## Supporting Information

## Investigating the Structure-Function Relationship in Triple Cation Perovskite Nanocrystals for Light-Emitting Diode Applications<sup>\*\*</sup>

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\*\* The experimental data for this study are provided as a supporting dataset from WRAP, the Warwick Research Archive Portal at https://wrap.warwick.ac.uk/134281.

## Experimental

**Powder X-ray Diffraction (XRD):** XRD measurement was conducted using a PANalytical X-ray diffractometer equipped with a 1.8kW Cu K $\alpha$  X-ray tube and operating at 45 kV and 30 mA. The diffraction patterns were collected in air at room temperature using Bragg-Brentano geometry. All XRD samples were prepared by drop casting a concentrated solution on a zero diffraction silicon holder.

**Transmission Electron Microscopy (TEM):** A Jeol 2010 was used for HR-TEM analysis at 200 kV of accelerating voltage and beam current of 108  $\mu$ A. Sample was prepared by diluting purified sample in hexane followed by sonication for two min. The sample was then drop casted on a Cu-200 mesh on forvar grid.

**Multinuclear Solid State** <sup>133</sup>Cs, <sup>207</sup>Pb <sup>13</sup>C and <sup>1</sup>H MAS NMR: Solid state <sup>133</sup>Cs MAS NMR data were acquired at 14.1 T using a Bruker Avance III-600 spectrometer operating at a <sup>133</sup>Cs Larmor frequency ( $\nu_0$ ) of 78.70 MHz. These measurements were undertaken using a Bruker 4 mm HX MAS probe which enabled a MAS frequency ( $\nu_r$ ) of 12 kHz for this study. A 'nonselective' <sup>133</sup>Cs (solution)  $\pi/2$  pulse length of 7  $\mu$ s was calibrated using a 0.1 M CsNO<sub>3</sub> (aq.) solution from which a 'selective' (solids)  $\pi/2$  pulse length of 1.75  $\mu$ s was determined for the <sup>133</sup>Cs (I = 7/2) nucleus. These <sup>133</sup>Cs MAS NMR measurements were undertaken using single pulse experiments using a  $\pi/3$  flip angle of ~1.2  $\mu$ s duration and a recycle delay of 10 s. The same 0.1 M CsNO<sub>3</sub> (aq) solution was also used as the IUPAC <sup>133</sup>Cs primary shift reference ( $\delta_{iso}$ = 0.0 ppm). The <sup>133</sup>Cs MAS NMR data were simulated using the DMFit program to elucidate the relative proportions of the individual components. Accompanying <sup>133</sup>Cs T<sub>1</sub> measurements were undertaken at 7.05 T on a Bruker Avance HD-300 spectrometer using the saturationrecovery method. A saturation comb of 100  $\pi/2$  pulse of 6  $\mu$ s duration (0.5  $\mu$ s delay between pulses) was implemented to achieve a complete scrambling of the <sup>133</sup>Cs magnetisation. A variable  $\tau$  delay range of 0.01-40 s was implemented in conjunction with a recycle delay of 1 s.

All solid state <sup>207</sup>Pb MAS NMR measurements were performed at 7.05 T using a Bruker Avance HD spectrometer operating at <sup>207</sup>Pb Larmor frequency ( $v_0$ ) of 62.8 MHz. These experiments were performed using a Bruker 2.5 mm HX probe that enabled a MAS frequency ( $v_t$ ) of 20 kHz to be implemented. Pulse length calibration was performed on Pb(NO<sub>3</sub>)<sub>2</sub> from which a  $\pi/2$  pulse time of 2.5  $\mu$ s was measured. These measurements were performed using a rotor-synchronised Hahn-echo pulse sequence ( $\pi/2 - \tau - \pi - \tau$  - acquire) was used with a pulse delay of 2 s. The <sup>207</sup>Pb chemical shifts were externally referenced against the IUPAC primary reference of (CH<sub>3</sub>)<sub>4</sub>Pb ( $\delta_{iso} = 0.0$  ppm) via the secondary solid Pb(NO<sub>3</sub>)<sub>2</sub> reference ( $\delta_{iso} = -3490$ ppm).

The 1D/2D <sup>1</sup>H and 1D <sup>13</sup>C MAS NMR measurements were undertaken using a Bruker Avance II-600 spectrometer operating at Larmor <sup>1</sup>H and <sup>13</sup>C frequencies ( $v_0$ ) of 600.13 and 150.93 MHz, respectively. The <sup>13</sup>C measurements used a Bruker 4 mm HX MAS probe that enabled a MAS frequency ( $v_r$ ) of 12 kHz for these measurements. All <sup>13</sup>C MAS NMR data were measured using single pulse (direct detection) methods that utilised high power <sup>1</sup>H decoupling of 100 kHz during data acquisition. A <sup>13</sup>C  $\pi/2$  pulse length of 4.0  $\mu$ s was calibrated using solid adamantane, and all <sup>13</sup>C MAS NMR measurements were undertaken using a  $\pi/4$  pulse length of 2.0  $\mu$ s and a recycle delay of 60 s. The <sup>1</sup>H  $T_{1p}$  measurements were implemented via the <sup>1</sup>H/<sup>13</sup>C cross-polarisation experiment which used an initial <sup>1</sup>H  $\pi/2$  pulse time of 3  $\mu$ s, a recycle delay of 10 s, a ramped 1 ms contact period (50 - 100 %), and additional incremented spin-lock delays ranging from 0.3 to 50 ms. Corresponding 1D and 2D <sup>1</sup>H MAS NMR data were acquired using a Bruker 1.3 mm HXY MAS probe that enabled a MAS frequency ( $v_r$ ) of 60 kHz. All 1D <sup>1</sup>H MAS NMR data were acquired using single pulse methods that utilised a  $\pi/2$  pulse length of 4.0  $\mu$ s (also calibrated using adamantane) and a recycle delay of 20 s. Both <sup>1</sup>H and <sup>13</sup>C chemical shifts were calibrated against the primary IUPAC reference TMS ( $\delta_{iso} = 0.0 \text{ ppm}$ ) via a secondary solid adamantane reference ( $\delta_{iso} = 1.9 \text{ ppm}$  for <sup>1</sup>H and 37.7 ppm for <sup>13</sup>C). The <sup>13</sup>C and <sup>1</sup>H methylammonium (MA) resonances (<sup>13</sup>C, 42.2 ppm; <sup>1</sup>H, 6.1 and 3.0 ppm) and formamidinium (FA) resonances (<sup>13</sup>C, 110.7 ppm; <sup>1</sup>H, 7.9 and 7.2 ppm) were sufficiently resolved from those of the other species present (crown ether and the capping agents) to obtain accurate relative ratios of FA<sup>+</sup> and MA<sup>+</sup> cation concentrations. The 2D homonuclear <sup>1</sup>H-<sup>1</sup>H NOESY experiments were undertaken using mixing times of 10, 50 and 100 ms, a recycle delay of 6s, with each experiment acquiring 1200 F1 slices. The 2D homonuclear <sup>1</sup>H-<sup>1</sup>H DQ/SQ BABA recoupling experiments utilised a rotor-synchronised F1 increment of 20.27  $\mu$ s which defined one rotor period of BABA recoupling, a recycle delay of 6s, with each experiment acquiring 688 F1 slices.

UV-Vis and PL Measurements: Samples were prepared by diluting the purified solution in 2.5 mL hexane in 1 cm path length quartz cuvettes. A Shimadzu UV-2550 and Horiba Fluoromax-4 spectrometer (slit width = 0.5 nm,  $\lambda_{ex}$  = 400 nm) were used for absorption and PL measurements respectively.

**Photoluminescence Quantum Yield (PLQY):** PLQY dependencies on the excitation fluence were measured with a Thorlabs IS20 integrating sphere. NC solutions in a cuvette were placed inside the sphere and excited using a 200mW continuous-wave laser beam. An optical fibre was attached to the sphere to direct the light to an Ocean Optics spectrometer. The excitation beam intensity was attenuated by means of calibrated Thorlabs neutral interference filters.

**Photoelectron Spectroscopy in Air (PESA):** Measurements on spin-coated NC thin films were conducted using a Riken Keiki AC-2 spectrometer with a power setting of 800 nW (power number of 0.5).

LED Fabrication: Patterned ITO substrates (sheet resistance ~8  $\Omega$ cm<sup>-1</sup>) were cleaned using consecutive 20 min sonication cycles in Hellmanex (10 % solution in deionized water), deionized water, acetone and isopropanol, followed by UV-ozone treatment for 15 min. PEDOT:PSS (Clevios Al4083) solution was filtered using 0.45 µl PVDF filter before spin coating on a cleaned ITO substrate at 4000 rpm for 60 s. The substrates were then annealed at 130 °C for 20 min. PEDOT:PSS coated substrates were then transferred to an argon-filled glove box for the remaining processes. Poly-TPD (2.5 mg ml<sup>-1</sup>) was spin coated at 4000 rpm for 60 s followed by annealing at 140 °C for 30 min. Triple cation NCs (in hexane) were spin coated at 2000 rpm (acceleration = 500 rpm s<sup>-1</sup>) for 60 s. A 45 nm layer of POT2T was thermally evaporated under 10<sup>-6</sup> Torr vacuum. 0.8 nm LiF and 80 nm Al electrode were then thermally evaporated through a shadow mask. All LEDs were encapsulated using UV-curable epoxy resin before removing from the glove box for electrical characterisation.

**LED Measurement:** A Keithley 2612B source measurement unit was used to obtain the current-voltage characteristics of the LED devices using a scan rate of  $1 \text{ V s}^{-1}$  (step size = 0.1 V, step interval = 0.1 s). The light emission was collected by an Ocean Optics FOIS-1 integrating sphere coupled to a calibrated spectrophotometer (Ocean Optics QEPro) through an optical fibre. An Ocean Optics HL-3 Plus vis-NIR light source was used to calibrate the absolute irradiance measurement of the spectrometer. LEDs were placed on the port of the integrating sphere and only forward emission was captured while the edge emission contribution was lost outside the integrating sphere. This method has also been widely used to measure the external quantum efficiency of LEDs.



**Figure S1.** TEM micrographs together with particle size distributions (histogram representations) describing the triple cation  $Cs_x(FA_{0.83}MA_{0.17})_{1-x}PbBr_3$  (x = 0 - 0.15) nanocrystal series (a) 0 mol% Cs, (b) 5 mol% Cs, (c) 10 mol% Cs, (d) 15 mol% Cs, and (e) a CsPbBr<sub>3</sub> nanocrystal sample. Each sample was prepared by drop casting NCs-hexane solution on Cu-200 mesh forvar grid. The high resolution TEM micrographs on the right highlighting the spherical morphology of these systems and the variation in *d* spacing measured throughout. The change in the orientation of lattice fringes in (b) and (c) indicates the spherical nature of these nanoparticles.



**Figure S2.** (a) The XRD patterns from precipitates of the triple cation  $Cs_x(FA_{0.83}MA_{0.17})_{1-x}PbBr_3$  (x = 0 - 0.15) nanocrystal series with varying Cs content demonstrating that preferred orientation was not evident in the data from powder samples. (b) simulated XRD patterns from CsPbBr\_3, MAPbBr\_3, and FAPbBr\_3 (inset shows the cubic CsPbBr\_3 crystal structure highlighting the (100), (200), and (110) planes). To estimate the relationship between relative intensity of (100)/(200) planes and average atomic number of atoms at A site, XRD patterns of each cubic perovskite for 10 nm particle size are simulated from crystallographic data.<sup>89</sup> It should be noted that XRD pattern of cubic FAPbBr\_3 is simulated from published structure of FAPbI<sub>3</sub> by replacing I with Br.<sup>10</sup> To observe the effect of particle size and preferred orientation on the XRD peak intensities, diffraction patterns with (c) different particle size and (d) with preferred orientation (PO) coincident with the 100 plane are simulated from Figure S2b can be confidently used for the analysis in Figure 1i.



**Figure S3.** FTIR spectrum of the v(N-H) stretching vibrations of the MA<sup>+</sup> and FA<sup>+</sup> cations in the triple cation  $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}PbBr_3$  (i.e. 5 mol% Cs) nanocrystal system.



**Figure S4.** Plots (a) - (e) show a comparison of the <sup>133</sup>Cs  $T_1$  data acquired from the CsPbBr<sub>3</sub> bulk and nanocrystalline phases with that measured from the Cs<sub>x</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>1-x</sub>PbBr<sub>3</sub> (x = 0.05 - 0.15) nanocrystal series. These room temperature (~25 °C)  $T_1$  measurements were undertaken at well separated external magnetic field strengths ( $B_0$ ) of 7.05 and 14.1 T.



**Figure S5**. An illustrative a survey of all possible H-H distances versus the number of protons contributing to these discrete distances, derived from the single crystal X-ray structure determination of a highly crystalline MAPbBr3 system.

Figure S5 above illustrates a survey of the available H-H distances comprising the highly ordered MAPbBr3 system. Although the lattice parameter of this cubic system is measured by PXRD to be 5.93 Å,<sup>11</sup> it is evident that many shorter H-H distances are manifested by H positions that are not centric to the interstitial cavity. This analysis shows a distinct demarcation between the intramolecular H-H distances (i.e. within one framework cavity, ranging between ~2.0 - 3.0 Å) and the intermolecular H-H distances (i.e. between neighboring framework cavities, ranging between ~3.5 - 6.0 Å). Previous reports have calculated the average H-H distance in MAPbBr3 could be much lower than 5 Å, which is consistent with survey of Figure 6d.<sup>11</sup> Similarly, the lattice parameters for the triple cation  $Cs_x(MA_{0.17}FA_{0.83})_{1-x}PbBr_3$  (x = 0 - 0.15) systems have been refined to be in the range of ~5.944 - 5.984 Å (see Figure 6d) suggesting that typical H-H distances governing the intramolecular MA<sup>+</sup>-FA<sup>+</sup> arrangements reside with the detection limits of the NOESY experiment. However, MA<sup>+</sup> and FA<sup>+</sup> cations in next-nearest-neighbour arrangements exhibit H-H distances of >10 Å which are outside the detection limits of this technique.



**Figure S6.** 2D homonuclear <sup>1</sup>H-<sup>1</sup>H MAS NMR data ( $B_0 = 14.1$  T,  $v_r = 60$  kHz) from the triple cation Cs<sub>x</sub>(MA<sub>0.17</sub>FA<sub>0.83</sub>)<sub>1-x</sub>PbBr<sub>3</sub> (x = 0.05 and 0.10) systems including (a), (d) 2D DQ/SQ BABA data showing through-bond connectivities (indicated with red dashed line) within the FA<sup>+</sup> cation and within the octylamine, passivating agent, and (b), (e) 2D NOESY data (mixing time 100 ms) indicating intramolecular and intermolecular through-space connectivities associated with the FA<sup>+</sup> and MA<sup>+</sup> cations, and the octylamine and oleic acid correlations passivating agents. Figures (c) and (f) show expanded representations of (b) and (e). The data from these triple cation systems exhibit exactly the same range of correlations as those examined in detail in Figure 6 within the main manuscript (15 mol% Cs system).



**Figure S7.** 2D homonuclear <sup>1</sup>H-<sup>1</sup>H MAS NMR data ( $B_0 = 14.1$  T,  $v_r = 60$  kHz) from the CsPbBr<sub>3</sub> nanocrystal system including (a) 2D DQ/SQ BABA data showing through-bond connectivities (indicated with red dashed line) within the octylamine, passivating agent, and (b) and (c) 2D NOESY data (mixing time 100 ms) highlighting through-space connectivities associated with intramolecular FA<sup>+</sup> (red) and octylamine (green) correlations, and intermolecular MA<sup>+</sup>/FA<sup>+</sup> correlations (black), octylamine/oleic acid correlations (blue). Figures (d) and (e) present an expansion of the 0 - 4 ppm region highlighting a key intramolecular correlation associated with the oleic acid passivating agent which suggests a folded configuration of the aliphatic chain back towards the nanocrystal surface.

**Figure S7 continued.** As observed above, the CsPbBr<sub>3</sub> nanocrystal system exhibits intramolecular CH<sub>3</sub> (oleic acid;  $\delta$  0.6 ppm)/vinyl CH (oleic acid;  $\delta$  4.9 ppm) correlations (see Figures S7b and c), and subtle CH<sub>2</sub>-vinyl (oleic acid;  $\delta$  1.7 ppm)/ $\alpha$ -CH<sub>2</sub> (oleic acid;  $\delta$  1.9 ppm) correlations (see Figures S7d and e), providing evidence supporting chain-folding arrangements in the oleic acid surface species as proposed in Figure 7d. Further evidence of this phenomenon is substantiated by an array of intermolecular correlations involving CH<sub>2</sub>-vinyl (oleic acid;  $\delta$  1.7 ppm)/NH<sub>3</sub><sup>+</sup> (octylamine;  $\delta$  6.6 ppm),  $\alpha$ -CH<sub>2</sub> (oleic acid;  $\delta$  1.9 ppm)/NH<sub>3</sub><sup>+</sup> (octylamine;  $\delta$  6.6 ppm),  $\alpha$ -CH<sub>2</sub> (oleic acid;  $\delta$  1.9 ppm)/NH<sub>3</sub><sup>+</sup> (octylamine;  $\delta$  6.6 ppm). These features demonstrate that mid-points of the oleic chain interact with regions near the nanocrystal surface as illustrated in Figure 7d indicating that a highly folded and entangled arrangement again emerges.



**Figure S8.** TRPL spectra of the 0 mol% Cs, 5 mol% Cs, 10 mol% Cs, and 15 mol% Cs thin films. The 5 mol% Cs sample shows the highest carrier lifetime of 14.5 ns which is consistent with the highest PLQY of ~93%.



**Figure S9.** (a) UV-Vis and PL spectrum of as synthesised CsPbBr<sub>3</sub>NCs and (b) EQE vs current density cruve of device fabricated using CsPbBr<sub>3</sub> NCs.



**Figure S10.** Photoelectron spectroscopy spectrum of 5 mol% Cs sample. The valance band position was calculated to be 5.77 eV in order to estimate the band diagram for NCs device structure.



**Figure S11.** Photophysical data showing (a) the normalized EL triple cation spectra, (b) a plot of EQE vs luminance, (c) a plot of current efficiency vs current density for devices constructed using 0 mol% Cs, 5 mol% Cs, 10 mol% Cs, 15 mol% Cs samples, and (d) EL peak position vs voltage (EL peak stability).



**Figure S12.** Current efficiency vs. current density and EQE vs. current density curves of 0 mol% Cs CS LEDs with and without crown ether (see Table S3).

**Table S1.** The precursor quantities of used in the synthesis of the triple cation  $Cs_x(MA_{0.17}FA_{0.83})_{1-x}PbBr_3$  (x = 0 - 0.15) nanocrystal series. These precursor quantities were dissolved in 1 mL of DMF to form a perovskite precursor solution for each nanocrystal synthesis.

Sample	Units	CsBr	FABr	MABr	PbBr <sub>2</sub>
0 mol% Cs	mmol	0	0.083	0.017	0.1
	mg	0	10.37	1.90	36.7
5 mol% Cs	mmol	0.005	0.079	0.016	0.1
	mg	1.06	9.85	1.80	36.7
10 mol% Cs	mmol	0.010	0.0747	0.0153	0.1
	mg	2.12	9.33	1.71	36.7
15 mol% Cs	mmol	0.015	0.0705	0.0144	0.1
	mg	3.19	8.81	1.61	36.7

**Table S2:** TEM EDXS data of the triple cation  $Cs_x(MA_{0.17}FA_{0.83})_{1-x}PbBr_3$  (x = 0 - 0.15) nanocrystal series. The relative Cs : Pb : Br ratio between the inorganic constituents are in good agreement with the starting material proportions, while the ratio between MA<sup>+</sup> and FA<sup>+</sup> cations was estimated from the solid state <sup>1</sup>H MAS NMR study (see Figure 4 and Table 1).

0	0 mol% Cs		5	5 mol% Cs		10 mol% Cs		15 mol% Cs			
Cs	Pb	Br	Cs	Pb	Br	Cs	Pb	Br	Cs	Pb	Br
0	20.3	56.7	1.2	19.7	54.3	1.8	19.4	57.5	3.1	21.3	60.9
0	19.5	57.8	1.6	18.9	53.2	2.3	22.3	59.8	3.2	21.6	60.2
0	21.3	61.8	1.1	20.7	58.2	2.4	18.5	59.5	2.9	22.8	61.2
0	22.4	61.0	1.2	21.8	59.8	2.0	18.6	58.3	3.0	23.8	60.3
0	20.9	59.3	1.2	20.3	56.3	2.1	19.7	58.7	3.0	22.4	60.6

Table S3. Device efficiency of 0 mol% Cs LED devices with and without crown ether.

<b>Device Name</b>	Current efficiency (cd A <sup>-1</sup> )	EQE (%)
0 mol% Cs without crown	12.7	3.1
ether		
0 mol% Cs with crown	12.5	3.0
ether		

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