SUPPORTING INFORMATION

Green Emitting Lead-Free Cs$_4$SnBr$_6$ Zero-Dimensional Perovskite Nanocrystals with Improved Air Stability

Rossella Chiara,$^a$ Yasemin O. Ciftci,$^b$ Valentin I. E. Queloz,$^c$ Mohammad Khaja Nazeeruddin,$^c$ Giulia Grancini,$^a$ Lorenzo Malavasi$^a,^*$
**Figure S1**: Absorbance spectrum of Cs$_4$SnBr$_6$ nanocrystal suspension

**Figure S2**: Optimized unit cell Cs$_4$SnBr$_6$ from DTF calculations.
Figure S3. Calculated charge density for Cs$_4$SnBr$_6$ from DFT calculations.

Figure S4: The HOMO (left) and LUMO (right) orbitals of Cs$_4$SnBr$_6$ as determined by DFT.
EXPERIMENTAL

Synthesis

Materials. All reagents were used without any purification: Cs$_2$CO$_3$ (cesium carbonate, 99%, Sigma-Aldrich), OA (oleic acid, 90%, Sigma-Aldrich), OLA (oleylamine, 90%, Sigma-Aldrich), ODE (1-Octadecene, 99%, Sigma-Aldrich), anhydrous n-hexane (99.98%, Sigma-Aldrich), 1-butanol (>99.4%, Sigma-Aldrich) TOP (Trioctylphosphine 97%, Sigma-Aldrich), SnBr$_2$ (99%, Sigma-Aldrich).

Synthesis of Cs$_4$SnBr$_6$ Nanocrystals. Nanocrystals were synthesized using a hot-injection method. In a typical procedure, the Cs-oleate precursor was synthesized separately. First, a mixture of 0.0656 g of Cs$_2$CO$_3$ and 0.2 mL of ODE, 0.2 mL of OLA and 0.2 mL of OA was stirred and degassed at 130 °C under vacuum for 1 hour to generate Cs-oleate precursor. Second, 0.3481 g of SnBr$_2$ are dissolved in 1.2 mL of TOP and quickly added to the mixture in a 10-mL three-neck flask, followed by mild degassing and nitrogen purging. The reaction was quenched after 1 minute. To the as-synthesized nanocrystals was added 1-butanol followed by centrifugation at 4000 rpm for 3 min and dispersion in 2 mL of hexane.

X-ray diffraction

The crystal structures of the samples were characterized by room temperature Cu-radiation Powder X-ray diffraction (XRD) on a Bruker D8 diffractometer. Scans were performed in the 10–40° range, with a step size 0.04° and a counting time of 3 s per step.

Transmission electron microscopy (TEM)
TEM images were collected on a JEOL JEM-1200 EX II microscope operating at 100 kV (tungsten filament gun) and equipped with the TEM CCD camera Olympus Mega View G2 with 1376 x 1032 pixel format. Samples were prepared by drop-casting the solution on coated copper grids.

**Steady State PL and Time-Resolved Photoluminescence Measurements**

Steady state and time resolved photoluminescence measurement were carried out on Horiba a Fluorolog-3, with a PMT as detector. The excitation source for the TCSPC is a Horiba nanoLED-370 with an excitation wavelength of 369nm, a pulse duration of 1.3ns and a repetition rate of 1 MHz.

**Time-Resolved Photoluminescence Measurements**

For TRPC measurements the samples have been loaded into air-tight resonant cavity (low intensity measurements) and open cell (high intensities) holders in a N\textsubscript{2} filled glovebox. The excitation source for the TCSPC is a Horiba nanoLED-39 370 with an excitation wavelength of 369 nm, a pulse duration of 1.3 ns and a repetition rate of 100 KHz.

**EDX Analysis**

Elemental analyses of the powders were performed by Energy Dispersive X-ray Analysis (EDX) by a X-max 50 mm\textsuperscript{2} probe (Oxford Instrument) connected to a EVO MA10 scanning electron microscope (SEM). The powders were dispersed on graphite bi-adhesive supports fixed on Al stubs.
inside a glove box under Ar atmosphere. The stubs were inserted in a home-made sample holder that was sealed in the glove box and in which the low vacuum was made by a rotary pump. In this way, the samples were transferred in the SEM chamber avoiding the exposition to air. Subsequently, the sample holder was open and the measurements performed under ultra-high vacuum at a working distance of 8.5 mm and with an electron generation voltage of 20 kV.

**Computation Details**

Periodic density functional calculations (DFT) were performed using the Dmol³ program in the Materials Studio package.¹ All calculations were carried out using Perdew-Burke-Ernzerhof exchange-correlation functions in the framework of general gradient approximation.² The double numerical basis set including d-polarization functions (DND) was utilized to describe the valence electrons, with the core electrons described by the effective core potential. The convergence criteria applied for geometry optimizations were $1.0 \times 10^{-5}$ Å, $2.0 \times 10^{-3}$ Å, and $5.0 \times 10^{-3}$ Å for energy change, maximum force, and maximum displacement, respectively. A double numerical basis sets, plus polarization functional version 3.5 and an orbital cutoff of 5.1 Å were used. The threshold for self-consistent-field density convergence was set to $1.0 \times 10^{-6}$ eV; while converging $(8 \times 8 \times 6)$ Monkhorst-Pack grids were employed to perform integration in the first Brillouin zone for Cs₄SnBr₆. Optimization of lattice constants and total energy calculations were performed with plane wave cutoff energy of 600 eV.

**References**

[1] J. B. Delley, *J. Chem. Phys.* **1990**, *92*, 508.

[2] P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244.
