Stable Hexylphosphonate-Capped Blue Emitting Quantum-Confined CsPbBr3 NanoPlatelets

Javad Shamsi,^a Dominik Kubicki,^{a,b} Miguel Anaya,^a Yun Liu,^a Kangyu Ji,^a Kyle Frohna,^a Clare P. Grey,^b Richard H. Friend,^a Samuel D. Stranks^{* a,c}

^a Cavendish Laboratory, University of Cambridge, 19 JJ Thomson Avenue, Cambridge CB3 oHE, United Kingdom

^b Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

^c Department of Chemical Engineering & Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge CB3 oAS, United Kingdom

* Email: <u>sds65@cam.ac.uk</u>

METHODS/EXPERIMENTAL SECTION

Chemicals:

Lead (II) bromide (PbBr₂, 99.999% trace metals basis), caesium carbonate (Cs₂CO₃, reagentPlus, 99%), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLA, 70%), oleic acid (OA, 90%), 2-propanol (IPA, anhydrous, 99.5%), n-hexylphosphonic acid (HPA, 95%) and toluene (anhydrous, 99.8%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

Preparation of caesium-oleate (CsOA) solution:

0.325 g Cs₂CO₃ was dissolved in 10 ml OA on a hotplate set at 120 °C until all Cs₂CO₃ reacted with OA.

Synthesis of CsPbBr₃ pristine nanoplatelets (OLA-NPLs):

All synthesis steps reported here were performed in air. 0.073 g of PbBr₂ was dissolved in 4 ml of ODE together with 0.5 ml of OLA and 0.5 ml of OA in a 20 ml vial at 110 °C. After the PbBr₂ was completely dissolved, the vial was moved to a room temperature (RT) stirrer, and the solution was allowed to reach room temperature (RT). 0.5 ml of the as-prepared CsOA precursor was then injected under stirring. After 30 seconds, 0.5 ml of IPA was added under stirring at RT. Then the transparent solution was transferred to another hotplate pre-set at 70 °C. After 10 minutes the reaction was quickly cooled down with a cold water bath.

Synthesis of hexylphosphonate-passivated nanoplatelets (HPA-NPLs):

The HPA-NPL synthesis followed the same protocol as for OLA-NPLs but including the addition of HPA with the IPA step. Specifically, 0.073 g of PbBr₂ was dissolved in 4 ml of ODE together with 0.5 ml of OLA and 0.5 ml of OA in a 20 ml vial at 110 °C. After the PbBr₂ was completely dissolved, the vial was moved to a room temperature (RT) stirrer, and the solution was allowed to reach room temperature (RT). 0.5 ml of the as-prepared CsOA precursor was then injected under stirring. After 30 seconds, 0.5 ml HPA/IPA solution (48 mg HPA in 0.5 ml

IPA) was added. Then the transparent solution was transferred to another hotplate pre-set at 70 °C. After 10 minutes the reaction was quickly cooled down with a cold water bath.

Purification:

To collect the NPLs, 4 ml toluene was added to the 2 ml crude solutions of as-synthesized NPLs then centrifuged at 3800 rpm for 5 min. After centrifugation, the supernatant was discarded and the NCs were redispersed in 3mL toluene.

NPL thin films preparation:

In our optimized procedure, 0.2 ml of washed NPL solution was spin coated on a 22mm x 22mm microscope slide coverslips at 2000 rpm for 45 seconds.

CHARACTERIZATION

UV–Vis and PL Measurements:

UV–vis measurements were collected on an Agilent 8453 UV–vis spectrophotometer with deuterium (190–800 nm) and tungsten (310–1100 nm) lamps. It is equipped with a photodiode array for detection. Photoluminescence (PL) spectra were measured on an Edinburgh Instruments FLS980 fluorimeter. Continuous illumination measurements were performed with excitation at 400 nm and intensity of ~50 mW/cm².

X-Ray Diffraction:

XRD measurements were performed using a Bruker X-Ray D8 Advance diffractometer with Cu K α 1,2 radiation (λ = 1.541 Å). Diffractograms were collected within an angular range of 10° \leq 2 θ \leq 50° and with Δ 2 θ = 0.01942° steps.

TEM:

TEM samples were prepared by drop casting 40ul of NPL solution in toluene on a TEM Grid (300 mesh Cu, Agar Scientific) and imaged employing a FEI Tecnai F20 microscope operated at 200 kV. The NPL size distributions were achieved by measuring 100 NPLs.

PLQY measurements:

The steady-state absolute PLQYs of the samples were measured using an integrating sphere method.¹ A continuous-wave 405-nm diode laser was used to excite the samples with an excitation intensity of ~100 mW cm⁻². The emission was measured using an Andor iDus Si detector, which was calibrated with a certified HL-3P-CAL Ocean Optics broadband source.

Transient PL measurements with TCSPC:

The samples were photoexcited using a 407 nm pulsed supercontinuum laser with a pulse width of 6 ps at 5 MHz repetition rate. The scattered laser light from the samples was filteredout using an absorptive 420 nm long-pass filter. The PL was focused and detected by a Sibased single photon avalanche photodiode (MPD-PDM-PDF) with an instrument response of around 0.2 ns.

Hyperspectral PL measurements:

PL maps were performed with a wide-field microscope (IMA VIS[™], Photon Etc.). We employed wide field air objectives of 20x magnification (0.45 Numerical aperture (NA)) and 100x (0.9 NA) to characterise the thin films in reflectance mode. For PL measurements a 405 nm, continuous wave laser was focused on the sample surface. The reflected laser beam was then filtered off with a 420 nm long pass filter before collecting the emission spectrum of the sample. Excitation power density was calibrated by measuring the laser intensity with a power meter and the size of the excitation spot. A halogen lamp (50 W) was employed to obtain the reflectance spectra. Broad signal (reflectance and PL) was measured with a calibrated 1040×1392 resolution silicon CCD camera. In order to obtain spectrally resolved images, we employed a volume tuneable Bragg filter.

NMR measurements:

Room temperature ¹³³Cs (91.8 MHz), ¹³C (176.0 MHz) and ³¹P (283.4 MHz) MAS NMR spectra were recorded on a Bruker Avance III 16.4 T spectrometer equipped with a 4.0 mm CPMAS probe. ¹³C were referenced using solid adamantane as a secondary reference (¹³C δ =29.456 ppm).² ¹³³Cs shifts were referenced using solid CsI as a secondary reference (δ =271.05 ppm).³ ³¹P spectra were referenced using 85% H₃PO₄ (³¹P δ =0 ppm). Calibrated RF strengths: ¹³³Cs (28 kHz), ³¹P (42 kHz). A contact times of 1 ms was used in the cross-polarization experiments. All solid-state experiments were carried out at 12 kHz MAS. Liquid-state ¹H (400 MHz) and ³¹P (162.0 MHz) NMR measurements were recorded on a Bruker Avance III 9.4 T. Further experimental details are given in the Table S1.

Details of solid-state NMR experiments:

sample (experiment)	recycle delay [s]	number of scans	acquisition time [min]	Lorentzian apodization [Hz]	notes
HPA-NPLs (¹ H- ¹³ C)	3	5144	257	50	
HPA-NPLs (¹ H- ³¹ P)	3	816	41	0	
HPA-NPLs (³¹ P)	500	4	33	0	
neat HPA (¹ H- ³¹ P)	1.3	40	1	0	
CsHPA (¹ H- ³¹ P)	1	64	1	0	
OLAHPA (¹ H- ³¹ P)	0.5	3039	25	100	
HPA-NPLs (¹³³ Cs)	15	1512	378	20	quantitative
microcrystalline CsPbBr ₃ (¹³³ Cs)	400	31	207	0	
CsHPA (¹³³ Cs)	7	16	2	20	

Table S1: Experimental parameters used to record the solid-state NMR spectra.

DFT calculations:

All DFT calculations were performed using the Quantum Espresso suite (v6.4).^{4,5} We used the PBE functional⁶ and norm-conserving pseudopotentials from the PSEUDODOJO library⁷ generated using the ONCVPSP code.⁸ The electronic wavefunctions were expanded in a plane wave basis with an energy cutoff of 60 Ry, and all atomic positions were relaxed until the residual forces were <0.01 eV/Å.

A vacuum spacing of 15 Å was added to the supercell in the *z*-dimension for the platelet calculations to remove any spurious interactions, and the Monkhorst-Pack⁹ *k*-point sampling scheme used for Brillouin zone has divisions of less than 0.03 Å⁻¹, and only the Γ point was sampled in the *z*-direction. The top surfaces were fully passivated. For isolated ligand, a vacuum of 15 Å was added in all 3 spatial directions and only the Γ point was sampled. For binding affinity calculations, each pair of ligand and counterion vacancies were created in a 3×3×1 supercell.



Figure S1: PL of the OLA-NPLs before and after the addition of various amount of HPA (dissolved in toluene).



Figure S2: (a) High-resolution TEM image of HPA-NPLs and (b) schematic illustration of NPL stacks.



Figure S3: CsPbBr₃ OLA-NPLs: (a) optical absorbance and PL; (b) TEM image. The black dots are metallic lead nanoparticles formed during the analysis.



Figure S4: PL of resulting HPA-NPLs when the HPA/Pb=2.



Figure S5: (a) PL decay kinetics of OLA-NPLs and HPA-NPL thin films at a fluence of 0.36 nJ/cm²/pulse. The decays are fit with functions of the form I(t) = A₁ exp(-t/ τ_1) + A₂ exp(-t/ τ_2) + A₃ exp(-t/ τ_3) + y₀ (solid lines), with the inset table reporting the fit lifetimes and amplitudes (y₀ = 0 for HPA-NPLs and 4.17 x 10⁻⁴ for OLA-NPLs). The average lifetime τ_{avg} reported in the text is determined by $\tau_{av} = ((A_1 \times \tau_1^2) + (A_2 \times \tau_2^2) + (A_3 \times \tau_3^2))/((A_1 \times \tau_1) + (A_2 \times \tau_2) + (A_3 \times \tau_3))$.¹⁰ (b, c) Evolution of PL decays as a function of excitation fluence (as stated in the legends) for (b) OLA- and (c) HPA-NPLs. The PL lifetime τ (assuming here τ_{avg}) represents the total decay rate $k_{tot} = 1/\tau$, where $k_{tot} = k_{rad} + k_{nonrad}$, and k_{rad} is the radiative rate, k_{nonrad} is the non-radiative rate. The PLQY is given by PLQY = k_{rad} / k_{tot} . The fact we observe an increased PLQY and an increased total rate (shorter PL lifetime) when moving from the OLA- to the HPA-NPLs suggests that the radiative rate is increasing; further work will be required to investigate this further.

Figure S6: Comparison of PL spectra from HPA-NPLs (fwhm 15 nm) and OLA-NPL (fwhm 19 nm, dash line) solutions.

Figure S7: The structure of n-hexylphosphonic acid (inset). Liquid-state ¹H NMR spectra in toluene-d₈ at 11.7 T of *n*-hexylphosphonic acid (HPA) and HPA-capped CsPbBr₃ nanoplatelets (NPLs).

Figure S8: Deconvolution of the ¹H-³¹P CP NMR spectrum of HPA-NPLs.

Figure S9: ³¹P MAS NMR spectra of HPA-NPLs acquired using a single pulse (Bloch decay, quantitative, recycle delay: 500 s) and ¹H-³¹P CP.

Figure S10: Deconvolution of the ¹³³Cs spectrum of HPA-NPLs

Figure S11: Reflectance images of (a) fresh OLA-NPL, (b) 1-month aged OLA-NPL (c) fresh HPA-NPL, (d) 1-week aged HPA-NPL and (e) 1-month aged HPA-NPL films.

Figure S12: PL map at 450 nm of 1-week aged HPA-NPL film.

Figure S13: plots of the average PL wavelength of films cast from solutions; (a) fresh OLA-NPL solution, (b) fresh HPA-NPL solution and (c) one-month aged HPA NPL solution.

Figure S14: Comparative UV-Vis absorption measurement for both OLA- and HPA-NPL films, normalized to the excitonic peak in each case. A small scattering background is present in the HPA-NPL sample due to a thicker film (cf. Figure S16).

Figure S15: PL spectra of encapsulated OLA-NPL films under continuous illumination at 405 nm over a period of 75 minutes.

Figure S16: Widefield hyperspectral PL microscopy characterization of an encapsulated HPA-NPL film with excitation at 405 nm at different illumination intensities. (a) Shows the averaged PL intensity across the entire field of view for ~100 mW/cm² (light grey), ~1,000 mW/cm² (dark grey) and ~10,000 mW/cm² (black) illumination intensity. PL maps corresponding to ~100 mW/cm² (b) and ~10,000 mW/cm² (c). The blue colour scale represents the emission of the confined NPLs averaged between 440-460 nm. The green color scale represents the emission averaged from 490-510 nm corresponding to emission from any aggregated CsPbBr₃ species. There is therefore no evidence of green impurities or degradation on the microscale.

Figure S17: PL spectra of HPA-NPLs before and after heating at 80°C in glove box and air for the stated time durations.

Figure S18: The partial density of states (a and b), wavefunction of the VBM (c and e) and CBM (d and f) of the methyl amine and methyl phosphonate passivated NPLs.

SUPPLEMENTARY NOTE

Estimation of buried Cs⁺ site population in HPA-capped CsPbBr₃ NPLs:

The average NPL size estimated from TEM is 26 nm \times 6 nm \times 2.4 nm, which in a Cs⁺-terminated NPL corresponds to the following number of Cs⁺ sites along the edges of the NPLs 44 \times 11 \times 5 or 2420 Cs⁺ sites in total (#total). Hence, the number of Cs⁺ sites along the edges, #edges, equals (5+11)·4+42·4 = 232. The number of Cs⁺ sites on the facets (without edges), #facets, equals 2·(3·9+3·42+9·42) = 1062. The number of buried Cs⁺ sites which are not in direct contact with the surface of the nanoplatelets is therefore equal to #buried = #total - #edges - #facets = 2420 - 1062 - 232 = 1126 which corresponds to 1126/2420 = 47% of all Cs⁺ sites.

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