## **Supporting Information**

# Colloidal Synthesis of Size-Confined CsAgCl<sub>2</sub> Nanocrystals:

## Implications for Electroluminescence Applications

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## **1. Experimental Details**

#### **1.1 Chemicals**

Europium chloride (EuCl<sub>3</sub>, 99.99%, Aldrich), trioctylphosphine oxide (TOPO, 99%, Aldrich), cesium acetate (Cs(OAc), 99.9%, Aldrich), silver acetate (Ag(OAc), 99.9%, Aldrich), oleic acid (OA, 90%, Aldrich), oleylamine (OAm, 70%, Aldrich), octadecene (ODE, 90%, Aldrich), methyl acetate (MeOAc, anhydrous 99.5%, Aldrich), 2,2',2"(1,3,5-benzenetriyl)tris-(1-phenyl-1H-benzimidazole) (TPBi, 99.5%, Aldrich), poly(9,9-dioctylfluorene-alt-N-(4-butylphenyl)-diphenylamine) (TFB, Art. L512036, Aldrich), antimony acetate (Sb(OAc)<sub>3</sub>, 97%, Alfa), antimony trichloride (SbCl<sub>3</sub>, 99%, Innochem), germanium (IV) chloride (GeCl<sub>4</sub>, 99.9999%, Alfa Aesar), yttrium chloride (YCl<sub>3</sub>, 99.99%, Aldrich), terbium chloride (TbCl<sub>3</sub>, 99.99%, Aldrich),

indium chloride (InCl<sub>3</sub>, 99.99%, Innochem), cerium chloride (CeCl<sub>3</sub>, 99.9%, Aldrich), erbium chloride (ErCl<sub>3</sub>, 99.9%, Aldrich), and zinc chloride (ZnCl<sub>2</sub>, 99.99%, Alfa). All chemicals were used as received without further purification.

1.2 Colloidal synthesis of the pristine and Sb<sup>3+</sup>-doped CsAgCl<sub>2</sub> nanocrystals (NCs) 0.5 mmol of EuCl<sub>3</sub> was mixed with 2 g of TOPO to prepare a TOPO-EuCl<sub>3</sub> stock solution. The mixture was vigorously stirred on a hot plate at 90 °C for 1 h until EuCl<sub>3</sub> was totally dissolved. In a 50 mL three-neck flask, 0.5 mmol of Cs(OAc), 0.5 mmol of Ag(OAc), 2.8 mL of OA, and 0.7 mL OAm were added into 10 mL of ODE. The mixture was degassed at 110 °C for 40 min with vigorous stirring and then heated to 120 °C under nitrogen atmosphere until the solution became clear. The temperature was then increased to 170 °C followed by the quick injection of the above prepared TOPO-EuCl<sub>3</sub> solution (note that because TOPO will solidify again upon decreasing the temperature, the hot TOPO-EuCl<sub>3</sub> solution should be used as soon as possible after being taken out from the hot vessel). About 10 secs after injection, the reaction was quenched by immediate immersion of the flask into an ice bath. NCs were precipitated by adding 10 mL of MeOAc, followed by centrifugation at 6000 rpm for 2 min. The supernatant was discarded and the precipitate was dispersed in 4 mL of hexane. Finally, the dispersed NCs were kept in the dark at 4 °C and centrifuged before use. For Sb<sup>3+</sup> doping, part of Ag(OAc) was replaced by Sb(OAc)<sub>3</sub> (0.03~0.30 mmol), while keeping the other parameters constant.

#### 1.3 Fabrication of the Sb-doped CsAgCl<sub>2</sub> NC LEDs

The ITO-coated glass substrates were rinsed with deionized water followed by sonication in deionized water, acetone, and isopropanol, respectively, each for 15 min. The substrates were then dried at  $125 \pm 5$  °C for 10 min and treated with UV ozone for 10 min before use. Thereafter, the aqueous solution of PEDOT:PSS (Clevios Al 4083) filtered through a 0.22 µm PTFE filter was spin-coated on the precleaned ITO glass at a speed of 4500 rpm for 40 s and then annealed at  $125 \pm 5$  °C for 30 min in the ambient conditions. TFB layers (dissolved in chlorobenzene, 8 mg/ml) were spin-coated at 4000 rpm, 30 s, followed by annealing at 150 °C for 30 min in a glove box. Subsequently, colloidal suspension of Sb-doped CsAgCl<sub>2</sub> NCs (in hexane, 20 mg/mL)

was spin-coated on TFB layer at 3600 rpm for 30 s, and then a 40 nm thick TPBi layer was deposited using a vacuum thermal evaporator. Finally, the cathode was fabricated by thermal evaporation of a LiF layer (1.0 nm), followed by an Al layer (100 nm). Each substrate is patterned to realize three devices, each with an active area of 0.36 cm<sup>2</sup>. All the devices were stored and characterized under the ambient atmosphere without encapsulation.

#### **1.4 Characterization**

The phase identification was carried out using a powder X-ray diffraction (XRD, TTR-III, Rigaku Corp., Japan). The morphology and crystal structure of the prepared samples were characterized using a high-resolution transmission electron microscopy (HRTEM, JEM-2100F, Japan). Field-emission scanning electron microscopy (FESEM) was carried out on a JEOL JSM-6340 F instrument (Japan). EDS spectrum was performed with an energy dispersive spectrometer equipped on the SEM equipment. UV-vis absorption spectra were recorded with a spectrophotometer (HITACHI, U-3900H, Japan). Fluorescence emission spectra were recorded on a FP-6500 spectrophotometer (JASCO, Japan). The inductively coupled plasma-mass spectrometry (ICP-MS) measurements were conducted using Perkin-Elmer ICP-MS NexION 300X. The absolute photoluminescence (PL) quantum yield of the NC solutions was measured by using an integrating sphere on an Absolute PL Quantum Yield Spectrometer C11347 at an excitation power of 0.1 mW (Hamamatsu, Japan). PL decay was measured using a NIR PL lifetime spectrometer (C12132, Hamamatsu Photonics). The EL spectra, *I-V-L* characteristics, and EQE were collected by using a Keithley 2400 source, a fiber integration sphere, and a PMA-12 spectrometer for light output measurements (the measurements equipment is designed by Hamamatsu Photonics Co., Ltd.).

### **2.** Computational methods

#### 2.1 Calculation of surface energies

Vienna *ab initio* simulation package (VASP)<sup>1-2</sup> was utilized to perform first-principles calculations based on the Density Functional Theory (DFT). The interactions between

electrons and nuclei were described by the projector augmented wave (PAW)<sup>3</sup> method. The exchange-correlation effect was described by the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functionals.<sup>4</sup> Kinetic energy cutoff for the planewave basis set expansion was set to 400 eV with a Gaussian smearing<sup>5</sup> of 0.1 eV in width. The first Brillouin zone (BZ) integration was sampled by a Monkhorst-Pack<sup>6</sup> *k*-point grid with resolution of 0.2 Å<sup>-1</sup>. For bulk model, the  $2 \times 2 \times 2$  supercell was constructed. The optimized lattice parameters are a = 13.39 Å, b = 19.57 Å, c = 11.58 Å. The slab models were constructed by cleaving the solid in the normal (1 1 1) direction. The three atomic layers at the bottom of the slab were fixed, while the rest of the atoms were fully relaxed. The vacuum layer of 15 Å was used to prevent the interaction between adjacent units. Dipole correction was also considered to minimize the polarization along the *z*-direction. The convergence criteria for the energy and Hellmann-Feynman force were  $1.0 \times 10^{-6}$  eV and 0.005 eV/Å, respectively.

The surface energy was calculated using

$$E_{\text{surface}} = [E_{\text{slab}} - (N_{\text{slab}}/N_{\text{bulk}})E_{\text{bulk}}]/2A,$$

where  $E_{\text{slab}}$  represents the surface slab,  $E_{\text{bulk}}$  stands for the bulk unit cell,  $N_{\text{slab}}$  is the atom number in slab,  $N_{\text{bulk}}$  is the atom number in bulk unit cell, and A is the surface area.

#### 2.2 Calculation of bond energies

All DFT calculations were carried out in the Kohn-Sham framework, using the Amsterdam Density Functional package (version ADF 2019.302).<sup>7-8</sup> For the calculation of bond energy, Mayer bond order, and Hirshfeld charge, the molecules are optimized at the PBE0 level of theory,<sup>9</sup> and zeroth-order regular approximation/triple-zeta with two polarization (ZORA/TZ2P) basis sets for all the atoms were used. Scalar relativistic effects are accounted, by using the zeroth-order regular approximation (ZORA) Hamiltonian.<sup>10-12</sup>



**Figure S1.** (a) TEM image, (b) TEM-EDS elemental mapping results, (c) XRD pattern (XRD pattern of the orthorhombic-phase CsAgCl<sub>2</sub> was provided for comparison), and (d) PL spectrum of the samples prepared by using TMSCl as halide precursor (excitation wavelength: 254 nm), similar to that synthesis of Cs<sub>2</sub>AgBiCl<sub>6</sub>.<sup>13</sup> Inset shows photographs of the corresponding samples taken under ambient light (left) and under 254-nm UV light (right), where we see no PL response.



Figure S2. XRD patterns of the samples prepared by different types of halide sources.

Table	<b>S1</b> .	The	Calculated	Mayer	Bond	Order,	Bond	Energy,	and	Hirshfeld
Charg	e of ]	Diffe	rent Types o	of Cl Do	nors.					

Halide	Bond type	Mayer bond	Bond	Hirshfeld	Hirshfeld
donor		order	energy	charge	charge
				(cation)	(Cl)
SbCl <sub>3</sub>	Sb-Cl	1.095	0.314	0.466	-0.155
YCl <sub>3</sub>	Y-Cl	0.964	0.312	0.824	-0.275
TbCl <sub>3</sub>	Tb-Cl	0.875	0.192	0.743	-0.248
GeCl <sub>4</sub>	Ge-Cl	1.117	0.352	0.399	-0.100
EuCl <sub>3</sub>	Sn-Cl	0.819	0.188	0.758	-0.253
InCl <sub>3</sub>	In-Cl	1.013	0.340	0.646	-0.215
CeCl <sub>3</sub>	Ge-Cl	1.005	0.287	0.770	-0.257
ErCl <sub>3</sub>	Er-Cl	0.849	0.232	0.730	-0.243
ZnCl <sub>2</sub>	Zn-Cl	1.081	0.362	0.506	-0.253
TMSCl	Si-Cl	1.070	0.320	0.148	-0.148



Figure S3. SEM-EDS mapping of the EuCl<sub>3</sub>-prepared CsAgCl<sub>2</sub> crystals.



**Figure S4.** XRD patterns of the NC samples prepared with and without OAm. The standard CsAgCl<sub>2</sub> (JCPDS No. 28-0377) was provided for comparison. The asterisk mark refers to the unknown phases and the circle mark indicates byproduct AgCl.

Table S2.	Quantitative	Analysis	Results	of	ICP-MS	for	Sb-Doped	CsAgCl <sub>2</sub>
Samples.								

Ag(OAc)	Sb(OAc) <sub>3</sub>	Molar percentage of
(mmol)	(mmol)	Sb <sup>3+</sup> in CsAgCl <sub>2</sub>
0.5	0	0
0.47	0.03	0.30%
0.45	0.05	0.70%

0.43	0.07	0.87%
0.40	0.10	1.00%
0.35	0.15	2.10%
0.30	0.20	3.91%
0.20	0.30	4.46%



Figure S5. Emission wavelength-dependent PLE spectra of the CsAgCl<sub>2</sub> NCs.



Figure S6. Excitation wavelength-dependent PL spectra of the CsAgCl<sub>2</sub> NCs.



Figure S7. Evolution of Sb 3d XPS spectra of CsAgCl<sub>2</sub> NCs with the etching cycle.



**Figure S8.** Temperature-dependent PL spectra and the integrated PL intensity as a function of inverse temperature for (a-b) the undoped and (c-d) Sb-doped CsAgCl<sub>2</sub> NCs.

**Supplementary Discussion 1** 

To gain more insight into the mechanism underlying the reduced particle size, surface energy of the CsAgCl<sub>2</sub> NCs was calculated by first-principles calculations based on DFT. It was found that after 1.0 mol% Sb<sup>3+</sup> doping, surface energy of the pristine CsAgCl<sub>2</sub> NCs was reduced by almost half (from 0.027 to 0.015 eV/A<sup>2</sup>), close to that of the most stable one, *i.e.*, the bulk state (surface energy ~0 eV/A<sup>2</sup>). This means that the doped CsAgCl<sub>2</sub> NCs become more stable and are easier to reach the stable state, making it unnecessary to increase their particle size to reduce surface energy. Therefore, compared to the undoped one, it would be easier for the doped NCs to retain their smaller particle size.



Figure S9. Energy band diagram of the LED devices with the use of TFB.



**Figure S10.** Time-dependent EL spectra of the fabricated LED devices working under bias voltage of 20 V. For all of these measurements the devices were completely unencapsulated, with RH ~40%.

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