Supporting Information for

Thermal Stability of the Black Perovskite Phase in Cesium Lead Iodide Nanocrystals Under Humid Conditions

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Tables S1 and S2. Indexation of the room temperature GIWAXS data in Figure 2 for the $CsPbI_3$ nanocrystals made with OAm and OA or DIOP.

Figure S1. GIWAXS of superlattices of $CsPbI_3$ nanocrystals at 25°C indexed to cubic $CsPbI_3$ crystal structure

Figure S2 and S3. GIWAXS of superlattices of $CsPbI_3$ nanocrystals made with OAm and OA heated to 200°C and 300°C indexed to δ-orthorhombic phase.

Figure S4. GIWAXS of superlattices of $CsPbI_3$ nanocrystals made with OAm and DIOP heated to 300°C indexed to γ-orthorhombic phase and δ-orthorhombic phase.

Figure S5. Thermogravimetric analysis (TGA) of $CsPbI_3$ nanocrystals synthesized with OAm and OA.

Figure S6. SEM images of $CsPbI_3$ nanocrystals synthesized with OAm and OA heated to 190°C in humid air.

Figure S7. Photographs of a film of $CsPbI_3$ nanocrystals made with OAm and OA on a glass substrate (1 cm × 1 cm) before and after heating in humid air (RH=42%) to 250°C.

Figure S8. *In situ* PL of a film of $CsPbI_3$ nanocrystals made with OAm and DIOP heated on a glass substrate and photos of a film of $CsPbI_3$ nanocrystals made with OAm and DIOP on glass before and after heating in humid air (RH=42%) under UV light illumination.

Figure S9. Photographs of a film of $CsPbI_3$ nanocrystals made with OAm and DIOP being heated on a glass substrate in humid air (RH=42%).

Figure S10. Photographs of a film of $CsPbI_3$ nanocrystals made with OAm and OA being heated on a glass substrate in nitrogen.

Figure S11. Photographs of a film of $CsPbI_3$ nanocrystals made with OAm and DIOP being heated on a glass substrate in nitrogen.

Video of a $CsPbI_3$ nanocrystal film being heated in air and then cooled back to room temperature: "cm9b03533_SI Movie 1.mp4"

Videos of 2D GIWAXS patterns with in situ heating in air of superlattices of $CsPbI_3$ nanocrystals made with OAm and OA or DIOP: "cm9b03533_SI Movie 2.mp4" and "cm9b03533_SI Movie 3.mp4"

Table S1. Indexation details for room temperature GIWAXS of $CsPbI_3$ OA nanocrystals. The spots are indexed to γ-orthorhombic phase (Pbnm)[1] with lattice parameters of a = 8.646 Å, b = 8.818 Å, and c = 12.520 Å. The best fit lattice parameters are a = 8.555 Å, b = 8.734 Å, and c = 12.251 Å.

			Indexation under $(002)_{NC}$				Indexation under $(110)_{NC}$			
Measured					Expected				Expected	
q (nm^{-1})	d (A)	Angle[a] (°)	(hkl)	BD[b]	d(A)	Angle (°)	(hkl)	BD	d(A)	Angle (°)
9.99	6.29	89.5	-110	[-110]	6.16	90.0	002	[-110]	6.24	90.0
14.45	4.35	46.0	-1-12	[-110]	4.38	45.4	112	[-110]	4.38	44.6
14.49	4.34	89.3	0-20	[100]	4.29	90.0	1-12	[-111]	4.38	89.2
16.95	3.71	72.8	211	[-120]	3.75	72.8	013	[-33-1]	3.74	72.6
17.87	3.52	55.0	0-22	[100]	3.53	54.8	202	[-111]	3.61	54.0
19.22	3.27	36.4	n/a[c]	n/a	n/a	n/a	212	[-221]	3.33	36.2
20.76	3.03	89.8	-2-20	[-110]	3.08	90.0	004	[-111]	3.12	90.0
23.29	2.70	89.6	-3-10	[-130]	2.79	90.0	1-14	[-221]	2.78	89.5
23.30	2.70	63.5	-2-22	[-110]	2.76	63.8	114	[-111]	2.78	63.1
23.37	2.69	25.5	-1-14	[-110]	2.78	26.9	222	[-110]	2.76	26.2
25.91	2.42	65.8	-3-12	[-130]	2.55	66.4	204	[-221]	2.55	65.2
26.02	2.41	34.7	0-24	[100]	2.52	35.4	312	[-111]	2.55	34.8
30.56	2.06	44.1	-2-24	[-110]	2.19	45.4	224	[-111]	2.19	44.6
32.29	1.95	47.3	-3-14	[-130]	2.08	48.8	314	[-221]	2.08	47.6

[a] Angle refers to the angle between the current spot and the vertical axis q_x=0. For indexation under $(002)_{NC}$, the (002) spot will fall on q_x=0, so the expected angle is calculated as the angle between the current spot and (002) spot; for indexation under $(110)_{NC}$, the (110) spot will fall on q_x=0, so the expected angle is calculated as the angle between the current spot and (110) spot.

[b] BD is the beam direction.

[c] n/a indicates that this spot does not appear for this beam direction and crystal orientation.

Table S2. Indexation details for room temperature GIWAXS of $CsPbI_3$ DIOP nanocrystals. The spots are indexed to γ-orthorhombic phase (Pbnm)[1] with lattice parameters of *a* = 8.646 Å, *b* = 8.818 Å, and *c* = 12.520 Å. The best fit parameters are *a* = 8.490 Å, *b* = 8.603 Å, and *c* = 12.086 Å.

			Indexation under $(002)_{NC}$				Indexation under $(110)_{NC}$			
Measured					Expected				Expected	
q (nm^{-1})	d (A)	Angle[a] (°)	(hkl)	BD[b]	d(A)	Angle (°)	(hkl)	BD	d(A)	Angle (°)
10.31	6.10	89.7	-1-10	[-110]	6.16	90.0	002	[-110]	6.24	90.0
14.60	4.30	89.4	0-20	[100]	4.29	90.0	1-12	[-111]	4.38	89.2
14.61	4.30	44.7	-1-12	[-110]	4.38	45.4	112	[-110]	4.38	44.6
17.12	3.67	72.7	211	[-120]	3.75	72.8	013	[-33-1]	3.74	72.6
18.05	3.48	54.8	0-22	[100]	3.53	54.8	202	[-111]	3.61	54.0
19.27	3.26	57.9	122	[-210]	3.28	57.9	n/a	n/a	n/a	n/a
19.31	3.25	35.5	n/a[c]	n/a	n/a	n/a	212	[-221]	3.33	36.2
20.76	3.03	89.6	-2-20	[-110]	3.08	90.0	004	[-110]	3.12	90.0
23.25	2.70	63.3	-2-22	[-110]	2.76	63.8	114	[-110]	2.78	63.1
23.51	2.67	89.6	-3-10	[-130]	2.79	90.0	1-14	[-221]	2.78	89.5
23.67	2.65	24.7	-1-14	[-110]	2.78	26.9	222	[-110]	2.76	26.2
25.62	2.45	65.7	-3-12	[-130]	2.55	66.4	204	[-221]	2.55	65.2
26.02	2.41	33.7	0-24	[100]	2.52	35.4	312	[-111]	2.55	34.8
30.25	2.08	43.6	-2-24	[-110]	2.19	45.4	224	[-110]	2.19	44.6
32.13	1.96	59.0	233	[-320]	2.08	59.8	n/a	n/a	n/a	n/a
32.43	1.94	46.7	-3-14	[-130]	2.08	48.8	314	[-221]	2.08	47.6

[a] Angle refers to the angle between the current spot and the vertical axis q_x=0. For indexation under $(002)_{NC}$, the (002) spot will fall on q_x=0, so the expected angle is calculated as the angle between the current spot and (002) spot; for indexation under $(110)_{NC}$, the (110) spot will fall on q_x=0, so the expected angle is calculated as the angle between the current spot and (110) spot.

[b] BD is the beam direction.

[c] n/a indicates that this spot does not appear for this beam direction and crystal orientation.

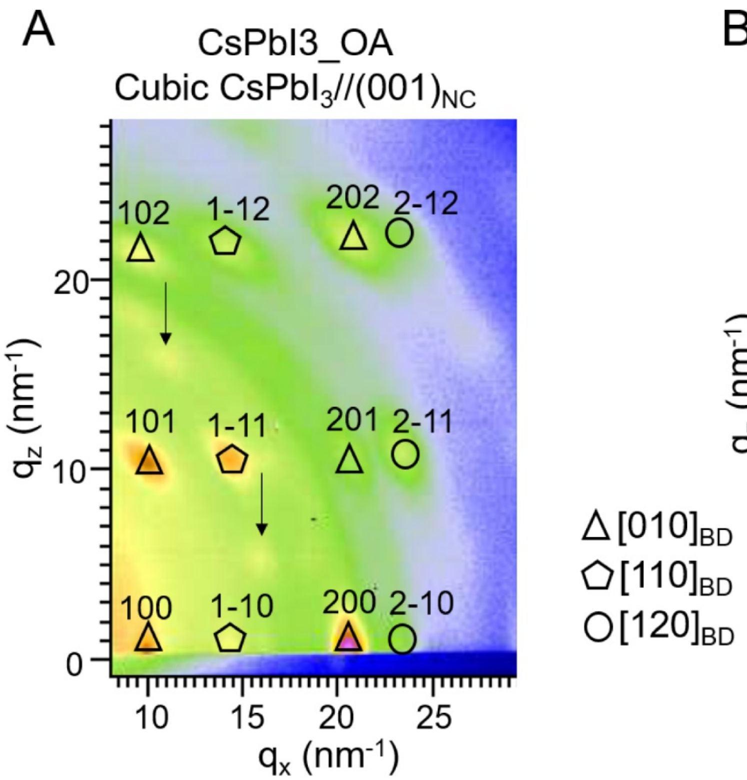

Figure S1. GIWAXS of superlattices of $CsPbI_3$ nanocrystals at 25°C indexed to cubic $CsPbI_3$ crystal structure with the (001) planes of nanocrystals parallel to the substrate: (A) $CsPbI_3$ nanocrystals synthesized with OAm and OA (same GIWAXS pattern as in Figures 2B and 2C); (B) $CsPbI_3$ nanocrystals synthesized with OAm and DIOP (same GIWAXS pattern as in Figures 2E and 2F). The associated beam directions (BD) needed to account for all of the diffraction spots are provided next to each image. The spots that cannot be indexed with cubic phase are pointed to with arrows. However, these spots are characteristic of γ-orthorhombic phase (Figure 2).

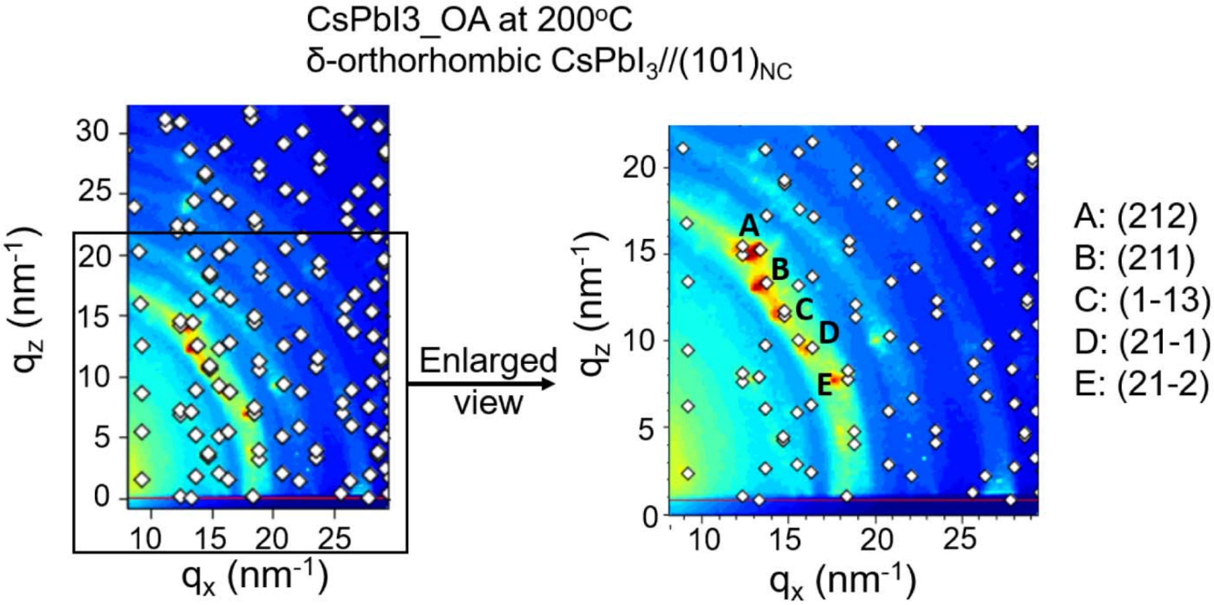

Figure S2. GIWAXS of superlattices of $CsPbI_3$ nanocrystals made with OAm and OA heated to 200°C (same pattern as in Figure 3E). The pattern is indexed to the yellow δ-orthorhombic phase using the indexGIXS-2M software. The (101) planes of nanocrystals are oriented parallel to the substrate. Due to the significant number of spots in the pattern and their close distances to each other, only the five most intense spots in the pattern are labeled and indexed for clarity. These five spots correspond to the (212), (211) (1-13) (21-1) and (21-2) planes of δ-phase.

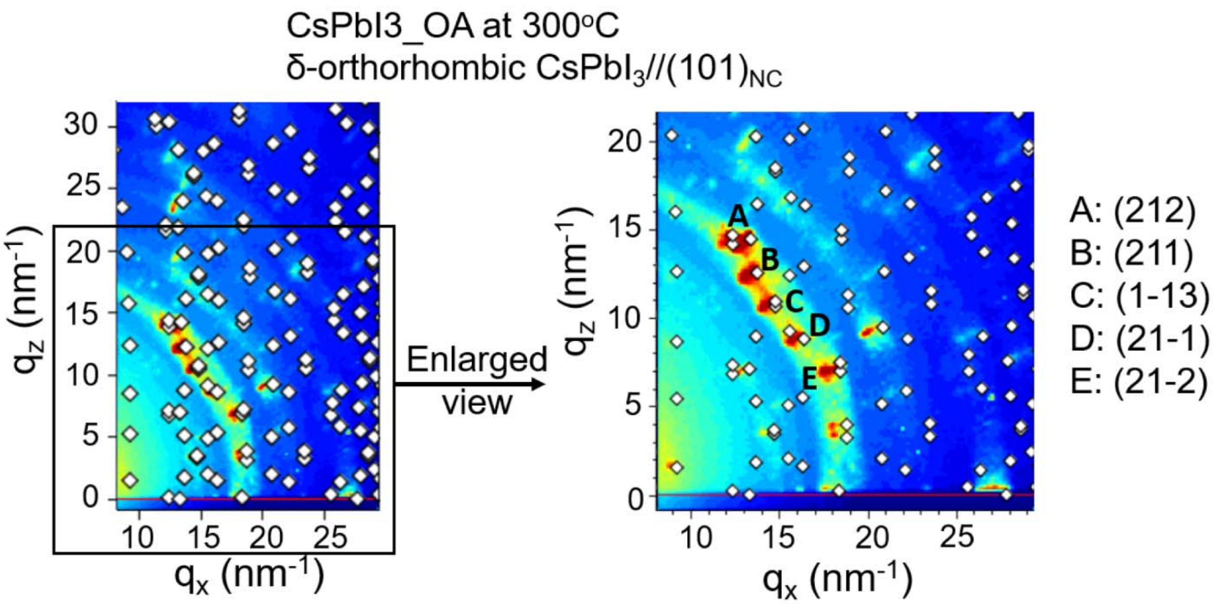

Figure S3. GIWAXS of superlattices of $CsPbI_3$ nanocrystals made with OAm and OA heated to 300^{o}C (same pattern as in Figure 3F). The pattern is indexed to the yellow δ-orthorhombic phase with (101) planes of nanocrystals oriented parallel to the substrate. The five most intense spots in the pattern correspond to the (212), (211) (1-13) (21-1) and (21-2) planes of δ-phase.

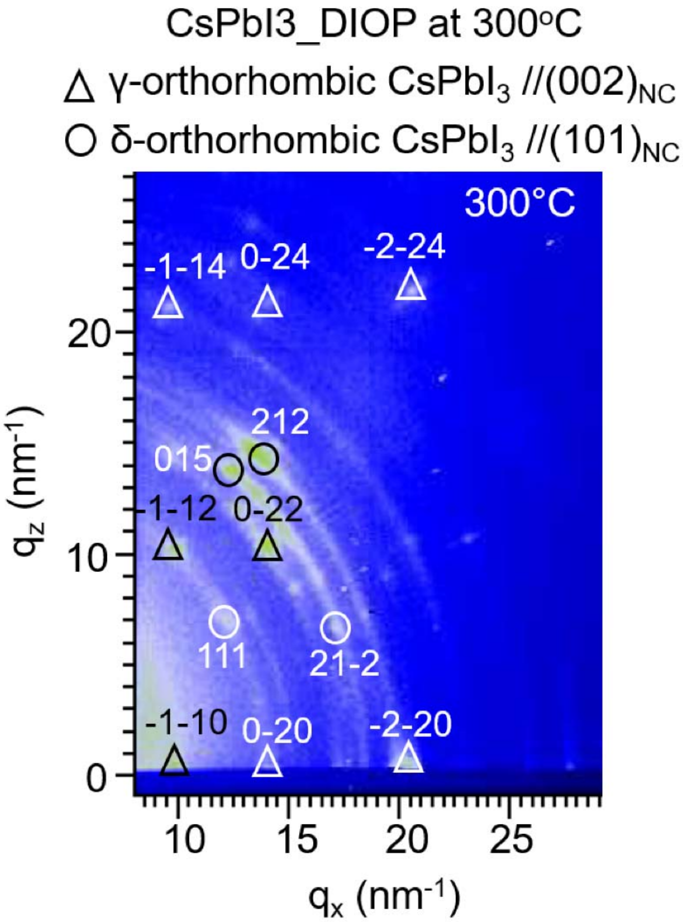

Figure S4. GIWAXS of superlattices of $CsPbI_3$ nanocrystals made with OAm and DIOP heated to 300°C (same pattern as in Figure 5F). The pattern is indexed to γ-orthorhombic phase with (002) nanocrystal orientation (labeled with triangles) and δ-orthorhombic phase with (101) nanocrystal orientation (labeled with circles).

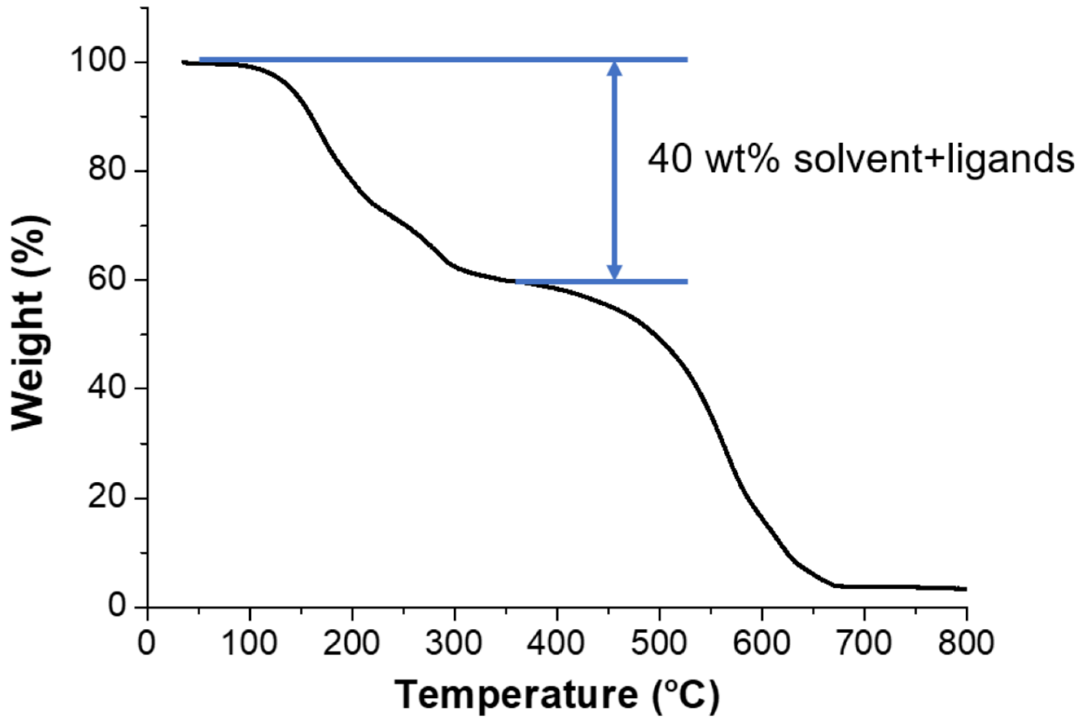

Figure S5. Thermogravimetric analysis (TGA) of $CsPbI_3$ nanocrystals synthesized with OAm and OA. TGA was performed on a Mettler Thermogravimetric Analyzer, Model TGA/DSC 1 using a dried dispersion of 2.6 mg of $CsPbI_3$ nanocrystals deposited in an alumina crucible and heated under nitrogen from 35°C to 800°C. The first two weight loss steps ending at ~350°C correspond to the loss of hexane, oleylamine, oleic acid, and octadecene. These two steps give a weight loss of 40 wt%, indicating that the solvent and ligands make up for 40 wt% of the nanocrystal sample.

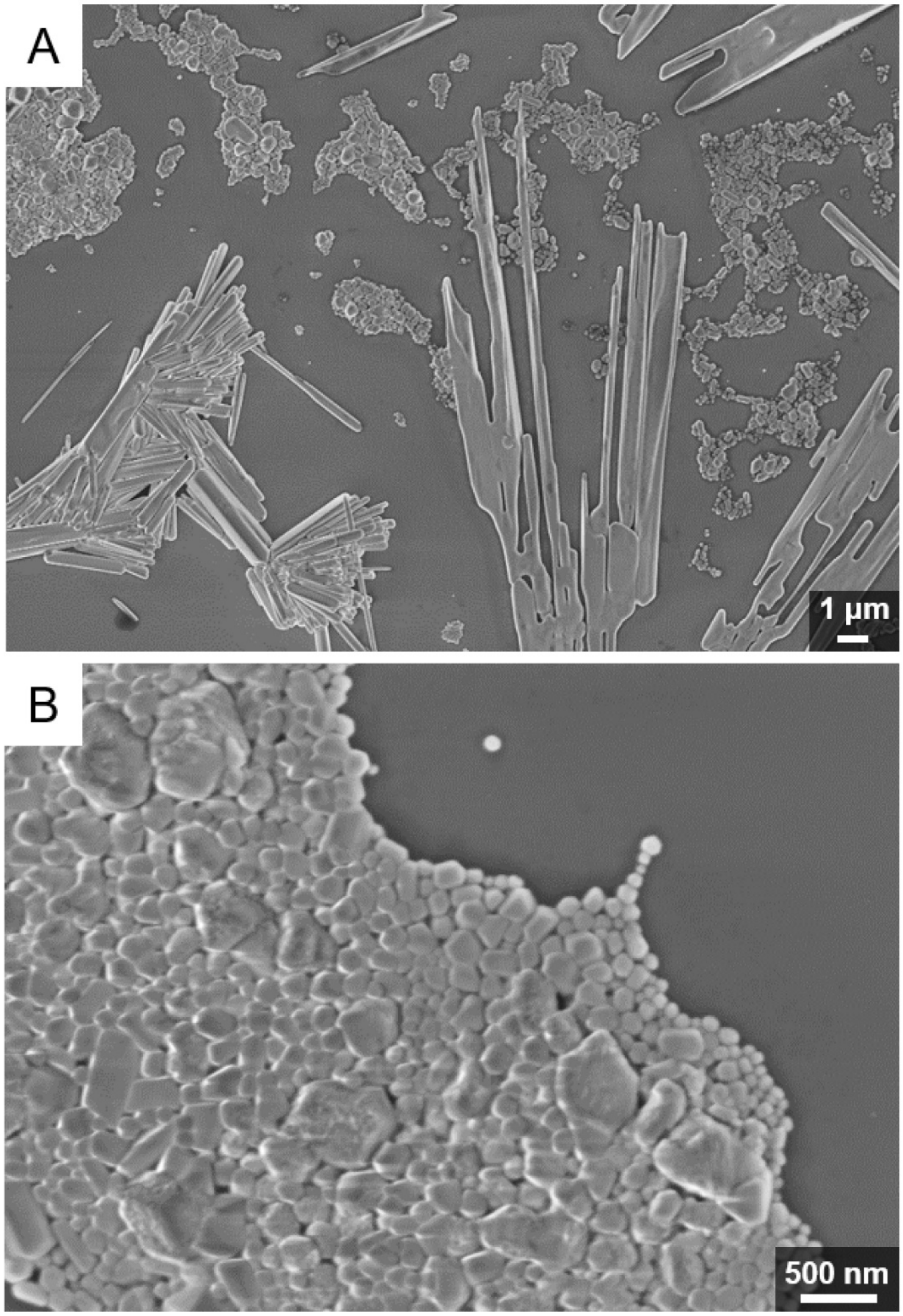

Figure S6. SEM images of $CsPbI_3$ nanocrystals synthesized with OAm and OA heated to 190^oC and cooled down to 25^oC in humid air. Heating results in the aggregation of the nanocrystals and the formation of nanorods and nanowires. The image in (A) shows a mixture of aggregated nanocrystals and nanorods. (B) shows a higher magnification image of a region with the aggregated and sintered nanocrystals, which are no longer cubic in shape.

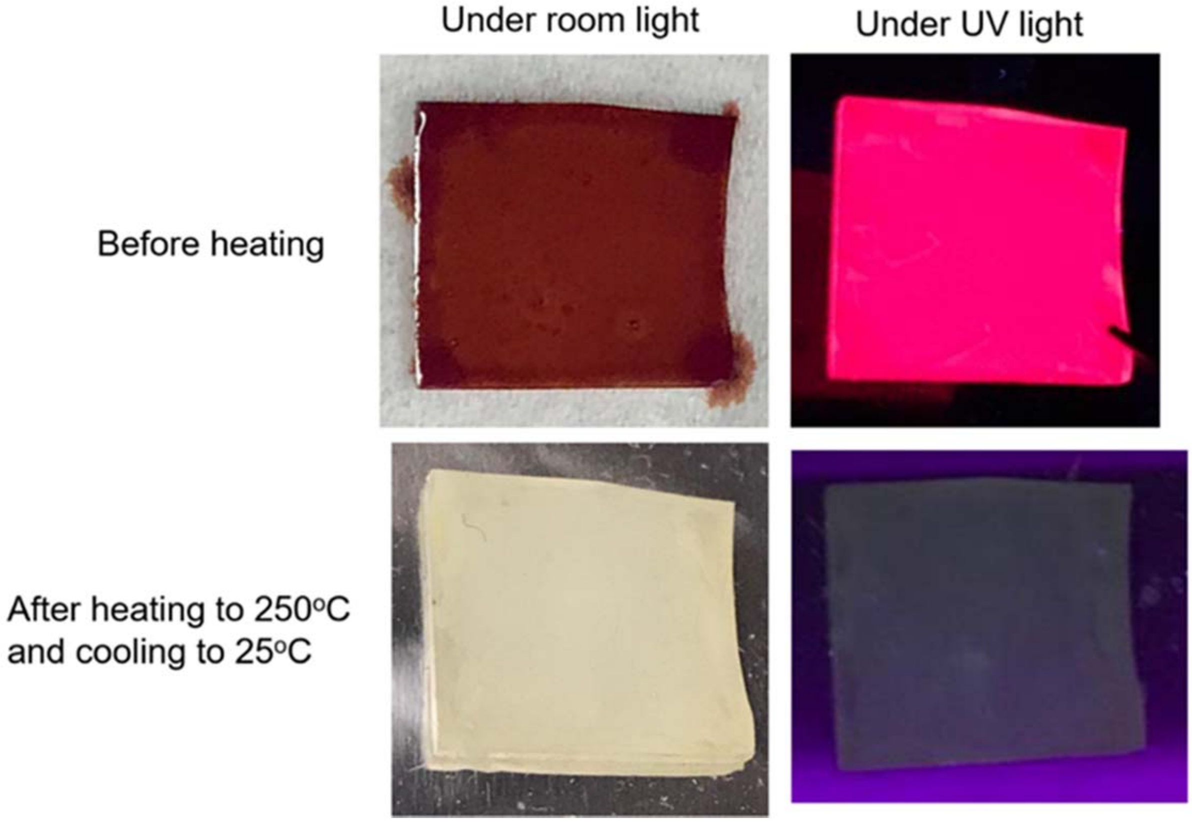

Figure S7. Photos of a film of $CsPbI_3$ nanocrystals made with OAm and OA on a glass substrate (1 cm × 1 cm) before and after heating in humid air (RH=42%) to 250°C. The images in the left column of the film are taken under room light. The images of the film in the right hand column are illuminated with UV light. Before heating, the film looks dark red because of the bright red fluorescence of the sample. After being heated to 250°C and cooled back to room temperature, the film has a pale yellow color and does not fluoresce.

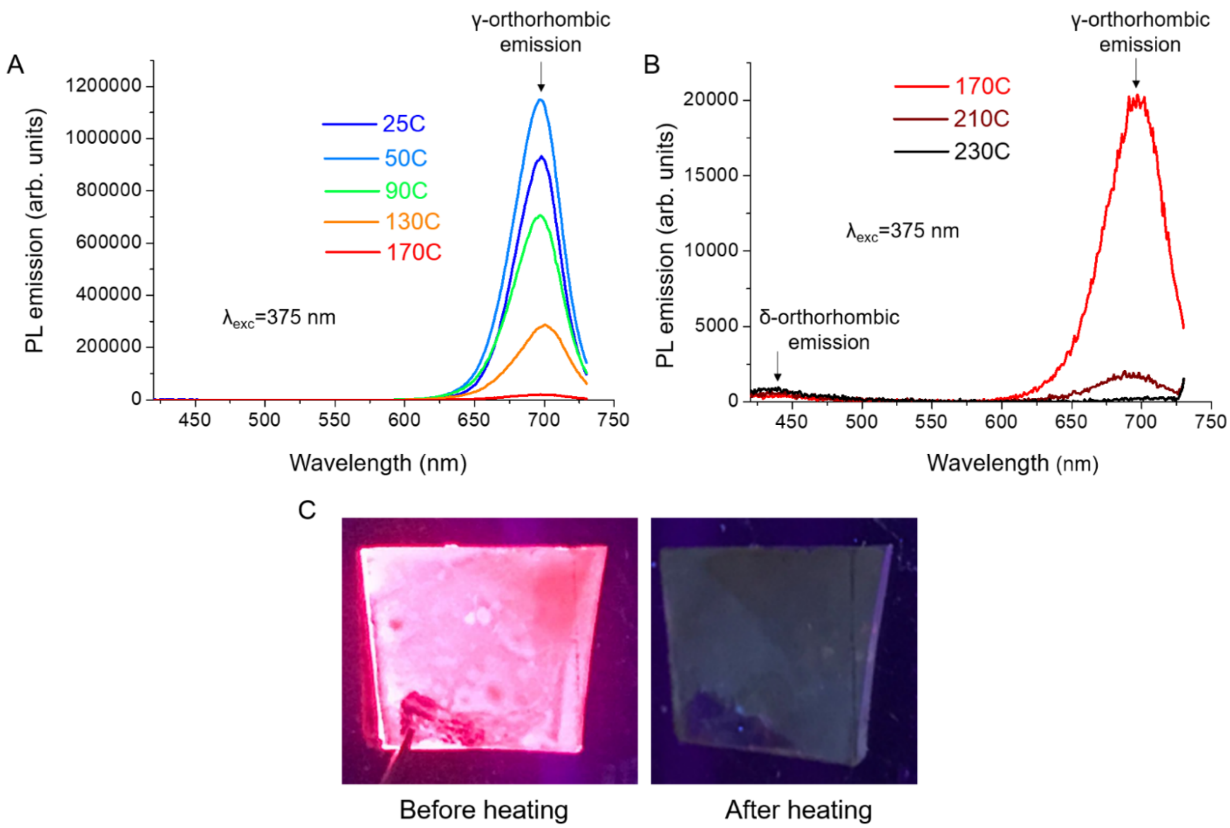

Figure S8. (A-B) *In situ* PL emission spectra (λ_{exc}=375 nm) of a film of $CsPbI_3$ nanocrystals synthesized with OAm and DIOP on a glass substrate (1cm×1cm) heated in humid air (RH=42%). The spectra were measured using the same slit size and data acquisition times and the intensity is plotted to scale. Initially, the film exhibits an emission peak at 698 nm. The PL peak intensity gradually decreases with increasing temperature. PL emission characteristic of δ-$CsPbI_3$ at ~440 nm becomes apparent when the temperature reaches 170°C. At 230°C, the primary source of light emission from the film is from δ-$CsPbI_3$. (C) Photos of a film of $CsPbI_3$ nanocrystals made with OAm and DIOP on glass before and after heating in humid air (RH=42%) under UV light illumination. Before heating, the film emits strongly in the pink-red color. After heating and cooling, the film is not emissive.

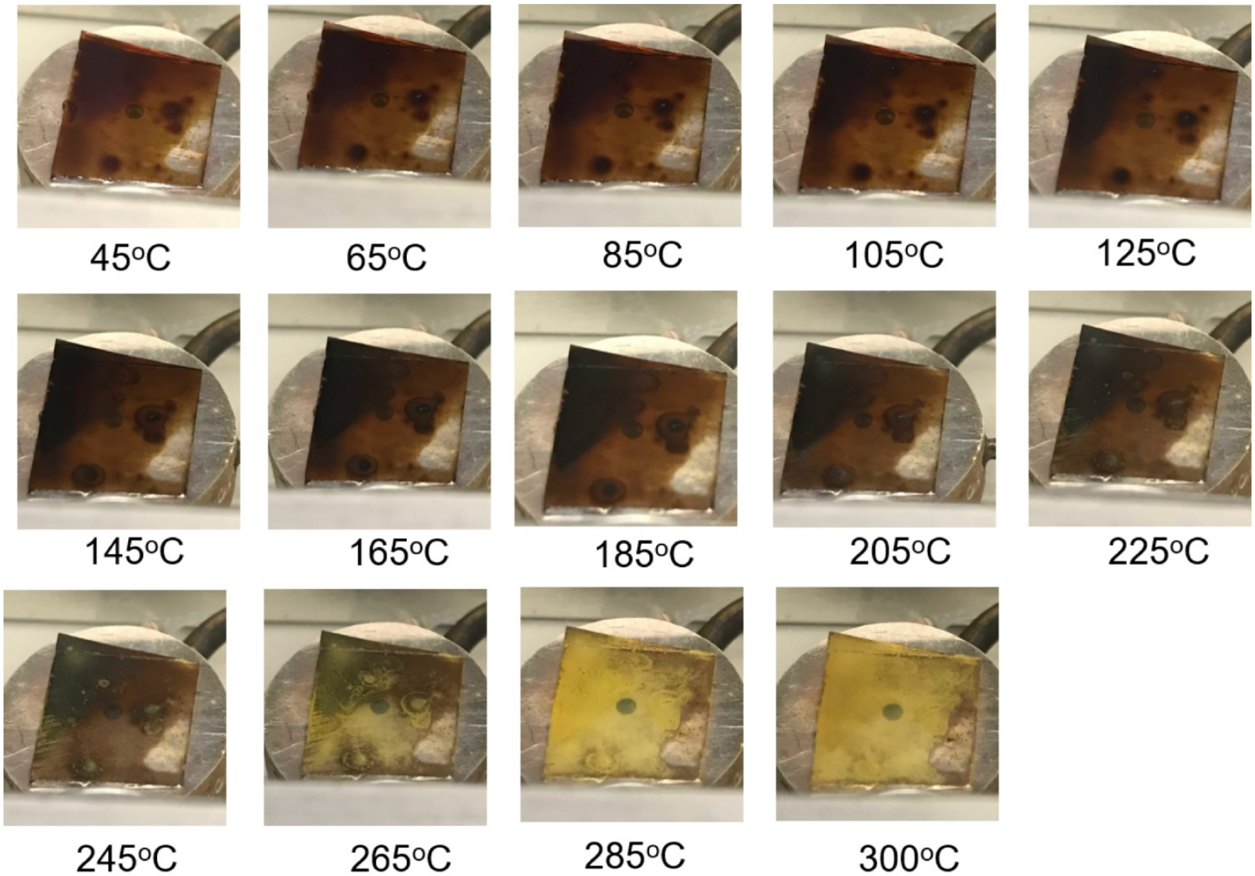

Figure S9. Photos of a film of $CsPbI_3$ nanocrystals made with OAm and DIOP being heated on a glass substrate (1 cm × 1 cm) in humid air (RH=42%). The temperature was increased at 20^{o}C min^{-1}. The yellow color of the film begins to appear at ~205^{o}C and has become completely yellow when the temperature reaches 300^{o}C.

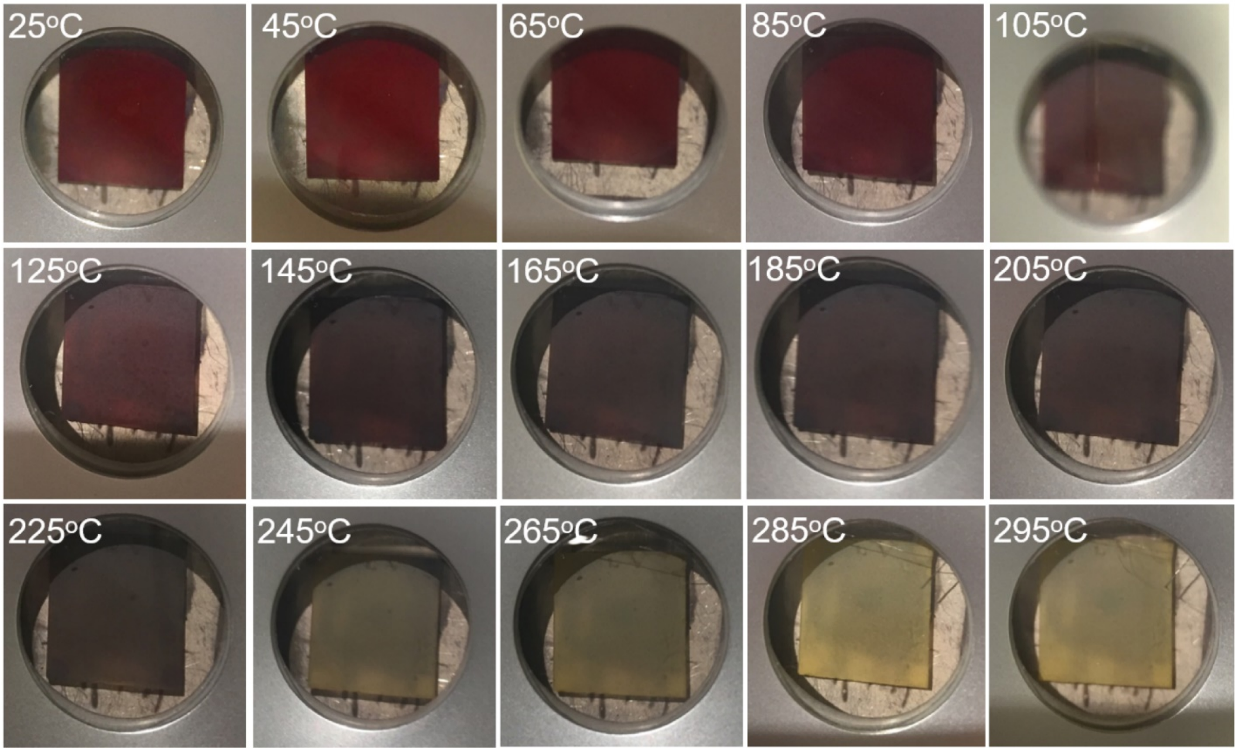

Figure S10. A film of $CsPbI_3$ nanocrystals made with OAm and OA being heated on a glass substrate (1 cm × 1 cm) in nitrogen. The heating experiment was performed using a Linkam LTS420 heating stage equipped with Linksys 32 software (Linkam Scientific). The temperature of the film was increased from 25°C to 300°C using a heating rate of 10 °C/min. The film begins to turn yellow at ~225°C, which is about 25°C higher than when a similar film was heated in humid air. The film has become completely yellow when the temperature reaches 300°C.

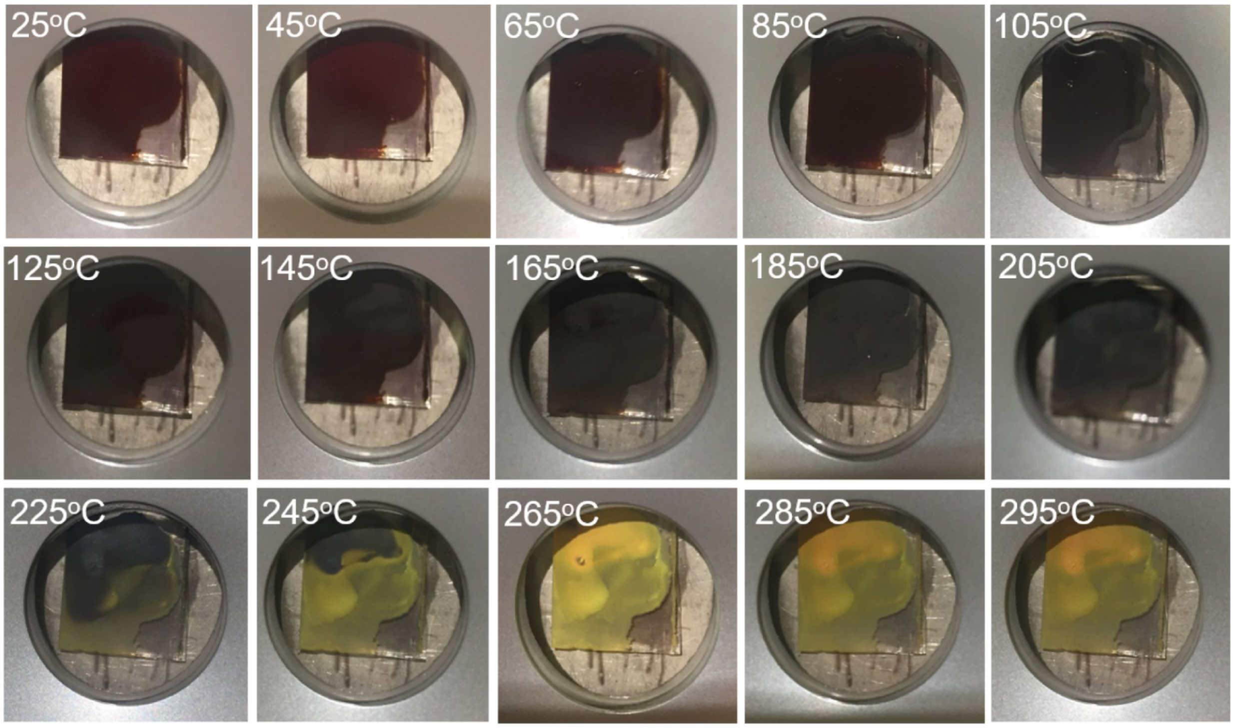

Figure S11. A film of $CsPbI_3$ nanocrystals made with OAm and DIOP being heated on a glass substrate (1 cm x 1 cm) in nitrogen using a Linkam heating stage. The temperature of the film was increased from 25°C to 300°C with a heating rate of 10 °C/min. The film begins to turn yellow at ~205^{o}C, which is the same temperature as when heated in humid air. It has become completely yellow when the temperature reaches 300^{o}C. (The brown color under the yellow films is a stain on the stage and not part of the sample).

References

1. Zhao, B.; Jin, S.-F.; Huang, S.; Liu, N.; Ma, J.-Y.; Xue, D.-J.; Han, Q.; Ding, J.; Ge, Q.-Q.; Feng, Y.; Hu, J.-S. Thermodynamically Stable Orthorhombic γ-$CsPbI_3$ Thin Films for High-Performance Photovoltaics. *J. Am. Chem. Soc.* **2018**, *140*, 11716-11725.