Electronic Supplementary Information (ESI) Influence of Shape on Carrier Relaxation Dynamics of CsPbBr₃ Perovskite Nanocrystals

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Method of Rietveld analysis

Rietveld powder structure refinement method is globally recognized as one of the best known methods for obtaining different (micro) structure parameters of a multiphase material.¹ The essence of this method remains in the minimization of the difference between observed (I_0) and structurally calculated (I_C) X-ray diffraction (XRD) spectra by refining different model parameters using Marquardt least-squares procedure. Evolution of refinement is reflected by Goodness of Fit (GoF), which is the ratio of R_{wp} (weighted R-factor) to R_{exp} (expected Rfactor).Pseudo-Voigt function is employed for peak shape analysis since it accounts for broadening resulting in from the combined effect of crystallite size and microstrain.² The angular dependence of full-width-at-half-maximum (FWHM) is taken care of using Caglioti function. Quantification of amorphous (glassy) phase in mixed crystalline and amorphous phases is achieved by using a poorly crystalline phase in the line shape calculation. For materials possessing some geometric shape, it is often noticed that relative intensities of Bragg reflections alter due to the presence of preferred orientation (PO).^{3,4} March-Dollase function is incorporated into the calculation to resolve and quantify the amount of PO in terms of texturing coefficient (r), where r>0 and r=1 signifies random distribution of orientation. In the present study, Rietveld software MAUD (V. 2.80) is utilized for simultaneous refinement of different (micro) structural parameters.

Calculation of PL quantum yield (PLQY) of CsPbBr₃ nanocrystals:

The PLQY of CsPbBr₃ NCs both in DCM and toluene are measured with respect to reference dye quinine sulphate in (0.1 M) H₂SO₄by using the following equation:

$$\phi_{s} = \phi_{r} \frac{I_{s} \frac{OD_{r}}{OD_{s}} \eta_{s}^{2}}{I_{r} \frac{OD_{r}}{OD_{s}} \eta_{r}^{2}}$$
(S1)

Where ϕ_s represents measured PLQY of CsPbBr₃NCs, ϕ_r represents standard PLQY of quinine sulphate (0.53) in 0.1 M H₂SO₄, OD_r and OD_s represents actual absorbance of reference and sample respectively at 370 nm. I_s and I_r represents integrated area of sample and reference, excited at 370 nm respectively. η refers to the refractive index of solvent medium.



Fig. S1 SAED patterns of CsPbBr₃NCs. (A) in toluene, (B) in DCM.



Fig. S2 TEM images of CsPbBr₃ NCs in (A) THF, (C) CHCl₃ and (E) ethyl acetate.

Analysis of XRD data of residue of CsPbBr₃ NCs:

The XRD pattern of the residue of the sample prior to redisperse in toluene and DCM is shown in Fig. S3. The XRD pattern looks very similar to that of CsPbBr₃ NCs in toluene. All peaks are identified to appear from crystalline cubic CsPbBr₃ and are indexed accordingly. Rietveld analysis also corroborates sole presence of crystalline cubic (Pm3m) phase with lattice constant, a= 5.8681(6) Å the value of which remains intermediate between that of CsPbBr₃ NCs in toluene (a = 5.8308 Å) and DCM (a= 5.8839 Å) respectively. However, presence of any crystalline orthorhombic phase is not observed unlike CsPbBr₃ NCs in DCM. An enhanced intensity along<200> direction is observed (shown inset) similar to that of cube shaped CsPbBr₃ NCs in toluene. The coefficient (*r*) of preferred orientation (PO) (where, r>0 and r=1signifies random orientation) along <200> is found to be, r=0.43 which is slightly greater than that of CsPbBr₃ NCs in toluene (r=0.33).



Fig. S3 The profile of the Rietveld analysis (black line) of the XRD pattern (red points) of the residue of the sample before redispersing in toluene and DCM. Inset of the pattern shows the presence of preferred orientation along <200>. (I_O-I_C), representing residue of Rietveld refinement, is plotted (grey colored line) below the fitted pattern. Bar sequence, denoting the peak positions of cubic CsPbBr₃ is plotted at the bottom.

Analysis of DADSs after using 375 nm excitation pulse:

The DADS1 is short lived (838 fs and 823 fs for NCs in toluene and DCM, respectively) and it is attributed to the initial excitation to the hot exciton state. This consists of exciton bleach (EB) nearly at 490 nm and photoinduced absorption (PIA) at 524 nm for cubic shaped NCs (in toluene). Whereas, for rod shaped NCs (in DCM) EB and PIA are found at 475 nm and at 512nm, respectively. DADS2 (shallow trap state) has a lifetime of 25 ps for cubic shaped NCs (in toluene) and 45 ps for rod shaped NCs (in DCM). For DADS2, EB peak and PIA are

observed at around 493 nm and 514 nm for cubic shaped NCs in toluene, whereas corresponding EB and PIA are found at 505 nm and 468 nm, respectively for rod shaped NCs in DCM. Similarly DADS 3 (deep trap state) has a lifetime of 163 ps for cubic shaped NCs and 303 ps for rod shaped NCs. For DADS3, EB and PIA are observed at around 513 nm and 487 nm for cubic shaped NCs, whereas EB and PIA are found at 501 nm and 483 nm, respectively for rod shaped NCs. DADS4 (band edge state) has a lifetime of 5 ns for cubic shaped NCs and 11ns for rod shaped NCs. For DADS4 EB and PIA are monitored at around 509 nm and 491 nm, respectively for cubic shaped NCs. For rod shaped NCs, EB is observed at 495 nm but PIA shows very negligible intensity. It is worth noting that measurement of slowest nanosecond time component is beyond our limitation, since maximum delay time available in our instrument is 8 ns.



Fig. S4 Decay-associated difference spectra (DADS) after performing global analysis of TA data of (A) cubic shaped CsPbBr₃ NCs in toluene and (B) rod shaped CsPbBr₃ NCs in DCM, respectively after using 375 nm excitation pulses.



Fig. S5 Goodness of fit TA data based on global and target analysis for (A) cubic shaped (in toluene) and (B) rod shaped (in DCM) NCs.

Analysis of TA data upon 400 nm excitation:



Fig. S6 Decay-associated difference spectra (DADS) after performing global analysis of TA data of (A) cubic shaped CsPbBr₃ NCs in toluene and (B) rod shaped NCs in DCM, respectively after using 400 nm excitation pulse.



Fig. S7 TA profile pictures of CsPbBr₃ NCs (A) in toluene and (B) in DCM after exciting the NCs at 400 nm. Typical TA contour plots (Ai, Bi), Time-gated spectra at short (50-800 fs) delay time (Aii, Bii), long (5-1000 ps) delay time (Aii, Bii) and time traces (Aiii, Biii) at selected probe wavelength for NCs in toluene and DCM, respectively. The time axis is linear up to 10 ps and logarithmic thereafter.



Fig. S8 Kinetic scheme used for target analysis of TA data and obtained Species-associated difference spectra (SADS) of (A, B) cubic shaped CsPbBr₃ NCs in toluene and (C D) rod shaped NCs in DCM, respectively after using 400 nm excitation pulse. Inset shows population profiles of the corresponding SADSs.

References:

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