## Bright Blue Emitting Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> Colloidal Nanocrystals

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Table S1. Composition of Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs measured by SEM-EDS and ICP-OES instrument. The amount of different elements was expressed relative to that Zn, which was assumed to be 1.

Cu/Zn precursors ratio	SEM-EDS analysis		
	Composition	Cu/Zn (%)	ICP-OES CU/Zn (%)
0/10	Cs <sub>1.96</sub> ZnCl <sub>4.57</sub>	/	/
0.1/9.9	Cs <sub>1.87</sub> ZnCl <sub>4.20</sub>	/	0.7
0.2/9.8	Cs <sub>2.00</sub> ZnCl <sub>4.48</sub>	/	2.1
0.5/9.5	Cs <sub>1.94</sub> ZnCl <sub>4.60</sub>	/	2.7
1/9	Cs <sub>1.95</sub> ZnCl <sub>4.57</sub>	4.0	4.3
2/8	Cs <sub>1.90</sub> ZnCl <sub>4.62</sub>	6.0	6.5
3/7	Cs <sub>1.84</sub> ZnCl <sub>4.30</sub>	7.0	7.5



Figure S1. SEM-EDS spectrum collected for the sample with analytical Cu concentration 7.5%.



**Figure S2.** Overview of TEM images with the corresponding size distribution histograms of (a) undoped and Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs with analytical Cu concentration of (b) 0.7%, (c) 2.1%, (d) 4.3%, (e) 6.5% and (f) 7.5%. The Cu concentration are defined as [Cu]/[Zn] by ICP-OES analysis.



**Figure S3.** HRTEM image and the corresponding Fast Fourier transforms (FFTs) of one of (a, b) 0.7 % Cu doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs and (c, d) 7.5 % Cu doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs, viewed along their [010] zone-axis.

## **EPR ANALYSIS**

In Figure S4 (right panel) the spectrum acquired for 4.3% Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs was simulated with the spin-Hamiltonian:

$$\hat{H} = \mu_B \hat{B} g \hat{S} + \hat{S} A_{Cu} \hat{I} + \hat{S} A_{Cl} \hat{I}$$

where **g** is the tensor,  $\mu_{\text{B}}$  is the Bohr magneton,  $\hat{B}$  is the magnetic field vector,  $\hat{S}$  and  $\hat{I}$  are the electron and nuclear spin operators respectively, and  $A_{cu}$  and  $A_{cl}$  are the hyperfine coupling tensors due to the interactions between the Cu(II) *d*-electron spins and the Cu and Cl nuclear spins respectively.

The simulation provides an axial spectroscopic *g*-factor with parallel and perpendicular values  $g_{\perp} = 2.089$  and  $g_{//} = 2.45$ , respectively; and anisotropic hyperfine interactions  $A_{Cu,\perp} = 119 \pm 5$  MHz,  $A_{Cu,//} = 50 \pm 5$  MHz,  $A_{Cl,\perp} = 30 \pm 5$  MHz and  $A_{Cl,//} = 60 \pm 5$  MHz.{Merks, et al. *J. Phys. C: Solid State Phys.* **1979**, *12*} The perpendicular and parallel components of the hyperfine tensor  $A_{cu}$  split in 4 lines (*i.e.* 2 I + 1) the EPR peaks centered around 270 mT and 330 mT, respectively; whereas the  $A_{cl}$  tensor provides a further split of the electronic energy levels in 4 lines which are responsible for the linewidth broadening of the EPR peaks.

The linewidth broadening of the EPR spectrum for 7.5% Cu-doped  $Cs_2ZnCl_4$  NCs (left panel) to the Cu(II) - Cu(II) electron spin interactions as result of the decreased averaged distance between the paramagnetic Cu(II) ions.



**Figure S4**. EPR spectra of 4.3% and 7.5% Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs (left) and the simulation of the EPR spectrum of the 4.3% Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NC sample (right).



**Figure S5.** Enlargement of the low-energy portion of the optical absorption spectra of Cu-doped  $Cs_2ZnCl_4$  NCs reported in Figure 2a, highlighting the emergence of an absorption feature at 3.05 eV (dashed vertical line) upon increasing the Cu concentration.



**Figure S6. (a)** PL spectra of Cu-doped  $Cs_2ZnCl_4$  NCs reported in Figure 2a and the respective Cu concentration dependences of (b) the PL maximum peak energy ( $E_{max}$ ) and (c) FWHM, both showing nearly invariance upon increasing [Cu].



**Figure S7.** Cu dependence of the Stokes shift of Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs calculated as the difference between the PLE maximum peak energy and the PL maximum peak energy.

## Alternative Synthesis Approach of Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub>

We synthesized Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs following a different colloidal route. A Cs-oleate precursor solution was prepared by dissolving 0.325 g of Cs<sub>2</sub>CO<sub>3</sub> with 5 ml of OA on hotplate at 150°C. 0.4 mmol of ZnCl<sub>2</sub>, 0.08 mmol CuCl, 2 ml ODE, 1 ml OA, 1 ml OLAM were mixed in a 20 ml vial and heated up to 100°C for 30min on a hotplate. Then, the temperature was further increased up to 130°C and 500  $\mu$ l of the Cs-oleate solution were swiftly injected. After 5min, the reaction was stopped by immersing the vial in a water bath. The TEM images, XRD analysis and optical properties of the obtained NCs are reported in Figure S12.



**Figure S8.** a) TEM micrograph, b) XRD pattern and c) optical properties of Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs obtained by employing an alternative colloidal approach.



Figure S9. PLE curve of the 0.7% Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NC sample with a magnification of the 380-420 nm region (inset).



**Figure S10.** Stretching factor,  $\beta$ , of Cu-doped Cs<sub>2</sub>ZnCl<sub>4</sub> NCs obtained by the fitting procedure of the PL decay curves with a stretched exponential function as reported in Figure 2c.



**Figure S11.** a) PL and b) absorption spectra of 2.1% Cu-doped  $Cs_2ZnCl_4$  NCs dispersed in hexane and exposed to air up to 60min. c) XRD patterns of 2.1% Cu-doped Cs2ZnCl4 NCs before and after 60 min of exposure to air.

Table S2. Bond and angle parameters of metal chloride units embedded in the 0D structure computed at the DFT/PBE level of theory on a 2x2x2 cell and at the  $\Gamma$  point. In some cases, the copper chloride moieties present geometrical parameters that slightly deviate from the ideal symmetry due to a different interaction with the surrounding embedding media.

Structural Parameter	Cs <sub>2</sub> ZnCl <sub>4</sub>	Cu(II):Cs $_2$ ZnCl $_4$ with Cu(II) as [CuCl $_4$ ] $^3$ -	Cu(I):Cs <sub>2</sub> ZnCl <sub>4</sub> (absorption)	$Cu(I):Cs_2ZnCl_4$ (emissive state)
[M = Zn, Cu]		unit	with Cu(I) as [CuCl <sub>3</sub> ] <sup>2-</sup> unit	with Cu(I) as $[CuCl_3]^{2-}$ unit
M-CI (Å)	~2.29	2.26/2.28/2.28/2.28	2.23/2.26/2.29	2.28/2.39/2.41
CI-M-CI (deg)	~109	98/102/122/132	113/118/129	95/100/113
CI-M-CI-CI (deg)	~120 (tetrahedral)	~115 (pseudo- tetrahedral)	~3-5 (trigonal planar)	~115 (trigonal pyramidal)



**Figure S12**. Molecular orbital plot of the lowest state of the conduction band, referred to the Figure 3e in the main text. An interesting feature here is that conduction band states are delocalized and composed by the linear combination of empty 4s orbitals of Cu with both the 6s of Cs and 4s of Zn. Color-code: Cs(cyan), Cu(blue), Zn(red), Cl(green).

## Synthesis of undoped and Cu-doped Cs<sub>2</sub>ZnBr<sub>4</sub> and Cs<sub>2</sub>ZnI<sub>4</sub> NCs

We employed the same reaction strategy reported in the main text and we substituted benzoyl chloride with either benzoyl bromide or iodide to produce also Cu-doped  $Cs_2ZnBr_4$  and  $Cs_2ZnI_4$  NCs. We could not obtain  $Cs_2ZnI_4$  nor Cu-doped  $Cs_2ZnI_4$  NCs, while in the case of both undoped and Cu-doped  $Cs_2ZnBr_4$  NCs we observed the formation of elongated parallelepiped NCs (rod-like) (Figure S13 c-d) exhibiting the orthorhombic  $Cs_2ZnBr_4$  crystal structure (ICSD number 41537) (Figure S13 a). The synthesis was carried out at 150°C and the reaction time was 0s, that is, the reaction was quenched immediately after the injection of Bz-Br. While undoped  $Cs_2ZnBr_4$  did not exibith any PL emission, Cu-doped NCs were characterized by a PL peak located at 465 nm with the corresponding PLE peak located at 270 nm (Figure S13 b).



Figure S13. a) XRD patterns, b) optical properties and c-d) TEM micrographs of undoped and Cu-doped Cs<sub>2</sub>ZnBr<sub>4</sub> NCs