

Supplementary Information: Structure and Surface Properties of Size-tuneable CsPbBr₃ Nanocrystals

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This investigation has characterised the structure and surface chemistry of CsPbBr₃ nanocrystals with controlled diameters between 6.4 to 12.8 nm. The nanocrystals were investigated via a thorough ¹³³Cs solid state NMR and nuclear relaxation study, identifying and mapping radially-increasing nanoscale disorder. This work has formalised ¹³³Cs NMR as a highly sensitive probe of nanocrystal size, which can conveniently analyse nanocrystals in solid forms, as they would be utilised in optoelectronic devices. A combined multinuclear solid state NMR and XPS approach, including ¹³³Cs-¹H heteronuclear correlation 2D (HETCOR) NMR, was utilised to study the nanocrystal surface and ligands, demonstrating that the surface is Cs-Br rich with vacancies passivated by didodecyltrimethylammonium bromide (DDAB) ligands. Furthermore, it is shown that a negligible amount of phosphonate ligands remain on the powder nanocrystal surface, despite the key role of octylphosphonic acid (OPA) in controlling the colloidal nanocrystal growth. The CsPbBr₃ NCs were shown to be structurally stable under ambient conditions for up to 6 months, albeit with some particle agglomeration.

Supplementary Experimental

Photoluminescence (PL) spectra were measured in Quartz cuvettes with a Horiba Fluoromax-4 spectrophotometer using an excitation wavelength of 365 nm with 0.1 nm steps and an integration time of 0.1 s. Stable nanocrystal dispersions were diluted by a factor of between 500 and 1000 for the measurements.

Variable temperature ¹³³Cs NMR experiments were performed on a 14.1 T Bruker Advance III HD 600 MHz spectrometer utilising 4mm Bruker HXY probe at an MAS frequency of 14 kHz. Specialised high temperature MACOR rotor caps were employed. The ¹³³Cs NMR ($\nu_0(^{133}\text{Cs}) = 78.724$ MHz) one-pulse experiments were acquired at an MAS frequency of 14 kHz, utilising a non-selective $\pi/2$ pulse of 7 μs (determined on CsCl_(s)) and a recycle delay 5 times the sample's T_1 to ensure quantitative spectra. Spin-lattice relaxation times, T_1 , were measured using saturation recovery pulse sequences with a 200 $\pi/2$ pulse saturation block.

The PLQY measurements were performed using a Labsphere integrating sphere. The sample was placed inside and excited with a Cobolt 445 nm continuous-wave diode laser. The output of the integrating sphere was coupled through an optical fibre to a charge-coupled device (Newton 920 CCD, Andor) in which the photon count was captured.

The proposed layer model of the CsPbBr₃ NCs was calculated utilising the relative integrals of the different ¹³³Cs resonances

to determine the volume ratios, and hence the radial boundaries, of the spherical layers by making the following assumptions: the CsPbBr₃ NCs were as perfect spheres with perfect spherical layers; Cs is uniformly distributed over the entire volume; that 100% of the Cs atoms are represented in the NMR (some surface environments could be so distorted that they are broadened beyond detection); the relative integral given by resonances at 120 ppm was not included since they are thought to be from anomalous aggregated particles; the surface layer was calculated from the combined relative integral of the ligand adjacent environments (163 ppm) and the 95 ppm environment. The following geometrical formula was utilised for the volume of the spherical layers.

$$V_n = \frac{4\pi r_n^3}{3} - \frac{4\pi r_{n-1}^3}{3}$$

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Supplementary Results

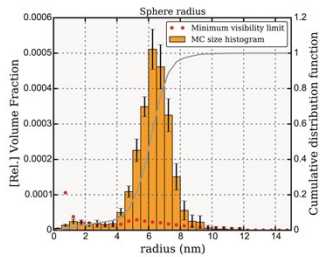
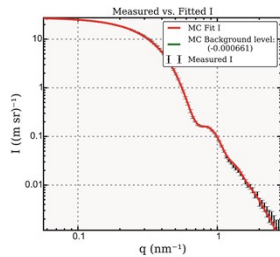
Table S1: The parameters of the spherical NC model derived from mean particle diameters and ^{133}Cs NMR relative integrals.

Sample name	Model particle diameter (nm)	Model sphere volume (nm ³)	Inner core (117 ppm)			Middle shell (108 ppm)			Outer shell (95 & 163 ppm)	
			^{133}Cs NMR rel. int. (%)	Shell volume (nm ³)	Radial boundary ^a (nm)	^{133}Cs NMR rel. int. (%)	Shell volume (nm ³)	Radial boundary ^a (nm)	^{133}Cs NMR rel. int. (%)	Shell volume (nm ³)
NC12.8	12.8	1098.1	28.3	310.9	2.2	44.7	490.5	0.6	27.0	296.5
NC10.4	10.4	589.0	17.3	101.9	2.3	46.8	275.6	0.7	35.9	211.4
NC9.9	9.9	508.0	15.6	79.3	2.3	49.5	251.5	0.7	34.9	177.3
NC8.9	8.9	369.1	14.0	51.7	2.1	42.9	158.3	0.8	43.0	158.9
NC8.3	8.3	299.4	8.3	24.9	2.3	39.1	117.1	0.9	52.6	157.4
NC7.7	7.7	239.0	6.7	16.1	2.3	40.8	97.5	0.8	52.5	125.6
NC6.4	6.4	137.3	0.0	0.0	3.2 ^b	38.4	52.7	0.9	61.6	84.6

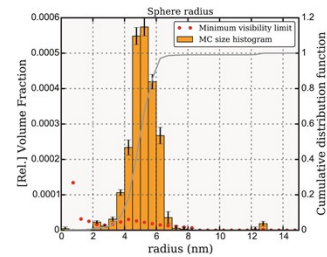
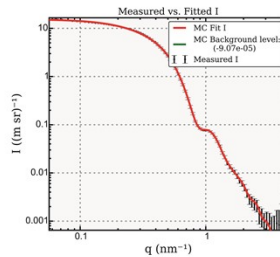
^a Radial boundaries given as distance from the surface of the NCs. Hence outer shell radial boundary is 0 nm by definition.

^b Anomalous value due to negligible 117 ppm resonance intensity for NC6.4. For example a 1% relative integral would give a radial boundary of 2.3.

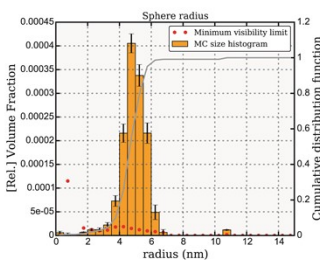
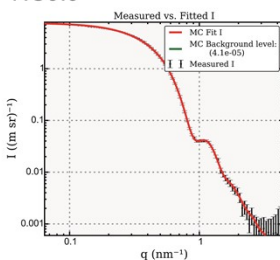
NC12.8



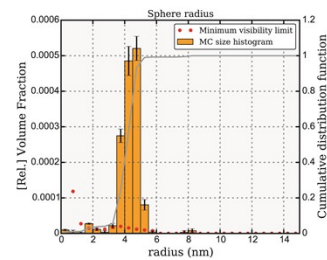
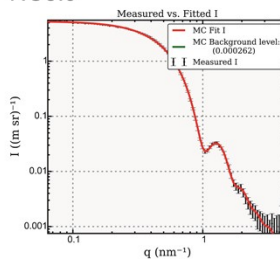
NC10.4



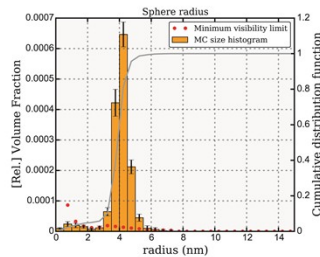
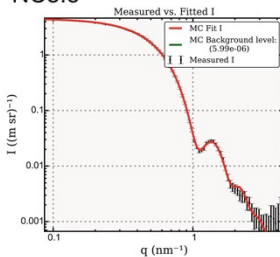
NC9.9



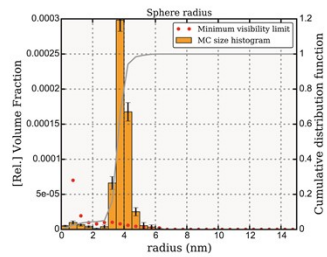
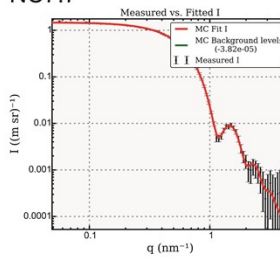
NC8.9



NC8.3



NC7.7



NC6.4

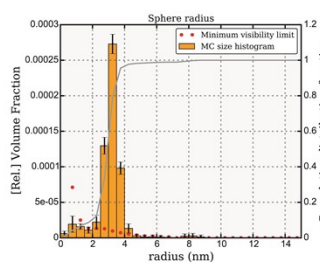
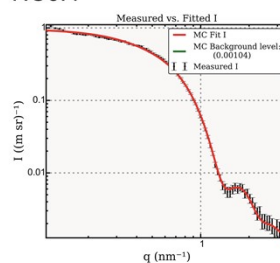


Figure S1. SAXS curves of each CsPbBr₃ NC sample fitted with a spherical particle model alongside the resulting particle radii histograms.

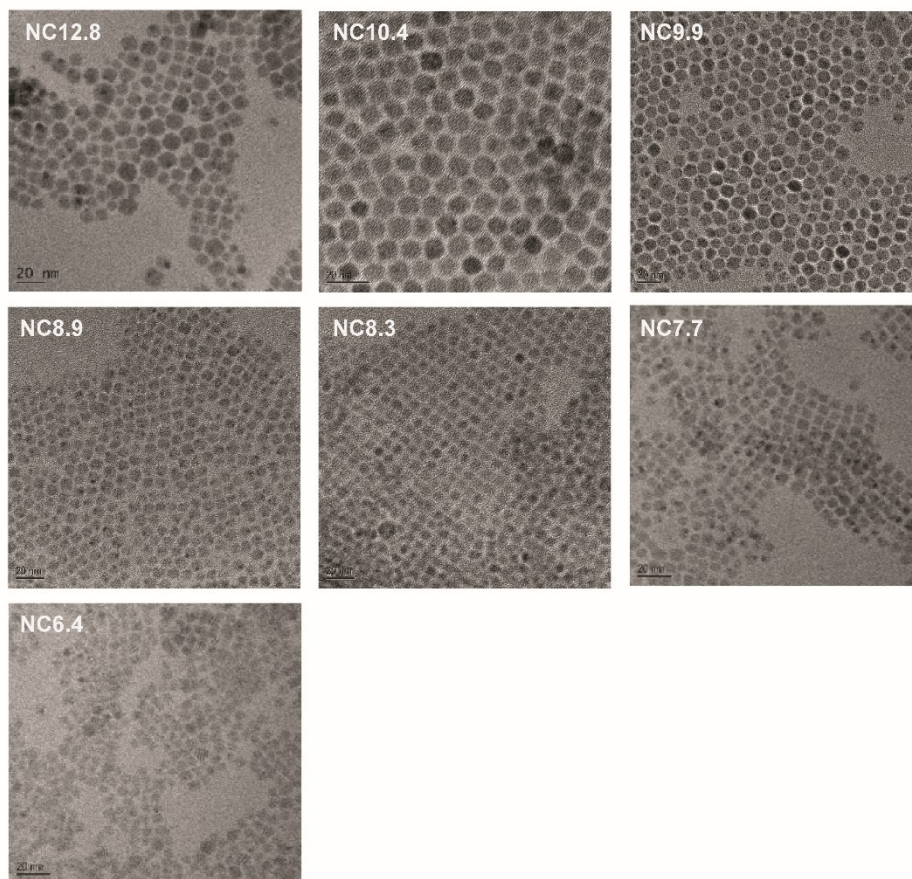


Figure S2. TEM images of the 7 CsPbBr₃ NCs colloidal solutions at varying degrees of magnification.

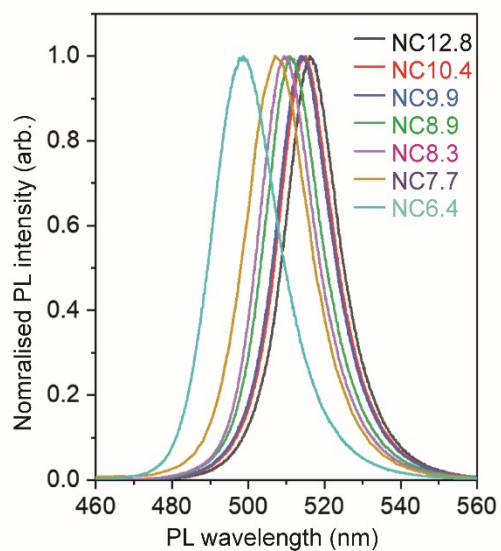


Figure S3. PL spectra of the colloidal CsPbBr₃ NCs with colloidal PLQY values of 88% for NC5.3, 87% for NC6.8, 88% for NC7.2, 87% for NC8.4, 90% for NC9.0, 90% for NC8.6, and 84% for NC11.8.

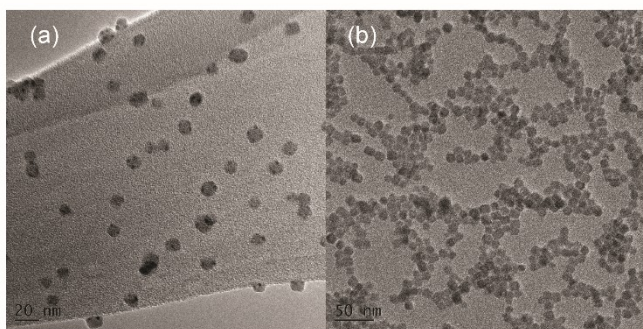


Figure S4. TEM images of (a) CsPbBr₃ NCs from the diluted colloidal solution and (b) CsPbBr₃ NC powders re-dispersed in heptane.

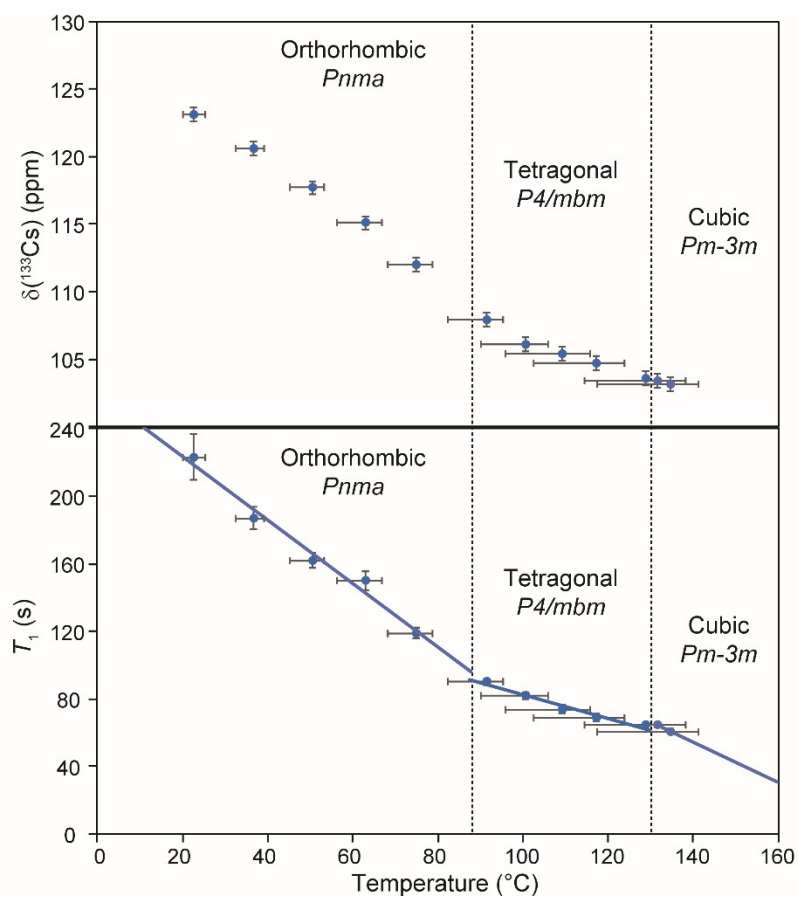


Figure S5. ¹³³Cs MAS NMR isotropic chemical shift (δ) and spin-lattice relaxation (T_1) of bulk CsPbBr₃ as a function of temperature over the structural phase regimes in CsPbBr₃ (*Pnma* - 88°C - *P4/mbm* - 130°C - *Pm-3m*).¹ The x-axis error bars represent the temperature gradient present in the sample within the NMR rotor due to imperfect *in-situ* temperature control. At higher heater powers and gas flow the temperature gradient becomes more pronounced.

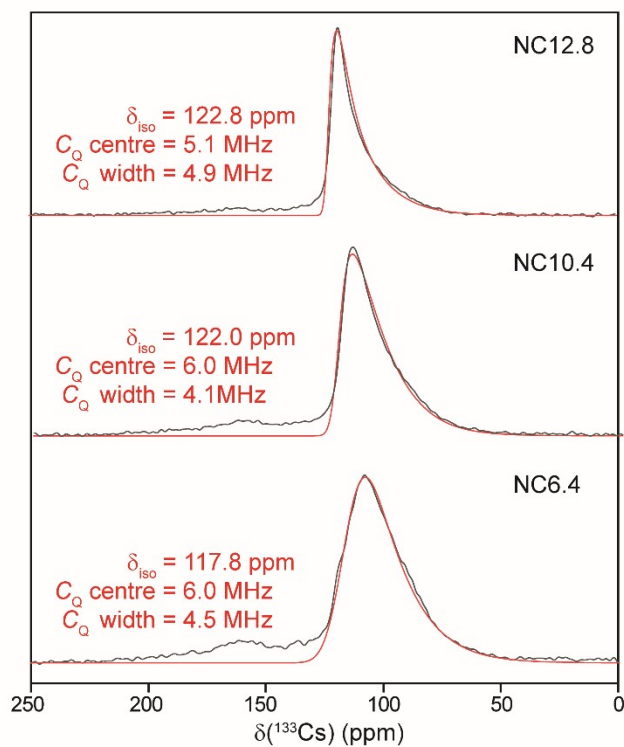


Figure S6. ^{133}Cs NMR spectra of three CsPbBr₃ NCs selected to cover the range of line shapes. Spectra have been fitted with simulated line shapes given by Gaussian distributions of the quadrupolar coupling constant, C_Q .

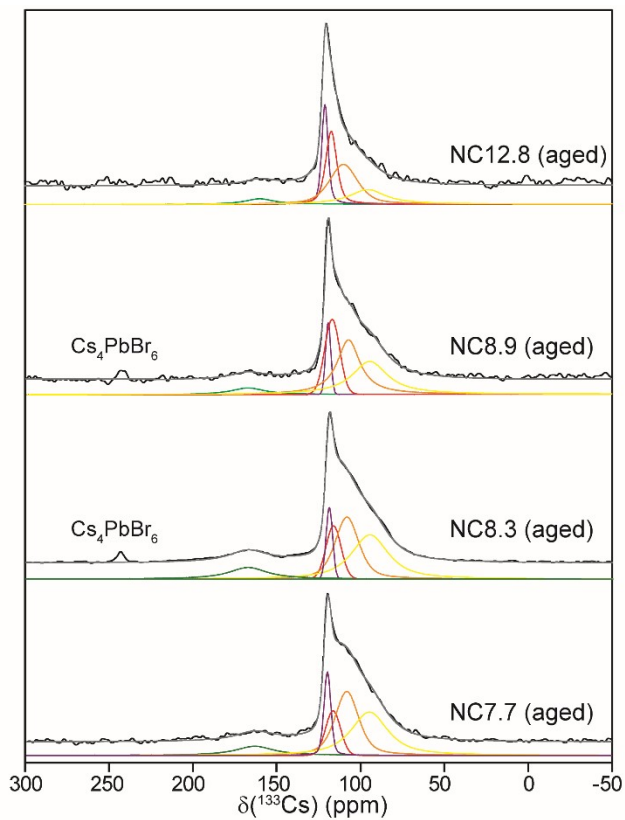


Figure S7. ^{133}Cs MAS NMR of selected NC samples post 6 months aging.

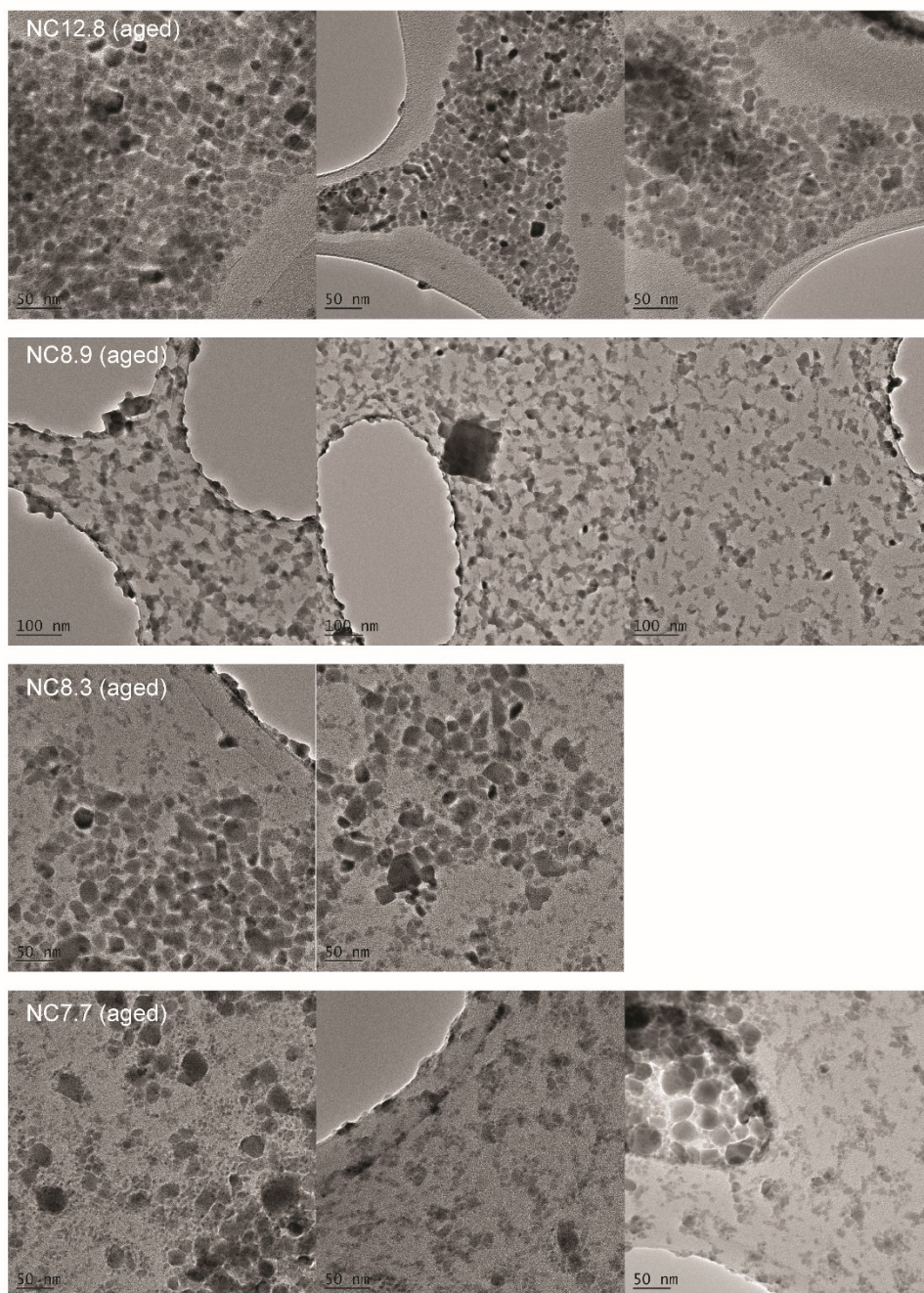


Figure S8. TEM imaging of samples NC12.8, NC8.9, NC8.3 and NC7.7 post 6 months aging in ambient conditions, showing regions containing larger agglomerated particles.

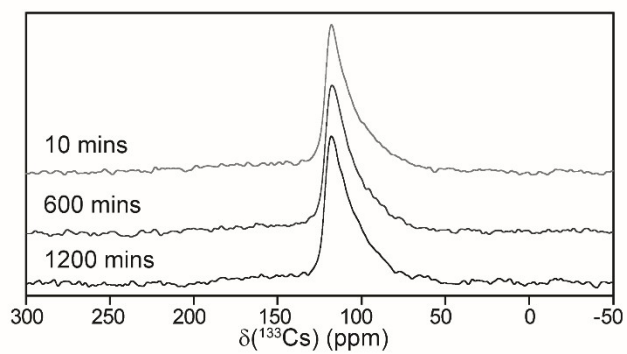


Figure S9. ^{133}Cs MAS NMR of the same CsPbBr_3 NC sample after MAS spinning in 1.9mm rotor at 24 KHz for 10, 600 and 1200 minutes (CsPbBr_3 NC samples were spun for a maximum of 60 minutes during initial ^{133}Cs NMR acquisition).

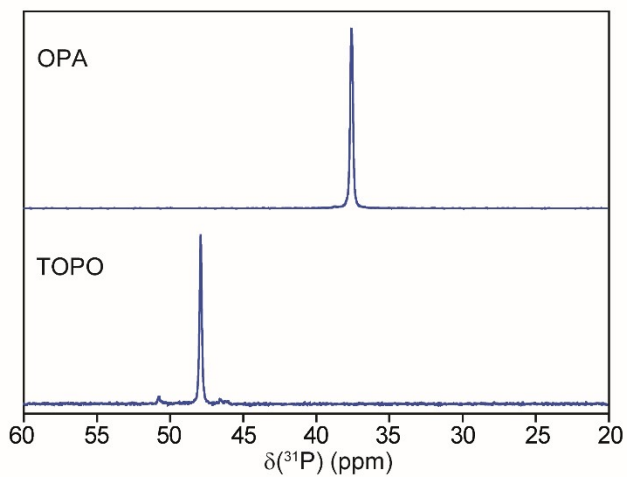


Figure S10. ^{31}P MAS NMR of OPA and TOPO ligands.

Notes and references

- 1 D. Yang and D. Huo, *J. Mater. Chem. C*, 2020, **8**, 6640–6653.