## **Electronic Supplementary Information**

## Nanocrystals of Divalent Europium-Doped CsPbCl<sub>3</sub> Perovskite: A Novel Optoelectronic Material with Dual-Emissions

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**Figure S1 (a)** XRD patterns of Eu: CsPbCl<sub>3</sub> samples prepared with different Eu doping concentrations. **(b-d)** Crystallite sizes evaluated from XRD results using the Scherrer equation for different crystalline planes.



**Figure S2 (a)** TEM image and **(b)** size distribution of the pristine CsPbCl<sub>3</sub> PeNCs. **(c)** HRTEM micrograph and **(d)** the corresponding FFT image showing atomic lattice fringes. **(e)** EDX mapping of the pristine CsPbCl<sub>3</sub> PeNCs.



**Figure S3** Typical EDX analyses of **(a)** the undoped and **(b)** Eu-doped CsPbCl<sub>3</sub> (red circle represents the presence of Eu element).



Figure S4 HRXPS profiles of Cs  $(3d_{3/2}, 3d_{5/2})$  energy states from the un-doped CsPbCl<sub>3</sub> and Eu-doped CsPbCl<sub>3</sub> PeNCs.



Figure S5 Two-dimensional excitation-emission mapping for (a) the CsPbCl<sub>3</sub> and (b)

Eu: CsPbCl<sub>3</sub> PeNCs.



**Figure S6 (a)** PL spectra for the broadband Eu<sup>2+</sup> emission of the Eu: CsPbCl<sub>3</sub> PeNCs prepared with different amounts of Eu concentrations. **(b)** PL spectra recorded by a FLS1000 spectrofluorometer equipped with an integrating sphere to determine PLQY.



**Figure S7** CIE color coordinates for the Eu: CsPbCl<sub>3</sub> samples, showing that the emitting color of the product changes from blue to orange upon increase of Eu doping content.



Figure S8 (a) Power-dependent PL spectra of the Eu: CsPbCl<sub>3</sub> sample and (b) the integrated PL intensity versus excitation power. The red line is a linear fitting.



Figure S9 The variation of PL intensity with the elongation of decay time.



**Figure S10** Pump-probe fs-TA spectra of (a) the CsPbCl<sub>3</sub> and (b) Eu: CsPbCl<sub>3</sub> PeNCs at different delay times.



Figure S11 Normalized temperature-dependent (11~300 K) PL spectra of the Eu: CsPbCl<sub>3</sub> PeNCs.

With elevation of temperature, host PL (i.e. exciton emission) quenches faster than  $Eu^{2+}$  emission owing to low exciton binding energy, which leads to the observed weak host PL and strong  $Eu^{2+}$  emission at room temperature.



**Figure S12** Temperature-dependent PL decay curves for **(a)** the CsPbCl<sub>3</sub> and **(b)** Eu: CsPbCl<sub>3</sub> PeNCs.



**Figure S13** Integrated PL intensity of exciton recombination for the Eu: CsPbCl<sub>3</sub> sample as a function of temperature, which is used to evaluate exciton binding energy.



**Figure S14** Orbital projected band structures and VBM/CBM orbital arrangements of CsEuCl<sub>3</sub>. The green, orange, blue, and yellow colors represent the Cl-3p, Eu-4f, Cs-4d and Eu-4d states, respectively.



Figure S15 Projected DOS for CsEuCl<sub>3</sub>.

Table S1 The calculated values of several key parameters for centroid shift and crystal

Parameter	Value
$R(Eu^{2+})$ (ppm)	117
$R(Pb^{2+}) (ppm)$	118
R(Eu-Cl) (ppm)	286
R(Eu-O) (ppm)	240
χ <sub>Cs</sub>	0.79
Хрь	2.33
χ <sub>av</sub>	1.82
αCl sp (10-30 m <sup>3</sup> )	2.46
αο sp (10 <sup>-30</sup> m <sup>3)</sup>	1.78
$\varepsilon_{c}(eV)$	0.75
$\epsilon_{cfs}(eV)$	0.81
D (eV)	1.16
$E_x(eV)$	3.06
$E_m(eV)$	2.22