

Electronic Supporting Information

Colloidal synthesis of emission tunable Cu-doped Zn-In-Se/ZnSe core/shell nanocrystals toward lighting and bioimaging applications

Joicy Selvaraj,¹ Arun Mahesh,² Vaseeharan Baskaralingam,³ Arunkumar Dhayalan², Miguel
Ángel Gracia Pinilla,⁴ Saravanan Rajendran⁴, and Thangadurai Paramasivam^{1,*}

1. Centre for Nanoscience and Technology, Pondicherry University, Puducherry - 605 014, India.

2. Department of Biotechnology, Pondicherry University, Puducherry - 605 014, India.

3. Department of Animal Health and Management, Alagappa University, Karaikudi – 630 003, Tamil
Nadu, India.

4. Faculty of Engineering, Department of Mechanical Engineering, University of Tarapacá, Avda,
General Velasquez, 1775, Arica, Chile

*thangaduraip.nst@pondiuni.edu.in / thangadurai.p@gmail.com

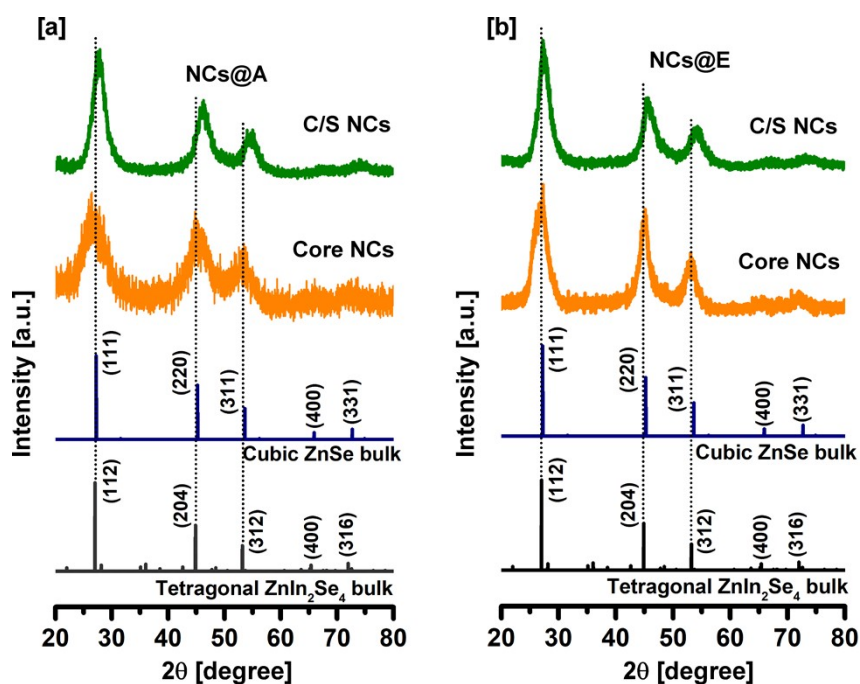


Figure S1. Comparative X-ray diffraction patterns of Cu^{I} :Zn-In-Se with the heavily doped and undoped core NCs along with their resulting C/S NCs after three batches of Zn-precursor injection. (a) NCs@A (Pristine, undoped) and (b) NCs@E (Cu-doped, 0.08 mmol of dopant concentration)

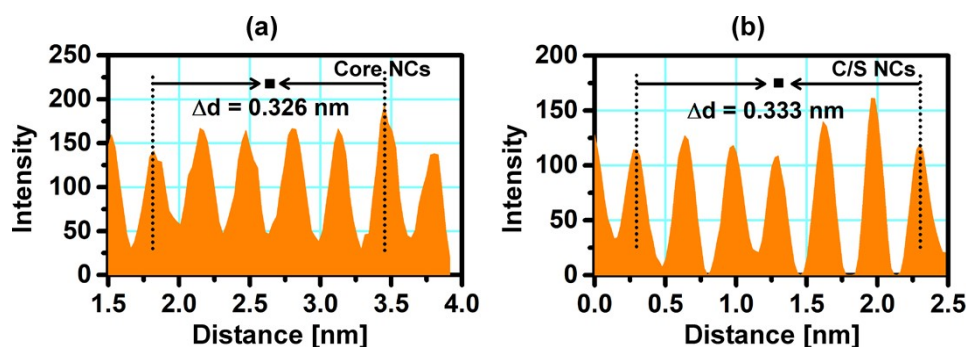


Figure S2. The intensity line profiles of lattice fringes obtained for (a) Cu^{I} doped Zn-In-Se alloy core NCs along the green line marked in Fig. S2b of main content and (b) Cu^{I} :Zn-In-Se/ZnSe C/S NCs along the green line marked in Fig. S2f of main content.

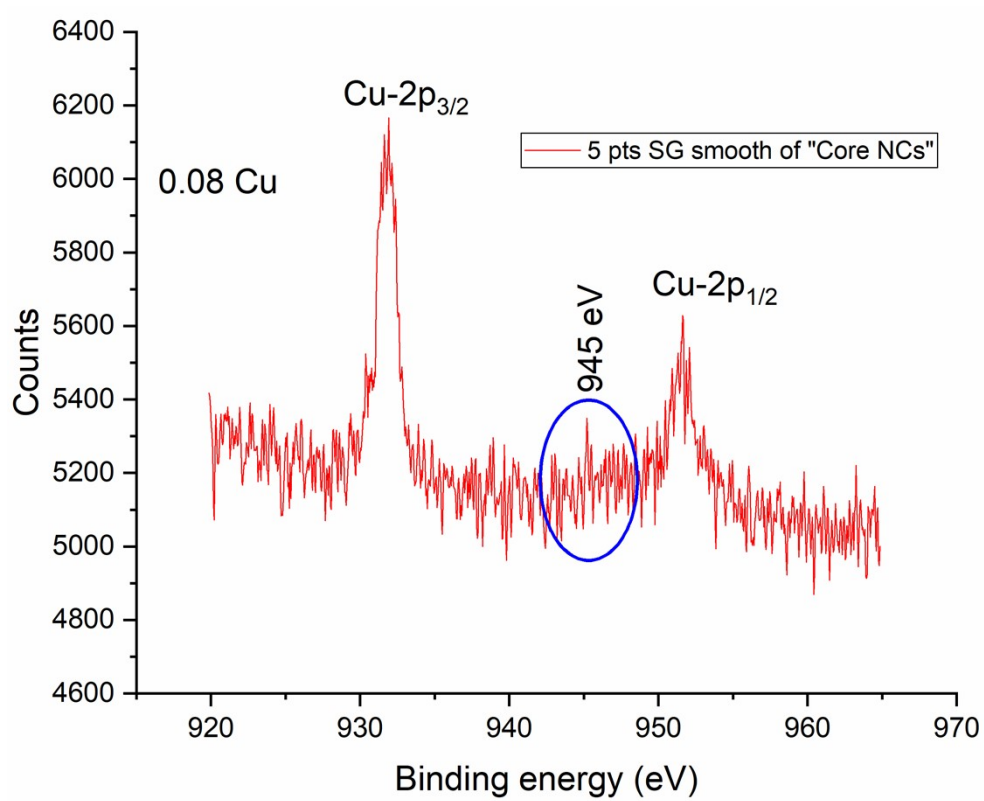


Figure S3. XPS spectra of core NC with 0.08 Cu doping.

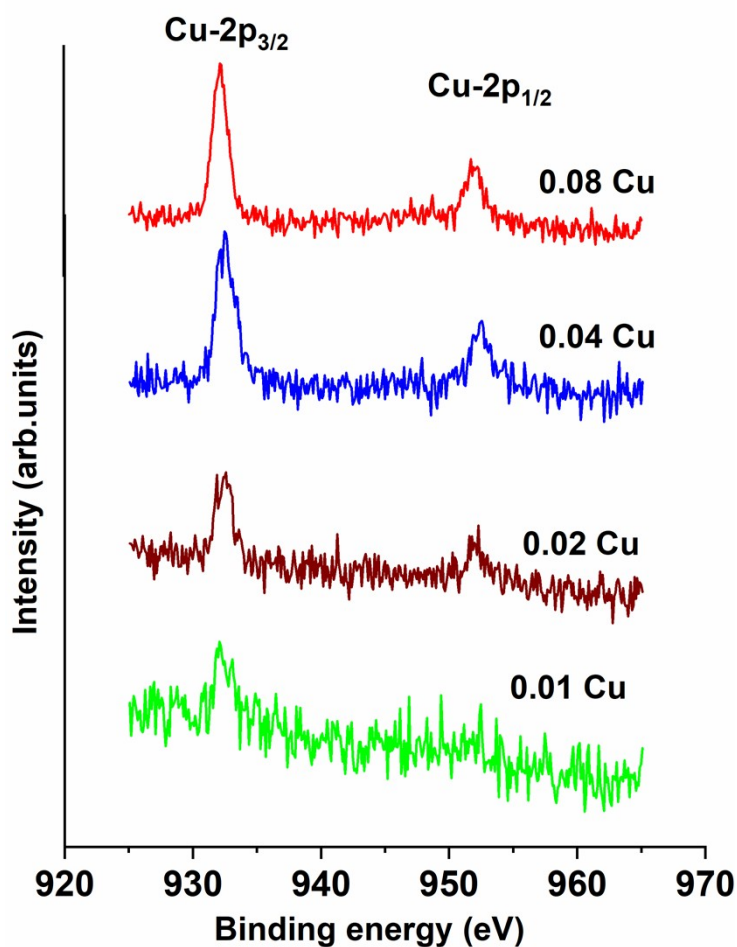


Figure S4. Cu-2*p* XPS spectra of Cu^I:Zn-In-Se core NCs.

Table T1: Quantification results obtained from XPS data for the core QDs with different Cu content.

0.01 mmol Cu

Name	Peak BE	Area (P) CPS.eV	Atomic %
Se 3d	56.07	239509.62	72.21
In 3d	445.29	591778.54	12.90
Cu 2p	932.83	101141.56	2.15
Zn 2p	1022.17	365539.33	12.74

0.02 mmol Cu

Name	Peak BE	Area (P) CPS.eV	Atomic %
Se 3d	55.24	306957.6	63.73
In 3d	445.33	1115213.49	14.68
Cu 2p	932.86	149187.95	3.8
Zn 2p	1022.29	740670.27	17.78

0.04 mmol Cu

Name	Peak BE	Area (P) CPS.eV	Atomic %
Se 3d	55.26	377815.42	62.62
In 3d	445.19	1377678.03	14.48
Cu 2p	932.27	210919.8	4.29
Zn 2p	1022.16	971346.34	18.61

0.08 mmol Cu

Name	Peak BE	Area (P) CPS.eV	Atomic %
Se 3d	55.46	279744.44	62.75
In 3d	445.73	895627.87	12.74
Cu 2p	953.04	214632.91	6.07
Zn 2p	1022.34	711025.96	18.44

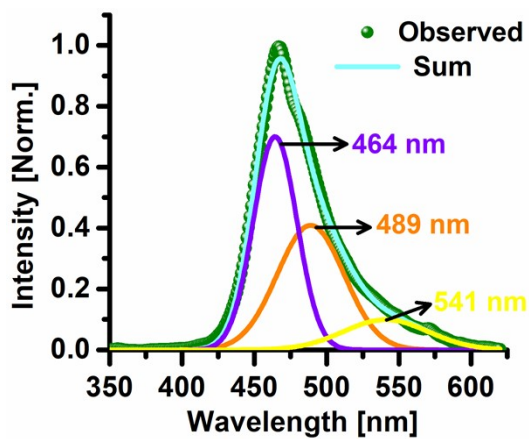


Figure S5. Deconvoluted fluorescence spectrum of pristine Zn-In-Se alloy core NCs excited at the wavelength of 320 nm.

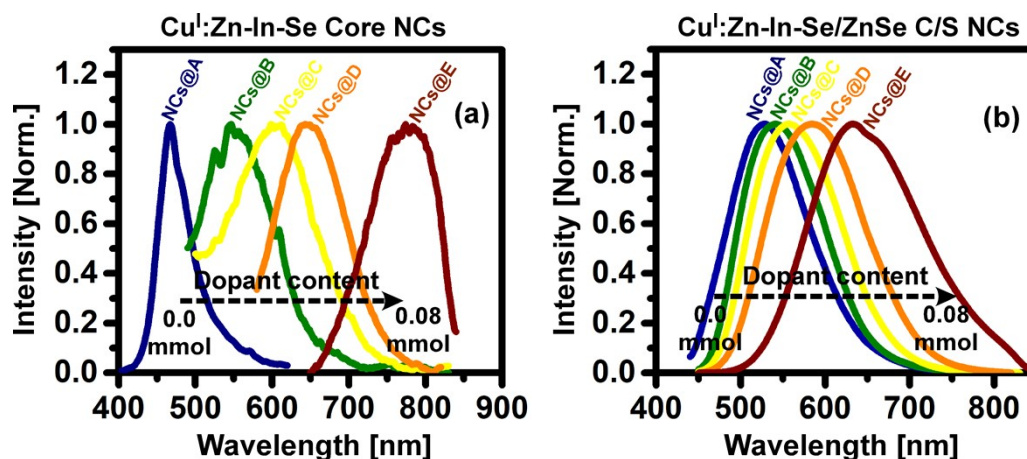


Figure S6. The normalized emission spectra of (a) Cu^I:Zn-In-Se core NCs and (b) Cu^I:Zn-In-Se/ZnSe C/S NCs (Batch 3) with various Cu dopant concentration in the core NCs.

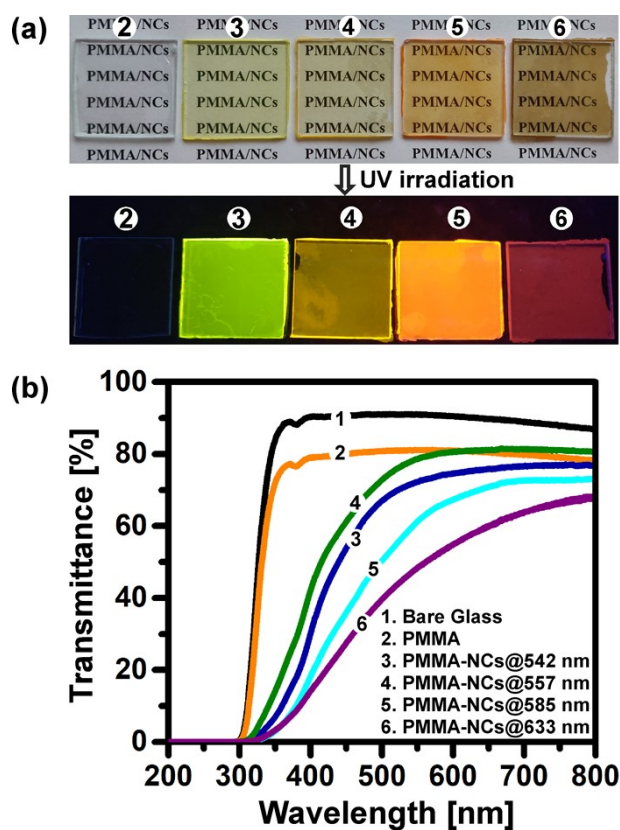


Figure S7. (a) Digital photographs of PMMA-NCs composite films coated on the glass slides excited under ambient light and UV light. (b) A series of optical transmittance spectra of PMMA-NCs composite films with various emission colors on the glass substrate. The numbers marked in (a) and (b) represent that they are from the same sample.

Table T2. The PL parameters of the color-tunable Cu^I:Zn-In-Se/ZnSe NCs before (NCs solution) and after embedding with the PMMA, the PMMA-NCs composite film.

Sample Code	Emission maximum (nm)		Emission linewidth (nm)	
	NCs solution	PMMA-NCs composite film	NCs solution	PMMA-NCs composite film
NCs@542nm	542	544	93.3	97.0
NCs@557nm	557	569	101.8	106.4
NCs@585nm	585	618	111.7	115.7
NCs@633nm	633	703	146.0	170.5

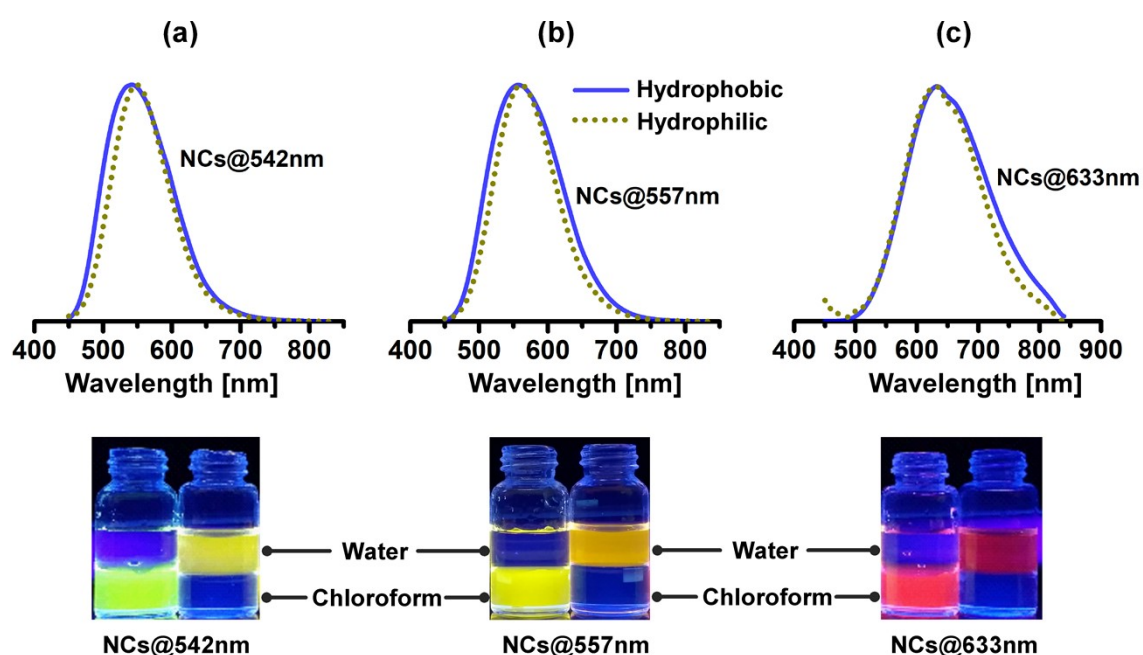


Figure S8. Normalized fluorescence intensity spectra of Cu^I:Zn-In-Se/ZnSe C/S NCs before (OLA coated) and after (11-MUA coated) ligand exchange. **(a)** NCs@542nm, **(b)** NCs@557nm and **(c)** NCs@633nm. The visual comparison of NCs before and after ligand exchange is shown in digital photographs acquired under UV excitation, below the emission spectrum.

Fitting and Calculations of Fluorescence Decay Curves:

The fluorescence decay curves were fitted by the tri-exponential function;

$$I(t) = \alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} + \alpha_3 e^{-t/\tau_3} \quad (\text{SE1})$$

where t represents time, τ_1 , τ_2 and τ_3 are florescence decay times, α_1 , α_2 and α_3 are the corresponding decay amplitudes fraction.

The amplitude weighted average lifetimes were calculated using the following equation

$$\langle \tau_{\text{avg}} \rangle = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2 + \alpha_3 \tau_3^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3} = f_1 \tau_1 + f_2 \tau_2 + f_3 \tau_3 \quad (\text{SE2})$$

The fractional intensities (f_1 , f_2 and f_3) give the weight of each recombination path and defined as

$$f_{1(2,3)} = \frac{\alpha_{1(2,3)} \tau_{1(2,3)}}{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3} \quad (\text{SE3})$$