\) (4) SCs, as well as T\(_2\)SnCl\(_6\) (5) and T\(_2\)Sn\(_{1-x}\)xBi\(_x\)Cl\(_6\) (6) NCs. Moreover, the tunable emissive wavelength and PL QY of T\(_2\)SnCl\(_6\) were achieved by Bi-, Sb- and Bi/Sb-doping. First, we synthesized SCs 1–4 through a hydrothermal crystallization method and then NCs via a room-temperature ligand-assisted re-precipitation (LARP) method (Fig. 1a) [29]. Phinctogen ion (Sb\(^{3+}\), Bi\(^{3+}\), and Bi\(^{3+}\)/Bi\(^{5+}\)-doped 0D-
3. Characterization

### 3.1. Physical characterizations

The powder X-ray diffraction measurements (PXRD) were performed on D/MAX2500V/PC diffractometer, Rigaku using Cu-rotating anode x-ray. PXRD were collected using K-alpha model, ThermoFisher. During the measurement, the Bragg’s diffraction angle ($2\theta$) range was set to 5–50° and scan rate was 2°/minute. Scanning electron microscopy (SEM) images were taken using SU8220 Cold FE-SEM, Hitach High-Technologies with an acceleration voltage of 10 kV, and EDX was used to characterize the elements of all the samples. X-ray photoelectron spectroscopy (XPS) was done using K-alpha (ThermoFisher) to analyze the chemical compositions. The optical diffuse reflectance spectra of all solid samples were recorded using a Cary 5000 UV–Vis-NIR Spectrophotometer with an integrated sphere in diffuse-reflectance mode and then converted to Kubelka-Munk function, $F(R)$. All the room temperature PL spectra of all the solid compounds were recorded using Cary Eclipse fluorometer, (Varian) in solid state. PL quantum yield (PL QY) of solid samples was experimentally evaluated using FP-8500ST Spectrofluorometer (Jasco International). PL QY was evaluated by integrating sphere, and the following equations have been used: PL quantum yield [%] = $S_2/(S_0-S_1) \times 100$.

### 3.2. DFT analysis

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [31] suite with the PBE exchange correlation functional [32]. Structural geometry optimization was performed with energy convergence and force convergence of $10^{-6}$ eV and 0.02 eV/Å, respectively. A $(1 \times 1 \times 2)$ supercell of cubic $T_2\text{SnCl}_6$ is used. We employed $\Gamma$-centered $(2 \times 2 \times 1)$ k-point mesh for sampling the Brillouin zone (BZ) and 500 eV energy cutoff for the projector augmented wave (PAW) plane wave basis sets.
4. Results and discussion

Metal-doped T$_2$SnCl$_6$ SCs were synthesized via hydrothermal crystallization while T$_2$SnCl$_6$ NCs were synthesized by using a room-temperature LARP process [33] (Fig. 1a). Due to the smaller B-site cation (Sn$^{4+}$) and larger A-site component (T$^+$), the [SnCl$_6$]$_2^-$ absorption peaks at 948 cm$^{-1}$ in infrared (FTIR) microscopy. Two large sharp absorbance peaks are observed in the XRD pattern of T$_2$SnCl$_6$ [35]. In Fig. 2d, the diffraction peaks match well with the simulated sample pattern, indicating that the T$_2$SnCl$_6$ structure is in the cubic phase for all of the samples. Slight shifts in the XRD peak positions within 0.1 cm$^{-1}$ between the doped and non-doped samples are due to the small doping amounts in both the NCs and SCs [36]. This finding is confirmed by the energy dispersive spectroscopy (EDS) results listed in Table 1 and Fig. S4-7. Moreover, X-ray photoelectron spectroscopy (XPS) results show a low concentration of dopant after surface etching of the SCs, which is consistent with the EDS results. However, high concentrations of dopant ions are observed in NCs which is due to metal oxycollyn chloride formation, confirmed by the existence of O element in high resolution deconvoluted XPS spectrum of T$_2$SnCl$_6$ (Fig. S13). Subsequently, cold field emission scanning electron microscopy (FE-SEM) (Fig. 2a) and high-resolution transmission electron microscopy (HR-TEM) images (Fig. 2c-e) were obtained to reveal the morphologies and structures of NCs. The SEM images of NCs exhibit uniform nanometer-sized particles, in contrast to SCs with an octahedral structure. The TEM images in Fig. 2 helped us to understand the crystalline phases of T$_2$SnCl$_6$ and 6. Uniform NCs of ~100 nm size observed in the TEM images are consistent with those observed in the SEM images. Then, the lattice diffraction pattern along with an FFT (fast Fourier-transform) was analyzed. In 6, a d-spacing of 0.329 nm corresponds to the (400) reflection plane of SnCl$_6$ matches well with the plane corresponding to the diffraction angle of 27.56° in the XRD pattern of T$_2$SnCl$_6$ [35]. In Fig. 2b, we investigated the presence of organic moieties in the NCs and SCs by Fourier transform infrared (FTIR) microscopy. Two large sharp absorption peaks at 948 cm$^{-1}$ and 1484 cm$^{-1}$ were assigned to the stretching and bending modes of C–N bonds [37]. Furthermore, a well-resolved N–C–H bending mode and a C–H stretching mode were observed, with peaks at 1200 ~ 1600 cm$^{-1}$ and 3035 cm$^{-1}$, respectively.

Thus, the presence of T$^+$ cations in the both SCs and NCs was verified. One more broad peak centered at 3500 cm$^{-1}$ was attributed to the O–H bond [38]. The appearance of which was probably due to the formation of an amorphous hydroxide coating. In addition, the corresponding FTIR peaks of oleic acid centered at 2921 cm$^{-1}$, 1721 cm$^{-1}$, 1035 cm$^{-1}$, and 727 cm$^{-1}$ were also observed, although the intensities were weak due to decoupling of the capping ligands and the in-situ formation of an oxycollyn chloride coating [39]. Then, inorganic chemical compositions analysis of SCs and NCs were elucidated by using XPS, as shown in Fig. S8–S13. In the high resolution XPS spectra, two spin–orbit doublet broad peaks originating from metal oxides can be observed beyond the Sn 3d, Bi 4f, and Sb 3d spectra. Moreover, Cl 2p sub-peaks corresponding to oxycollyn chloride appeared beside Cl 2p doublet peaks for all of the samples, thereby confirming the existence of oxycollyn chloride instead of oleic acid as the capping ligand.

Previously, metal-doped Cs$_2$SnCl$_6$ has been widely studied because of the efficiently STE induced emission from OD 5 2$^+$/metal halides [15,17,27,34]. We recorded UV–Vis absorption and PL spectra to investigate the detailed optical properties of SC 1–4 (Fig. 3a and Fig. S16). A strong broad absorption edge at 320 nm for all the samples is attributed to pristine T$_2$SnCl$_6$ [40]. An absorption peak located between 320 nm and 425 nm after doping was due to the transition of the dopant ions from ground state $^2$S$_0$ to excited state $^1P_1$, via SOC interaction [27]. The PL excitation (PLE) spectra of the NCs and SCs 2–4 show peaks among 300 nm to 425 nm of the absorption range of host 1, which indicates that there is no energy transfer process between the host and the dopant. Furthermore, PL characterizations of the SCs based on confocal laser scanning microscopy were conducted to confirm the crystal luminescence (Fig. S14). Millimeter-scale octahedral crystals showed pure red, blue, and green PL without any impurity phase. The PL spectra of SCs 2–4 at selected points revealed single broad peaks centered at 470, 625, and 500 nm, respectively. This indicates that PL emissions of SCs are due to the intrinsic properties of their structures, rather than the aggregation effect or surface defects.

To further examine the PL mechanism, we conducted PL experiment and DFT calculations shown in Fig. 3. The PL spectra of the SCs shown in Fig. Sb exhibit the STE-featured emission from metal-doped Cs$_2$SnCl$_6$ [15,30], which provides more evidence of the discrepancy between the absorption and PLE spectra. Moreover, 3 shows excitation wavelength-dependent PL and PLE spectra shown in Fig. S16, which can be ascribed to the dual emission centers with singlet ($^1P_1$–$^1S_0$) and triplet ($^3P_n$–$^1S_0$) STE transitions, respectively [17]. Bi and Sb co-doped 4 shows one broad emission peak centered at 490 nm with a tail extending to 600 nm and with PLE properties similar to 3 (Fig. 3 and Fig. S16). Moreover, the XPS results show a higher concentration of Sb than Bi in crystalline 4 (Table 1). We speculate that the green emission of 4 can be attributed to the single STE transition in the Bi and Sb co-doped system. As the Sb 5 s and 5p orbitals occupy energy levels similar to Bi 6 s, orbital hybridization occurs them. The new orbital-driven band structure gives rise to green emission with a red-shift of nearly 30 nm as compared to 2 [41]. In the case of the vacancy-ordered cubic perovskite, the formation of additional halide dimers (Cl–Cl') in the excited state creates new valence holes localized on this new chemical bond by occupying the highest bonding orbital of the bonded pair [22,34]. In order to balance the dopant ion charge, the Sn sites substituted by dopant ions provide electron trap sites that are complementary to the hole centers [34]. As shown in Fig. 3d, upon excitation, the host attains large bandgap absorption while the dopant ions undergo featured $^1S_0$–$^1P_1$ absorption. When electrons are excited to high-energy excitation states, electrons enter self-trapped states and form the STE. However, the emission induced by singlet STE dominates the transition $^1P_1$–$^1S_0$ in 2 and 4, while triplet STE dominates the emission transition in 3. And as a result, orange, green, and blue emissions with large Stokes shifts occur. To gain more insight, we conducted density of states (DOS) calculations to investigate the emission shift by DFT, as shown in Fig. 3c. The Bi 6 s and Sb 5 s orbitals dominate the highest bonding orbital and give rise to recombination of blue and red emission in 2 and 3, respectively. Due to the orbital hybridization of Sb and Bi in 4, the Sb orbitals lead to an energy change in the highest bonding orbital, resulting in green emission. This was also confirmed by the slightly shifted states between 2 and 4. This fur-
ther corroborates that Bi/Sb co-doping in \( 4 \) induces a PL red-shift compared with \( 2 \) (Fig. 3b). However, after conversion SCs to NCs, \( 5 \) shows shoulder peaks centered at 365 nm and 446 nm with a PL QY of 9.6% when excited at 309 nm (Fig. 4a). The blue emission peak at 446 nm is caused by surface defects or defects states [17] while the peak located at 365 nm originates from free exciton
recombination. Intriguingly, 6 exhibits an enhanced PL QY of 41%. To elucidate the highly efficient PL of NCs, PL imaging and spectra are shown in Fig. 4a, 4b and Fig. S15. The broad peak centered at 615 nm is due to intrinsic 3P1-1S0 triplet transition. The single partial PL imaging of 6 shown in Fig. S15 demonstrates pure emission due to aggregation of the NCs. The PL spectrum of the selected area also exhibits similar peaks with spectrum to a solution of 6.
In contrast to 3, the PL of 6 shows a strong peak at 615 nm as well as a weak peak at 480 nm upon excitation from 310 to 365 nm (Fig. 4b). We conclude that the $^1P_1$-$^1S_0$ transition peak at 480 nm is partially suppressed and the $^3P_1$-$^1S_0$ transition peaked at 615 nm dominates the emission. This is because of the efficient charge transfer from the singlet state to the triplet state. Due to the large constant of SOC, we expected that the intersystem crossing (ISC) between singlet STE and triplet STE is significantly efficient and the $^3P_1$-$^1S_0$ transition rate becomes relatively high [42,43].

In the case of 2 and 4, the ISC process of the Sb$^{3+}$-doped T$_2$SnCl$_6$ is attributed to the $^3P_n$-$^1S_0$ transitions ($n = 0, 1, 2$). The ground state of s$^2$ ion of an activator is $^1S_0$ whereas it has four energy levels at excited states, $^1P_1$, $^3P_0$, $^3P_1$, and $^3P_2$ [17,44]. The HOMO-LUMO energy gap increases more in Sb$^{3+}$ and Bi$^{3+}$ co-doped T$_2$SnCl$_6$ samples as compared to the Sb$^{3+}$-doped T$_2$SnCl$_6$ because of the mixing of s-orbitals of Sb$^{3+}$ and Bi$^{3+}$. This is also evidenced from our DFT calculations. The mixing of s-orbitals prevents the ISC process. Hence, Sb$^{3+}$ and Bi$^{3+}$ co-doped T$_2$SnCl$_6$ sample do not show ISC between singlet STE and triplet STE. The ISC process in 6 was confirmed by similar PLE spectra monitored at 475 nm and 615 nm. Therefore, efficient PL with enhanced PL QY for orange emission occurs even under ambient conditions. Finally, we fabricated thin films using the colloidal solution of 5 and 6 shown in Fig. 4c and 4d. Under 365 nm-irradiated UV light, bright blue and orange PL emissions were observed for 5 and 6, respectively. This indicates the bright future of using these 0D lead-free perovskites in thin-film based optoelectronic devices.

The poor stability of perovskite materials has been a major factor restricting their development [45], and the stability of Pb-based perovskites in water has been widely studied [46–48]. We investigated the water and thermal stability of 0D lead-free perovskites 2–4, as exhibited in Fig. 5. All of the samples exhibited bright luminescence in water even after immersion for 7 days (Fig. 5a). The compounds collected from the water were characterized by HP-XRD to check their stability (Fig. 5b and Fig. S3). The XRD pattern of 2–4 before and after water immersing showed similar peak positions indicating that the main phase of the samples remained unaltered. However, there was a slight change in crystallinity. We have checked the PL QY of 2, 3, and 4 after immersing them in water. In the case of Cs$_2$SnCl$_6$:Bi and Cs$_2$SnCl$_6$:Sb [15,30] the PL QY decreased due to loss in crystallinity. PL images and the PL QYs of samples 2–4 before and after water immersing were shown in Table S1 and Fig. S3. After drying the samples that had been immersed in water for 7 days, the resulting powder of 2, 3, and 4 still showed bright PL with PL QYs of 4.7%, 13.4%, and 4.8%, respectively. The good water stability was attributed to an oxygen-resistant passivating layer of

![Fig. 5.](https://example.com/fig5.png)

(a) Digital PL images of 2–4 under UV light (365 nm); (b) XRD patterns for 2–4 before and after immersion in water; (c) SDT curves for 2–4. (d) PL images of 5 (blue) and 6 (orange) dispersed in toluene under UV light (before and after 7 days).
oxychloride in the presence of water. The presence of oxychloride was confirmed by FTIR (Fig. S18). Broad FTIR peak at 3430 cm⁻¹ were observed for 2, 3, and 4, which indicate the formation of layer of oxychloride.

To investigate the thermal stability of the samples, simultaneous differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA) analysis (SDT) were conducted to illustrate their temperature tolerance capability (Fig. 5c and Fig. S17). In TGA curves, weight loss from all of the samples started at 335 °C and ended at 400 °C, which is attributed to the decomposition of the tin halide [49]. Furthermore, the endothermal process suddenly occurred at 351 °C due to decomposition reactions, as shown in their DSC curves. Meanwhile, there were slight weight losses below 335 °C and above 400 °C (the TGA curves) in Fig. S17 due to the dehydration process and decomposition of the oxychloride compounds, respectively [50,51]. Residue remained even above 800 °C, which provides further evidence of the oxychloride compound coating outside the lattice structure. Thus, 2-4 revealed excellent thermal and water stability. The stability of 5 and 6 NCs dispersed in toluene is shown in Fig. 5d. After 7 days, 5 and 6 still showed bright fluorescence even though the NC particles had precipitated out. This was attributed to NC aggregation caused by the loss of surface-passivating ligands.

5. Conclusion

We synthesized 0D organic–inorganic Sn⁴⁺-based perovskite pure SCs as well as their Sb³⁺, Bi³⁺, and Sb³⁺/Bi³⁺ doped SCs via a hydrothermal method. Brightly photoluminescent pure Sn⁴⁺ 0D perovskite colloidal NCs and their Sb³⁺-doped counterpart were also synthesized from their corresponding SCs. Thus, we demonstrated optically tunable Sn⁴⁺-based perovskite phosphors capable of stable and efficient blue, green, and red PL. Using DFT calculations, we revealed that Sb³⁺/Bi³⁺ co-doping led to a new Sb 5p and 5 s orbital-driven band structure which was not present in pure SCs as well as their Sb³+, Bi³+, and Sb³+/Bi³+ doped SCs via a

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jciis.2021.08.083.

References


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