Room Temperature Synthesis of Stable, Printable $Cs_3Cu_2X_5$ (X=I, Br/I, Br, Br/ Cl, Cl) Colloidal Nanocrystals with Near Unity Quantum Yield Green Emitters (X=Cl)

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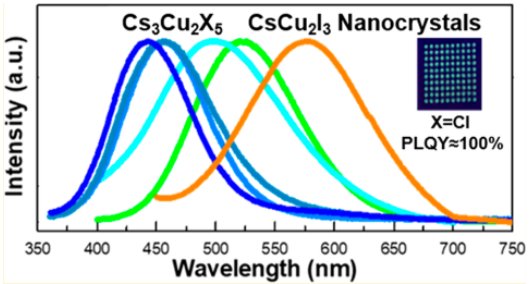
Abstract

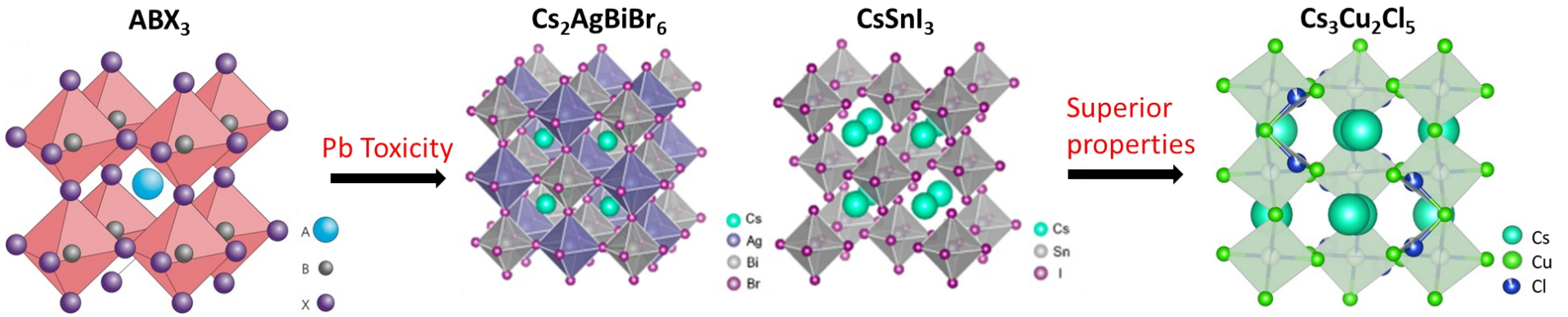
Lead halide perovskite nanocrystals (NCs) have shown remarkable properties for emission applications, but their toxicity and instability are a hindrance to many commercial uses. Herein, we synthesized lead-free all-inorganic $Cs_3Cu_2X_5$ (X = I, Br/I, Br, Br/Cl, Cl) colloidal nanocrystals as members of the metal-metal halide family of materials. These nanocrystals have uniform sizes less than 10 nm in diameter and show excellent optical properties, including composition-tunable emission spectra over the spectral region of 440-530 nm; high photoluminescence quantum yields of ~100, 20, and 30% for X = Cl, Br, and I, respectively; and large effective Stokes shifts of over 100 nm for all species. Pure- and mixed-halide materials show tunable emission with the halide concentration, with a large fwhm of 80-110 nm due to a widely reported exciton self-trapping emission mechanism. Notably, the $Cs_3Cu_2Cl_5$ NCs exhibit a near-unity quantum yield with an emission at 520 nm, high crystallinity, and good stability. These materials can be processed and maintained in adequately stable dispersions to enable inkjet printing of these materials into arbitrary patterns. These results indicate that cesium copper chloride NCs may have great potential for the future display or lighting applications.



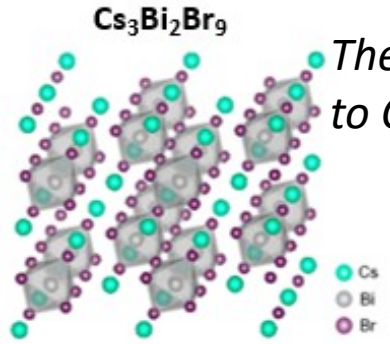
Introduction

Luo *et al. ACS Appl. Mater. Interfaces* (2019)
Green . *et al. Nature Photonics* (2014)

Pb-based perovskites → Lead-free perovskites → Cu-based perovskite variants



$[BX_6]^{4-}$ octahedra is oraganized in an all-corner sharing 3D network



The Cu^+ ions are tetrahedrally coordinated to Cl- and disordered over two sites

Advantages of $CsPbX_3$ (X= Cl, Br, I)

- Excellent optical absorption
- Low exciton binding energy
- Tunable bandgap
- Relatively long diffusion length of charge carriers
- High photoluminescence quantum yield (PLQY)

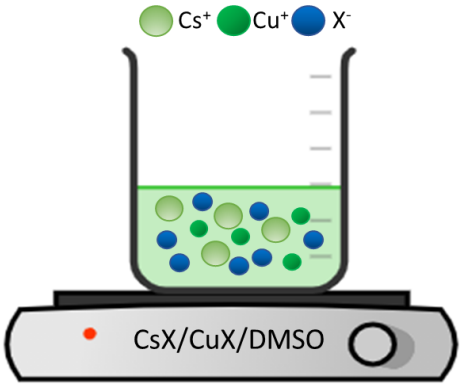
Advantages of Cu-based halides:

- Outstanding optoelectronic properties
- Abundance
- Low cost
- Low environmental impact

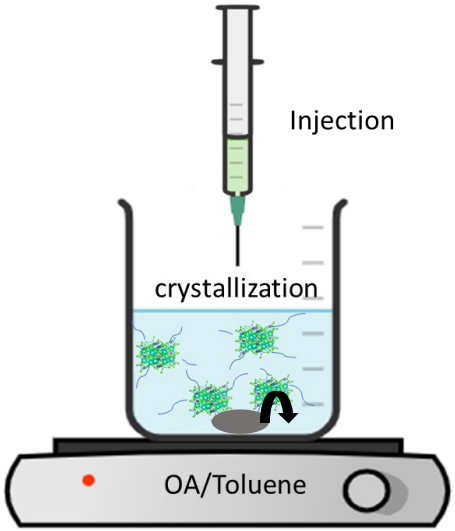
Methods

Li, Y. *et al. Chem. Mater.* (2020)

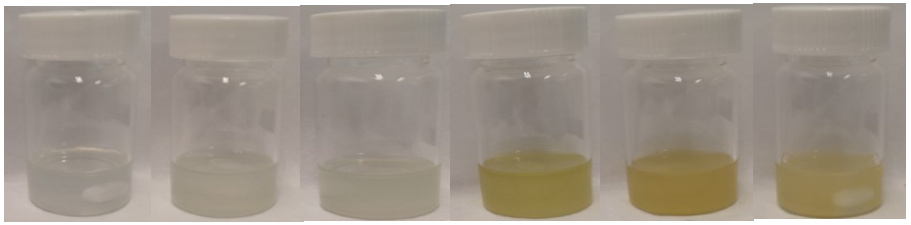
Anti-solvent recrystallization: Adding a polar precursor solution in a good solvent to a nonpolar poor solvent. The mixture of the two solvents under vigorous stirring induces an instantaneous supersaturation, triggering the nucleation and growth of NCs.



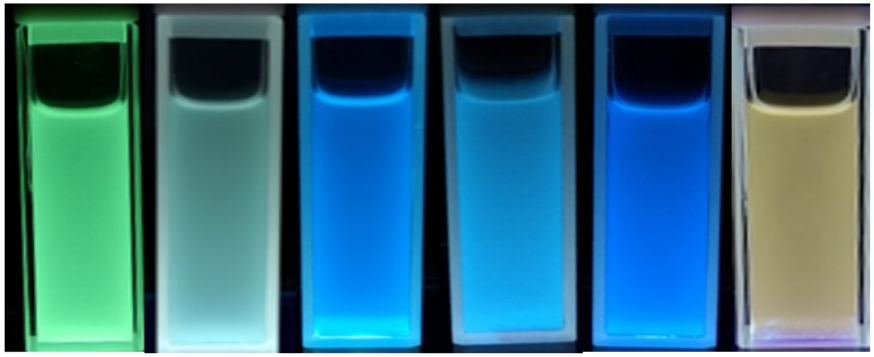
Precursor



After synthesis



UV



X=Cl X=Cl/Br X= Br X=Br/I X=I **$CsCu_2I_3$**

$Cs_3Cu_2X_5$ NCs

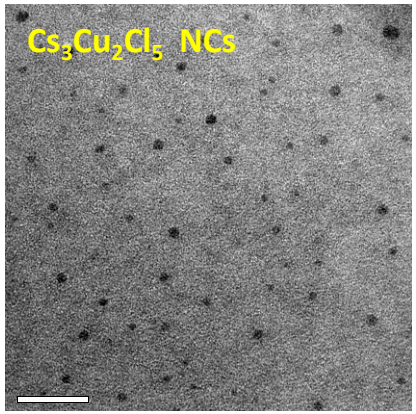
Easy to fabricate:

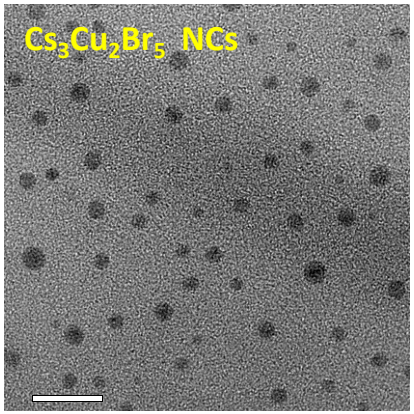
- Room temperature
- Under ambient condition

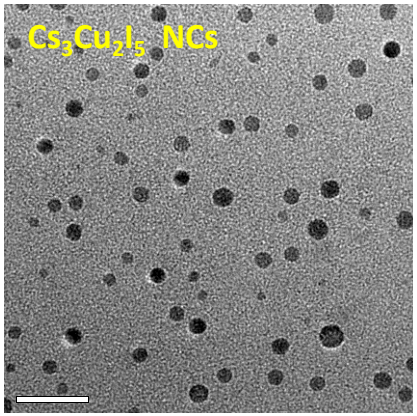
Results

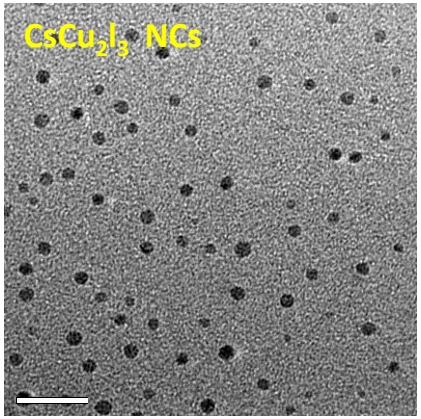
Li, Y. *et al. Chem. Mater.* (2020)

Transmission electron microscopy (TEM) images

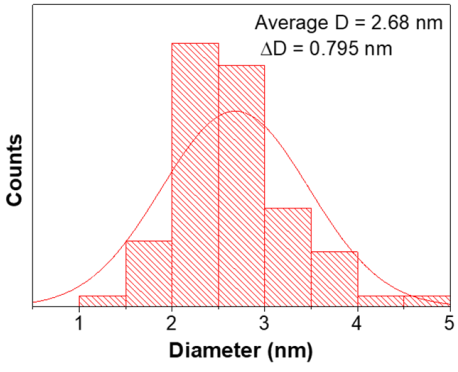


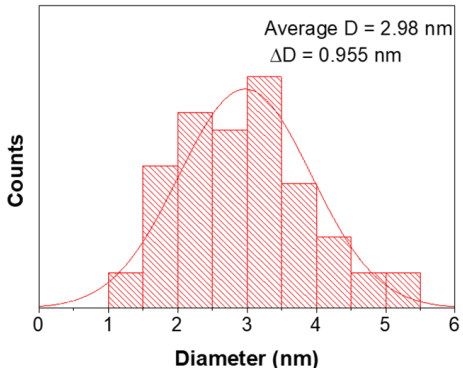


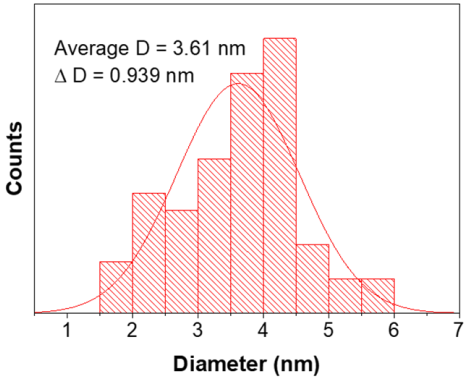


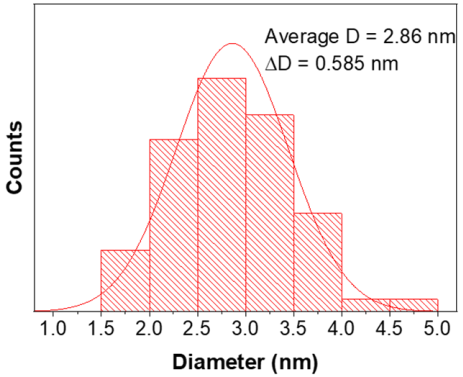


Size distribution histograms







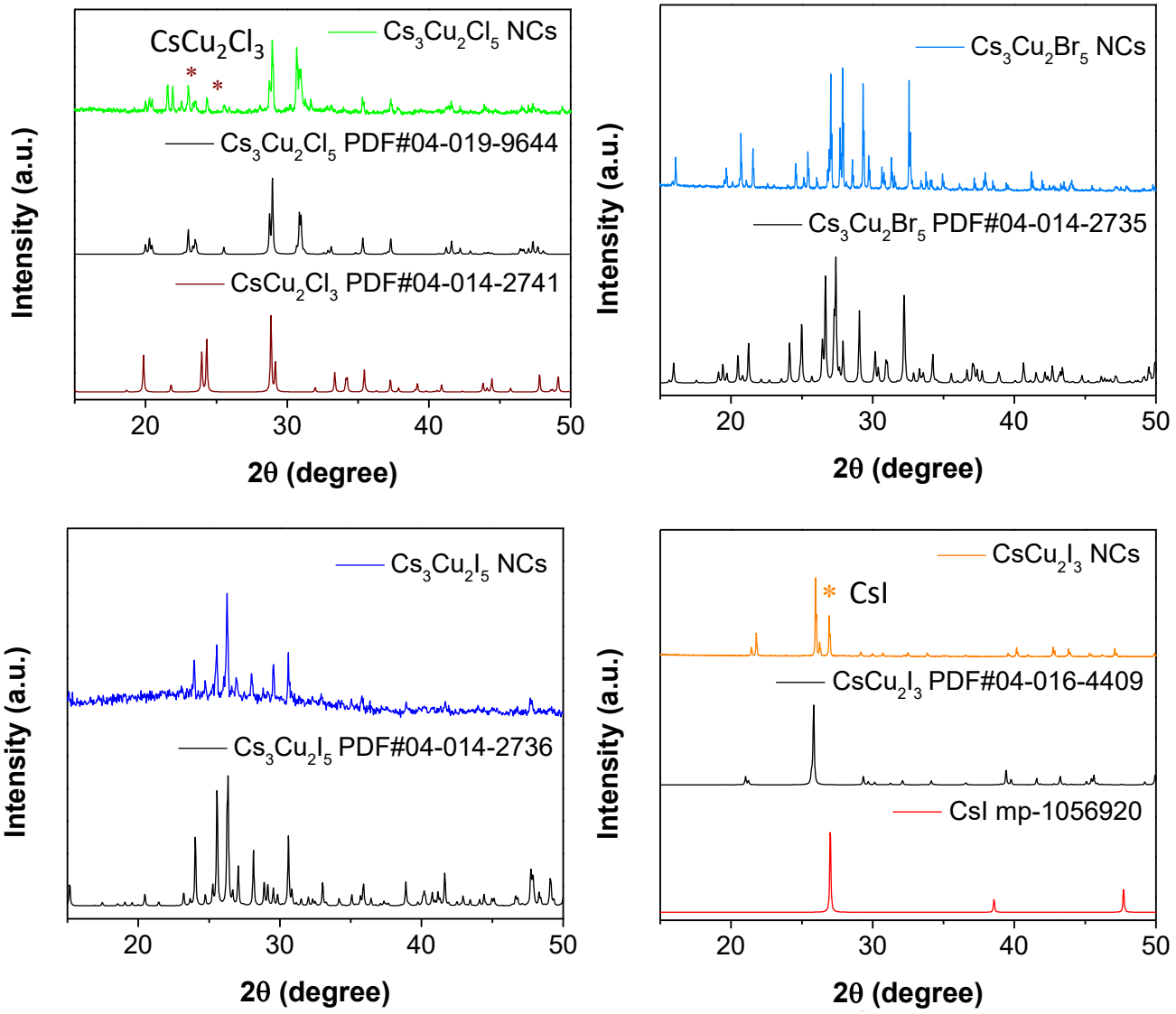


Spherical shapes with average diameters of 2 - 4 nm for $Cs_3Cu_2X_5$ (X=Cl, Br, I) and $CsCu_2I_3$ NCs

Results

Li, Y. *et al. Chem. Mater.* (2020)

X-ray diffraction (XRD)



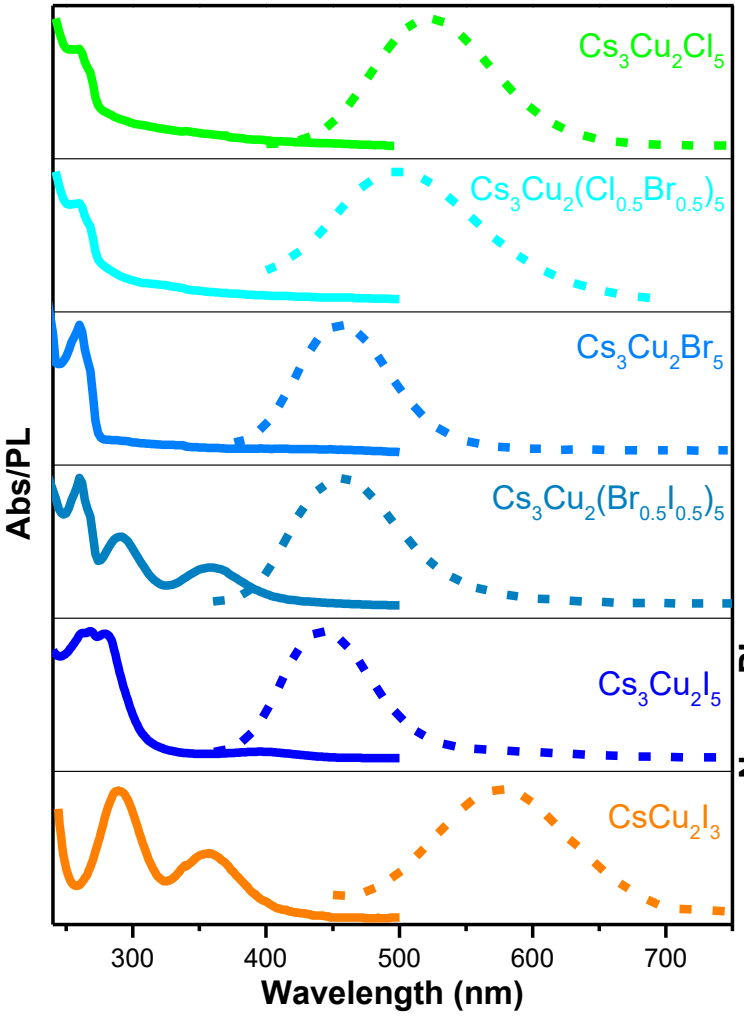
Good match with the standard XRD patterns: confirmation of the formation of the materials

Results

Li, Y. *et al. Chem. Mater.* (2020)

Optical properties

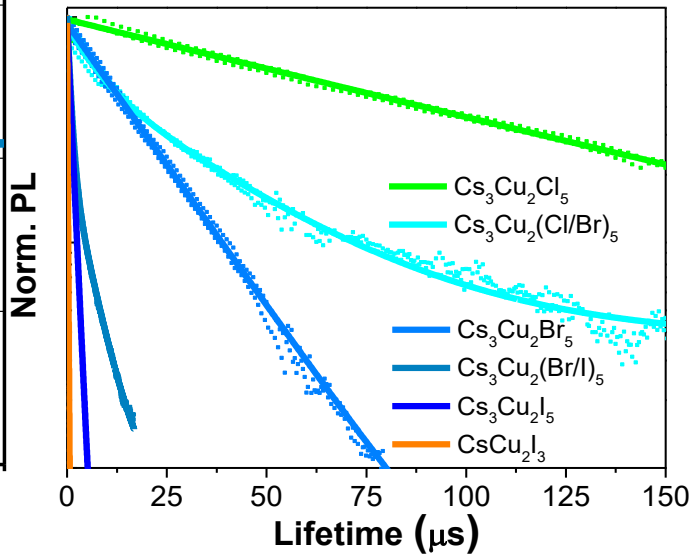
Composition-tunable UV-vis and PL spectra



Summary of PL parameters for colloidal $Cs_3Cu_2X_5$ and $CsCu_2I_3$ NCs

NCs	PLQY (%)	Emission peak (nm)	FWHM (nm)	Lifetime (μs)
$Cs_3Cu_2Cl_5$	≈ 100	521	104	97.7
$Cs_3Cu_2(Cl_{0.5}Br_{0.5})_5$	6	508	85	22.5
$Cs_3Cu_2Br_5$	20	458	82	17.3
$Cs_3Cu_2(Br_{0.5}I_{0.5})_5$	36	457	93	1.4
$Cs_3Cu_2I_5$	30	443	80	1.1
$CsCu_2I_3$	11	569	112	0.12

Time-resolved PL decays



Features:

- Broad spectra
- Large Stokes shifts
- Long PL lifetimes

Applications

Li, Y. *et al. Chem. Mater.* (2020)

Inkjet printing

- **Ink preparation:**

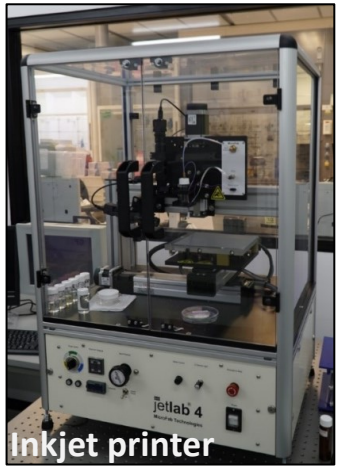
Purified $Cs_3Cu_2Cl_5$ NCs solution is mixed with crystal monomer and dichlorobenzene.

- **Silicon substrate preparation:**

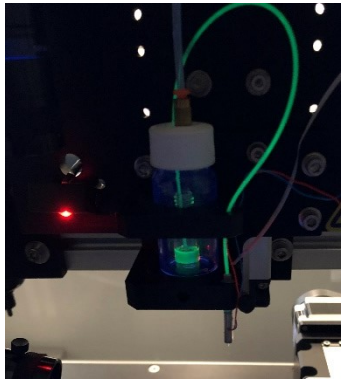
Clean silicon substrates coated with 1H,1H,2H,2H-perfluorodecyltricholorosilane.

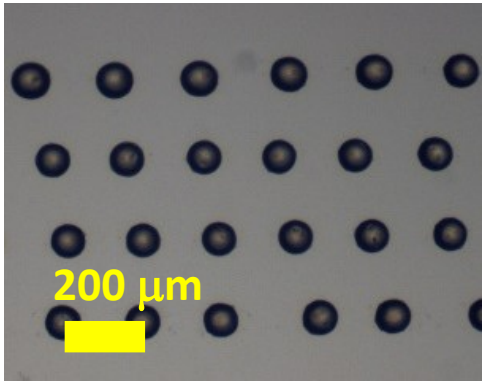
- **Inkjet printing process:**

MacroFab Jetlab 4 Inkjet deposition system → Liquid crystal polymerizes under 365 nm UV.

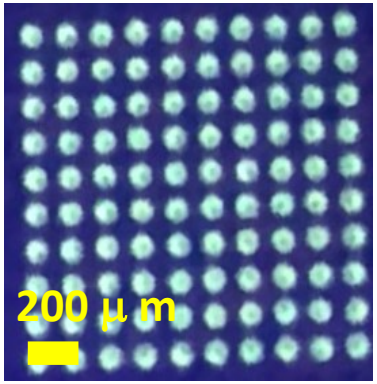


Inkjet printer


During printing (under UV)



Array on silicon substrate



Under UV light

Applications

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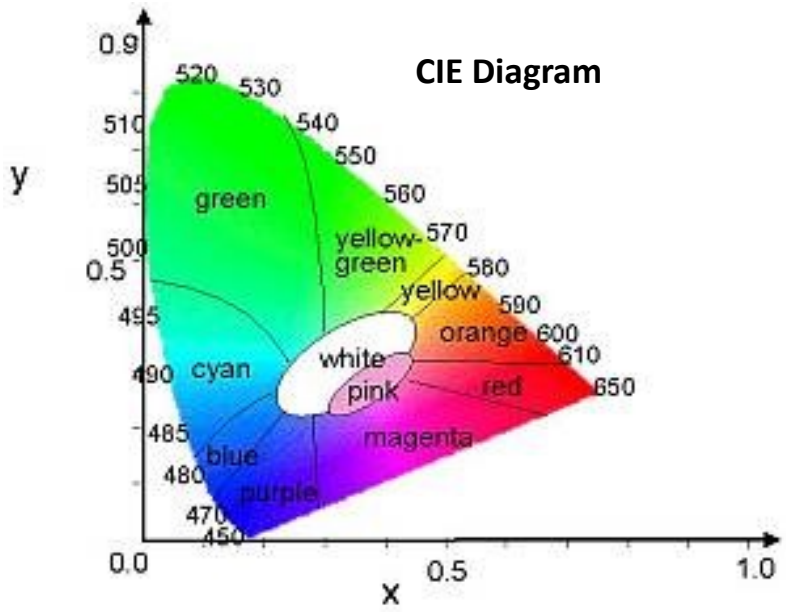
Display

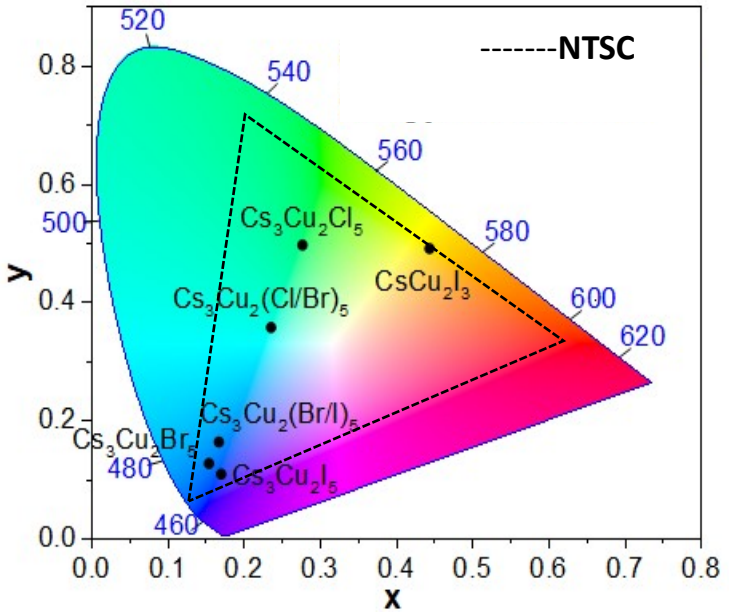
- **CIE (Commission Internationale de l'Eclairage) chromaticity diagram:**

Allows the comparison of the quality of colors by mapping colors visible to the human eye in terms of hue and saturation.

- **NTSC:**

The first broadcast standards for color TV.





Color gamut of $Cs_3Cu_2X_5$ and $CsCu_2I_3$ NCs (black dots)

Applications

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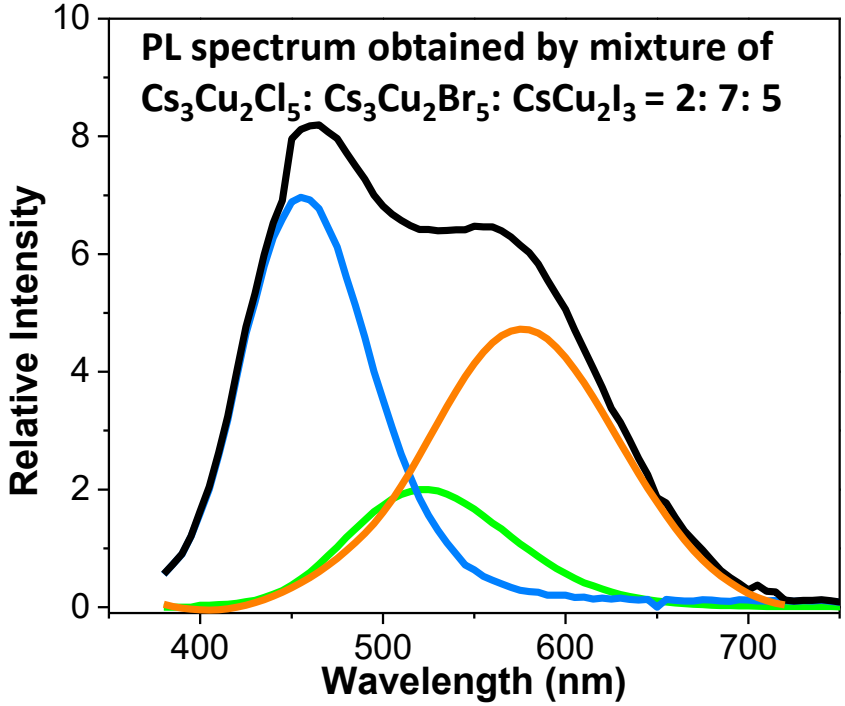
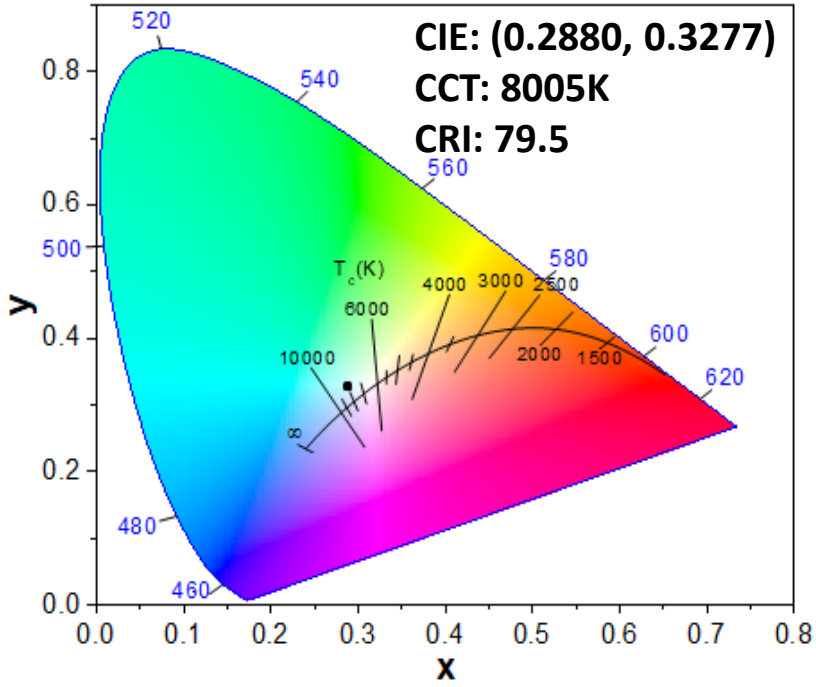
White light

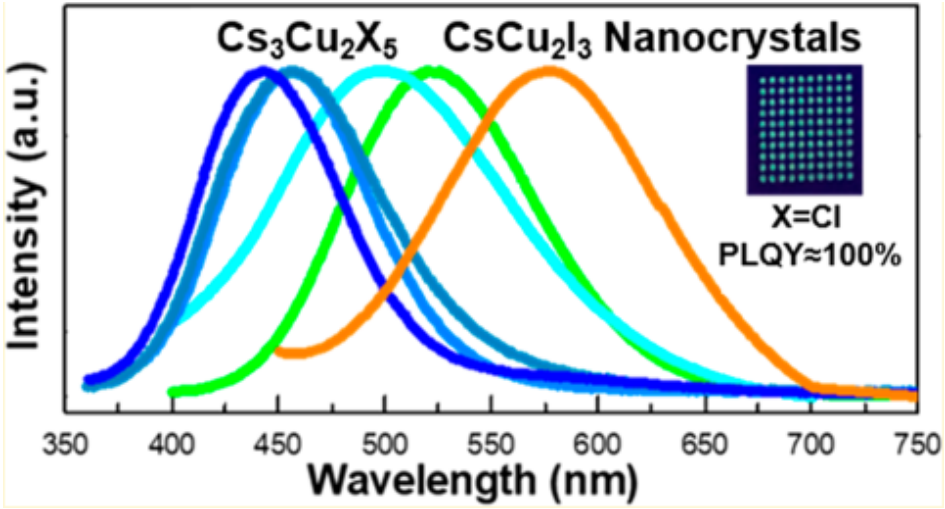
- **CIE** and **CRI** is the primary metric for how "white" light is
- **Color Rendering Index (CRI)** describes how other objects appear when subjected to "white" light sources
- 100% means that the white light fits to a blackbody emitter at a set color temperature
- After choosing a target "heat" the apparent brightness for each colour under a test light lamp is compared to that of a blackbody emitter





Conclusions

- Non-toxicity
- Outstanding optical properties (emission tunability, high PLQY)
- Easy fabrication
- Printable
- Potential for low-cost, non-toxic LED, displays or white light



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