

Supplemental Information

HF-free synthesis of colloidal Cs₂ZrF₆ and (NH₄)₂ZrF₆ nanocrystals

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EXPERIMENTAL METHODS

Zirconium(IV) acetylacetonate (Zr(C₅O₂H₇)₄, 97%), zirconium(IV) carbonate basic (Zr(OH)₂CO₃ · ZrO₂, ≥ 40% ZrO₂ basis), trifluoroacetic acid (TFA, 99%), cesium(I) hydroxide hydrate (CsOH · H₂O, ≥ 90%), cesium(I) carbonate (Cs₂CO₃, 99%), oleic acid (OA, 90%), oleylamine (OAm, 70%), trioctylphosphine (TOP, 97%), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich. Ammonium fluoride hydrate (NH₄F · xH₂O, x ≈ 0.5, 99.9975%) was purchased from Alfa Aesar. All reagents were used without further purification.

Serious care and attention are needed when working with any fluoride material. NH₄F is a hydrophilic crystalline solid and should be stored in a cool dry area and always remain in a sealed plastic container when not in use. Long neoprene gloves and a neoprene apron were worn during all handling of NH₄F, in addition to typical personal protective equipment. A face mask or shield is also recommended when working with fluorides. Always have calcium gluconate paste nearby in case of accidental skin exposure to NH₄F.

All reaction liquids with any amount of assumed free fluoride anions should not remain in glass containers (flasks, beakers, etc.) for more than a few hours to avoid etching and possible cracking. A fluoride waste stream separate from incompatible compounds should be prepared, well-labeled, and handled with care.

Synthesis Attempt of Cs₂ZrF₆ with Trifluoroacetic Acid. Synthesis was attempted following literature procedure for NaYF₄ nanocrystals.¹ 410 mg (2.5 mmol Cs) of Cs₂CO₃, 390 mg Zr(OH)₂CO₃ · ZrO₂ (2.5 mmol Zr), and 10.0 mL of TFA were added to a 100-mL 3-neck round bottom flask. The solution was put under N₂ flow and the temperature was raised to 80 °C. The solution was kept at temperature for 40 min, at which the solution was clear yellow. The solution was brought to room temperature before placing the flask under vacuum to pull off excess TFA. A faint orange solid was observed. 10.0 mL OA and 5.0 mL ODE were added, and the solution was degassed at 120 °C for 1 h. A separate 100-mL flask of 10.0 mL OA and 15.0 mL ODE was degassed at 120 °C for the same time. The TFA-precursor solution was kept at 120 °C and turned to N₂ flow while the second solution was heated to 310 °C under N₂ flow. A cannula transfer of the TFA-precursor solution to the receiving solvent and ligand solution occurred over a 15 min span, with periodic vapor bursts observed in the receiving flask. The reaction solution was stirred under N₂ at 305 °C for 1 h before cooling to room temperature. The solid was precipitated from solution with ethanol and centrifuged at 10,000 rpm for 10 min before collecting the solid and washing again with ethanol.

Synthesis of Cs₂ZrF₆ Microcrystals. 490 mg (1.0 mmol) of Zr(C₅O₂H₇)₄ was added to 10.0 mL OA and 15.0 mL ODE in a 100-mL 3-neck round bottom flask and heated to 160 °C under N₂ flow for 30 min with constant stirring. The clear light-yellow solution was cooled to room temperature. 280 mg (6.1 mmol) of

$\text{NH}_4\text{F} \cdot x\text{H}_2\text{O}$ and 340 mg (2.0 mmol) of $\text{CsOH} \cdot \text{H}_2\text{O}$ were added at a N_2 overpressure then 6.0 mL of methanol was injected through a septum cap into the reaction mixture, and the solution was stirred as the methanol was pulled off under vacuum. The solution was then slowly heated to 60°C and let sit for 1 h to ensure the removal of all methanol. The solution was heated to 250°C under N_2 flow and the reaction was quenched in a water bath after 10 min at temperature.

Synthesis of Cs-oleate. 200 mg (1.2 mmol Cs) of Cs_2CO_3 was added to 0.7 mL of OA and 7.5 mL of ODE in a 100-mL 3-neck round bottom flask. The solution was degassed at 120°C under vacuum for 1 h. The clear solution was then heated to 150°C under N_2 flow for 40 min before letting cool to room temperature.

Synthesis of Hollow Cs_2ZrF_6 Nanocrystals. 150 mg (0.31 mmol) of $\text{Zr}(\text{C}_5\text{O}_2\text{H}_7)_4$ was added to 3.4 mL OA and 5.0 mL ODE in a 50-mL 3-neck round bottom flask and heated to 160°C under N_2 flow for 30 min with constant stirring. The clear light-yellow solution was cooled to room temperature. 85 mg (1.8 mmol) of $\text{NH}_4\text{F} \cdot x\text{H}_2\text{O}$ was added at a N_2 overpressure then 2.0 mL of methanol was injected through a septum cap into the reaction mixture. The solution was stirred as the methanol was pulled off under vacuum at room temperature. The solution was then slowly heated to 85°C and let sit for 40 min then raised to 110°C and left for another 40 min under vacuum to ensure the removal of all methanol. The solution was heated to 250°C under N_2 flow at which 8.2 mL of Cs-oleate, gently heated until clear at 100°C in the glovebox, was swiftly injected into the reaction solution. The reaction was quenched in a room temperature water bath after 10 min (timer began upon reaction solution returning to 250°C).

Synthesis of Hollow Cs_2ZrF_6 Nanocrystals with Multiple Ligand Types. 150 mg (0.31 mmol) of $\text{Zr}(\text{C}_5\text{O}_2\text{H}_7)_4$ was added to 2.2 mL OA, 0.2 mL OAm, and 5.0 mL ODE in a 50-mL 3-neck round bottom flask and degassed at 100°C for 10 min. The solution was put under N_2 flow and 0.5 mL TOP from a glovebox was added, then returned to vacuum for another 10 min. The solution was then heated to 160°C under N_2 flow for 30 min with constant stirring. The clear light-yellow solution was cooled to room temperature. 85 mg (1.8 mmol) of $\text{NH}_4\text{F} \cdot x\text{H}_2\text{O}$ was added at an overpressure then 2.0 mL of methanol was injected through a septum cap into the reaction mixture. The solution was stirred as the methanol was pulled off under vacuum at room temperature. The solution was slowly heated to 85°C and let sit for 40 min then raised to 110°C and left for another 40 min under vacuum to ensure the removal of all methanol. The solution was heated to 250°C under N_2 flow at which 8.2 mL of Cs-oleate, gently heated until clear at 100°C in the glovebox, was swiftly injected into the reaction solution. The reaction was quenched in a room temperature water bath after 3 min (timer began upon reaction solution returning to 250°C).

Synthesis of Cs_2ZrF_6 Nanocrystals. 150 mg (0.31 mmol) of $\text{Zr}(\text{C}_5\text{O}_2\text{H}_7)_4$ was added to 2.5 mL OA and 5.0 mL ODE in a 50-mL 3-neck round bottom flask and heated to 160°C under N_2 flow for 30 min with constant stirring. The clear light-yellow solution was cooled to room temperature. 85 mg (1.8 mmol) of $\text{NH}_4\text{F} \cdot x\text{H}_2\text{O}$ was added at an overpressure then 2.0 mL of methanol was injected, and the solution was stirred as the methanol was pulled off under vacuum. The solution was slowly heated to 85°C and let sit for 40 min then raised to 110°C and left for another 40 min under vacuum to ensure the removal of all methanol. The solution was heated to 180°C under N_2 flow at which 8.2 mL of Cs-oleate, gently heated until clear at 100°C in the glovebox, was swiftly injected into the reaction solution. The reaction was quenched in a room temperature water bath after 1 min (timer began upon reaction solution returning to 180°C).

Washing of Cs_2ZrF_6 Nanocrystals. The mother-liquor reaction solution was collected into microcentrifuge tubes and spun at 6,800 rpm for 10 min. The white precipitate was then collected and resuspended in anhydrous hexane solution. To prepare samples for XRD, the product solid was washed with ethanol and spun at 12,000 rpm for 10 min in a N_2 -atmosphere glovebox, then resuspended in hexane

before being dropcast onto a Si wafer. To separate the Cs_2ZrF_6 nanocrystals from the larger CsF salt impurity, the product solution was spun at 9,000 rpm for 3 min in a N_2 -atmosphere glovebox and the supernatant of Cs_2ZrF_6 nanocrystals was collected.

Synthesis of $(\text{NH}_4)_2\text{ZrF}_6$ Nanocrystals. 150 mg (0.31 mmol) of $\text{Zr}(\text{C}_5\text{O}_2\text{H}_7)_4$ was added to 2.5 mL OA and 5.0 mL ODE in a 50-mL 3-neck round bottom flask and heated to 160°C under N_2 flow for 30 min with constant stirring. The clear light-yellow solution was cooled to room temperature. 85 mg (1.8 mmol) of $\text{NH}_4\text{F} \cdot x\text{H}_2\text{O}$ was added at an overpressure then 2.0 mL of methanol was injected, and the solution was stirred as the methanol was pulled off under vacuum. The solution was slowly heated to 85°C and let sit for 40 min then raised to 110°C and left for another 40 min under vacuum to ensure the removal of all methanol. The solution was heated to 180°C under N_2 flow. The reaction was quenched in a room temperature water bath 30 sec after reaching temperature.

Washing of $(\text{NH}_4)_2\text{ZrF}_6$ Nanocrystals. The mother-liquor reaction solution was collected into microcentrifuge tubes and spun at 12,000 rpm for 10 min. The white precipitate was then collected and resuspended in anhydrous hexane solution. The resuspended product solution was spun at 2,000 rpm for 1 min and the supernatant was collected. To prepare samples for XRD, the product solid was washed with ethanol and spun at 12,000 rpm for 10 min in a N_2 -atmosphere glovebox, then resuspended in hexane before being dropcast onto a Si wafer.

POWDER X-RAY DIFFRACTION AND TRANSMISSION ELECTRON MICROSCOPY

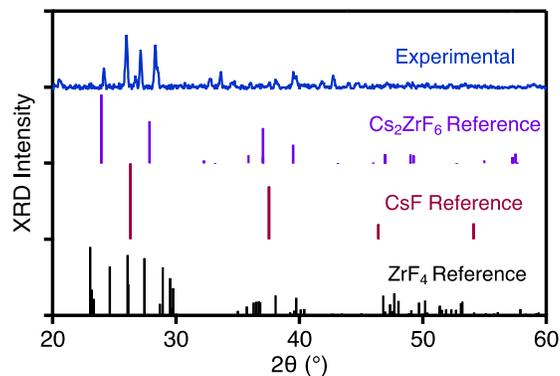


Fig. S1. Powder X-ray diffraction (pXRD) data of attempted synthesis of Cs_2ZrF_6 using trifluoroacetic acid (TFA) as fluoride source. For comparison Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598), CsF (cubic, ICSD Coll. Code 61563), and ZrF_4 (tetragonal, ICSD Coll. Code 35100) references are given. No references match the crystalline sample data.

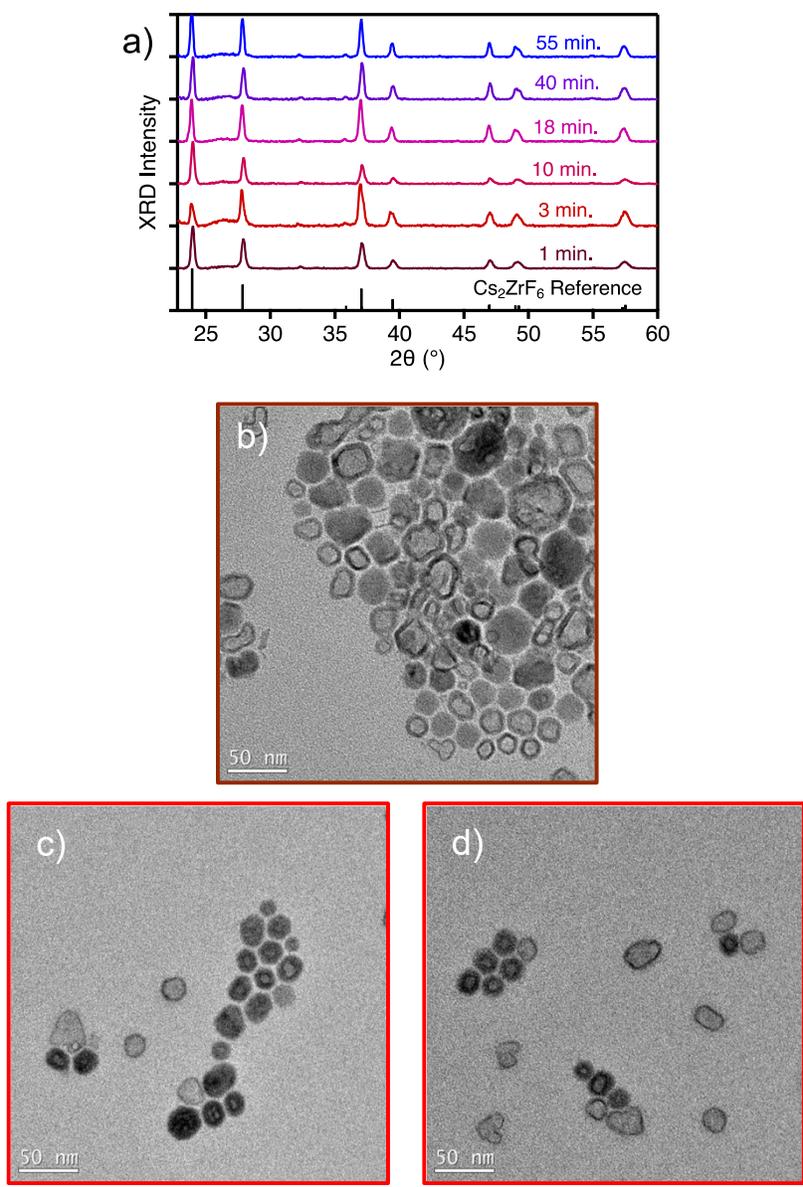


Fig. S2. (a) pXRD data of hollow Cs₂ZrF₆ nanocrystals ($T_{\text{rxn}} = 250\text{ }^{\circ}\text{C}$) with reaction times indicated on spectra. pXRD data are compared to Cs₂ZrF₆ (trigonal, ICSD Coll. Code 25598) reference. (b) Transmission electron microscope (TEM) image of hollow Cs₂ZrF₆ nanocrystals after 1-min reaction time. (c), (d) TEM images of hollow Cs₂ZrF₆ nanocrystals after 3-min reaction time.

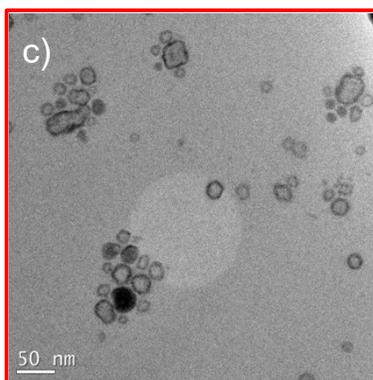
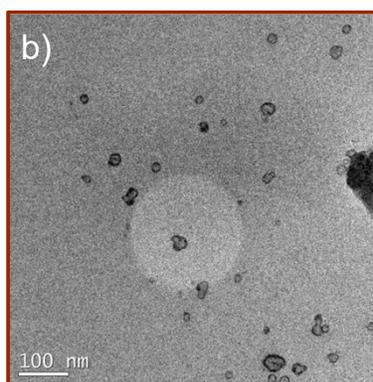
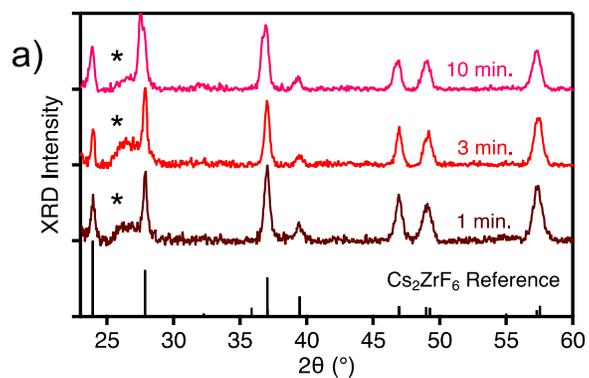


Fig. S3. (a) pXRD data of hollow Cs_2ZrF_6 nanocrystals ($T_{\text{rxn}} = 250^\circ\text{C}$) with TOP and OAm ligands included. pXRD data are compared to Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598) reference. Asterisk (*) indicates diffuse Kapton tape peak. Kapton tape is used to cover the sample to avoid water adsorption in air. (b) TEM image of hollow Cs_2ZrF_6 nanocrystals after 1-min reaction time. (c) TEM image of hollow Cs_2ZrF_6 nanocrystals after 3-min reaction time.

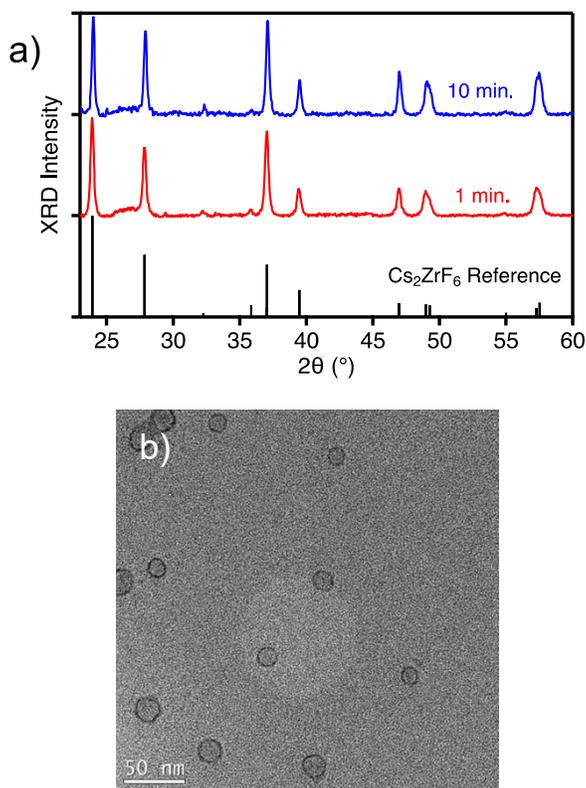


Fig. S4. (a) pXRD data of hollow Cs_2ZrF_6 nanocrystals ($T_{\text{rxn}} = 220\text{ }^\circ\text{C}$) with reaction times indicated on the data. pXRD data are compared to Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598) reference. (b) TEM image of hollow Cs_2ZrF_6 nanocrystals after 1-min reaction time.

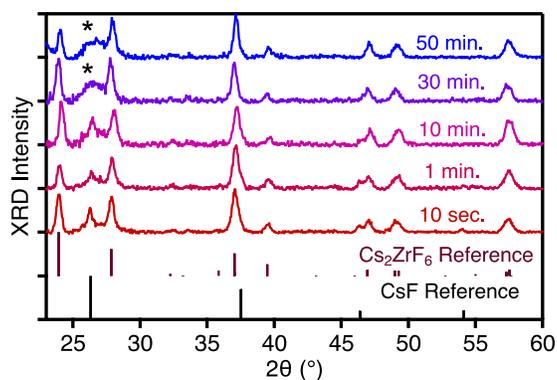


Fig. S5. pXRD data of low-temperature synthesis Cs_2ZrF_6 nanocrystals ($T_{\text{rxn}} = 180\text{ }^\circ\text{C}$) showing diminishing CsF impurity with increased reaction time, with reaction times indicated on the data. pXRD data are compared to Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598) and CsF (cubic, ICSD Coll. Code 61563) references. Asterisk (*) indicates diffuse Kapton tape peak. Kapton tape is used to cover the sample to avoid water adsorption from air.

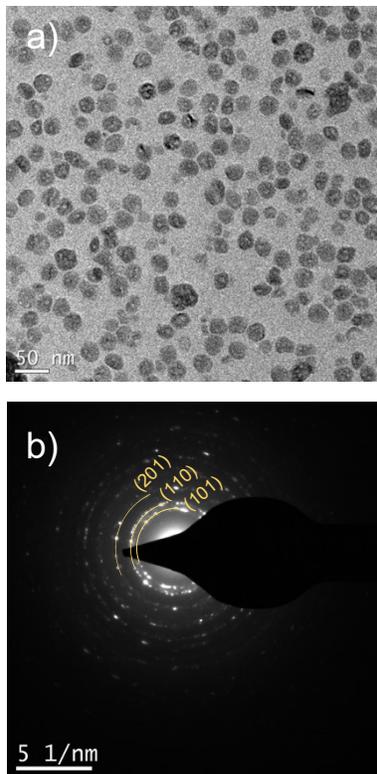


Fig. S6. (a) TEM image of Cs_2ZrF_6 nanocrystals ($T_{\text{rxn}} = 180^\circ\text{C}$) after additional washing procedure to separate CsF from colloid solution. (b) Electron diffractogram of sample showing a pure diffraction pattern of Cs_2ZrF_6 without CsF impurity. Diffraction rings matched to Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598) reference.

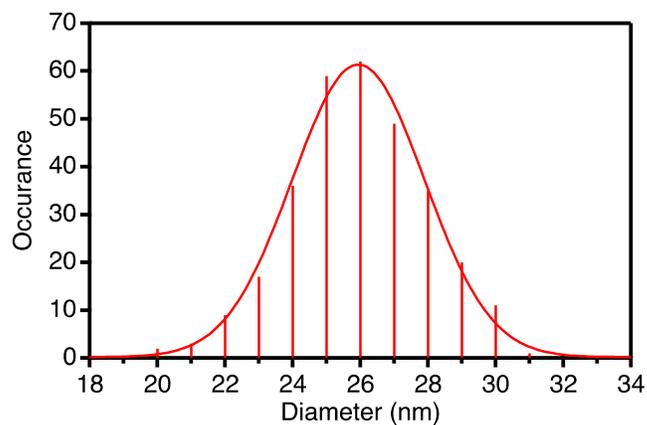


Fig. S7. Histogram containing measured diameters of 300 Cs_2ZrF_6 nanocrystals ($T_{\text{rxn}} = 180^\circ\text{C}$, 1-min reaction time) and fit to a Gaussian distribution with an average and standard deviation of 26.5 ± 2.0 nm.

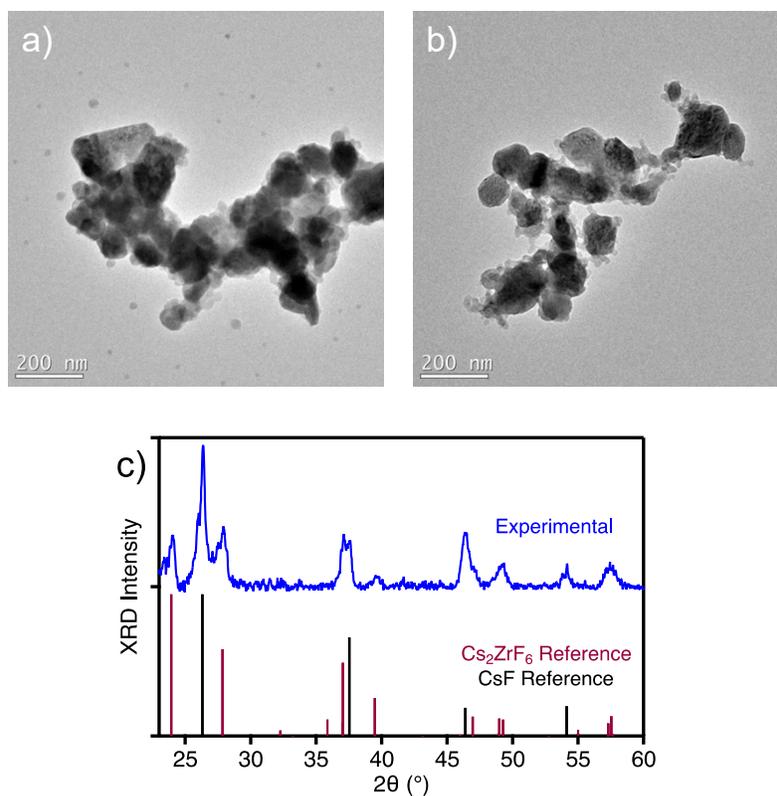


Fig. S8. In a follow-up low temperature synthesis ($T_{\text{rxn}} = 180\text{ }^{\circ}\text{C}$), an aliquot was taken 30 sec after hot-injection, as the solution temperature was returning to $180\text{ }^{\circ}\text{C}$. (a,b) TEM images indicate that among the smaller Cs_2ZrF_6 nanocrystals, large particle clusters $>100\text{ nm}$ in size are also observed. (c) Scherrer analysis of the pXRD CsF linewidths indicates that the grain size of CsF is $>>50\text{ nm}$ at time of reaction collection whereas pXRD Cs_2ZrF_6 linewidths yield an estimated average grain size of $<20\text{ nm}$, implying that the larger particles are likely CsF precipitate. pXRD data is compared to Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598) and CsF (cubic, ICSD Coll. Code 61563) references.

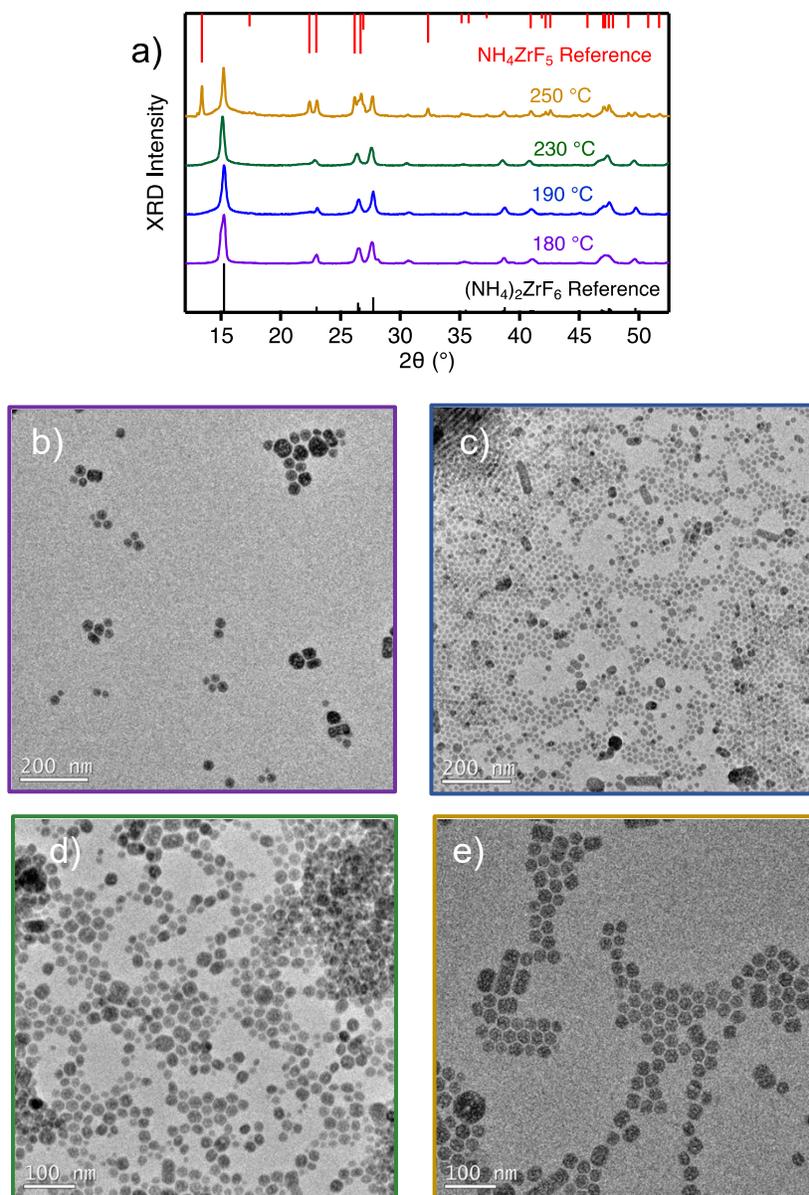


Fig. S9. (a) pXRD data of $(\text{NH}_4)_2\text{ZrF}_6$ nanocrystals prepared at reaction temperatures between 180 °C and 250 °C, collected immediately after reaching temperature. The formation of NH_4ZrF_5 is observed at $T_{\text{rxn}} = 250$ °C. pXRD data are compared to $(\text{NH}_4)_2\text{ZrF}_6$ (orthorhombic, PDF ID 04-014-8036) and NH_4ZrF_5 (orthorhombic, PDF ID 00-020-1460) references. (b) TEM image of $(\text{NH}_4)_2\text{ZrF}_6$ nanocrystals prepared at $T_{\text{rxn}} = 180$ °C. (c) TEM image of $(\text{NH}_4)_2\text{ZrF}_6$ nanocrystals prepared at $T_{\text{rxn}} = 190$ °C. (d) TEM image of $(\text{NH}_4)_2\text{ZrF}_6$ nanocrystals prepared at $T_{\text{rxn}} = 230$ °C. (e) TEM image of $(\text{NH}_4)_2\text{ZrF}_6$ nanocrystals prepared at $T_{\text{rxn}} = 250$ °C.

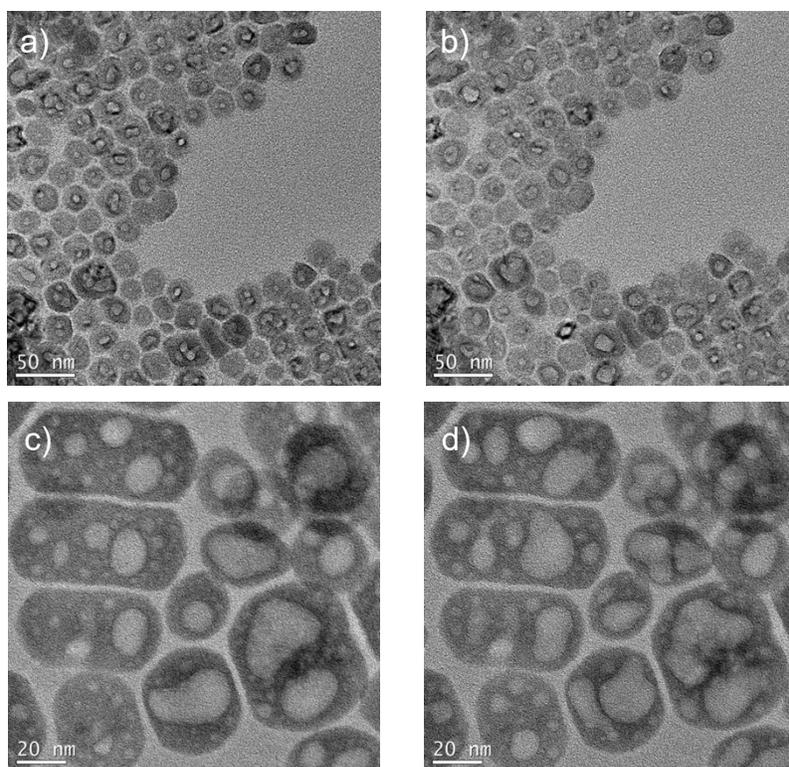


Fig. S10. To study the appearance of electron-beam sample damage when imaging on the transmission electron microscope, a region of Cs₂ZrF₆ nanocrystals ($T_{\text{rxn}} = 180\text{ }^{\circ}\text{C}$) was placed under the electron beam for an extended period. (a) TEM image of a Cs₂ZrF₆ nanocrystal sample shortly after being placed under the electron beam, (b) after 1 min under the beam. A region of (NH₄)₂ZrF₆ nanocrystals ($T_{\text{rxn}} = 180\text{ }^{\circ}\text{C}$) was also placed under the electron beam for an extended period. (c) TEM image of a (NH₄)₂ZrF₆ nanocrystal sample shortly after being placed under the electron beam, (d) after 1 min under the beam. Dispersed holing that increases with beam exposure is observed in both nanocrystals, but this phenomenon is explicitly different from the hollowing observed in Cs₂ZrF₆ nanocrystals prepared at reaction temperatures above 200 °C.

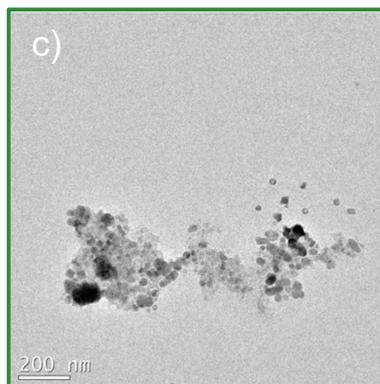
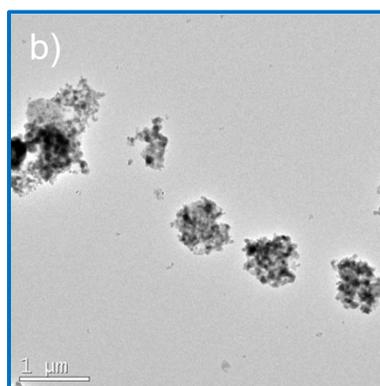
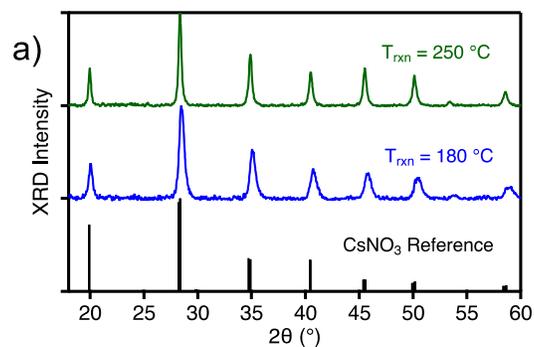


Fig. S11. Experiments at $T_{\text{rxn}} = 180\text{ }^{\circ}\text{C}$ and $250\text{ }^{\circ}\text{C}$ in which all parameters were kept the same as previously described *en route* to Cs_2ZrF_6 nanocrystals, except that $\text{Zr}(\text{C}_5\text{O}_2\text{H}_7)_4$ was omitted. (a) pXRD data of reaction products at $T_{\text{rxn}} = 180\text{ }^{\circ}\text{C}$ (blue trace, 1-min reaction time) and $T_{\text{rxn}} = 250\text{ }^{\circ}\text{C}$ (green trace, 10-min reaction time). pXRD data are compared to CsNO_3 (trigonal, ICSD Coll. Code 64600) reference. (b) TEM image of $T_{\text{rxn}} = 180\text{ }^{\circ}\text{C}$ product after 1-min reaction time, showing agglomerated CsNO_3 nanocrystals. (c) TEM images of $T_{\text{rxn}} = 250\text{ }^{\circ}\text{C}$ product after 10-min reaction time, showing agglomerated CsNO_3 nanocrystals.

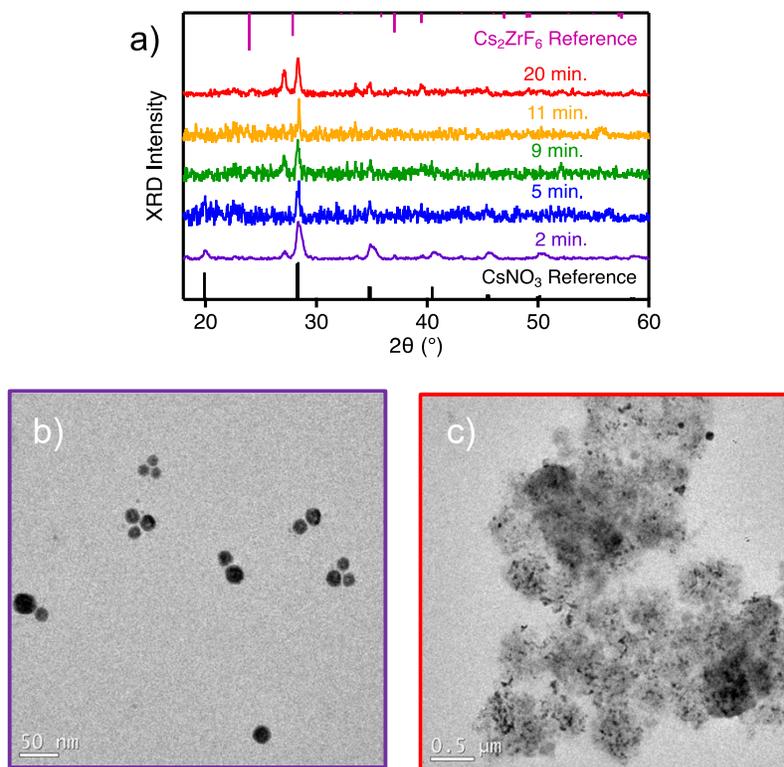


Fig. S12. To assess if the CsNO_3 product observed when $\text{Zr}(\text{C}_5\text{O}_2\text{H}_7)_4$ is omitted from the reaction is a critical precursor *en route* to Cs_2ZrF_6 NC formation, Zr-oleate was injected into a solution of CsNO_3 at 250 °C. (a) pXRD data of the reaction products collected at various time points after Zr-oleate injection. At early time points, the only crystalline material observed is CsNO_3 . Conversion to Cs_2ZrF_6 is also not observed at longer reaction times. pXRD data are compared to CsNO_3 (trigonal, ICSD Coll. Code 64600) and Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598) references. (b) TEM image of product after 2-min reaction time, showing CsNO_3 nanocrystals. (c) TEM image after 20-min reaction time, showing large agglomerations of nanocrystals.

HIGH-ANGLE ANNULAR DARK FIELD SCANNING TRANSMISSION ELECTRON MICROSCOPY

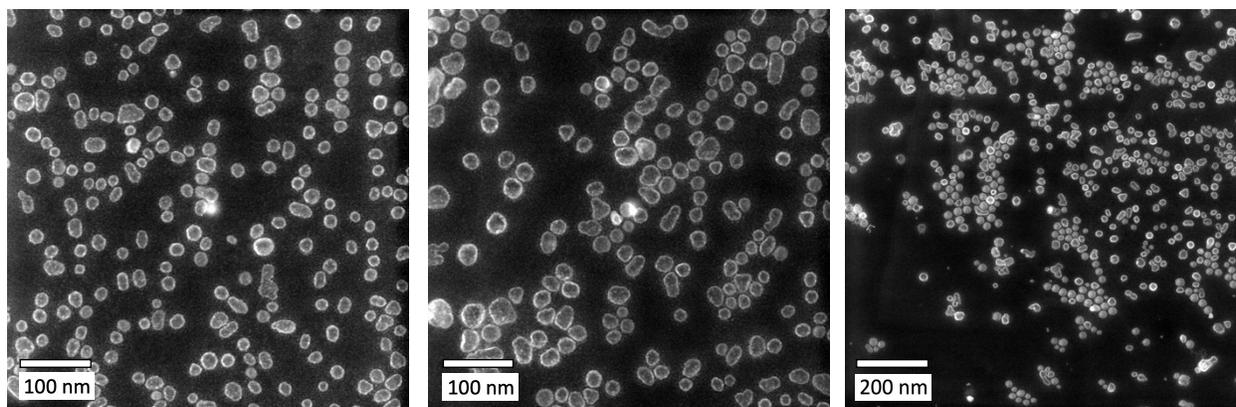


Fig. S13. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images confirm that Cs₂ZrF₆ nanocrystals prepared at $T_{\text{rxn}} = 250$ °C are predominantly hollow nanocrystals.

SCANNING ELECTRON MICROSCOPY WITH ENERGY DISPERSIVE X-RAY SPECTROSCOPY

For better imaging, an ethanol wash of the Cs_2ZrF_6 nanocrystals was performed prior to imaging to strip ligands off the nanocrystal surfaces. This procedure resulted in the particle agglomeration observed in the images.

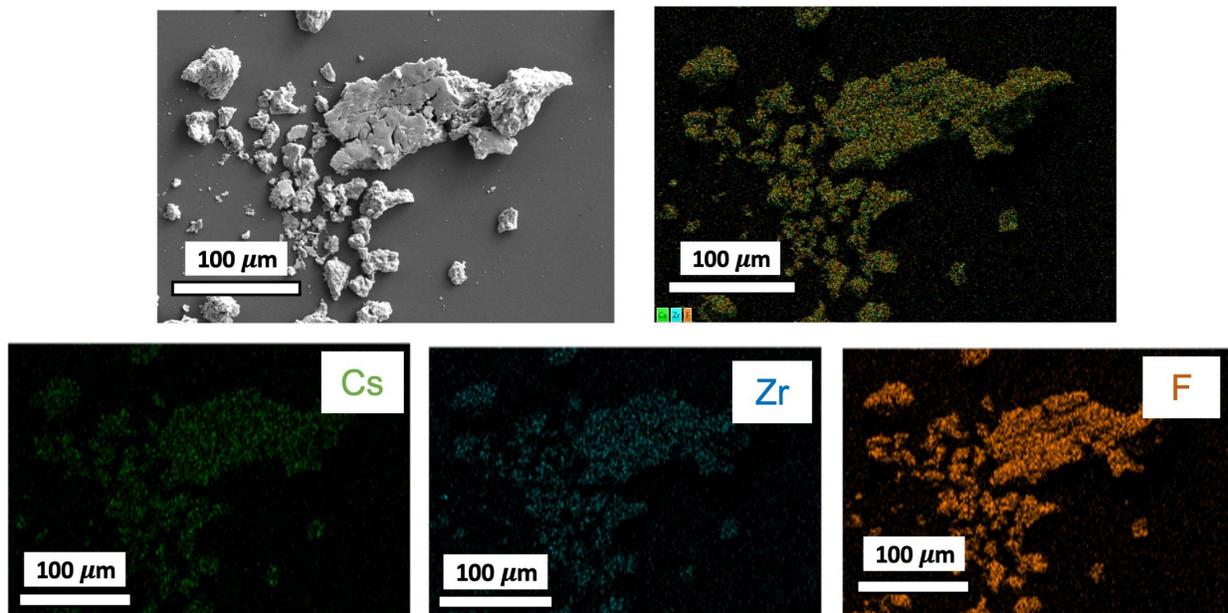


Fig. S14. Scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) elemental mapping of Cs_2ZrF_6 crystals prepared at $T_{\text{rxn}} = 180\text{ }^\circ\text{C}$.

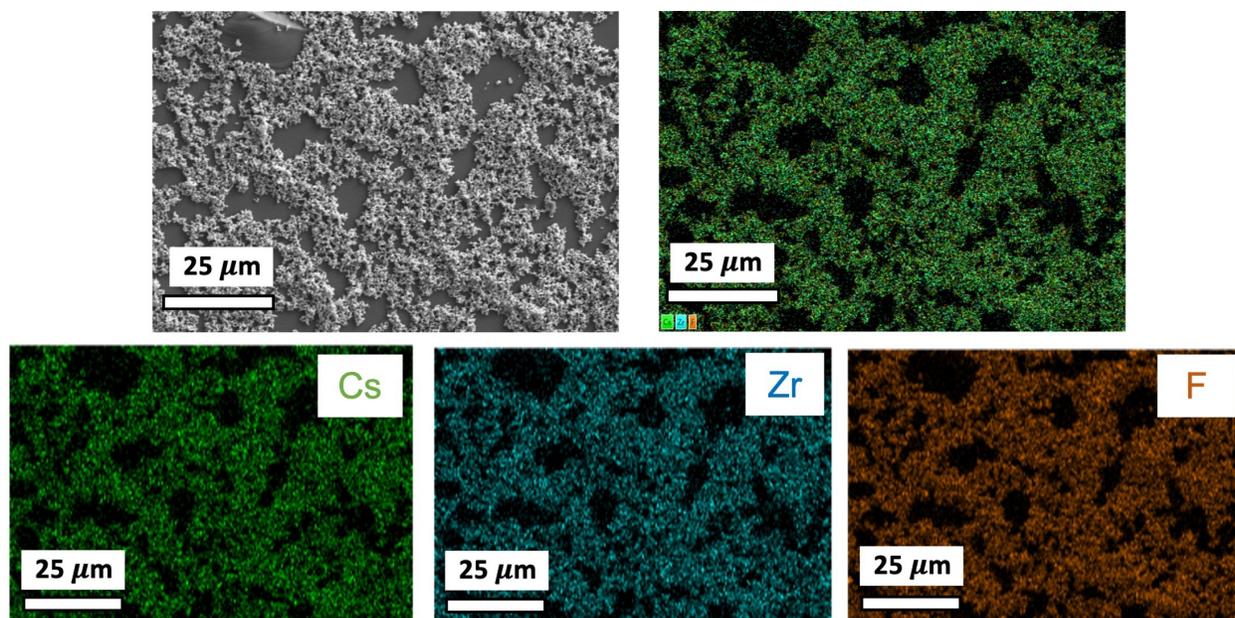


Fig. S15. SEM-EDX elemental mapping of Cs_2ZrF_6 nanocrystals prepared at $T_{\text{rxn}} = 250\text{ }^\circ\text{C}$.

Table S1. Atomic ratios of elements from EDX elemental analysis on Cs_2ZrF_6 nanocrystal samples prepared at different reaction temperatures.

Sample	Cs	Zr	F
Hexagonal NCs at $T_{\text{rxn}} = 180\text{ }^\circ\text{C}$	2.3	1.0	5.9
Hollow NCs at $T_{\text{rxn}} = 250\text{ }^\circ\text{C}$	2.2	1.0	5.2

References

1. J. C. Boyer, L. A. Cuccia, J. A. Capobianco, *Nano Lett.*, 2007, **7**, 847.
2. C. Rüssel, *J. Non-Cryst. Solids*, 1993, **152**, 161.