# **Supporting Information**

## Room Temperature Synthesis of Low-Dimensional Rubidium Copper Halide Colloidal Nanocrystals with Near Unity Photoluminescence Quantum Yield

Parth Vashishtha<sup>†</sup>\*, Thomas J.N. Hooper<sup>‡</sup>, Yanan Fang<sup>†</sup>, Deviana Kathleen<sup>†</sup>, David Giovanni<sup>§</sup>, Maciej Klein,<sup>II</sup><sup>§</sup> Tze Chien Sum<sup>§</sup>, Subodh G. Mhaisalkar<sup>†</sup>I, Nripan Mathews<sup>†</sup>I\*, and Tim White<sup>†</sup>\*

<sup>†</sup>School of Materials Science and Engineering, Nanyang Technological University (NTU), 50 Nanyang Avenue, Singapore 639798, Republic of Singapore

<sup>\*</sup>*High Field NMR Facility, School of Physics and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Republic of Singapore* 

*Energy Research Institute @NTU (ERI@N), Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive, Singapore 637553, Republic of Singapore* 

<sup>§</sup>Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Republic of Singapore

### **Experimental Section**

**Materials:** Rubidium bromide (RbBr, 99.9%, Sigma Aldrich). Copper(I) bromide (CuBr, 99.8%, Sigma Aldrich), Rubidium Chloride (RbCl,  $\geq$ 99.0%, Sigma Aldrich), Copper(I) Chloride (CuCl, >99.995%, Sigma Aldrich), Dimethylsulfoxide (DMSO, Anhydrous,  $\geq$ 99.0%, Sigma Aldrich), Isopropyl alcohol (IPA, Anhydrous, 99.5%, Sigma Aldrich), Toluene (Anhydrous, 99.8%, Sigma Aldrich), Oleic Acid (Sigma Aldrich).

Synthesis of  $Rb_2CuBr_3$  and  $Rb_2CuCl_3$  nanocrystals: Both nanocrystals were synthesised using a ligand assisted re-precipitation (LARP) method. For  $Rb_2CuBr_3$  synthesis, 0.8 mmol (132.30 mg) of RbBr and 0.4 mmol (57.38 mg) of CuBr were first dissolved separately in 2 mL and 1 mL DMSO solvent, respectively. After that, both solutions were mixed together to form  $Rb_2CuBr_3$  precursor solution under a nitrogen filled glove box. 80 µL of DMSO precursor solution was added dropwise into a solution containing 5 mL toluene and 400 µL oleic acid under ambient conditions with constant stirring. The nanocrystals were instantly precipitated and a white-transparent solution was obtained.

For Rb<sub>2</sub>CuCl<sub>3</sub> synthesis, exact similar method was used in which, 0.8 mmol (96.74 mg) of RbCl and 0.4 mmol (39.59 mg) of CuCl were dissolved separately in 2 mL and 1 mL of DMSO, respectively. After that, both solutions were mixed together to form Rb<sub>2</sub>CuCl<sub>3</sub> precursor solution under a nitrogen filled glove box. 80 µL

of DMSO precursor solution was added dropwise into a solution containing 5 mL toluene and 200  $\mu$ L oleic acid under ambient conditions with constant stirring. The nanocrystals were instantly precipitated and a white-yellow solution was obtained.

Both nanocrystals were the purified by centrifuging at 8,000 RPM for 6 min. The supernatant was discarded and the precipitate was dispersed in 2 mL isopropyl alcohol for further optical and microscopy characterization. However, resulting precipitate was dried under vacuum for NMR, powder XRD, and TGA measurements.

#### **Characterizations:**

X-ray diffraction (XRD) measurements were held by using PANalytical X-ray diffractometer equipped with a Cu K $\alpha$  X-ray tube operating at accelerating voltage of 40 kV and current of 30 mA. Diffraction patterns were collected under ambient conditions using Bragg–Brentano geometry. All XRD samples were prepared by placing vacuum dried and ground powder of the nanocrystals on a zero-background holder to clearly resolve each peak.

XPS measurements were conducted using an AXIS Supra spectrometer (Kratos Analytical, U.K.) equipped with a hemispherical analyzer and a monochromatic Al K $\alpha$  source (1487 eV) operating at 15 mA and 15 kV. The XPS spectra were acquired from an area of 700 × 300 µm with a take off angle of 90°. These measurements were undertaken on nanocrystals powder sample coated on a glass substrate. The binding energies (BEs) were charge-corrected based on the C 1s at 284.8 eV.

Thermal Gravimetric Analysis (TGA) measurements were performed using TA Q500 instrument. For one measurement, 5-15 mg of nanocrystals dry powder were loaded in an alumina crucibles, which was placed in a platinum pan. Each powder sample was placed inside the alumina crucibles which held by a platinum pan. Samples were measured from room temperature to 800°C under nitrogen atmosphere and with the ramp rate of 10°C/min.

Transmission Electron Microscopy (TEM) measurements were performed by Jeol 2100F. The measurements were taken with beam current of 146  $\mu$ A and accelerating voltage of 200 kV. The colloidal solution of both

nanocrystals were further diluted in isopropyl alcohol before drop-casting on a holey carbon grids for the TEM analysis. Elemental analysis was performed using a Jeol 7600 FESEM at operating voltage of 20kV. Samples were prepared by drop-casting concentrated colloidal solution of nanocrystals on an ITO coated glass substrate. In order to create histogram, 64 and 102 nanoparticles were measured for Rb<sub>2</sub>CuBr<sub>3</sub>, and Rb<sub>2</sub>CuCl<sub>3</sub>, respectively.

The photoluminescence measurements were performed using a Cary Eclipse spectrophotometer. The samples are diluted in IPA inserted in 1 cm path length quartz cuvettes. The excitation wavelengths are observed at 285 nm and 292 nm for Rb<sub>2</sub>CuCl<sub>3</sub> and Rb<sub>2</sub>CuBr<sub>3</sub> nanocrystals respectively, while the emission is 400 nm for Rb<sub>2</sub>CuCl<sub>3</sub> and 387 nm for Rb<sub>2</sub>CuBr<sub>3</sub>. An excitation-dependent PL spectra were also obtained for both samples. Similar sample preparation was used for absorption spectra using a Cary 5000 UV-Vis-NIR spectrophotometer.

For TRPL measurements, nanocrystals solution were photoexcited using a 300 nm ~50 fs pulsed laser, with 1 kHz repetition rate. The PL lifetime was measured by first collecting the PL using a lens pair, before directing the emission toward a Princeton Instrument SP2360i monochromator coupled with Optoscope streak camera. This yielded time- and spectrally resolved PL spectra. A similar setup was also used for the excitation power dependent PL measurements. PLQY of both samples were measured using EXALITE 398 fluorescent dye. Later on, near unity PLQY of Rb<sub>2</sub>CuBr<sub>3</sub> nanocrystals was verified using a femtosecond laser system.<sup>1</sup> A Coherent LIBRA laser with output wavelength of 800 nm, repetition rate of 1 kHz, and pulse width of 50 fs was utilized. This fundamental laser light was targeted to a Coherent OPeRa Solo optical parametric amplifier (OPA), to generate tunable wavelength output from 290–2600 nm. In the experiment, excitation source of 290 nm was used. Sample was placed inside the centre of a BaSO<sub>4</sub>-coated ø15 cm integrating sphere, before being photoexcited by the laser. The integrating sphere was connected to a monochromator and CCD using an optical fiber. The pump scattering and emission from the solvent (IPA) and sample were collected for spectrally resolved measurement. Finally, PLQY of nanocrystals was calculated by using the following formula:

$$PL QY = \frac{\int_{\lambda_{PL1}}^{\lambda_{PL2}} d\lambda S(\lambda) [I_{sample}(\lambda) - I_{solvent}(\lambda)]}{\int_{\lambda_{pump2}}^{\lambda_{PL1}} d\lambda S(\lambda) [I_{solvent}(\lambda) - I_{sample}(\lambda)]}$$

Here,  $S(\lambda)$  is the instrument spectral response function;  $I_{solvent}$  and  $I_{sample}$  are the intensity of collected spectra for the solvent and sample, respectively; and  $[\lambda_{PL1}, \lambda_{PL2}]$  and  $[\lambda_{pump1}, \lambda_{pump2}]$  are the spectral region for the sample PL and the pump, respectively.

Temperature-dependent photoluminescence spectra were measured using Fluorolog spectrofluorometer coupled with iHR550 spectrometer and CCD detector (Horiba). Sample was placed on FTIR600 heating/cooling stage (Linkam) mounted inside spectrofluorometer. The excitation wavelength was set at 292 nm.

Solid-state NMR data was acquired on a Bruker Avance III HD spectrometer utilising a Bruker 4 mm MAS probe. All data was referenced to the unified scale using IUPAC recommended frequency ratios and processed with the Topspin processing software.<sup>2</sup> The <sup>87</sup>Rb MAS NMR data was completed at 14.1 T ( $v_0 = 196.40$  MHz) with a spinning frequency of 14 kHz. The <sup>87</sup>Rb one pulse sequence utilised a selective  $\pi/6$  pulse length of 1.2  $\mu$ s, calibrated on RbBr<sub>(s)</sub>, and relaxation delays of 0.5-1.2 s. The <sup>87</sup>Rb spin-lattice relaxation times were measured using a saturation recovery pulse sequence utilising a 200 pulse saturation pulse-train. The <sup>1</sup>H MAS NMR data was completed at 14.1 T ( $v_0 = 600.18$  MHz) with a spinning frequency of 14 kHz. The <sup>1</sup>H one pulse sequence utilised a non-selective  $\pi/2$  pulse length of 3.4  $\mu$ s, calibrated on adamantane<sub>(s)</sub>, and relaxation delays of 1-2 s.



**Figure S1.** Powder XRD of (a) Rb<sub>2</sub>CuBr<sub>3</sub> (b) Rb<sub>2</sub>CuCl<sub>3</sub>, and (c) Rb<sub>2</sub>Cu(Br/Cl)<sub>3</sub> nanocrystals with comparison to their calculated structure of each phase present in the system. As evident the mixed halide sample exhibits several impurities, the synthesis is not feasible using LARP method.



**Figure S2.** XRD pattern of (a)  $Rb_2CuBr_3$  and (b)  $Rb_2CuCl_3$  nanocrystals recorded over 6 days with storage under ambient conditions. The phase degradation study reveals the formation of  $Cu^{2+}$  structure such as  $RbCuCl_3$  and  $CuBr_2$  over time with side products of RbBr and RbCl.



**Figure S3.** TEM micrographs of (a), (b)  $Rb_2CuBr_3$  and (d), (e)  $Rb_2CuCl_3$  nanocrystals with histogram of  $Rb_2CuBr_3$  and  $Rb_2CuCl_3$  nanocrystals created using Figure b and e, respectively. SEM EDXS mapping of (g)  $Rb_2CuBr_3$  and (h)  $Rb_2CuCl_3$  drop casted NCs solution on ITO substrate.



**Figure S4.** (a) Cu 2p XPS spectra of  $Rb_2CuBr_3$  and  $Rb_2CuBr_3$  nanocrystals. As evident,  $Rb_2CuCl_3$  sample shows some strong Cu<sup>2+</sup> satellite peaks confirming the surface oxidation in this sample, which could be the cause of faster structural and PL degradation in this material, and (b) <sup>1</sup>H MAS NMR of  $Rb_2CuBr_3$  (blue) and  $Rb_2CuCl_3$  (green) nanocrystal powders.



**Figure S5.** (a) Absorption spectra of  $Rb_2CuBr_3$  and  $Rb_2CuCl_3$  nanocrystals with a photograph of  $Rb_2CuBr_3$  colloidal nanocrystals solution under room light, and excitation dependent PL spectra of (b)  $Rb_2CuCl_3$  nanocrystals and (c)  $Rb_2CuBr_3$  nanocrystals. 3D PL spectra shows no peak shift as a function of excitation wavelength.



**Figure S6.** Normalized PL intensity as a function of time (days), while the colloidal solution of nanocrystals were stored under ambient conditions. Sample showed reasonable stability over 7 days under ambient condition, as only 13% of maximum PL intensity were found to be dropped for Rb<sub>2</sub>CuBr<sub>3</sub> nanocrystals, whereas Rb<sub>2</sub>CuCl<sub>3</sub> nanocrystals showed 50% reduction in PLQY.



**Figure S7. (a)** Power dependent PL measurement of Rb<sub>2</sub>CuBr<sub>3</sub> nanocrystals embedded in PDMS polymer matrix depicting the linear dependency of PL intensity with excitation power, and (b) Temperature dependent PL measurements of Rb<sub>2</sub>CuBr<sub>3</sub>nanocrystals embedded in PDMS polymer matrix.

| Atom | Wyck. | Occupancy | x/a    | y/b | z/c    |
|------|-------|-----------|--------|-----|--------|
| Rb1  | 4c    | 1         | 0.1727 | 1/4 | 0.4750 |
| Rb2  | 4c    | 1         | 0.5123 | 1/4 | 0.6761 |
| Cu1  | 4c    | 1         | 0.2543 | 1/4 | 0.1896 |
| Br1  | 4c    | 1         | 0.1381 | 1/4 | 0.0517 |
| Br2  | 4c    | 1         | 0.4366 | 1/4 | 0.1384 |
| Br3  | 4c    | 1         | 0.2755 | 1/4 | 0.7825 |

Table S1. Refined position coordinates for Rb<sub>2</sub>CuBr<sub>3</sub> nanocrystals

| Atom | Wyck. | Occupancy | x/a    | y/b | z/c    |
|------|-------|-----------|--------|-----|--------|
| Rb1  | 4c    | 1         | 0.1705 | 1/4 | 0.4743 |
| Rb2  | 4c    | 1         | 0.5134 | 1/4 | 0.6711 |
| Cu1  | 4c    | 1         | 0.2530 | 1/4 | 0.1883 |
| Cl1  | 4c    | 1         | 0.1390 | 1/4 | 0.0509 |
| Cl2  | 4c    | 1         | 0.4370 | 1/4 | 0.1399 |
| Cl3  | 4c    | 1         | 0.2771 | 1/4 | 0.7799 |

**Table S2.** Refined position coordinates for Rb<sub>2</sub>CuCl<sub>3</sub> nanocrystals

**Table S3.** EDXS data of Rb<sub>2</sub>CuBr<sub>3</sub> and Rb<sub>2</sub>CuCl<sub>3</sub> drop casted on ITO substrate. Elemental analysis confirms the estimated ratio of 1.97:1.00:3.01 for Rb<sub>2</sub>CuBr<sub>3</sub> and 1.96:1.00:2.95 for Rb<sub>2</sub>CuCl<sub>3</sub> nanocrystals.

| Rb <sub>2</sub> CuBr <sub>3</sub> Nanocrystals |                  |                  |                  |  |  |
|--|------------------|------------------|------------------|--|--|
| No.  | Rb               | Cu               | Br               |  |  |
| 1  | 35.82            | 18.16            | 54.90            |  |  |
| 2  | 35.18            | 18.10            | 53.86            |  |  |
| 3  | 35.96            | 17.98            | 54.22            |  |  |
| Mean $\pm$ Std. deviation                      | $35.65 \pm 0.33$ | $18.08 \pm 0.07$ | $54.32 \pm 0.43$ |  |  |
| Ratio  | 1.97             | 1.00             | 3.01             |  |  |
| Rb <sub>2</sub> CuCl <sub>3</sub> Nanocrystals |                  |                  |                  |  |  |
| No.  | Rb               | Cu               | Cl               |  |  |
| 1  | 35.90            | 18.04            | 54.06            |  |  |
| 2  | 35.34            | 17.86            | 53.58            |  |  |
| 3  | 35.66            | 18.58            | 53.18            |  |  |
| Mean $\pm$ Std. deviation                      | $35.63 \pm 0.22$ | $18.16 \pm 0.30$ | $53.60 \pm 0.36$ |  |  |
| Ratio  | 1.96             | 1.00             | 2.95             |  |  |

**Table S4.** <sup>87</sup>Rb solid state NMR chemical shift ( $\delta_{iso}$ ) and spin-lattice relaxation times ( $T_1$ ) of Rb<sub>2</sub>CuBr<sub>3</sub> and Rb<sub>2</sub>CuCl<sub>3</sub> nanocrystals compared to RbBr and RbCl.

| <sup>87</sup> Rb NMR              |                                |          |  |  |
|-----------------------------------|--------------------------------|----------|--|--|
| Powders                           | $oldsymbol{\delta_{iso}}$ /ppm | $T_1$ /s |  |  |
|                                   | (±0.5)                         | (±0.05)  |  |  |
| Rb <sub>2</sub> CuBr <sub>3</sub> | 123.5                          | 0.15     |  |  |
| Rb <sub>2</sub> CuCl <sub>3</sub> | 104.2                          | 0.12     |  |  |
| RbBr                              | 158.6                          | 0.23     |  |  |
| RbCl                              | 132.5                          | 0.20     |  |  |

### **Reference:**

- 1. P. Vashishtha, G. V. Nutan, B. E. Griffith, Y. Fang, D. Giovanni, M. Jagadeeswararao, T. C. Sum, N. Mathews, S. G. Mhaisalkar and J. V. Hanna, *Chemistry of Materials*, 2019, **31**, 9003-9011.
- 2. R. K. Harris, E. D. Becker, S. M. C. De Menezes, R. Goodfellow and P. Granger, *Pure and Applied Chemistry*, 2001, **73**, 1795-1818.