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Supplementary Information for

Devising Novel Methods for the Controlled Synthesis with Morphology and Size Control of Scintillator Materials

Nathaniel Hurley,[1] Federico Moretti,[2] Hanfei Yan,[3] Edith Bourret-Courchesne,[2]

Yong S. Chu,[3] and Stanislaus S. Wong[1,*]

Email: stanislaus.wong@stonybrook.edu; sswong@bnl.gov

[1]Department of Chemistry, State University of New York at Stony Brook,
Stony Brook, NY 11794-3400

[2]Materials Sciences Division, Lawrence Berkeley National Laboratory,
Berkeley, California 94720

[3]National Synchrotron Light Source II, Building 743, Brookhaven National Laboratory,
Upton, NY 11973

*To whom correspondence should be addressed.

Justification for Study

To highlight the necessity of our study, it is worth pointing out that previously reported synthesis methods used to make these scintillator materials are relatively limited in scope. These include (i) a vertical Bridgman-Stockbarger technique, (ii) slow evaporation, and (iii) the Czochralski method.[1] The Bridgman-Stockbarger protocol is a high temperature procedure, involving heating of precursors within a vacuum-sealed quartz ampoule for an extended period of time in an oven with designated 'temperature controlled' zones.[2] This method works well for generating either 'millimeter-scale' or larger single crystals from 'high purity' powder precursors. However, this is a relatively energy-intensive method that not only necessitates both specialized equipment and high temperatures (i.e., 300°C or higher) but also takes 24 hours or more to complete, based upon the sample size and the rate at which the ampoule is lowered. It is noteworthy that the precursors used must be of a very high purity, considering that there is no way to properly wash out impurities, even after the desired crystals have been formed.[3]

Another reported synthesis method is associated with 'slow evaporation'. This technique involves dissolution of the precursor salts in either water or other solvents, and growing of the crystals by slowly evaporating off the solvent.[4, 5] This technique requires no special equipment, but it can take either days or weeks to grow the crystals. Moreover, a time-consuming purification of crystal precursors must also be performed, since even minor impurities can either inhibit the growth of or contaminate the final crystal formed.[6]

The final commonly used procedure involves a Czochralski methodology. This procedure starts off with a single crystal seed placed within a melt of the crystal, and, using mechanical means, it is pulled slowly upward. As the crystals are 'raised', a single crystal is formed. This protocol requires very high temperatures, typically over 1000°C, and takes a relatively long time to occur, since crystals must be grown very slowly or they will not form properly.[1]

References

1. M. J. Weber, *Journal of Luminescence*, 2002, **100**, 35-45.
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3. A. G. Ostrogorsky, V. Riabov and N. Dropka, *Journal of Crystal Growth*, 2018, **498**, 269-276.
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5. A. R. Lim, *Journal of Applied Physics*, 2010, **107**, 1-6.
6. M. Senthil Pandian, K. Boopathi, P. Ramasamy, and G. Bhagavannarayana, *Materials Research Bulletin*, 2012, **47**, 826-835.
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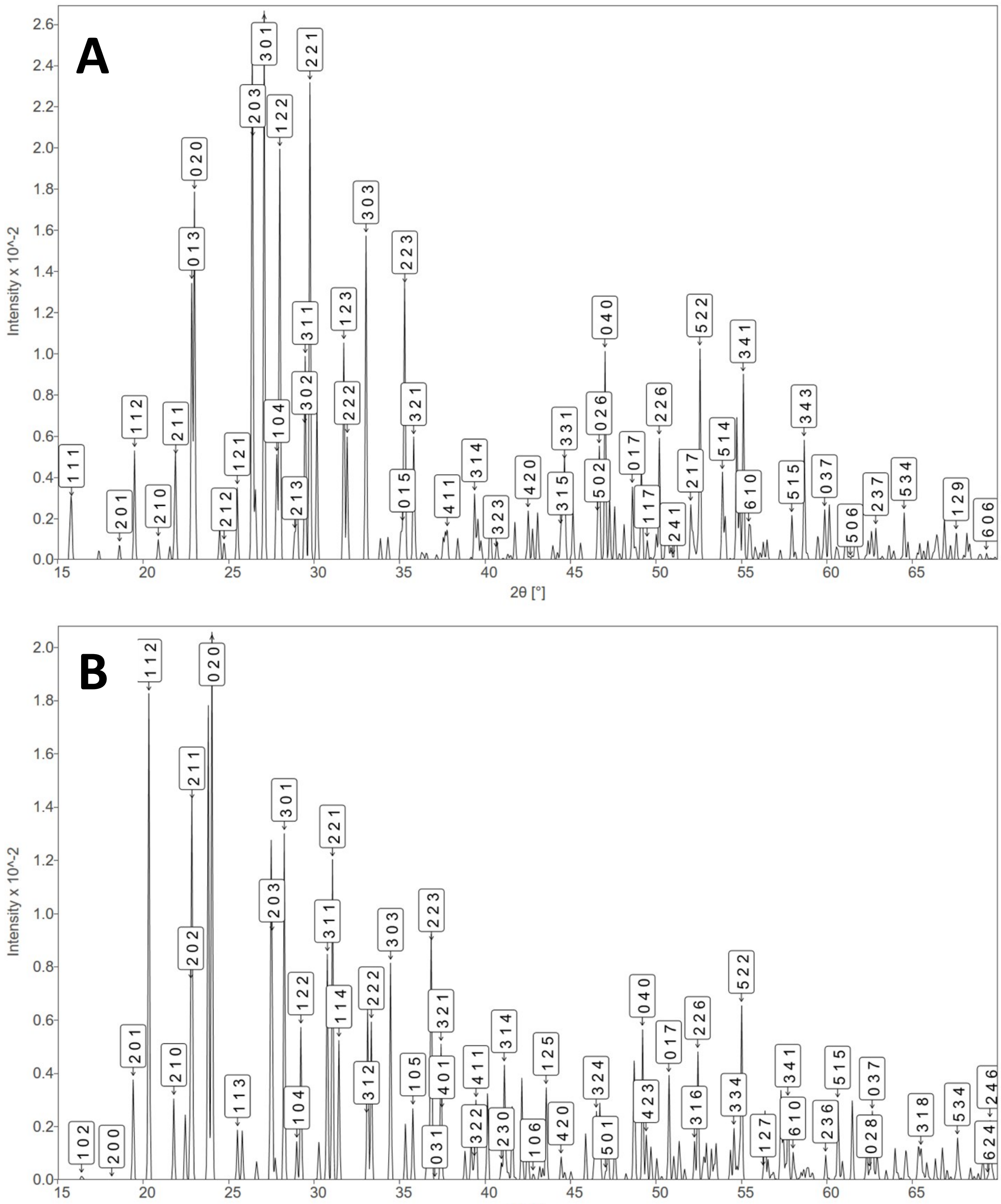


Figure S1. Indexed peaks (*hkl*) of (A) Cs_2ZnBr_4 and (B) Cs_2ZnCl_4.

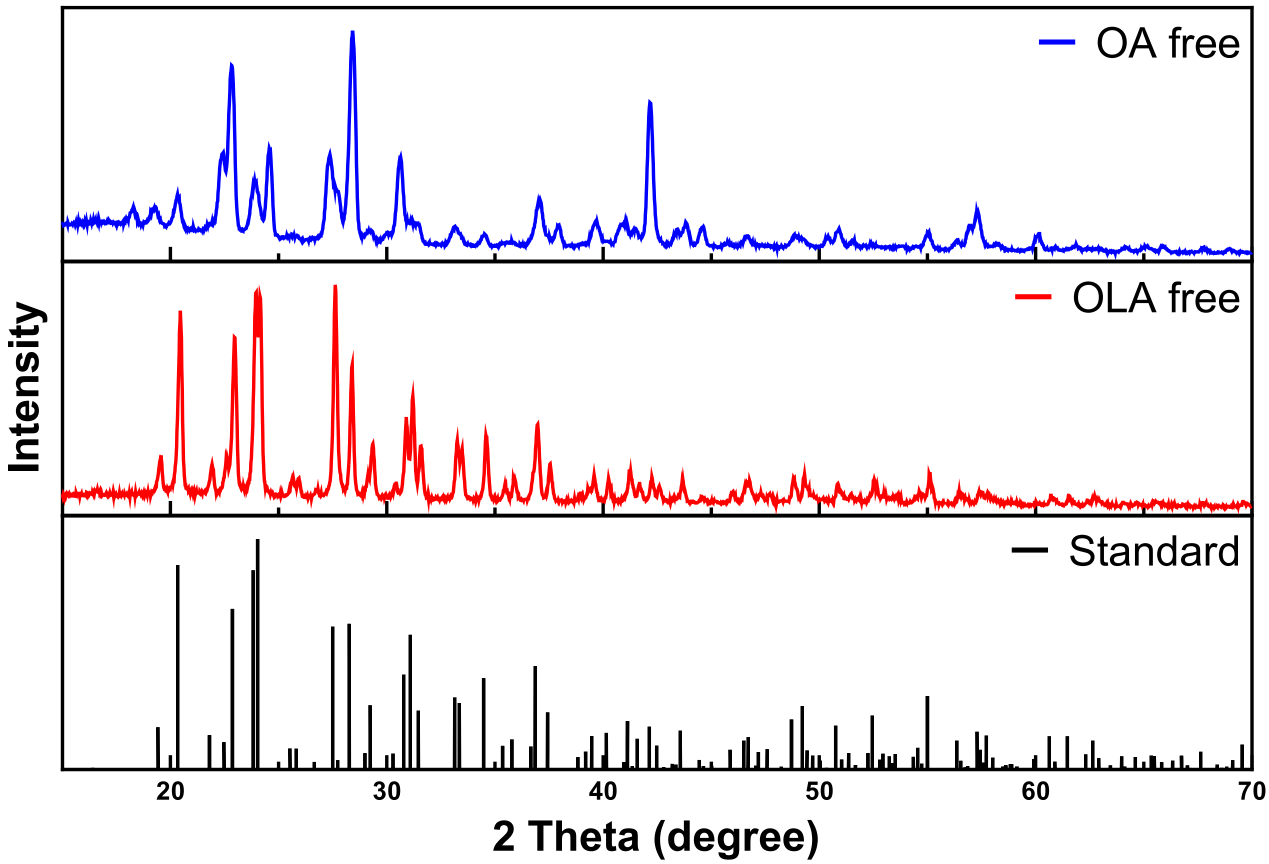


Figure S2. Hot Injection Method. *Effect of surfactant.* XRD patterns of OA-free (blue) and OLA-free (red) samples, shown along with the standard diffraction pattern of Cs_2ZnCl_4 (black).[7]

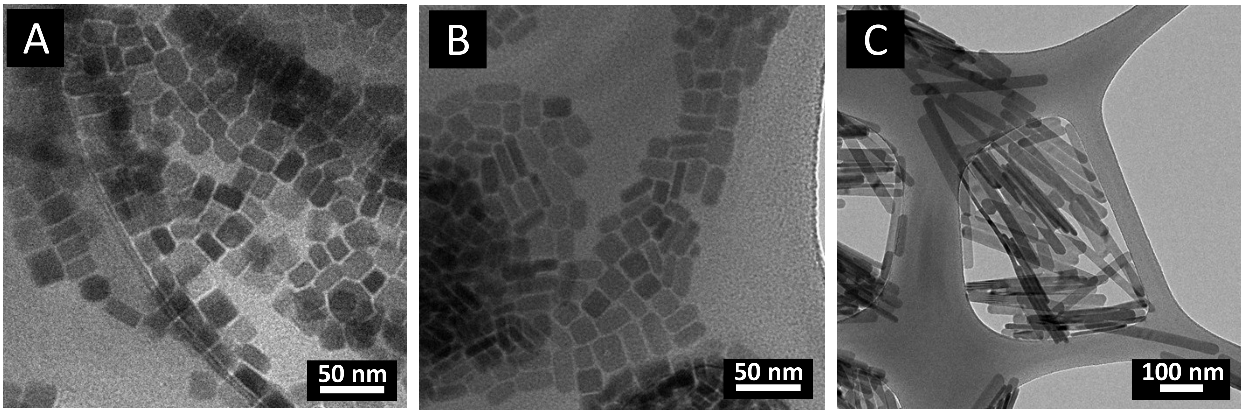


Figure S3. Effect of Varying Surfactant Quantities. Reducing oleylamine levels to (A) 150 μL and (B) 350 μL. Increasing the amount of oleylamine to (C) 6 mL.

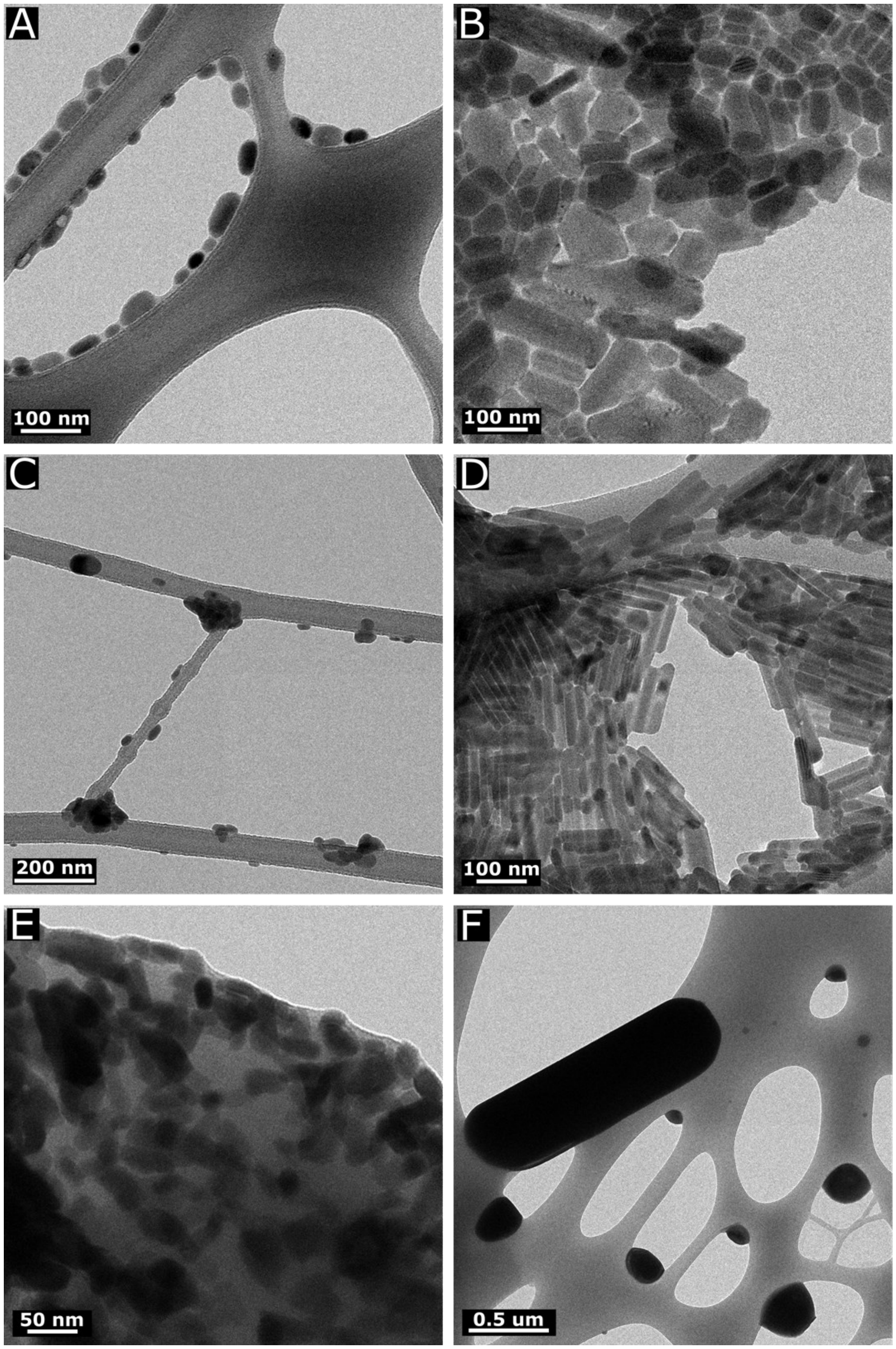


Figure S4. Effect of reaction time on Cs_2ZnCl_4. Samples, heated to 100°C, were prepared at the (A) 5 second and (B) 60 minute mark, respectively. Analogous samples, heated to 150°C, were generated at the (C) 5 second and (D) 60 minute interval, while the ones, heated to 200°C, were produced after (E) 5 seconds and (F) 60 minutes, respectively.

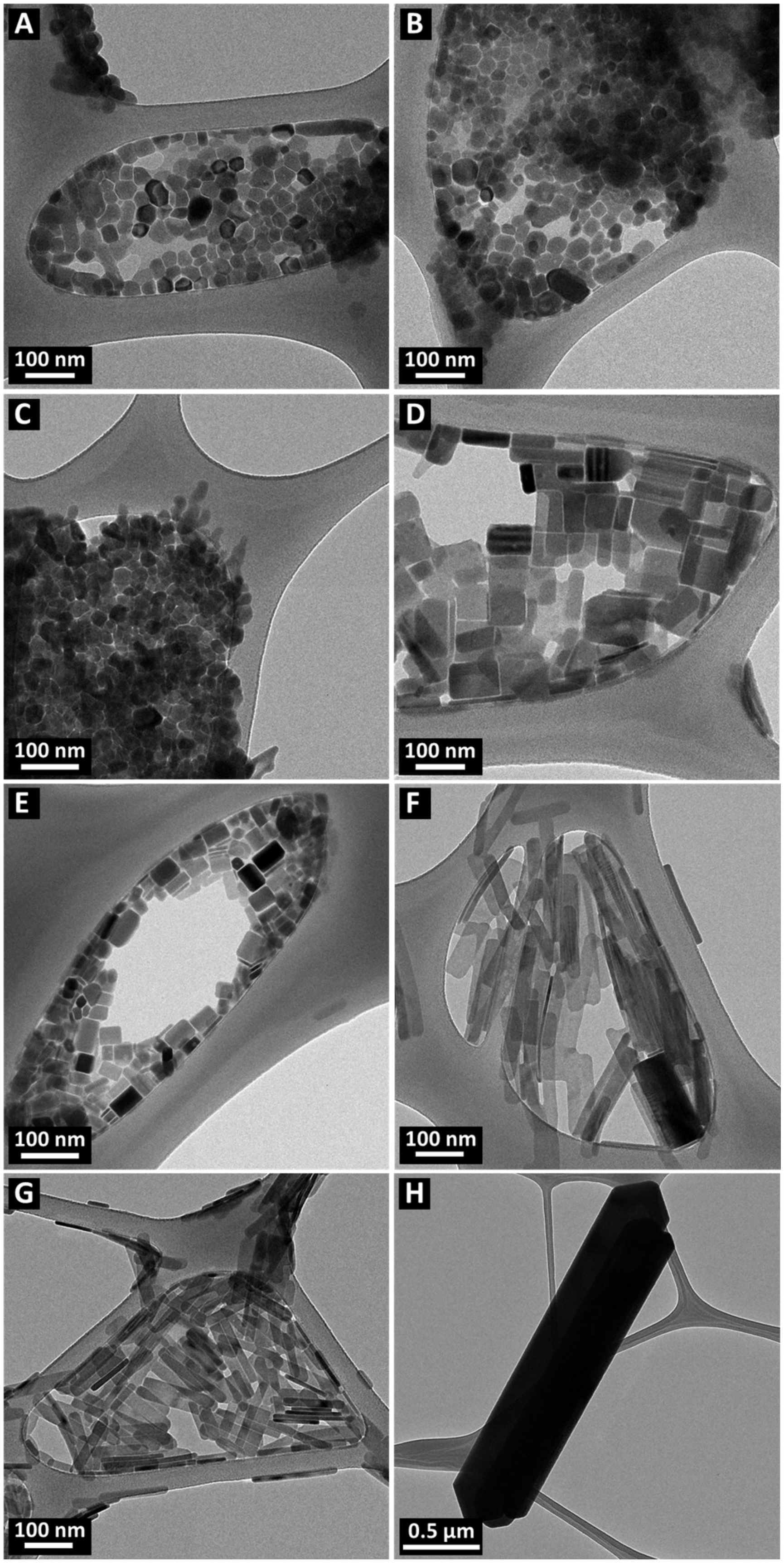

A
100 nm
B
100 nm
C
100 nm
D
100 nm
E
100 nm
F
100 nm
G
100 nm
H
0.5 µm

Figure S5. Effect of reaction time on Cs_2ZnBr_4. Samples, heated to 100°C, were prepared at the (A) 5 second and (B) 60 minute mark, respectively. Analogous samples, heated to 150°C, were generated at the (C) 5 second and (D) 60 minute interval, while the ones, heated to 200°C, were produced after (E) 5 seconds and (F) 60 minutes, respectively. Finally, samples heated to 200°C are presented after (G) 5 seconds and (H) 60 minutes, respectively

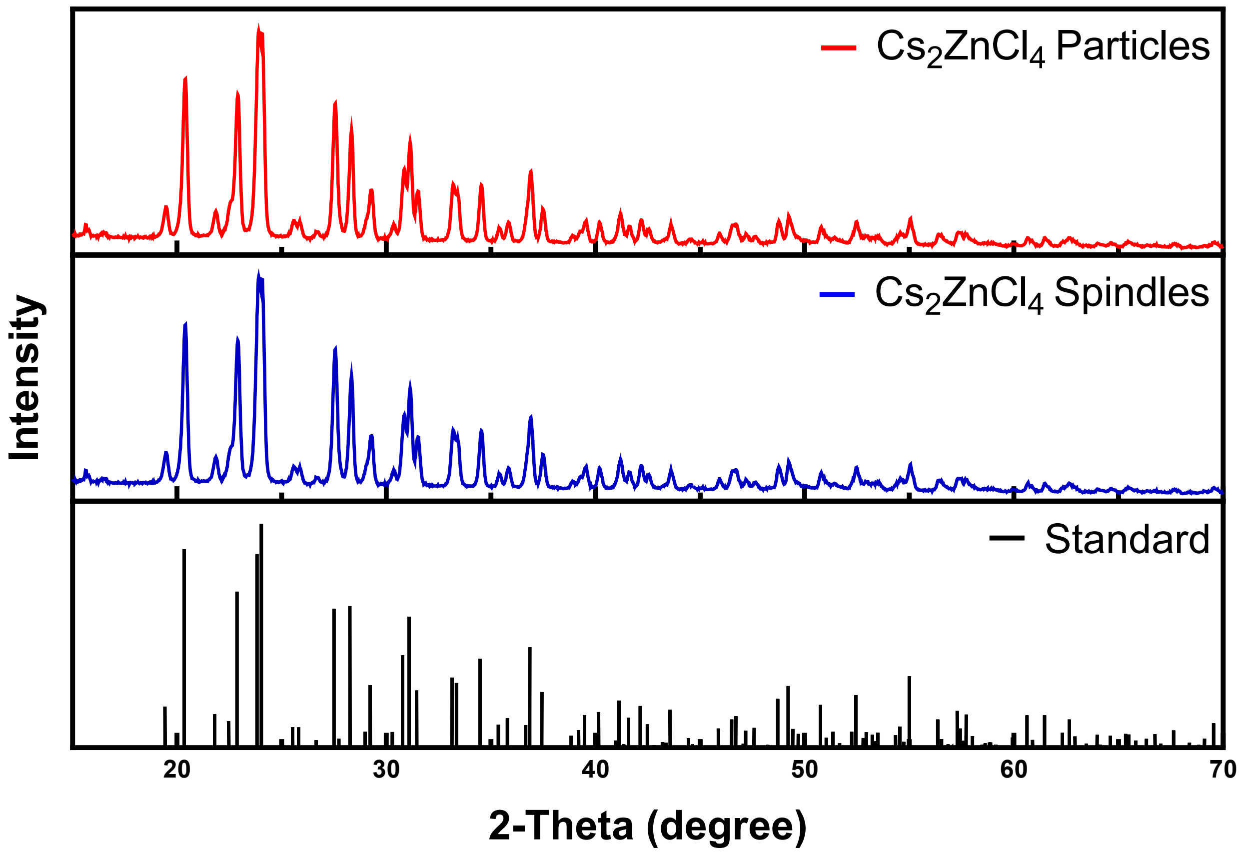


Figure S6. LARP method. XRD patterns of Cs_2ZnCl_4 corresponding to spindles (blue) and particles (red), along with the published database standard (black).[7]

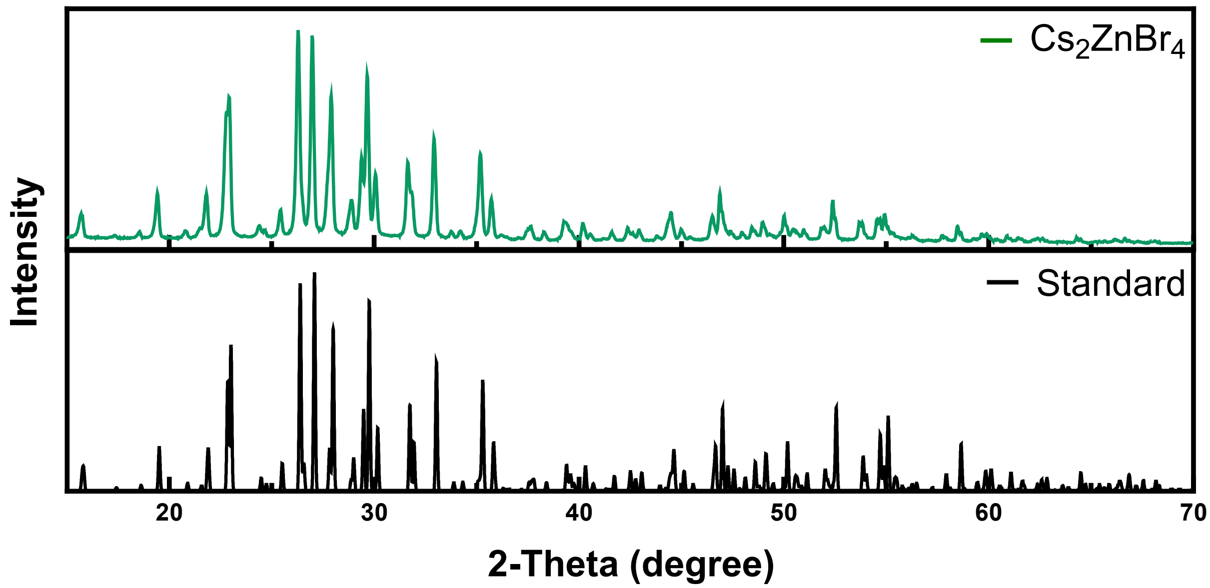


Figure S7. LARP Method. XRD patterns of Cs_2ZnBr_4 plates (green) and the published database standard (black).[8]

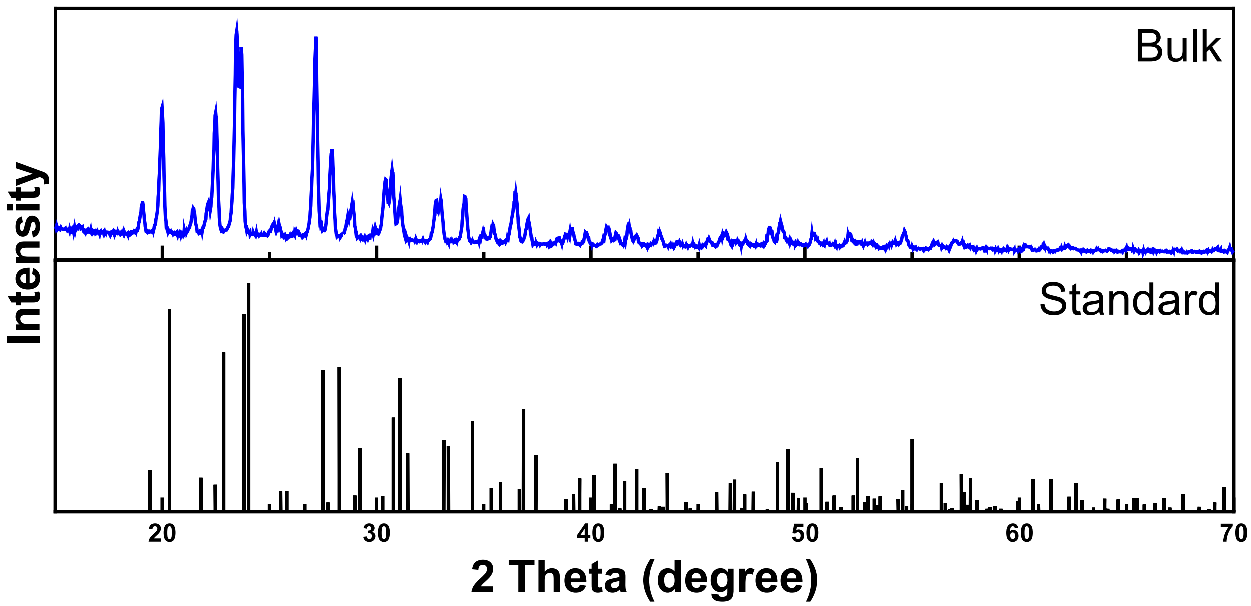


Figure S8. XRD pattern of bulk Cs_2ZnCl_4 that had been created by slow evaporation.

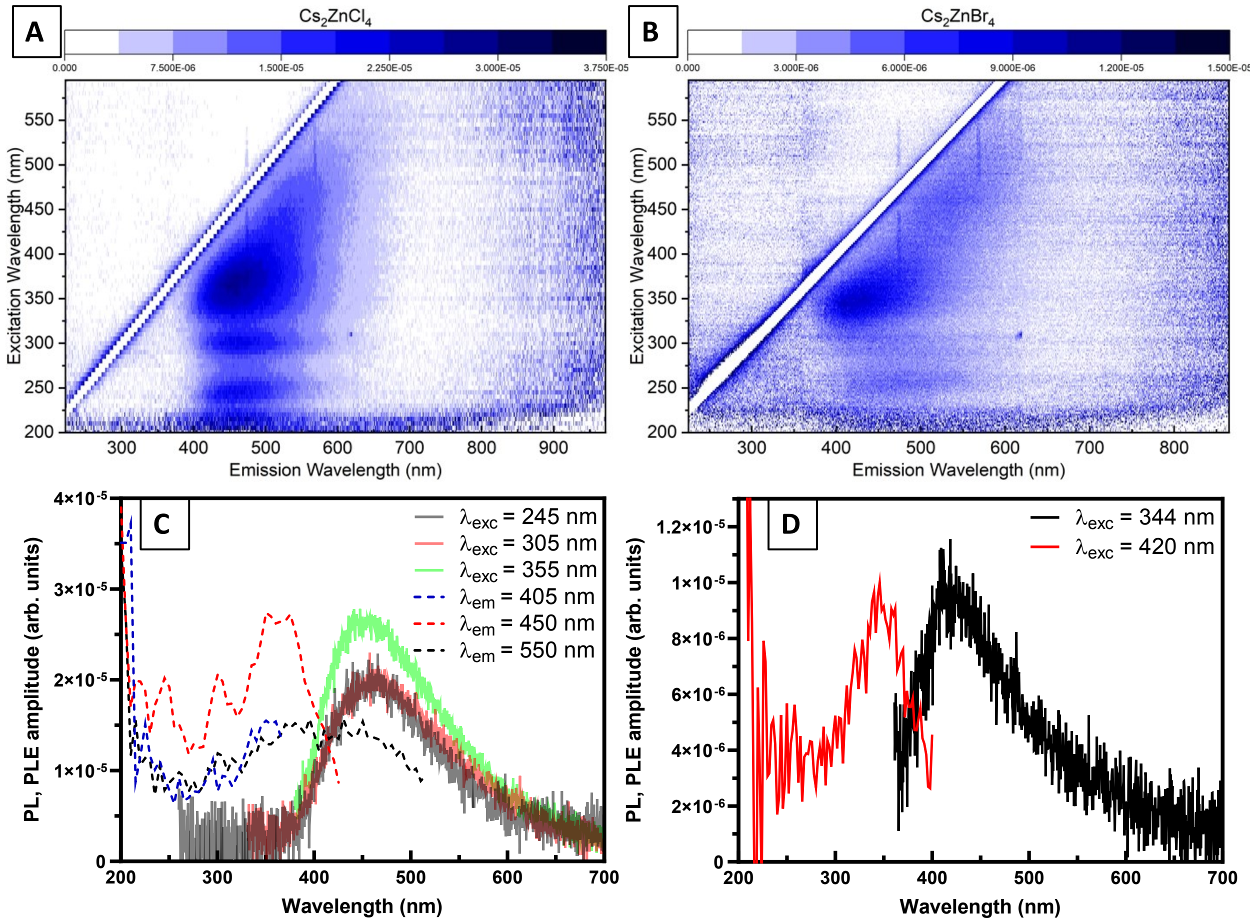


Figure S9. 2D photoluminescence maps and selected excitation and emission spectra of (A and C, respectively) Cs_2ZnCl_4 and of (B and D) Cs_2ZnBr_4.

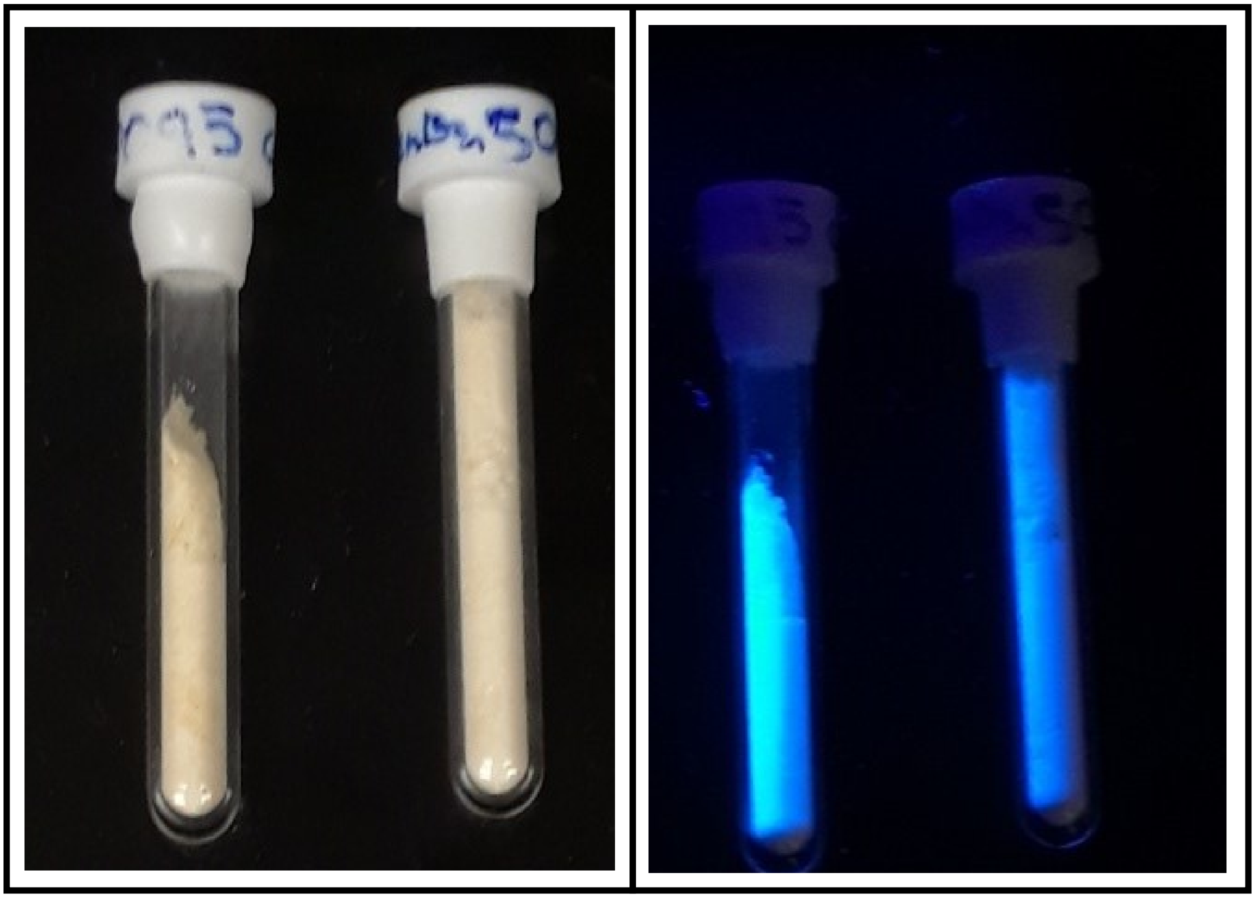


Figure S10. Images of Cs_2ZnCl_4 (left vial) and Cs_2ZnBr_4 (right vial) in neon light (right-hand set of images) and under 254 nm Hg light excitation (left-hand set of images).

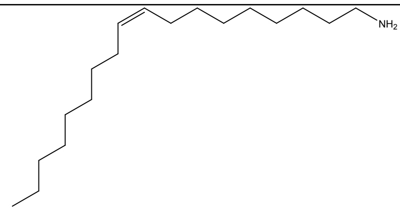
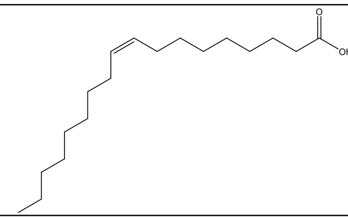
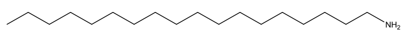
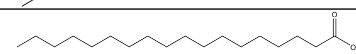
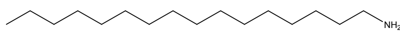
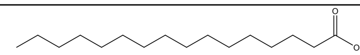
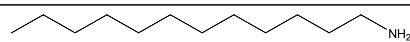
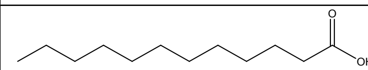
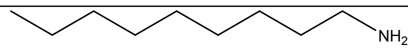
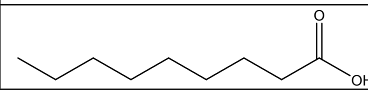
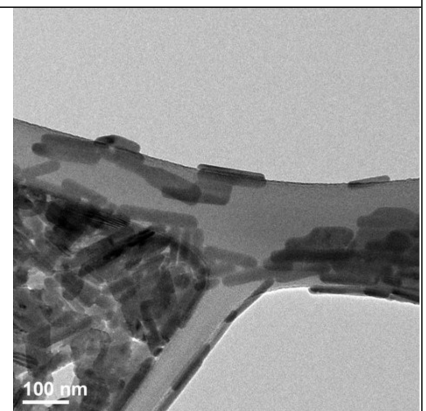
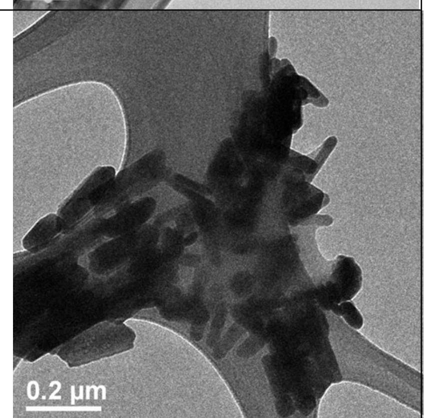
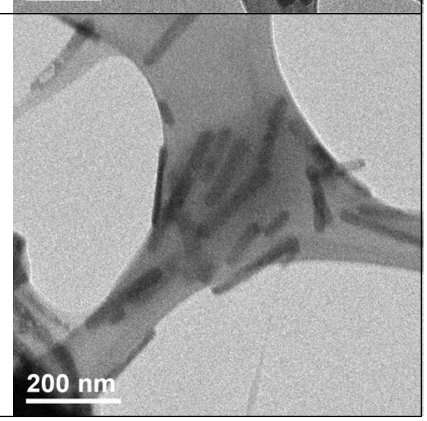
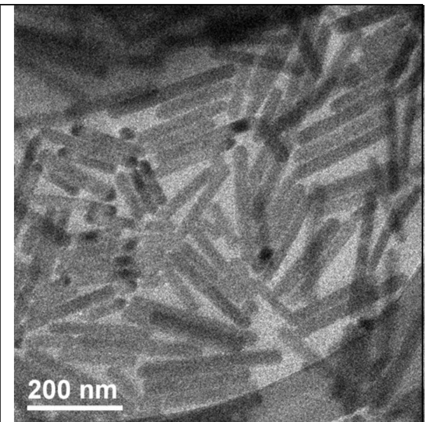
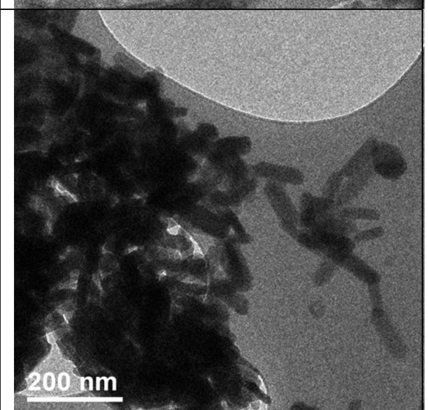
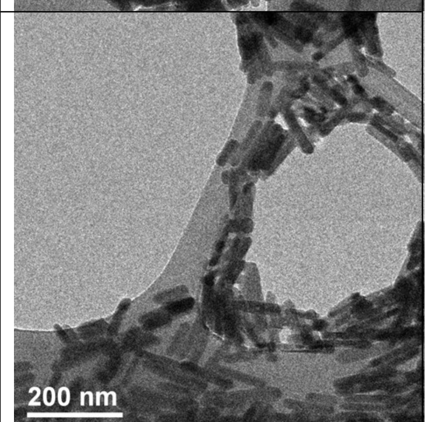
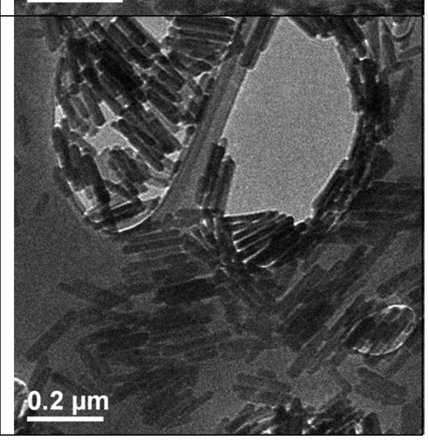
‘Basic’ Surfactant	Structure	‘Acidic’ Surfactant	Structure
Oleylamine (OLA)		Oleic Acid (OA)	
Octadecylamine (ODA)		Stearic acid (SA)	
Hexadecylamine (HDA)		Palmitic acid (PA)	
Dodecylamine (DDA)		Lauric acid (LA)	
Nonylamine (NLA)		Nonanoic acid (NA)	

Table S1. Surfactants, abbreviations, and associated chemical structures (made in Chemdraw).

Material	Acid Surfactant	Base Surfactant	Results	Image
Cs_2ZnCl_4	Oleic Acid (18 carbons)	Oleylamine (18 carbons)	Nanorods Length: 124.6 nm ± 26.8 nm (21% error); Width: 25.1 nm ± 3.5 nm (14% error). Taken from above table for comparison	
Cs_2ZnCl_4	Lauric acid (12 carbons)	Oleylamine (18 carbons)	A mixture of rods and particles	
Cs_2ZnCl_4	Palmitic acid (14 carbons)	Oleylamine (18 carbons)	Length: 94.3 ± 50.1 nm (53% error) Width: 26.6 ± 4.7 nm (18% error)	

Cs_2ZnCl_4	Stearic acid (18 carbons)	Oleylamine (18 carbons)	Length: 175.9 ± 54.7 nm (31% error) Width: 25.7 ± 4.0 nm (16% error)	
Cs_2ZnCl_4	Oleic acid (18 carbons)	Dodecylamine (12 carbons)	Mixture of rods and particles	
Cs_2ZnCl_4	Oleic acid (18 carbons)	Hexadecylamine (16 carbons)	<u>Nanorods</u> Lengths: 86.9 ± 19.2 nm (error: 22%) Width: 21.5 ± 3.7 nm (error: 17%)	
Cs_2ZnCl_4	Oleic acid (18 carbons)	Octadecylamine (18 carbons)	<u>Nanorods</u> Length: 149.6 ± 17.3 nm (error: 12%) Width: 19.0 ± 4.6 nm (error: 24%)	

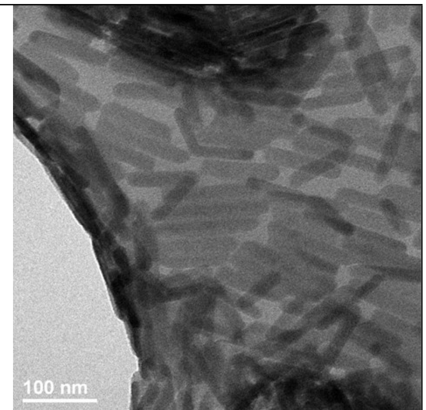
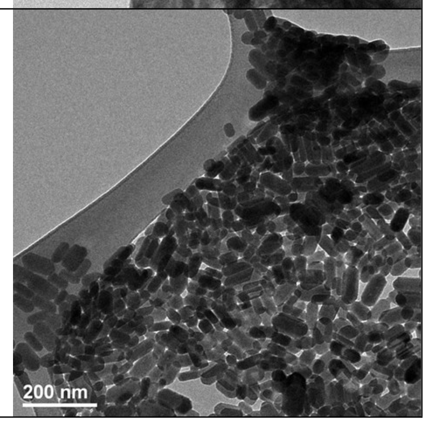
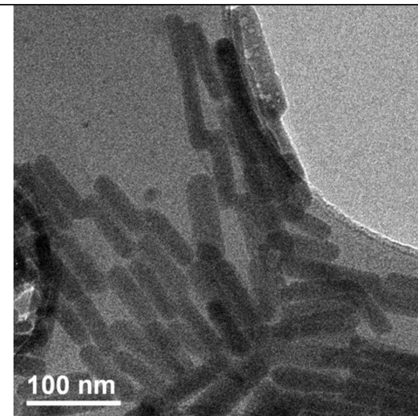
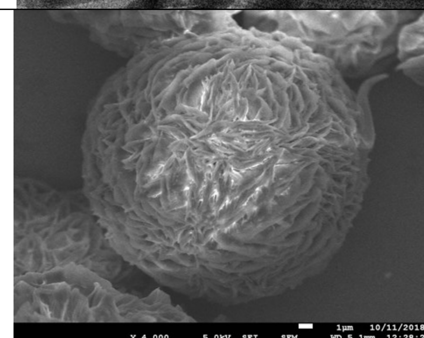
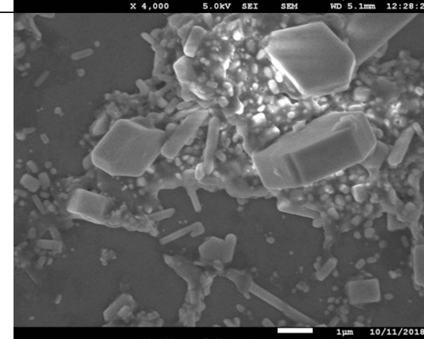
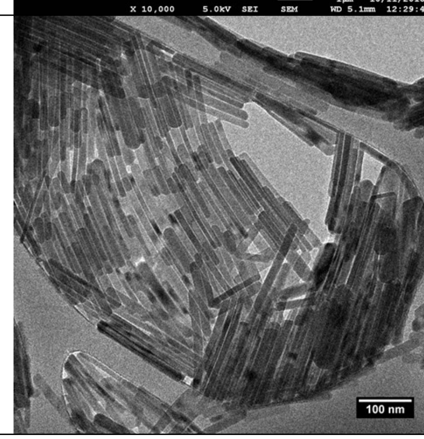
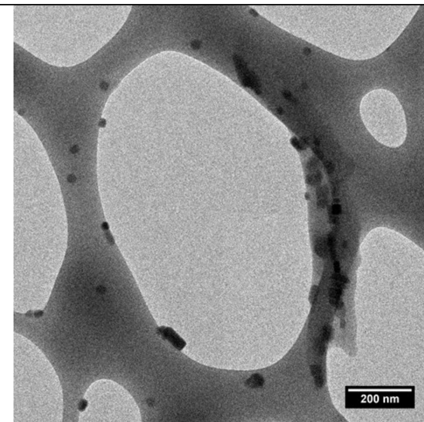
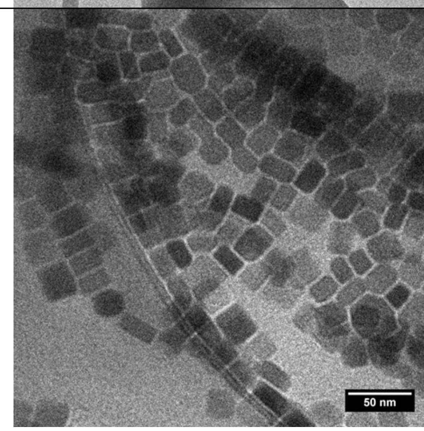
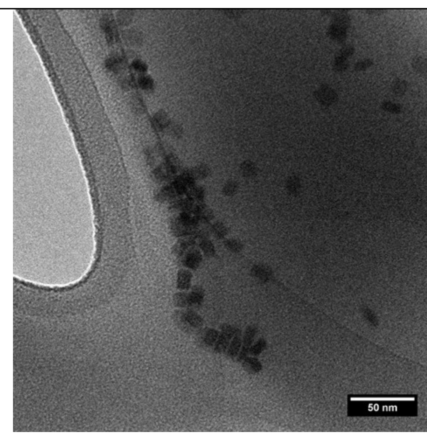
Cs_2ZnCl_4 (changed solvent)	Oleic acid (18 carbons)	Oleylamine (18 carbons)	Nanorods Length: 95.8 ± 25.3 nm (26% error); Width: 18.1 ± 2.5 nm (13% error) Used tetradecane as solvent.	
Cs_2ZnCl_4 (changed solvent)	Oleic acid (18 carbons)	Nonylamine (9 carbons)	Short nanorods Length: 78.3 ± 15.4 nm (20% error) Width: 34.4 ± 8.3 nm (24% error) Used tetradecane as solvent.	

Table S2. Cs_2ZnCl_4. Effect of **changing the identity of acid and amine surfactants by reducing nonpolar tail length** from the 18-carbon oleic acid and oleylamine. Reaction time was kept at 20 minutes, and the corresponding reaction temperature was held at 150°C. These conditions were chosen, as they yielded the most reproducible morphology from previous trials.

Material	Acid Surfactant	Base Surfactant	Results	Image
Cs_2ZnCl_4	Oleic acid: 0.4 ml	Oleylamine: 0.4 ml Reduced surfactant amount by 5x.	Length: 89.6 ± 19.5 nm (21% error) Width: 21.4 ± 3.0 nm (14% error)	
Cs_2ZnCl_4	Oleic acid: 4.0 ml	Oleylamine: 0.0 ml	Micron sized textured spheres Diameter: 21.2 ± 4.9 µm	
Cs_2ZnCl_4	Oleic acid: 0.0 ml	Oleylamine: 4.0 ml	No morphology control	
Cs_2ZnCl_4 3x scale up	Oleic acid: 6.0 ml	Oleylamine: 6.0 ml	<u>Rods</u> Length: 183.70 nm ± 26.38 (14% error) Width: 13.16 nm ± 4.41 nm (33% error)	

Cs_2ZnCl_4	Oleic acid: 2.0 ml	Oleylamine: 30 µL	Irregularly-shaped particles	
Cs_2ZnCl_4	Oleic acid: 2.0 ml	Oleylamine: 150 µL	<u>Cubes</u> Size: 24.45 nm ± 4.11 nm (17% error)	
Cs_2ZnCl_4	Oleic acid: 2.0 ml	Oleylamine: 250 µL	Irregular particles	

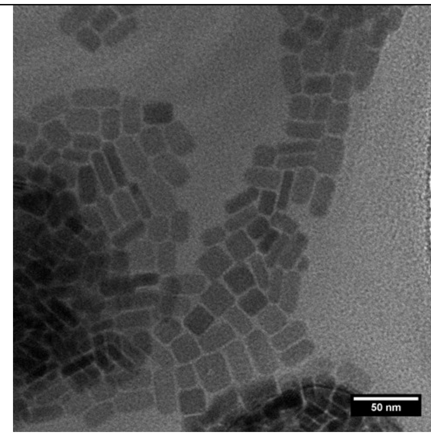
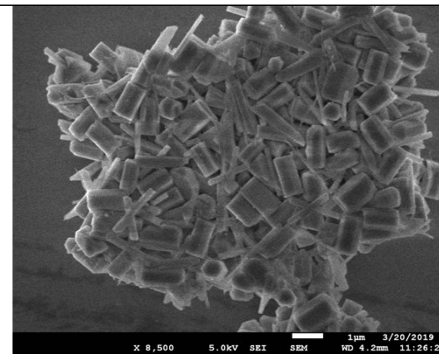
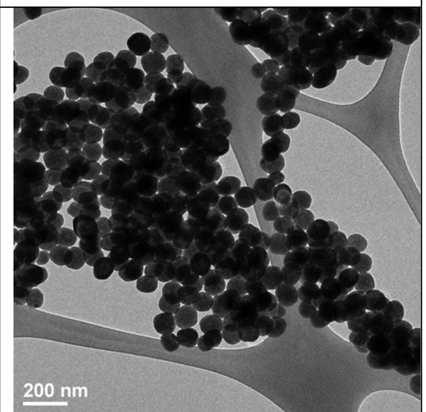
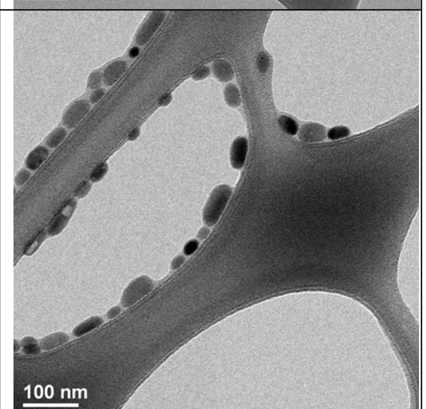
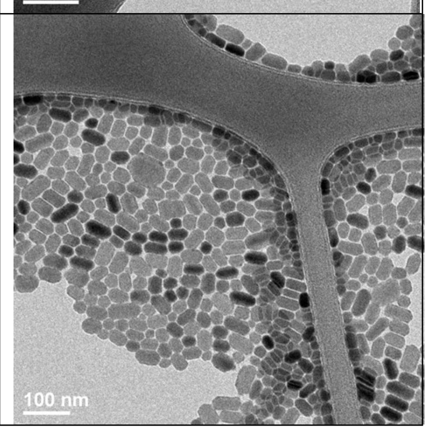
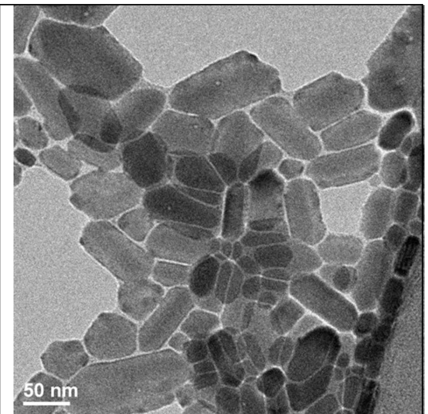
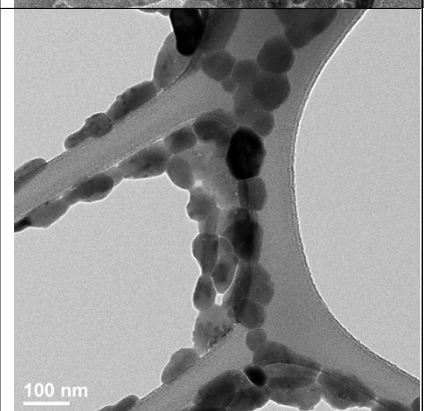
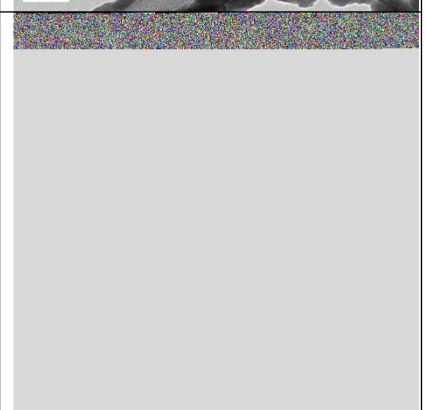
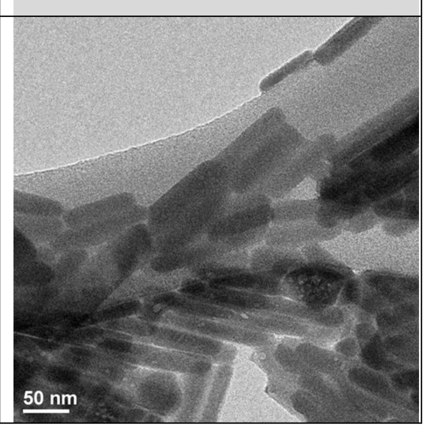
Cs_2ZnCl_4	Oleic acid: 2.0 ml	Oleylamine: 350 µL	Mixture of cubes and rods Size: 27.40 ± 6.18 nm (23% error)	
Cs_2ZnCl_4	Oleic acid: 12.0 ml	Oleylamine: 12.0 ml	Micron-sized rods, cubes, and particles No morphology control No octadecene used as solvent	

Table S3. Cs_2ZnCl_4. All trials are highlighted, wherein **the amounts of oleic acid and oleylamine ratios were changed**. Reaction time and temperature were kept at 20 minutes and 150°C. The total volume was kept constant by either adding in or removing octadecene.

Material	Reaction Temperature	Reaction Time	Results	Image
Cs_2ZnCl_4	50°C	20 minutes	Nanospheres Size: 93.3 ± 9.9 nm (10% error) Best morphology of the 50°C trials	
Cs_2ZnCl_4	100°C	5 seconds	Irregularly-shaped particles Size: 38.9 ± 14.3 nm (37% error)	
Cs_2ZnCl_4	100°C	20 minutes	More regularly-shaped particles Size: 36.3 ± 10.9 nm (29% error) Best morphology of the 100°C trials	

Cs_2ZnCl_4	100°C	60 minutes	Particles become less uniform at longer reaction times. Size: 54.9 ± 27.2 nm (50% error)	
Cs_2ZnCl_4	150°C	5 seconds	Irregularly-shaped particles and significant particle aggregation	
Cs_2ZnCl_4	150°C	20 minutes	<u>Nanorods</u> Length: 124.6 nm ± 26.8 nm (21% error); Width: 25.1 nm ± 3.5 nm (14% error). Best morphology of the 150°C trials	
Cs_2ZnCl_4	150°C	60 minutes	Little change from the 20 minute sample. Some more aggregation and particle formation	

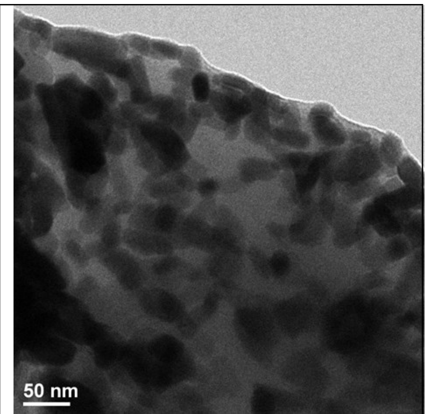
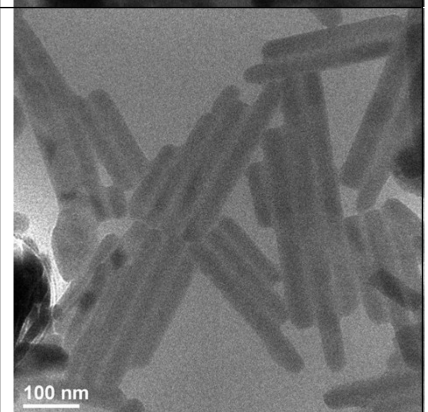
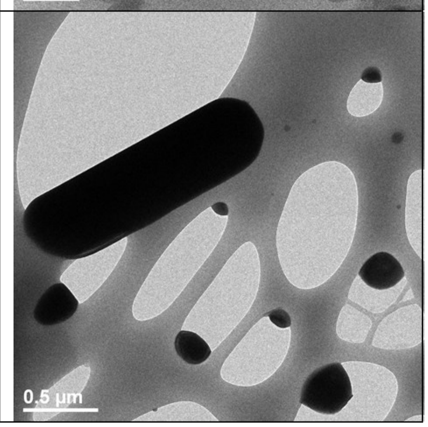
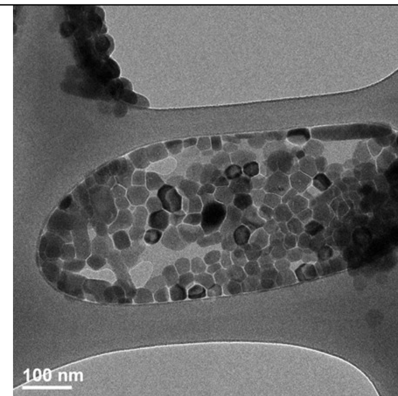
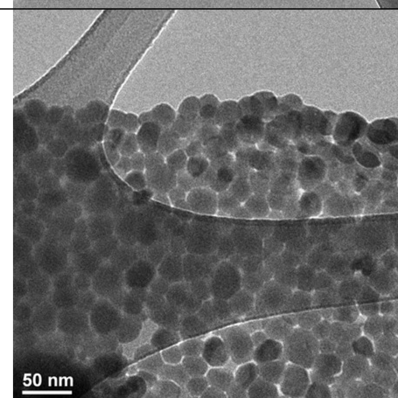
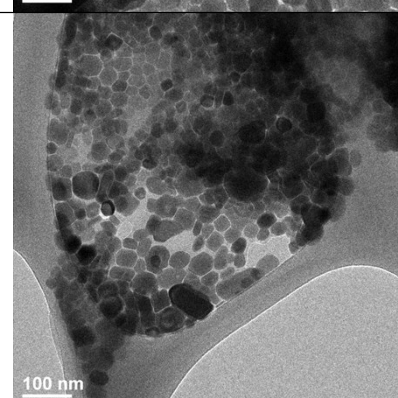
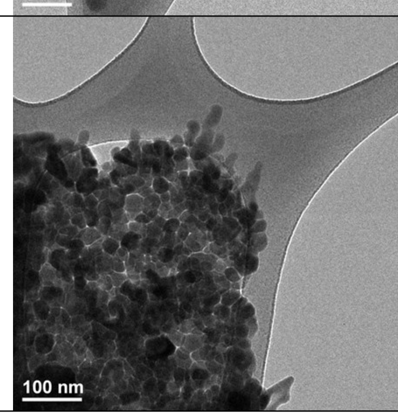
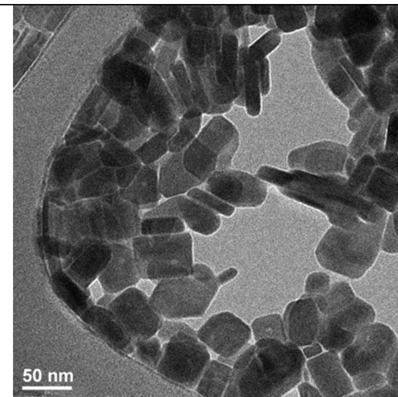
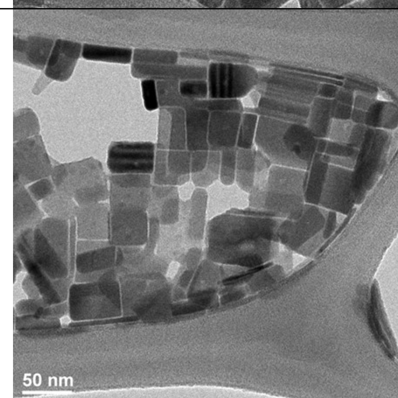
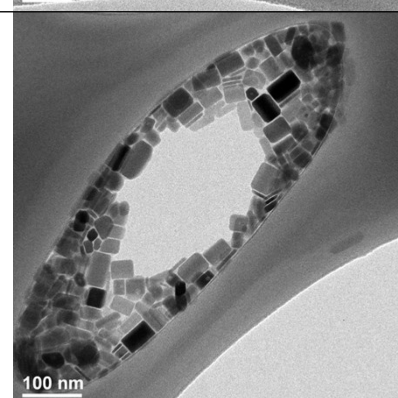
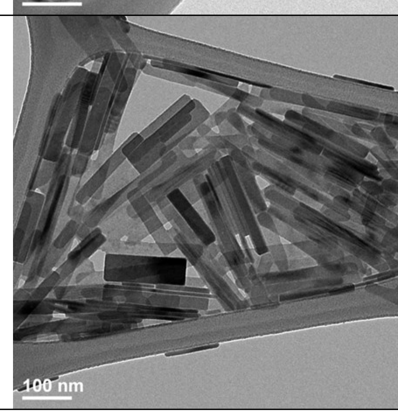
Cs_2ZnCl_4	200°C	5 seconds	Irregular particles suspended in a film.	
Cs_2ZnCl_4	200°C	20 minutes	<u>Nanorods</u> Length: 239.6 ± 101.7 nm (42% error) Width: 25.7 ± 4.6 nm (18% error) Larger overall rods than with the 150°C samples, but with larger size variation	
Cs_2ZnCl_4	200°C	60 minutes	Large irregularly-shaped particles. Rod morphology was completely degraded.	

Table S4. Cs_2ZnCl_4. The effects upon morphology of **changing reaction time** with samples tested at 5 seconds, 20 minutes, and 60 minutes, respectively. Effects of reaction time upon morphology were probed at **different reaction temperatures,** systematically ranging from 50°C to 200°C in increments of 50°C. Amounts of oleic acid, oleylamine, cesium-oleate, zinc chloride, and octadecene were kept constant throughout all of the trials.

Material	**Reaction Temperature**	**Reaction Time**	**Results**	**Image**
Cs_2ZnBr_4	50°C	5 seconds	Irregular particles Size: 34.85 ± 8.75 nm (25% error)	
Cs_2ZnBr_4	50°C	20 minutes	Irregular particles Size: 26.34 ± 5.38 nm (20% error)	
Cs_2ZnBr_4	50°C	60 minutes	Irregular particles Size: 34.18 ± 9.92 nm (29% error)	
Cs_2ZnBr_4	100°C	5 seconds	Irregular particles Size: 23.30 ± 7.56 nm (32% error)	

Cs_2ZnBr_4	100°C	20 minutes	Cubes with rounded corners Size: 43.88 ± 10.36 nm (24% error) Thickness: 4.63 ± .90 nm (19% error)	
Cs_2ZnBr_4	100°C	60 minutes	Cubes Size: 46.06 ± 12.27 nm (27% error) Thickness: 4.31 ± .51 nm (12% error)	
Cs_2ZnBr_4	150°C	5 seconds	Cubes Size: 36.05 ± 11.36 nm (31% error) Thickness: 4.29 ± 0.84 nm (20% error)	
Cs_2ZnBr_4	150°C	20 minutes	Rods Length: 206.88 ± 50.17 nm (24% error) Width: 26.66 ± 12.59 nm (47% error) Thickness: 6.87 ± 1.17 nm (17% error)	

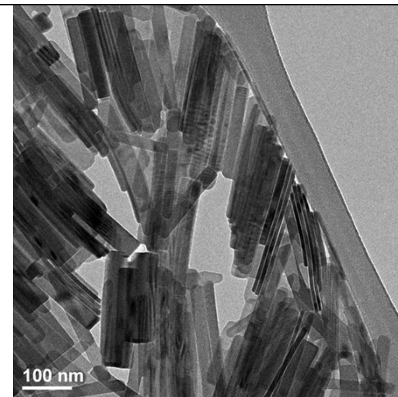
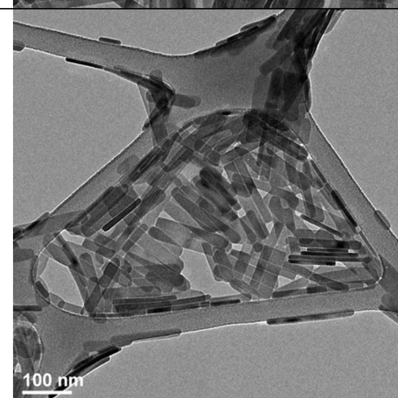
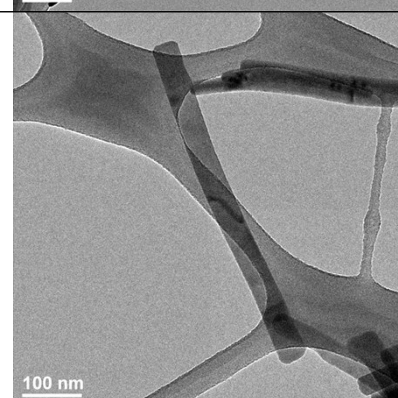
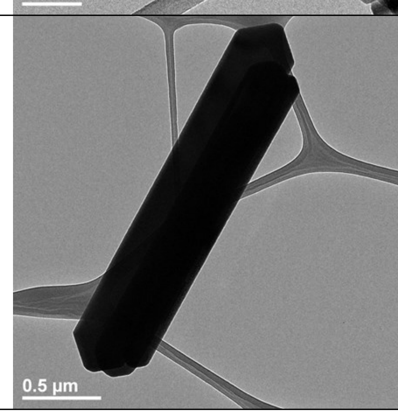
Cs_2ZnBr_4	150°C	60 minutes	Rods Length: 217.02 ± 56.20 nm (26% error) Width: 30.38 ± 9.32 nm (31% error) Thickness: 6.38 ± 1.34 nm (21% error)	
Cs_2ZnBr_4	200°C	5 seconds	Rods Length: 118.35 ± 32.66 nm (28% error) Width: 22.11 ± 4.27 nm (19% error) Thickness: 7.56 ± 1.12 nm (15% error)	
Cs_2ZnBr_4	200°C	20 minutes	Longer rods Length: 642.16 ± 334.40 nm (52% error) Width: 40.72 ± 29.11 nm (71% error)	
Cs_2ZnBr_4	200°C	60 minutes	Micron sized rods Length: 2.57 ± .37 µm (14% error) Width: 0.32 ± 0.09 µm (28% error)	

Table S5. Cs_2ZnBr_4. The effects upon morphology of **changing reaction time** with samples tested at 5 seconds, 20 minutes, and 60 minutes, respectively. Effects of reaction time upon morphology were probed at **different reaction temperatures,** systematically ranging from 50°C to 200°C in increments of 50°C. Amounts of oleic acid, oleylamine, cesium-oleate, zinc chloride, and octadecene were kept constant throughout all of the trials.

Sample	Surfactants	‘Good’ solvent	‘Poor’ solvent	Results
1. Cs_2ZnI_4	None	Triethylene glycol	2-ethylhexanol	CsI precipitated
2. Cs_2ZnI_4	None	DMF	2-ethylhexanol	CsI precipitated
3. Cs_2ZnI_4	None	Triethylene glycol	Toluene	No precipitation
4. Cs_2ZnI_4	None	DMF	Toluene	CsI precipitated
5. Cs_2ZnI_4	Oleic acid	Triethylene glycol DMF	Isopropanol	No precipitation

Table S6. All trials associated with the LARP method, run for Cs_2ZnI_4 . These were organized by the choice of the poor solvent.

Sample	Surfactants	'Good' solvent	'Poor' solvent	Results
1. Cs_2ZnCl_4	Oleic acid	Triethylene glycol, water,	Isopropanol	1.045 ± 0.321 microns; Irregularly-shaped particles
2. Cs_2ZnCl_4	Oleic acid	Triethylene glycol, DMF	Isopropanol	0.498 ± 0.152 microns; Irregularly-shaped particles
3. Cs_2ZnCl_4	Oleic acid (0.2x the volume)	Triethylene glycol, water	Isopropanol	1.611 ± 0.951 microns, irregularly-shaped particles
4. Cs_2ZnCl_4	Oleic acid (2x the volume)	Triethylene glycol, water	Isopropanol	Large plates: 4.535 ± 1.067 microns (long edge) 2.881 ± 0.577 microns (short edge) 0.298 ± 0.061 microns (width)
5. Cs_2ZnCl_4	Oleic acid (0.058 ml)	Triethylene glycol	Isopropanol	1.011 ± 0.310 microns, lumpy, oblong structures
6. Cs_2ZnCl_4	Oleic acid (0.116 ml)	Triethylene glycol	Isopropanol	2.760 ± 0.284 microns, uniform spindles
7. Cs_2ZnCl_4	Oleic acid (0.232 ml)	Triethylene glycol	Isopropanol	1.580 ± 0.162 microns, uniform spindles
8. Cs_2ZnCl_4	Oleic acid	Triethylene glycol	Isopropanol	0.684 ± 0.169 microns, less uniform smaller spindles
9. Cs_2ZnCl_4	Oleic acid	ethylene glycol, water	Isopropanol	0.801 ± 0.348 microns; Irregularly-shaped particles
10. Cs_2ZnCl_4	Oleic acid	Propylene glycol, DMF	Isopropanol	0.835 ± 0.331 microns, irregularly-shaped particles
11. Cs_2ZnCl_4	None	Triethylene glycol	Isopropanol	0.953 ± 0.223 microns, Lumpy, oblong structures
12. Cs_2ZnCl_4	Linoleic acid	DMF	Isopropanol	Irregularly-shaped particles
13. Cs_2ZnCl_4	Myristic acid	DMF	Isopropanol	Irregularly-shaped particles
14. Cs_2ZnCl_4	Oleic acid	DMF	Isopropanol	Irregularly-shaped particles
15. Cs_2ZnCl_4	Palmitic acid	DMF	Isopropanol	Irregularly-shaped particles

16. Cs_2ZnCl_4	Stearic acid	DMF	Isopropanol	Irregularly-shaped particles
17. Cs_2ZnCl_4	None	Triethylene glycol	DCM	Irregularly-shaped particles
18. Cs_2ZnCl_4	Oleic acid (0.116 ml)	Triethylene glycol	DCM	Irregularly-shaped particles
19. Cs_2ZnCl_4	Oleic acid (1.166 ml)	Triethylene glycol	DCM	Irregularly-shaped particles
20. Cs_2ZnCl_4	None	Triethylene glycol	Butanol	Micron sized irregularly-shaped spindles
21. Cs_2ZnCl_4	None	Triethylene glycol	2-ethylhexanol	Irregularly-shaped particles
22. Cs_2ZnCl_4	Linoleic acid	DMF	Toluene	Irregularly-shaped particles
23. Cs_2ZnCl_4	Myristic acid	DMF	Toluene	Irregularly-shaped particles

Table S7. All trials associated with the LARP method, run for Cs_2ZnCl_4 organized by the choice of poor solvent.

Sample	Surfactants	‘Good’ solvent	‘Poor’ solvent	Results
1. Cs_2ZnBr_4	None	Triethylene glycol	Isopropanol	Large irregularly-shaped plates
2. Cs_2ZnBr_4	Oleic acid	water	Isopropanol	Only CsBr precipitated
3. Cs_2ZnBr_4	Oleic acid (0.116 ml)	Triethylene glycol	Isopropanol	Large irregularly-shaped plates
4. Cs_2ZnBr_4	Oleic acid (1.166 ml)	Triethylene glycol	Isopropanol	Large irregularly-shaped plates
5. Cs_2ZnBr_4	Oleic acid	DMF	Octanol	Large irregularly-shaped CsBr crystals
6. Cs_2ZnBr_4	Oleic acid	DMF	Chloroform	355 ± 154 nm, irregularly-shaped rounded particles
7. Cs_2ZnBr_4	Oleic acid	Ethylene glycol, DMF	Chloroform	1.211 ± 0.438 microns, irregularly-shaped particles
8. Cs_2ZnBr_4	Oleic acid	Ethylene glycol, DMF	DCM	1.211 ± 0.438 microns, irregularly-shaped particles
9. Cs_2ZnBr_4	None	Triethylene glycol	DCM	Irregularly-shaped particles
10. Cs_2ZnBr_4	Oleic acid (0.116 ml)	Triethylene glycol	DCM	Irregularly-shaped particles
11. Cs_2ZnBr_4	Oleic acid (1.166 ml)	Triethylene glycol	DCM	Irregularly-shaped particles
12. Cs_2ZnBr_4	Oleic acid	Triethylene glycol, DMF	Toluene	764 ± 207 nm, rectangular plates
13. Cs_2ZnBr_4	Oleic acid	Ethylene glycol, DMF	Toluene	0.967 ± 0.393 microns, irregularly-shaped particles
14. Cs_2ZnBr_4	CTAB	DMF	Toluene	Irregularly-shaped particles
15. Cs_2ZnBr_4	Linoleic acid	DMF	Toluene	Irregularly-shaped particles
16. Cs_2ZnBr_4	Myristic acid	DMF	Toluene	Irregularly-shaped particles
17. Cs_2ZnBr_4	Palmitic acid	DMF	Toluene	Irregularly-shaped particles
18. Cs_2ZnBr_4	Stearic acid	DMF	Toluene	Irregularly-shaped particles
19. Cs_2ZnBr_4	None	Triethylene glycol	2-ethylhexanol	Irregularly-shaped particles

Table S8. All trials associated with the LARP method, run for Cs_2ZnBr_4 organized by the choice of the poor solvent.

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