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Influence of Ligand Shell Ordering on Dimensional Confinement of Cesium Lead Bromide ($CsPbBr_3$) Perovskite Nanoplatelets

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Experimental

Materials

All chemicals were used as received without further purification. Cs_2CO_3 (99.9%, Alfa Aesar), oleic acid (OLAc, 90%, Aldrich), octadecene (ODE, 90%, Aldrich), lead bromide ($PbBr_2$, 98%, Alfa Aesar), *n*-butylamine (BA, 99%, TCI America), *n*-octylamine (OA, 98%, TCI America), dodecylamine (DA, 98%, Alfa Aesar), tetradecylamine (TA, 95%, Aldrich), octadecylamine (ODA, 97%, Alfa Aesar), di-*n*-octylamine (96%, Alfa Aesar), and tri-*n*-octylamine (95%, Alfa Aesar) were used in the synthesis of $CsPbBr_3$ nanoplatelets.

Synthesis of 2D $CsPbBr_3$ nanoplatelets

In a typical reaction, cesium oleate (Cs-OA) was prepared by adapting a previously reported method wherein 0.032 g Cs_2CO_3 and 10 mL OLAc were loaded in a 50 mL three-neck round-bottomed flask, degassed under vacuum at 120°C, and heated to 150°C under Ar flow to ensure complete dissolution of the solids.[21] In parallel, 0.015 g of $PbBr_2$ was dissolved in 5 mL ODE and 0.250 mL of OLAc; the lead oleate thus formed was mixed with a desired stoichiometric ratio of alkylamine (RA:C4—C18) in a three-neck round-bottomed flask and degassed under vacuum for 20 min at 100°C; for C4 mixture was heated at 80—90°C because of low boiling point of C4 (78°C). The alkylamine (RA) concentration (x) was systematically varied. After complete dissolution of $PbBr_2$, the temperature of the flask was set at the desired temperature (which was varied from 50–150°C). Next, 1 mL of the as-prepared Cs-OA solution was rapidly injected under Ar flow. The reaction mixture was maintained for 10 s and immediately quenched with 15 mL of cool hexanes to 30—40 °C). The pale yellow-colored precipitate was collected by centrifugation at 12,000 rpm for 10 min and then resuspended to form a colloidal dispersion in hexanes. The colloidal dispersion of the nanoplatelets in hexanes was used for further characterization.

Characterization

Single-particle PL emission spectra from individual perovskite nanoplatelets were measured with a home-built wide-field microscope equipped with an imaging spectrograph (Princeton Instruments, Acton SpectraPro SP-2300) and an electron multiplying charge-coupled device (EMCCD) (Princeton Instruments, ProEM 16002). A Xe-lamp (Oriel Instrument, 300 W) in conjunction with a monochromator (Newport, Oriel Cornerstone 130) was used as the excitation light source. The nanoplatelets were excited via an attenuated total reflection scheme using a quartz prism to minimize the interference from the excitation light during the PL measurement. A dilute dispersion of colloidal nanoplatelets was cast onto a thin quartz plate to deposit well-separated individual nanoplatelets. Next, the plate was placed on top of the prism using an index matching liquid (hexanes). The PL from individual nanoplatelets was collected using an objective lens (Olympus, PLanFL N 40×) and was focused onto the EMCCD either as an image or as a spectrum using a tube lens (Nikon) through the imaging spectrograph.

High-resolution transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G2 F20 ST instrument at accelerating voltage 200 kV.

Powder X-ray diffraction (XRD) measurements were performed using a Bruker D8-Focus Bragg-Brentano X-ray Powder Diffractometer with a Cu Kα radiation source ($\lambda = 1.5418$ Å) in the range of 10—60°.

Small angle X-ray scattering (SAXS) measurements were performed using a Rigaku S-Max3000 Pinhole SAXS Camera in the range of 0.02 – 0.30 Å^{-1}.

UV-Vis absorption spectra were obtained using a Hitachi U-4100 UV-Vis-NIR spectrophotometer. PL emission spectra were acquired using a Horiba PTI Quanta-Master series spectrofluorometer with a Xenon arc lamp as the light source and a photomultiplier tube (PMT) as the light detector.

Fourier transform infrared (FTIR) spectra were obtained using Bruker VERTEX 70 in the range of 4000—400 cm^{-1} with a spatial resolution of 4 cm^{-1}.

Calculation of the average octahedra layer thickness (*n*) of nanoplatelets

The average octahedral layer thickness of nanoplatelets is reported as per the following equation.

$$n_{avg} = \sum_{i=1}^{\infty} (a_i \times n_i) \quad \cdots\cdots(6)$$

$$a_i = \frac{\mathit{Integrated\ area\ of\ } n_i \mathit{\ in\ PL\ spectra}}{\mathit{Totally\ integrated\ area\ in\ PL\ spectra}} \ldots\ldots \quad (7)$$

where n_{avg} is average octahedral layer thickness for a specific sample, a_i (i = 1—6 and bulk) is the weighting factor representing the population of a specific layer thickness, andn_i (i = 1—6 and bulk) is the number of octahedral; layers of few-layered nanoplatelets. For nanoplatelets thicker than n = 6 in the bulk limit, a value of n = 30 has been approximated, based on TEM measurement for thick perovskite approaching to bulk limit. In order to calculate the relative proportion of each population, the integrated area of individual nanoplatelets at a specific PL maximum emission wavelength is obtained and then divided by the total integrated area in the PL spectrum.

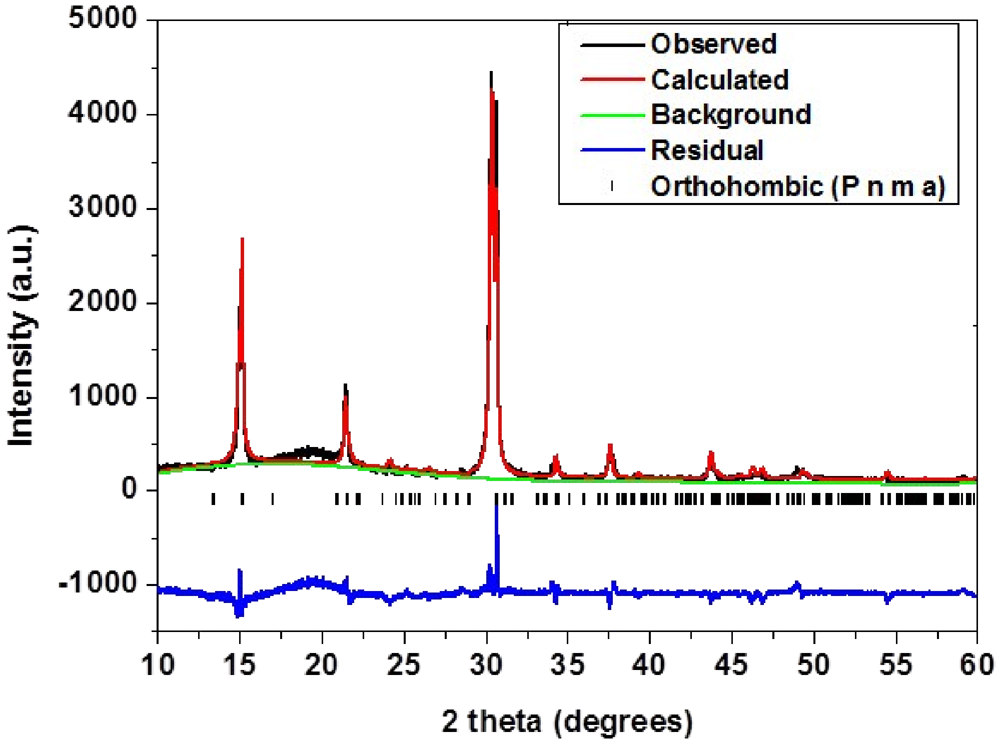

Fig. S1 Rietveld refinement of powder XRD pattern of $CsPbBr_3$ nanoplatelets obtained using C8 at 150°; tick marks indicate the position of Bragg reflections corresponding to the *Pnma* orthohombic space group of $CsPbBr_3$.

Table S1. Rietveld refinement parameters corresponding to the refinement of the power XRD pattern of $CsPbBr_3$ nanoplatelets obtained using C8 at 150°C as shown in Figure S1. Refinement statistics, including goodness of fit (χ^2), weighted goodness of fit (wRp) and the individual point residuals (Rp) show good agreement between the observed and calculated patterns. The orthorhombic structure provides a better fit to the diffraction data as compared to the cubic polymorph.

Orthorhombic Fit: $CsPbBr_3$ (using C8 at 150°C)// Space Group: *Pnma* // Vol: 804.83(6) Å^3		
α = 90.000(0)°	β = 90.000(0)°	γ = 90.000(0)°
a = 8.2934 (5)	*b* = 11.7941 (4)	*c* = 8.2281(6)
χ^2 = 5.809	wRp = 0.1482	Rp = 0.1150

Table S2. PL emission maxima (nm) measured for 2D $CsPbBr_3$ nanoplatelets from single-particle PL emission spectroscopy experiments and assignments to layer thicknesses in terms of number of octahedral layers (*n*). The assignments are in good agreement with previous assignments available from Refs. 16 and 17.

Thickness of nanoplatelts in terms of number of octahedra layers (*n*)	Experimental result based on emission maximum (nm), (*this paper*)	Emission maximum (nm), Ref. 18	Emission maximum (nm), Ref. 19	Emission maximum (nm), Ref. 29
1	406	-	405	-
2	430	-	435	-
3	458	438	462	452
4	475	450	477	478
5	490	459	488	489
6	505	-	-	-
Bulk	520	-	-	516

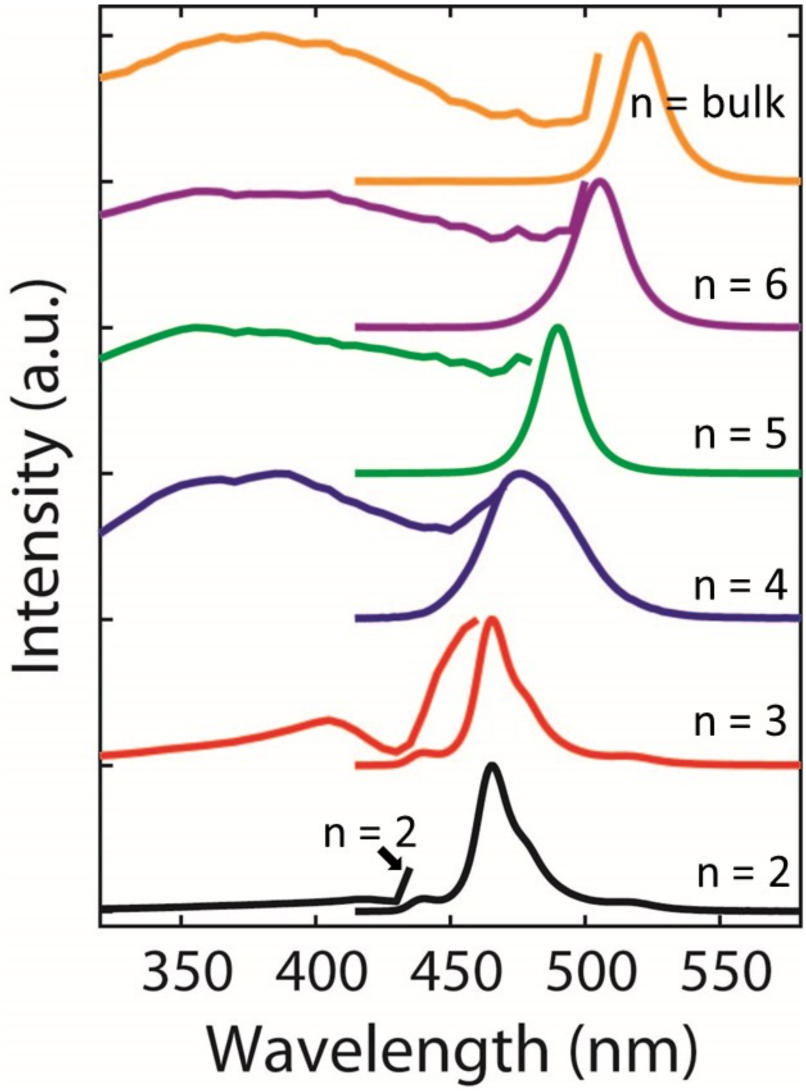

Fig. S2. PL excitation spectra along with emission spectra for $CsPbBr_3$ nanoplatelets with different layer thickness (*n* = 2, 3, 4, 5, 6, and bulk): *n* = 2 and *n* = 3 nanoplatelets are obtained from dispersions prepared using C12 amine at 100°C; *n* = 4 and *n* =5 nanoplatelets are isolated from dispersions prepared using C12 amine at 150°C; and *n* = 6 and *n* = bulk nanoplatelets are isolated from samples prepared using C8 amine at 100°C.

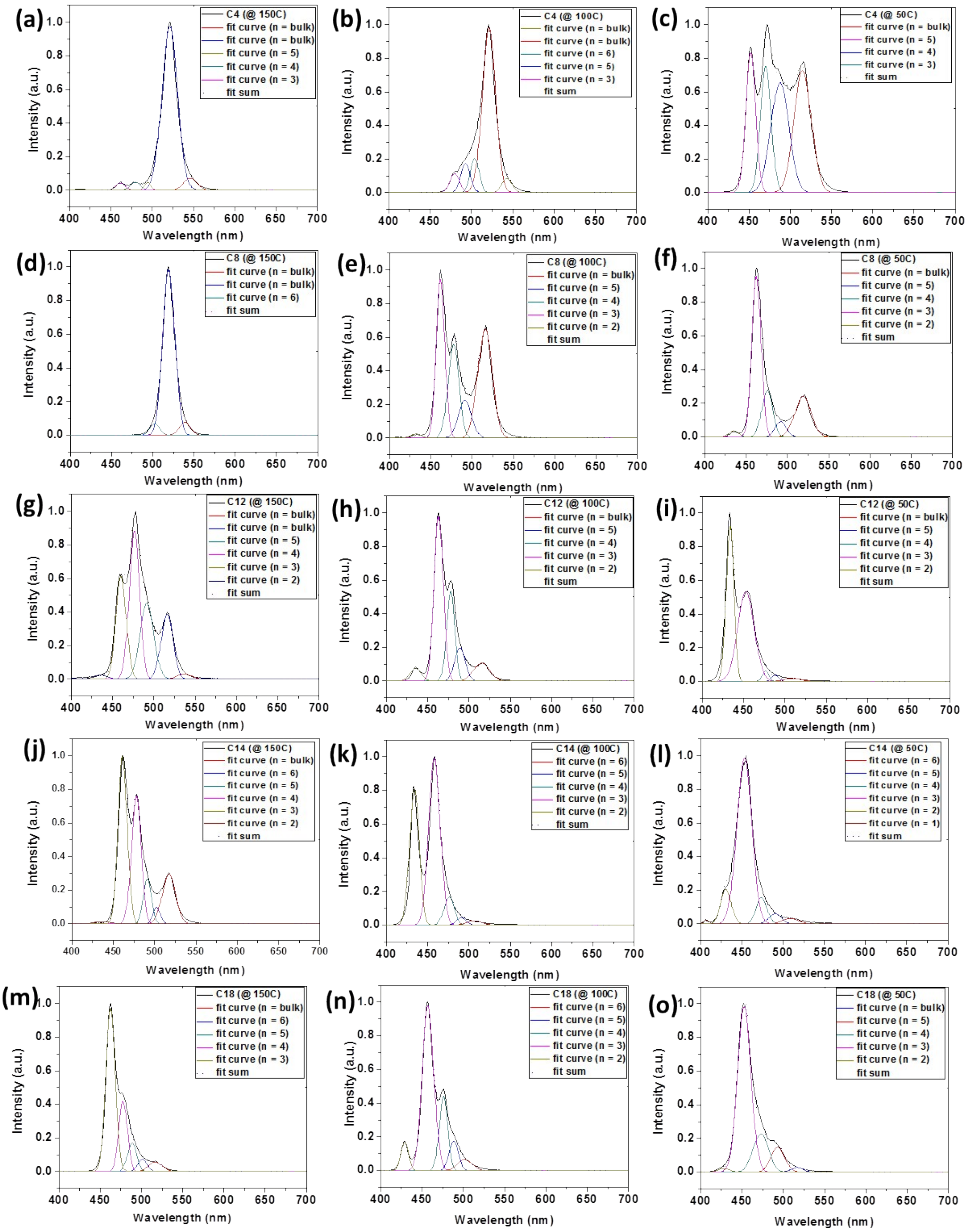

Fig. S3 Deconvolution of ensemble PL emission spectra of $CsPbBr_3$ nanoplatelets to contributions from nanoplatelets of different layer thicknesses exemplified for spectra collected for nanoplatelets prepared using C4—C18 alkylamine ligands at 100°C. In each case, the spectra have been fitted to Gaussian peaks derived from *n* = 1, 2, 3, 4, 5, 6, and bulk species. The spectra correspond to nanoplatelets prepared at 150 (left), 100 (middle), and 50°C (right column) using (a-c) C4, (d-f) C8, (g-i) C12, (j-l) C14, and (m-o) C18.

Table S3. Deconvolution of PL emission spectra using Gaussian fitting results and emission peak position for different layer thickness (*n* = 1, 2, 3, 4, 5, 6, and bulk) at specific synthetic condition using various chain length amines at various temperature.

Used Ligand chain length at reaction temperature	*n* = 2	*n* = 3	*n* = 4	*n* = 5	*n* = 6	*n* = bulk	*n* = bulk (larger species)
C4 at 150°C	-	461	479	493	-	520	546
C8 at 150°C	-	-	-	-	502	519	538
C12 at 150°C	435	460	476	491	-	516	539
C14 at 150°C	-	460	476	490	502	515	-
C18 at 150°C	-	462	477	489	502	516	-
C4 at 100°C	-	-	479	493	504	521	543
C8 at 100°C	432	461	477	491	-	515	-
C12 at 100°C	435	463	477	489	-	515	-
C14 at 100°C	433	458	476	490	506	-	-
C18 at 100°C	430	457	475	488	501	-	-
C4 at 50°C	-	452	470	487	-	515	-
C8 at 50°C	435	462	475	492	-	519	-
C12 at 50°C	432	455	475	489	-	510	-
C14 at 50°C	430	455	473	489	508	-	-
C18 at 50°C	433	453	476	488	-	510	-

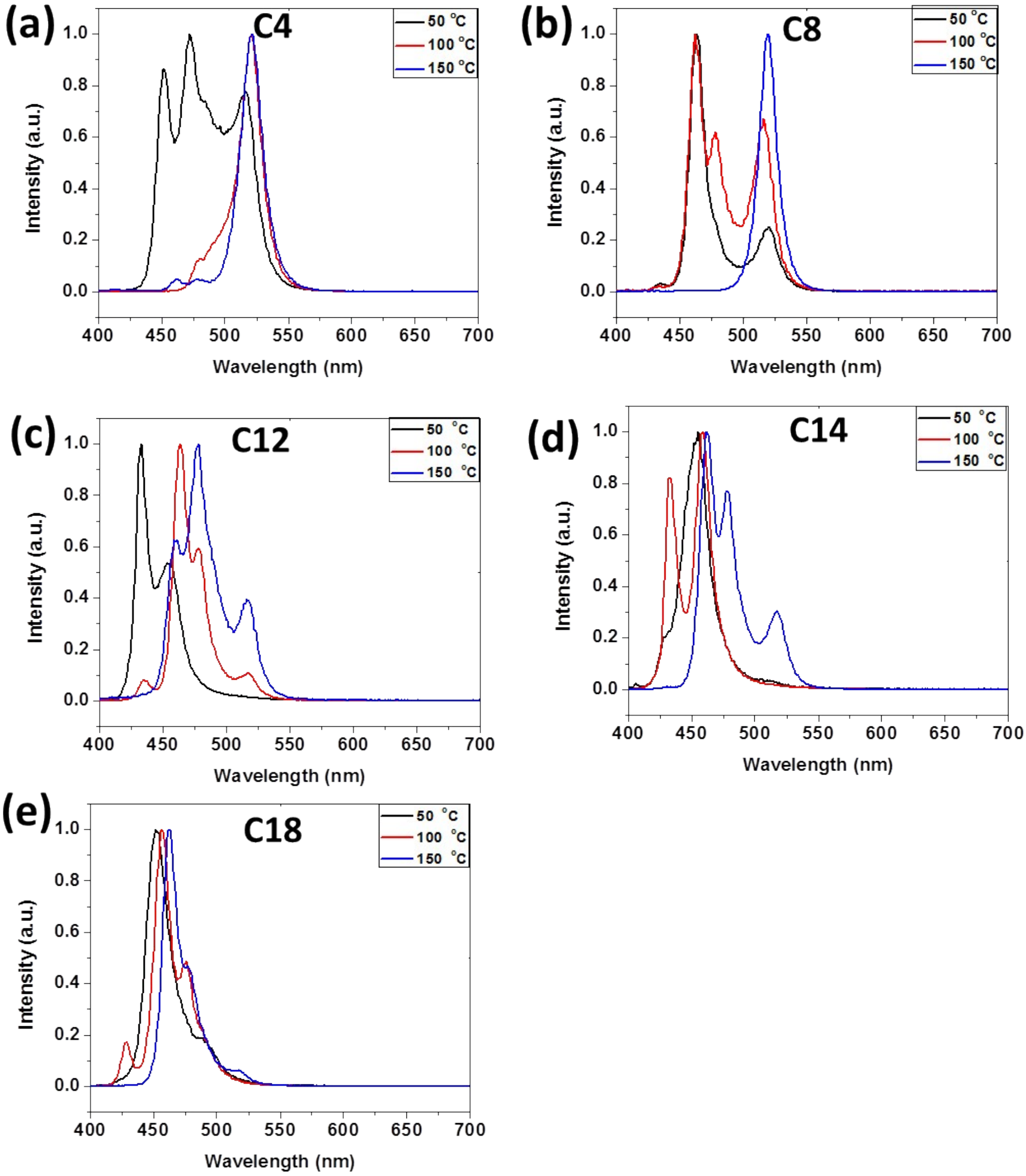

Fig. S4 PL emission spectra of of $CsPbBr_3$ nanoplatelets plotted as a function of temperature for nanoplatelets obtained using (a) C4, (b) C8, (c) C12, (d) C14, and (e) C18 alkylamine ligands.

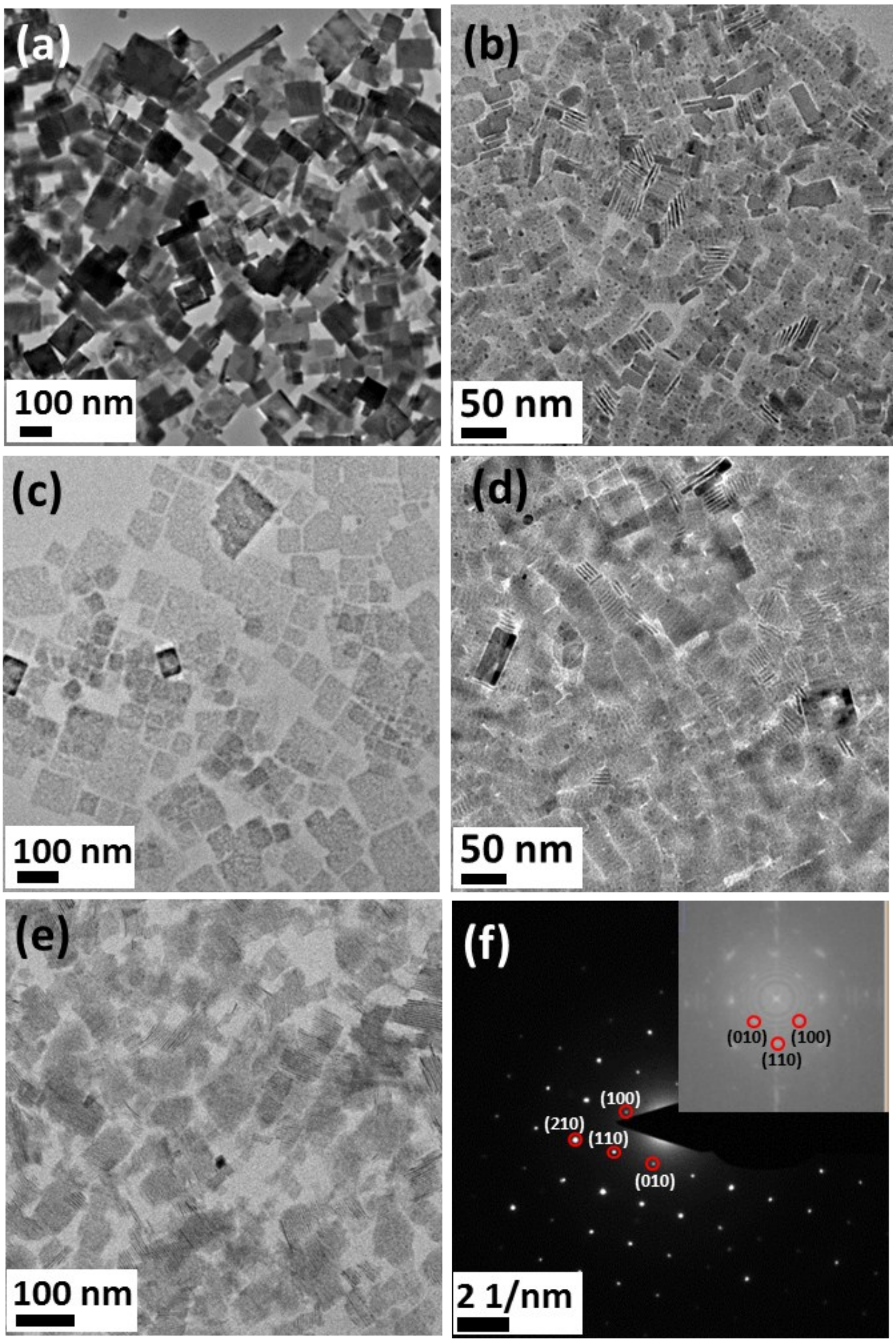

Fig. S5 TEM images of $CsPbBr_3$ nanoplatelets prepared at 100°C using different alkylammonium chain-lengths of a) C4, b) C8, c) C12, d) C14, and e) C18. f) Selected area electron diffraction and its fast Fourier transform acquired for an individual $CsPbBr_3$ nanoplatelet prepared using a C4 amine.

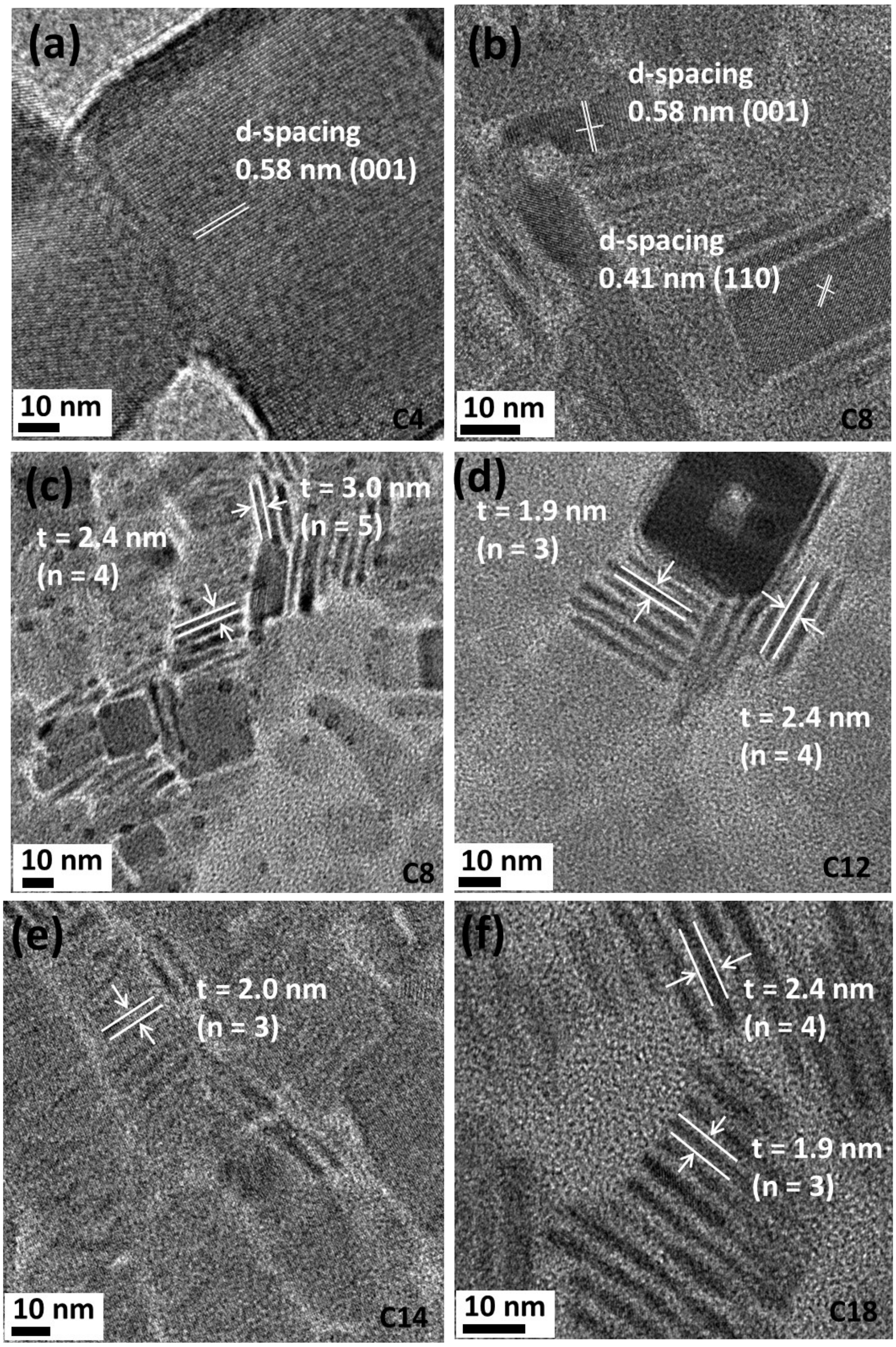

Fig. S6 High-resolution TEM images of $CsPbBr_3$ nanoplatelets obtained using different chain-lengths of ligands and representative measurements of the thickness spans of nanoplatelets. The images correspond to $CsPbBr_3$ nanoplatelets prepared using: a) C4; b,c) C8, d) C12, e) C14, and f) C18.

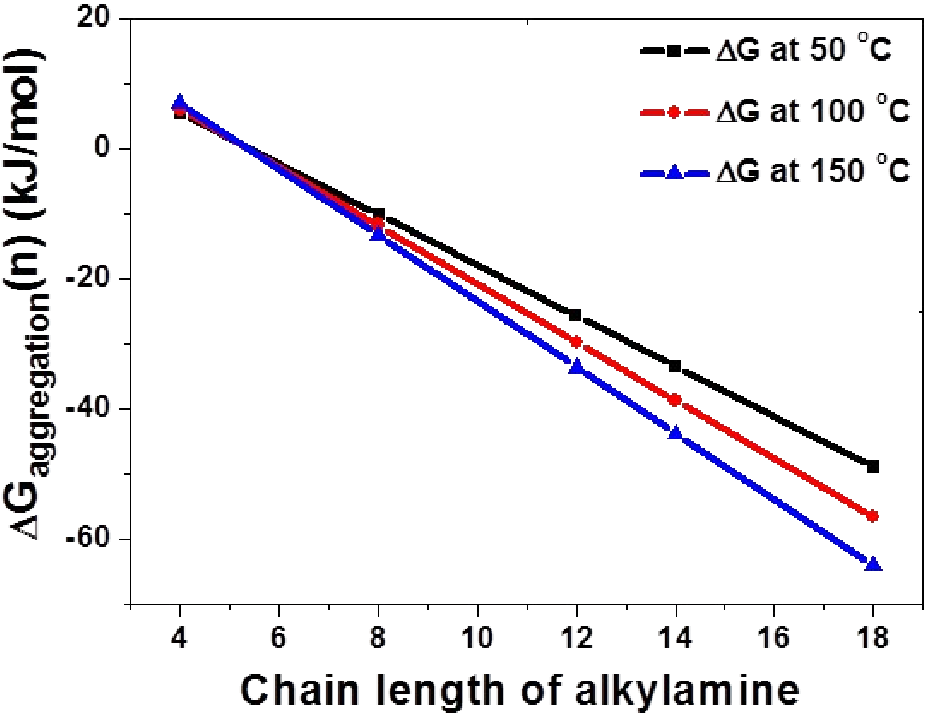

Fig. S7 Gibbs free energy of aggregation of ligand packing as a function of chain-length at different reaction temperatures.

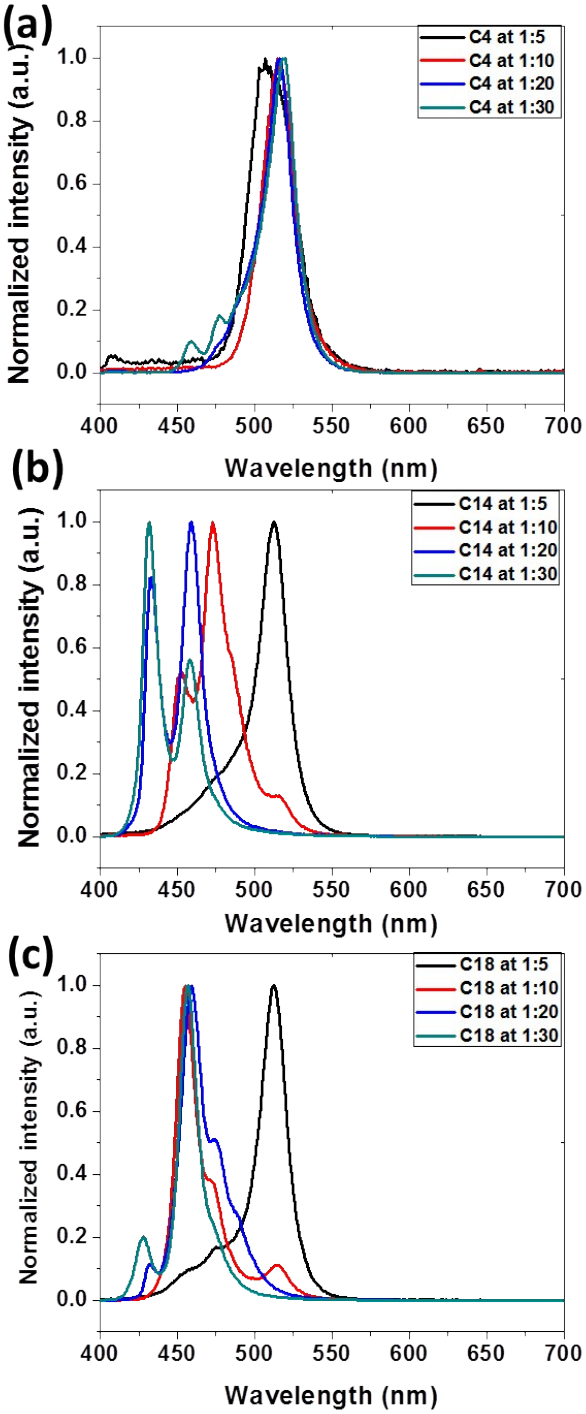

Fig. S8 PL emission spectra of $CsPbBr_3$ nanoplatelets plotted as a function of ligand concentration (Pb-OA:RA=1:5—1:30) for nanoplatelets obtained using (a) C4, (b) C14, and (c) C18 at 100 °C.

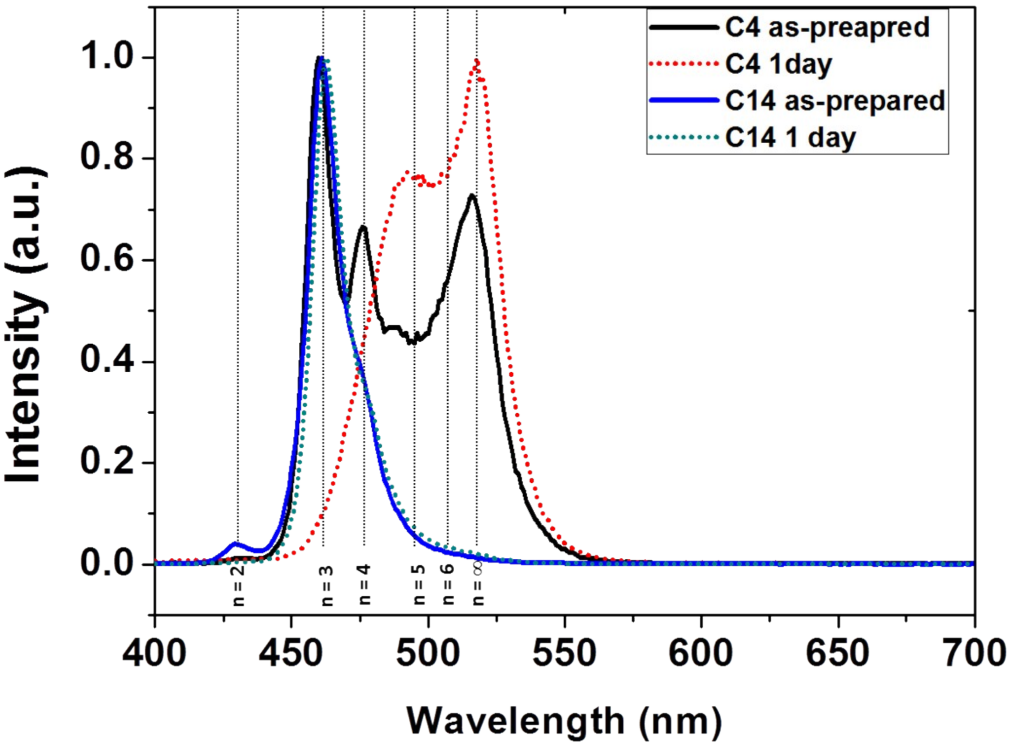

Fig. S9 PL emission spectra of $CsPbBr_3$ nanoplatelets obtained immediately after synthesis (solid line) and after 1 day (dotted line) using C4 at 50°C and C14 at 80°C.