Electronic Supplementary Material (ESI) for ChemComm.

Chirality in Luminescent $Cs_3Cu_2Br_5$ microcrystals produced via ligand assisted reprecipitation

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Electronic Supplementary Information

1 Materials and Methods

1.1 Chemicals:

CsBr 99.9% Alfa Aesar, $CuBr_2$ 99% Sigma Aldrich, N,N-dimethylformamide (DMF) ACS reagent ≥ 99.8% Sigma Aldrich, HBr 48% Merck, L-arginine ≥ 98% Sigma Aldrich, D-arginine 98% Sigma Aldrich, L-lysine ≥ 98% Sigma Aldrich, D-lysine 98% Alfa Aesar, Thioglycolic acid 98% Sigma Aldrich. All the chemicals were used without further purification.

1.2 Synthetic procedure:

L/D- Arginine $Cs_3Cu_2Br_5$ synthesis: in a typical synthesis, L/D-arginine (62 mg, 0.36 mmol) are solubilised in DMF (0.5 ml) and HBr 2.0 M (375 µl), then thioglycolic acid (22.5 µl, 0.32 mmol) is added. CsBr (48 mg, 0.22 mmol) and $CuBr_2$ (33 mg, 0.15 mmol) are added to the ligand solution. The copper(II) addition is followed by a rapid colour transition, the solution turns rapidly from colourless to green due to the formation of Cu(II) complexes, this first transition is immediately followed by a second colour change to yellow that is associated to the reduction to Cu(I) due to the thioglycolic acid. The final mixture is sonicated for 30 min in a sonication bath to ensure the complete solubilisation of the precursors. Then, the metal halide precursor solution (270 µl) is added dropwise to 90.0 ml of isopropyl alcohol under constant stirring at room temperature. During the additions, the antisolvent solution turns cloudy due to the precipitation of the metal-halide crystals. The reaction mixture is stirred for 5.0 min, then, the product is precipitated by centrifugation (7000 rpm, 3.0 min). The supernatant is discharged, the pellet is washed three times with 10.0 ml of isopropyl alcohol and collected by centrifugation (7000 rpm, 3.0 min). After cleaning, the product is redispersed in 10.0 ml of isopropyl alcohol under sonication, the colloidal solutions are stored in a fridge.

1.3 Characterisation

Structural characterisation: the powder diffraction measurements are recorded with a Panalytical Advanced Powder Diffractometer.

Morphological characterisation: The high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) high-angle annular dark-field imaging (HAADF) is carried out using a FEI Titan 80 operating at a beam voltage of 300 kV, situated at the Advanced Microscopy Laboratory at Trinity College, Dublin, Ireland. SEM analyses are performed using a Zeiss sigma VP field emission Scanning Electron Microscope and a Bruker Quantarax 200 detector is employed for the EDS analysis working with an ETH voltage of 10 kV.

Absorption spectra: The UV/Vis analysis is carried out with a Cary 60 (Agilent) UV/Vis spectrophotometer.

Photoluminescence Quantum Yield: the quantum yield is estimated by comparison with a known fluorescence standard according to **Eqs. 1** and **2**:[2,3]

$$= \frac{^{2}}{\cdot} \quad (1)$$

Where the subscripts *QDs* and *st* refer to the quantum dots or the fluorescence standard respectively. The PLQY is represented by Φ, *I* represents the integrated intensity corrected by the fluorimeter sensitivity and the source intensity, *n* represents the diffraction index of the solvent and *f* the absorption factor:

$$, = 1 - 10\text{^}(- \quad ,). \quad (2)$$

Where *A* represents the absorbance for quantum dots (*QDs*) and fluorescence standard (*st)*.

Tryptophan is chosen as the standard considering a quantum yield of 0.15 ± 0.01 in a water solution.[1] The metal halide colloidal dispersion is prepared in isopropanol (η = 1.377) and the standard solution in deionised water (η = 1.333), adjusting the dilution in order to obtain absorbance of 0.05 at the excitation wavelength (280 nm). The emission spectra are collected by exciting with radiation at 280 nm and measuring the emission in the 300 – 550 nm range. A spectral resolution of 2.0 nm is employed in both excitation and emission.

Steady state luminescence spectra: luminescence excitation and emission spectra are collected using a Horiba Jobin Yvon FluoroMax-4.

FTIR spectra: FTIR spectra are recorded using a NEXUS-FTIR instrument implementing a Nicolet Diffuse Reflectance accessory (DRIFT).

CD measurements: the CD spectra are collected with a Jasco J815 using colloidal dispersion in isopropanol and adjusting the particles concentration to keep the absorbance at 310 nm around 0.8. For the spectra acquisitions, the scan speed is set to 50 nm/min using 5 accumulations for each spectrum.

2. Miscellaneous data

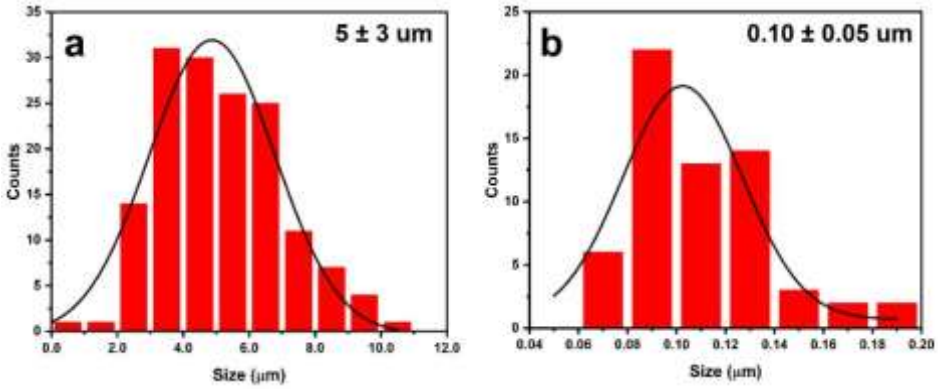

Figure S1: Size distributions of length a) and width b) of L-CCB microwires, the average values (inset) are evaluated according to the normal distribution.

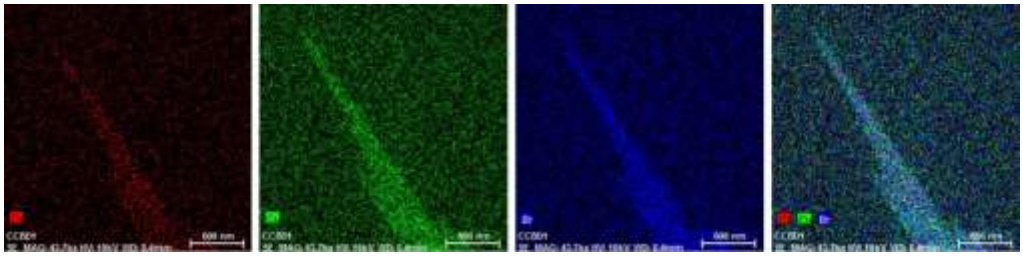

Figure S2: SEM-EDS elemental mapping of L-CCB microwires.

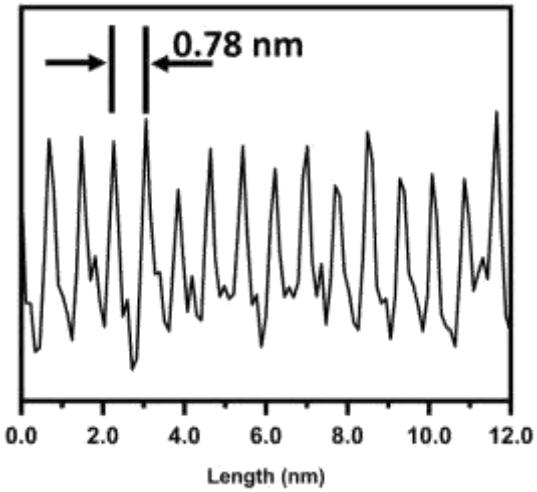

Figure S3: Typical line profile analysis of the electron diffraction fringes of L-CCB sample.

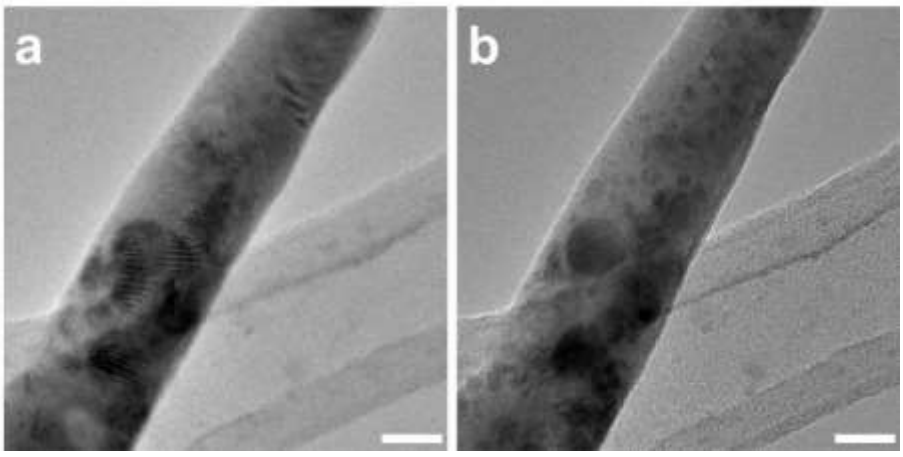

Figure S4: Observation of the microneedle decomposition under constant irradiation with an electron beam at 300 kV, scale bars: 25 nm.

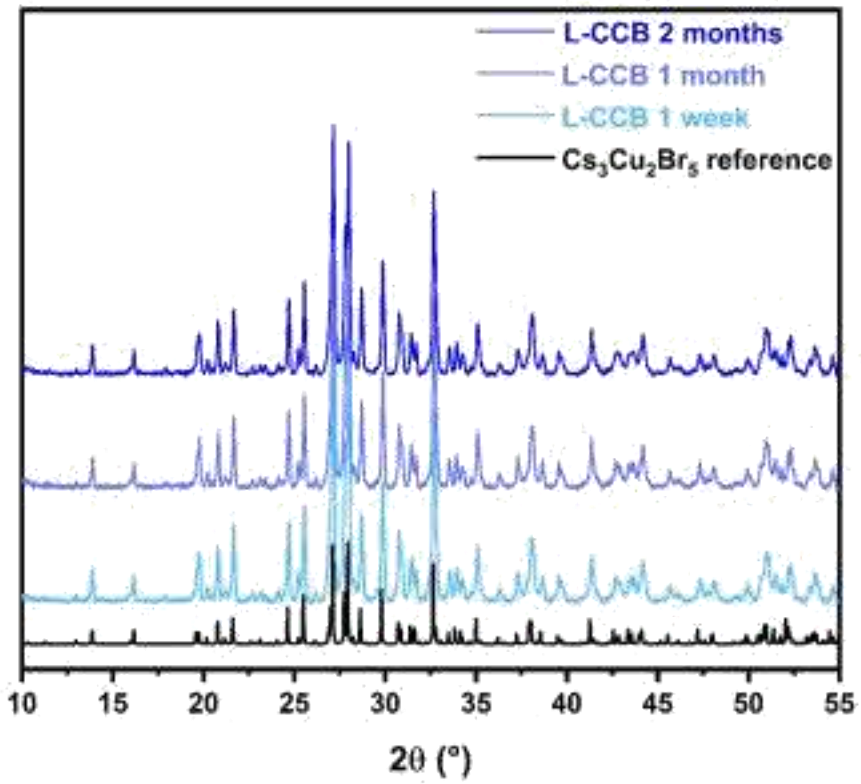

Figure S5: XRD patterns of L-CCB samples stored in air for different periods.

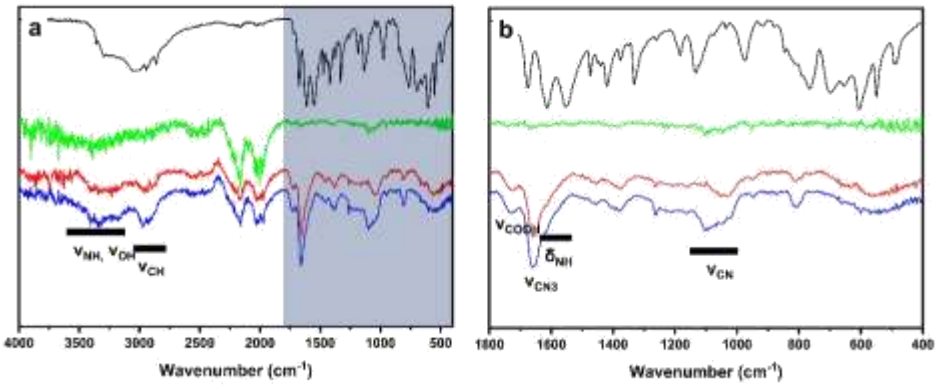

Figure S6: a) FTIR spectra of L-Arg (black), bulk-CCB (green), D-CCB (red) and L-CCB (blue). b) expanded graph for the 1800-400 cm^{-1} region, highlighted in blue in panel (a).

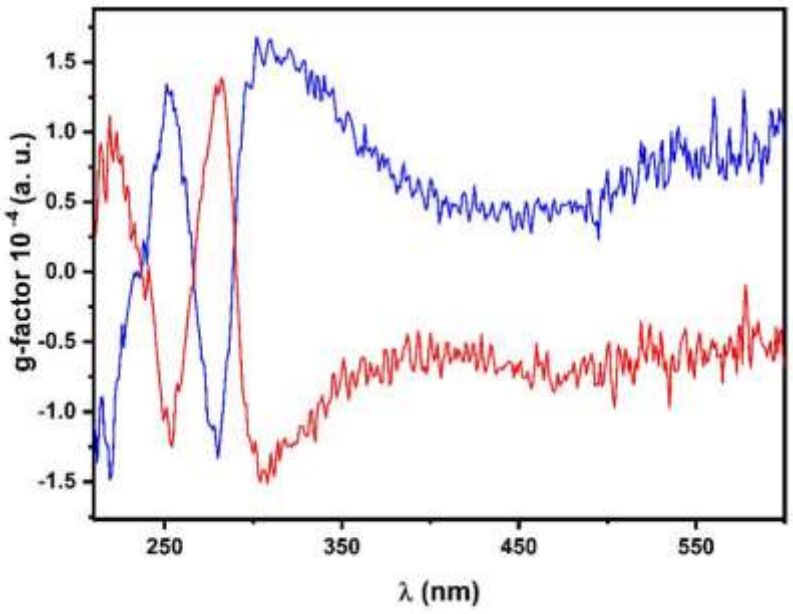

Figure S7: g-factor for L-(blue) and D-CCB (red).

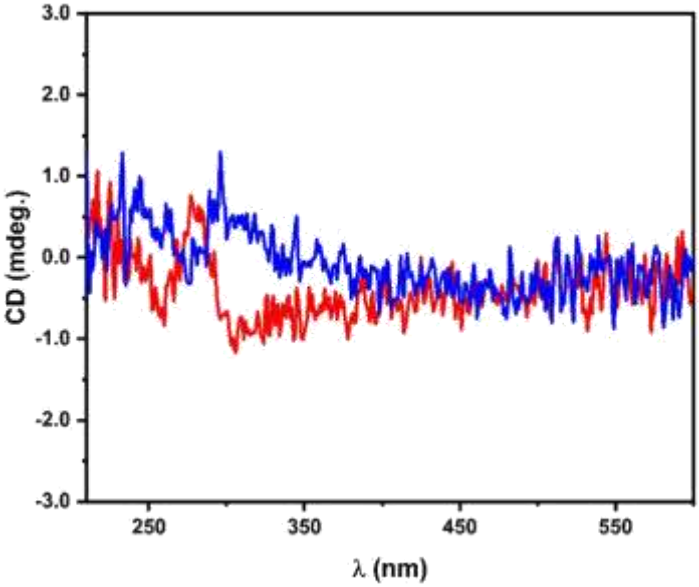

Figure S8: CD spectra of L-(blue) and D- (red) lysine stabilised $Cs_3Cu_2Br_5$.

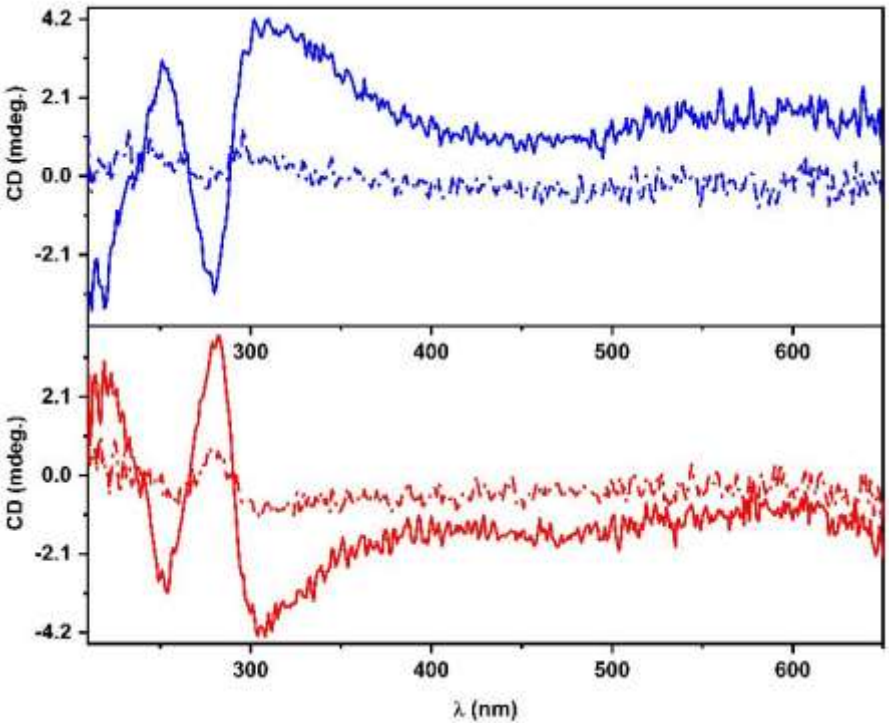

Figure S9: CD spectra of $Cs_3Cu_2Br_5$ microcrystals produced in the presence of L amino acids (top panel) L-Arg (solid line), L-Lys (dashed line) and D amino acids (bottom panel) D-Arg (solid line) and D-Lys (dashed line)

3 References

1 K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9850–9860.

2 U. Resch-Genger and K. Rurack, *Pure Appl. Chem.*, 2013, **85**, 2005–2026.

3 A. M. Brouwer, *Pure Appl. Chem.*, 2011, 83, 2213–2228.