Supporting Information for:

Colloidal Synthesis of Strongly Fluorescent $CsPbBr_3$ Nanowires with Width Tunable Down to the Quantum Confinement Regime

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Materials: Lead(II) bromide ($PbBr_2$, 99.999% trace metals basis), cesium carbonate (Cs_2CO_3, reagentPlus, 99%), 1-octadecene (ODE, technical grade, 90%), oleylamine (OlAm, 70%), oleic acid (OlAc, 90%), Hexanoic acid (HexAc, ≥99.5%), Octanoic acid (OctAc, 99%), Octylamine (OctAm 99,5%), Toluene (anhydrous), Hexane (anhydrous, 95%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

Methods:

Preparation of Cesium-oleate solution:

The Cs-oleate solution was prepared following the approach developed by Protesescu *et al*[1]. Briefly, 0.4 g Cs_2CO_3 and 1.2 mL OA were loaded into a 3-neck flask along with 15 mL ODE, degassed and dried under vacuum at 120 °C for 60min, and then heated under N_2 to 150 °C until all Cs_2CO_3 reacted with OA.

Synthesis of $CsPbBr_3$ NWs:

NWs with widths of 10 nm or above. In order to grow NWs with widths of 10 nm and above, the following procedure was followed: 8 mL ODE, 0.069g $PbBr_2$, and proper amounts of OlAm and OctAm (see table S1 for details) were loaded into a 25 mL 3-neck flask and dried under vacuum for 45 minutes at 95ºC, leading to a *cloudy* solution. *Note that in these syntheses no short chain acid was added*. Subsequently, the temperature was raised to 120ºC under N_2. After 10 min at 120 °C, 0.6mL of Cs-oleate solution (prepared as described above) were swiftly injected in the flask. The NWs were then allowed to grow for 50 minutes at 120 °C, after which the reaction mixture was slowly cooled down to room temperature using a water bath. The NWs were isolated by centrifugation at 3000 rpm for 10 mins and re-dispersed in hexane/toluene for further use. A sketch of the temperature ramp for the 10 nm width NW synthesis is reported in Figure S1A.

NWs with widths below 10 nm. In order to grow NWs with widths below 10 nm, the following procedure was followed: 8 mL ODE, 0.069g $PbBr_2$, 500 µL OlAm, 500 µL OctAm and a proper volume of a hexanoic acid (see table S1 for details) were loaded into a 25 mL 3-neck flask and dried under vacuum for 45 minutes at 95ºC, leading to a *clear* solution. Subsequently, the temperature was increased to 120ºC under N_2 and kept at 120°C for 10 mins. The temperature was then lowered to 65ºC and 0.6mL of Cs-oleate solution (prepared as described above) were swiftly injected in the flask. The NWs were then allowed to grow for 50 minutes at 65 °C, after which the reaction mixture was slowly cooled down to room temperature using a water bath. The NWs were isolated by centrifugation at 3000 rpm for 10 mins and re-dispersed in hexane/toluene for further use. A sketch of the temperature ramp for the 5.1 nm width NW synthesis is reported in Figure S1B.

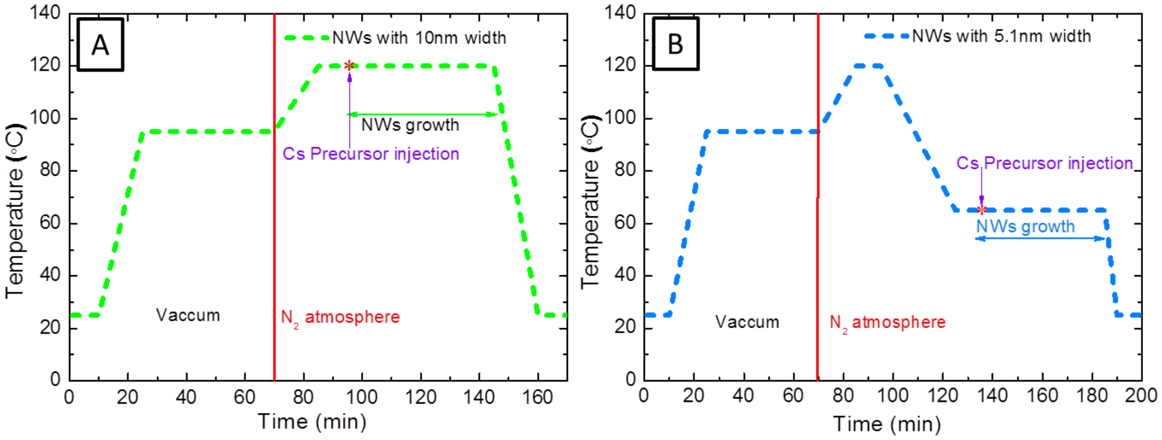

Figure S1. Examples of temperature ramps for the syntheses of NWs with (a) 10 nm width, and (b) 5.1 nm width. Reaction conditions for (a) and (b) were: 0.069g $PbBr_2$, 8mL ODE, 500µL OctAm, 500µL OlAm, with an additional 50 µL of HexAc in (B).

Table S1: Synthetic conditions for the various $CsPbBr_3$ NWs. All syntheses had in common the following parameters: ODE: 8mL; $PbBr_2$: 0.069g; Cs-oleate: 0.6ml; Reaction time: 50min.

NWs width (nm)	OlAm (µl)	OctAm (µl)	HexAc (µl)	Reaction Temp (°C)
20±3	1000	200	0	120
10±1	500	500	0	120
5.1±0.5	500	500	50	65
4.1±0.7	500	500	100	65
3.4±0.5	500	500	150	65
2.8±0.3	500	500	250	65

Characterization:

Conventional TEM images were acquired on a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. HRTEM, selected area electron diffraction (SAED) and HAADF-STEM analyses were performed on a JEOL JEM-2200FS microscope equipped with a Schottky emitter operated at 200 kV, a CEOS spherical aberration (C_s) corrector for the objective lens, and an in-column energy filter (Omega-type). The SAED patterns were acquired using a conventional CCD camera (Gatan, Ultrascan 894 US1000), while HRTEM imaging of wide FOV regions was possible thanks to a direct detection camera (Gatan, K2 Summit™). The HRTEM images in Figure 2 in the main manuscript correspond to a magnification of 80K, over an area of 164 nm x 169 nm, with pixel number of 7420 x 7626, and obtained by integrating over a stack of 60 frames after drift correction among bandpass-filtered frames. Each frame was acquired with dose of 44 $e^-/Å^2$ for 3.4 nm NWs, 14 $e^-/Å^2$ for 5.1 nm NWs, and 21 $e^-/Å^2$ for 10 nm NWs. The HRTEM images were acquired by filtering elastically scattered electrons by a 5 eV energy-selecting slit, and two-fold astigmatism was manually optimized within the CEOS software. Samples were prepared by dropping diluted NWs suspensions onto ultrathin carbon film-coated holey carbon film on 400 mesh copper grids.

Atomic force microscopy (AFM) was employed to obtain a detailed three-dimensional representation of the NW topography. AFM images were acquired with a Nanowizard III AFM setup (JPK Instruments, Germany), working in tapping mode in ambient conditions. Single beam silicon cantilevers (NCHV, Bruker, USA) with a nominal spring constant of 42 N/m and resonance frequency of 320 kHz were used. The typical radius of curvature of the tip was 10 nm. 3 µl aliquots of solution containing NWs were spread on freshly cleaved graphite substrates and subsequently dried under a mild nitrogen flow.

The UV-Vis absorption spectra were recorded on a Varian Cary 5000 UV−vis−NIR spectrophotometer. The NWs solutions were prepared by diluting the mother solution in toluene (20 µL in 1 mL), in 1 cm path length quartz cuvettes. PL spectra, PLQY and time-resolved PL measurements were carried out with an Edinburgh Instruments fluorescence spectrometer (FLS920). The system was equipped with a Xenon lamp and monochromator for steady-state PL excitation, and a time-correlated single photon counting unit coupled with a pulsed laser diode (λ = 405 nm, pulse width = 50 ps) for time-resolved PL. PLQY values were measured using 400 nm as excitation wavelength and a calibrated integrating sphere. PL decays were fitted with a two-exponential function: $I = A_1 e^{-(t/\tau_1)} + A_2 e^{-(t/\tau_2)} + y_0$ and the reported average lifetime $< \tau >$ was calculated as: $< \tau >= (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$.

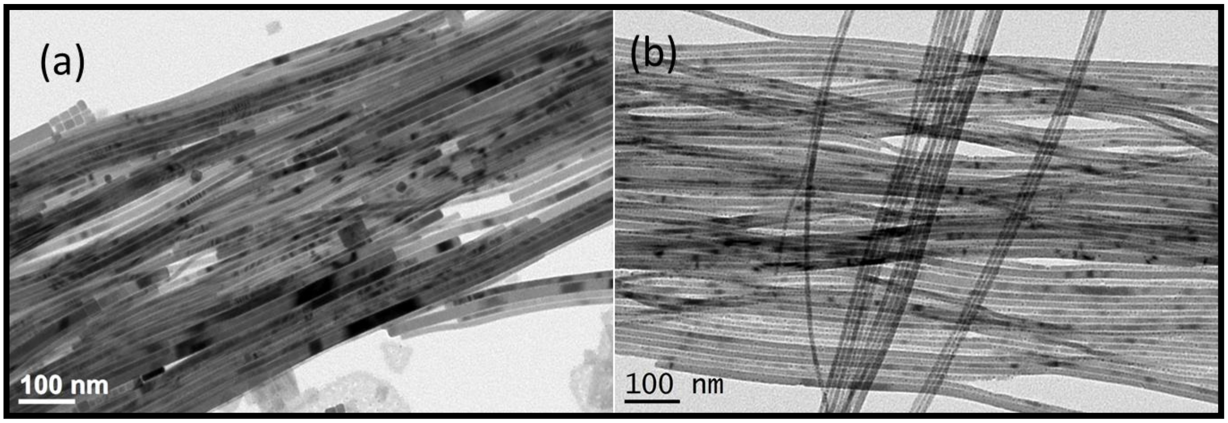

Figure S2. BF-TEM images of NWs prepared without any acid (neither oleic acid nor hexanoic acid). Reaction conditions: 0.069g $PbBr_2$, 8mL ODE, (a) 200µL OctAm, 1000µL OlAm, (b) 500µL OctAm, 500µL OlAm. Reaction temperature: 120°C, Reaction time: 50 min.

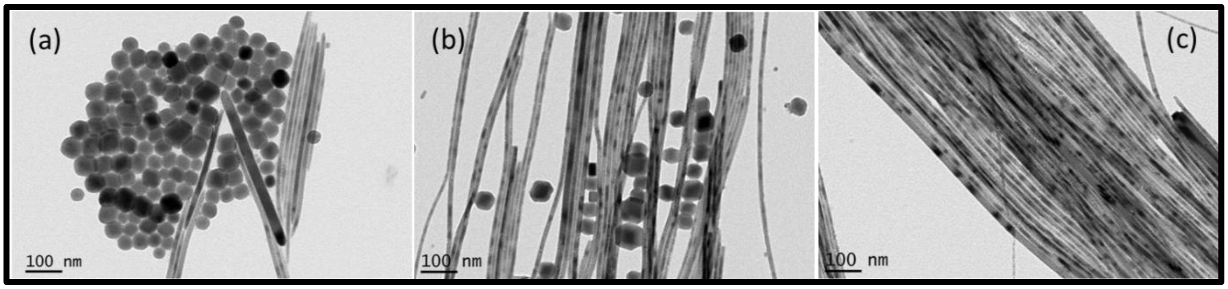

Figure S3: BF-TEM images showing the growth of 10nm NWs with time. (a) 5min, (b) 30min, (a) 50min.

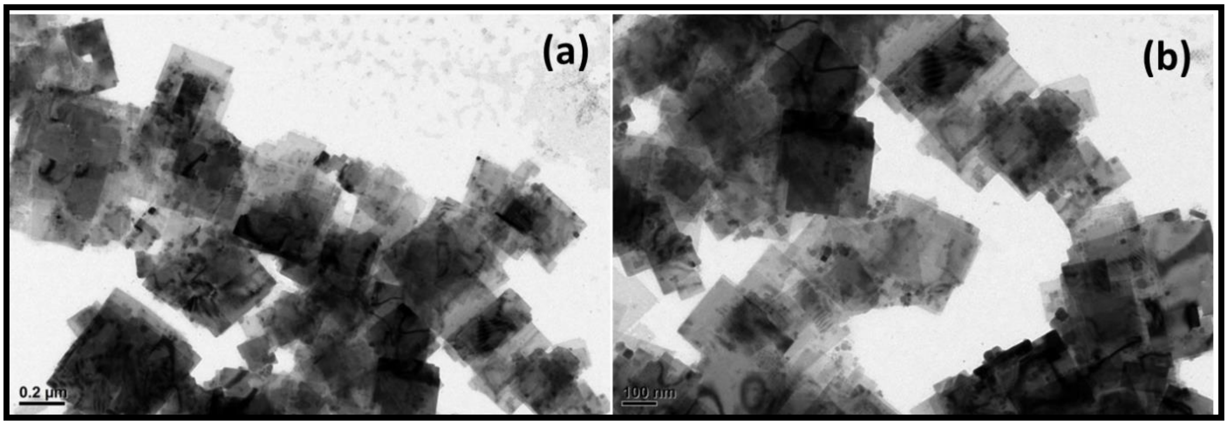

Figure S4. BF-TEM images of NWs prepared using oleic acid:. Reaction conditions: 0.069g $PbBr_2$, 8 mL ODE, 500µL OlAc, 500µL OlAm and 500µL OctAm, Reaction temperature: 120°C, Reaction time: 50 min.

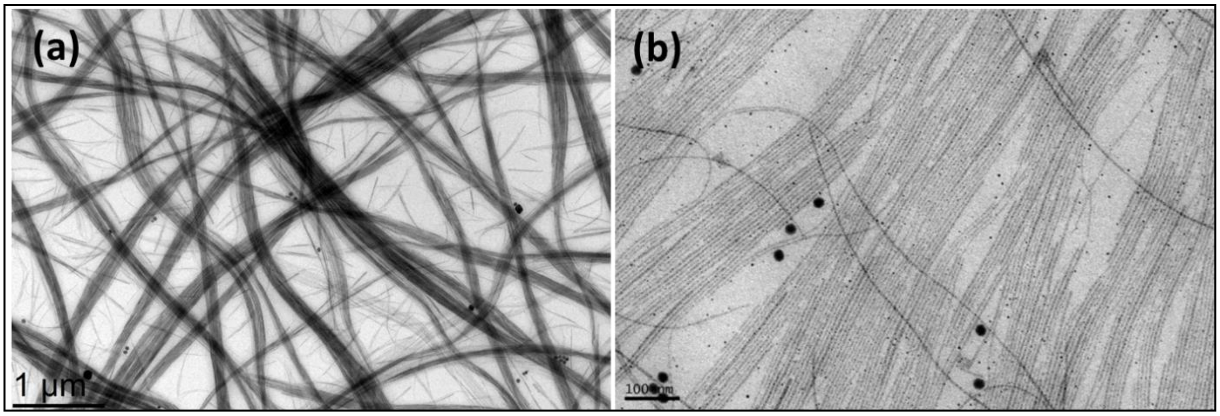

Figure S5. BF-TEM images of NWs prepared using hexanoic acid instead of Oleic acid: Reaction conditions: 0.069g $PbBr_2$, 8 mL ODE, 500µL OlAm, 500µL OctAm, and 50µL of HexAc. Reaction temperature: 65˚C, Reaction: time 50min.

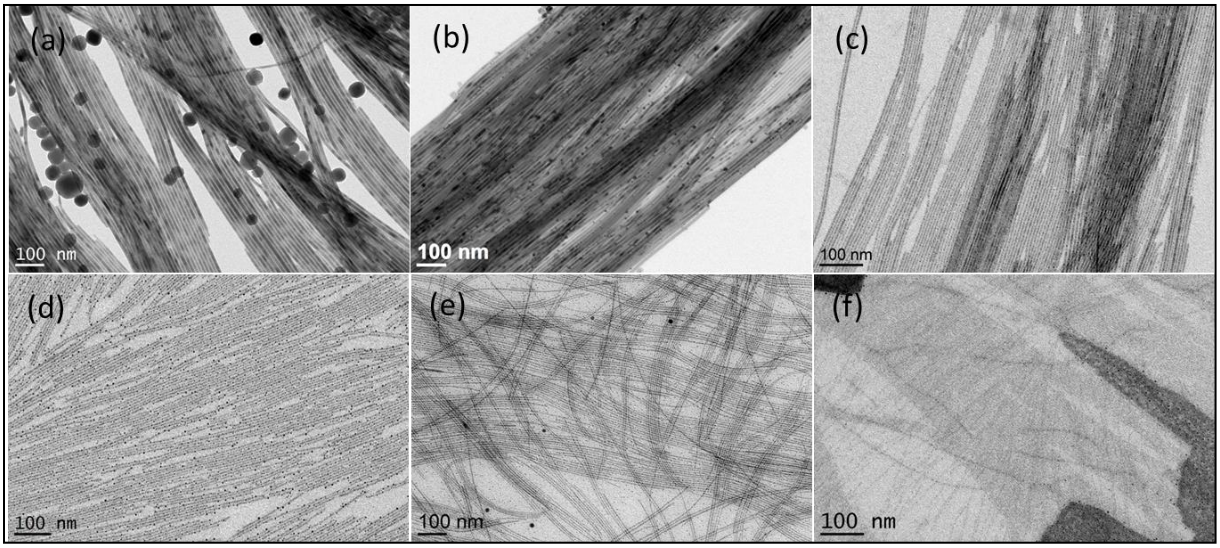

Figure S6. BF-TEM images of NWs prepared with different ratios of short acids to amine ligands. The widths of the wires are: (A) 20 nm, (B) 10 nm, (c) 5.1 nm, (d) 4.1 nm, (e) 3.4 nm, (f) 2.8 nm (the latter NWs were not stable over time). See Table S1 for synthesis details.

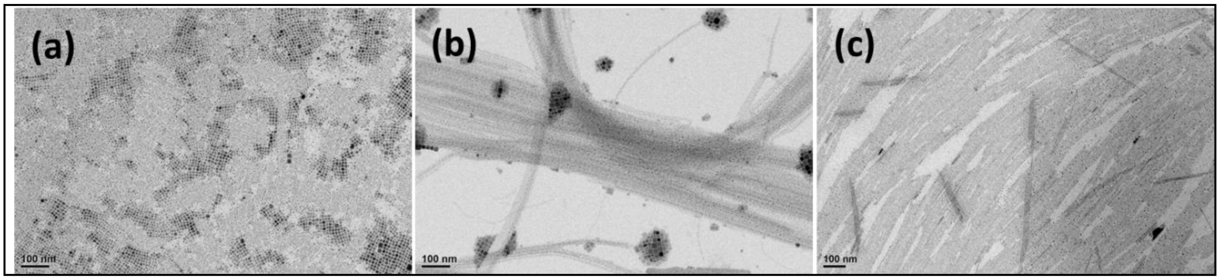

Figure S7. BF-TEM images of NWs prepared at different temperatures: (A) 165˚C, (B) 120˚C, and (c) 65˚C. Reaction time: 50 min. Reaction conditions: 0.069g $PbBr_2$, 8 mL ODE, 500µL OlAm, 500µL OctAm, and 50µL of HexAc.

The 10 nm NW image in Figure 2(a) of the main manuscript shows additional information, which is investigated in Figure S9. As noticed from Figure S9(a), the spacing between 10 nm NWs is only few nm, and some of the neighboring NWs (Figure S9 (b, c)) merge into one single wire. The sizes of the individual NWs in (a) are all labelled, and there are two sets of sizes, clearly indicating the rectangular cross section of this NW sample, with width of 9.5 nm, and thickness 7.7 nm.

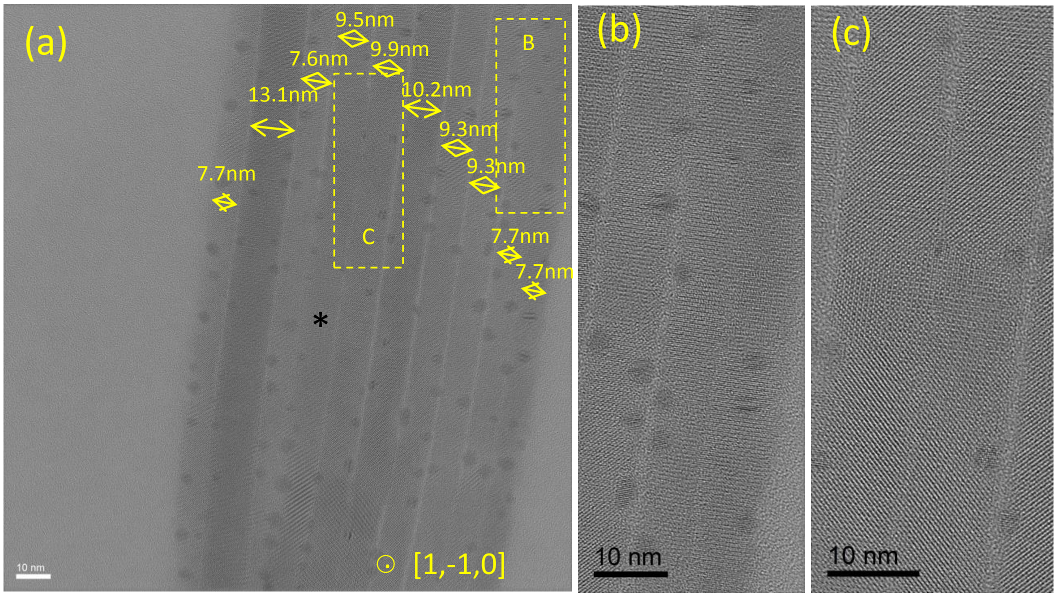

Figure S8: HRTEM image of 10 nm NWs. (b, c) are the magnified view of region B and C labelled in (a), showing merging of the 10 nm NWs at some of the locations.

The SAED pattern in Figure S8 (b) was taken for 10 nm NWs without tilting the sample, while the patterns (d, f) were taken for 5.1 nm NWs, and 3.4 nm NWs by tilting the sample 20° around the sample holder axis, in order to enhance the contribution of planes parallel to the support film. The camera length was 30 cm for all three diffraction patterns. The azimuthal integration of the SAED patterns in Figure S8 (b, d, f) is compared with the powder XRD data for reference orthorhombic (ICSD 97851) and cubic phases (ICSD 29073) of $CsPbBr_3$. The 10 nm wires show distinctive peaks for orthorhombic phase, labelled by purple arrows in the panel. One weak peak unique for orthorhombic phase is shown for 5.1 nm wires, which indicates the orthorhombic phase is maintained despite the addition of acid in the synthesis. The peaks for the 3.4 nm wires are broad due to their low thickness, thus distinctive features for the orthorhombic phase cannot be appreciated. However, the phase of the 3.4 nm wires is likely to remain orthorhombic since the synthesis protocol is the same as 5.1 nm NWs, with the only difference being the amount of short chain acid added.

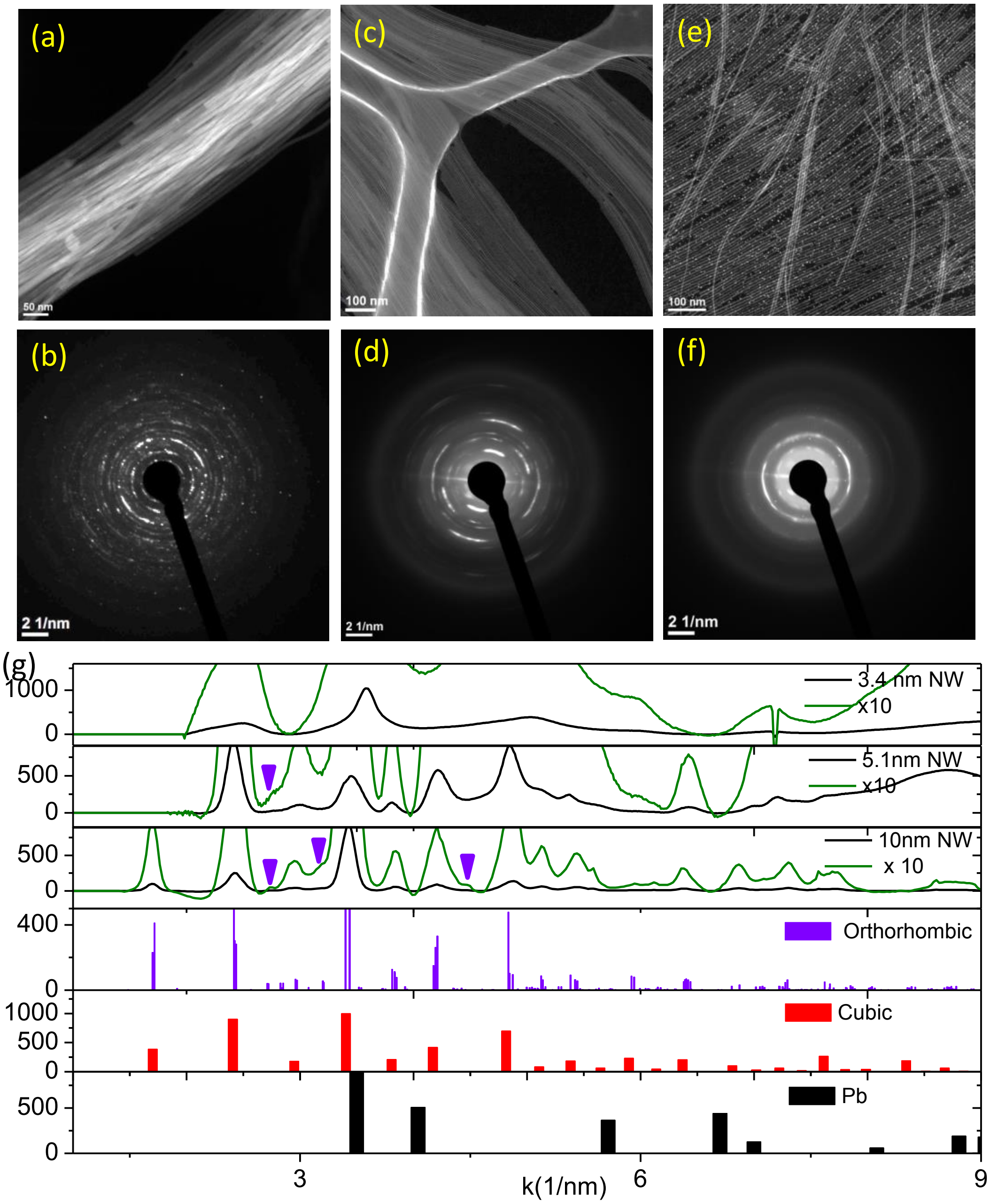

Figure S9. HAADF-STEM images and the SAED patterns of the 10 nm (a, b), 5.1 nm (c, d), and 3.4 nm (e, f) NWs respectively. The SAED pattern in (b) was taken without tilting the sample for 10 nm NWs, while the patterns in (d, f) taken with samples tilted 20° for both 5.1 nm and 3.4 nm NWs. (g) Azimuthal integration of the SAED patterns, and comparison with the powder XRD data for reference orthorhombic (ICSD 97851) and cubic phases (ICSD 29073) of $CsPbBr_3$, as well as Pb crystal (ICSD 96501).

Table S2 Summary of the parameters used for fitting the PL decays of the different NWs samples.

Sample	λ_{PL} (nm)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	$<\tau>$ (ns)
20±3	**524**	4952	6.9	5048	34.1	20.6
10±1	**517**	4685	2.4	5315	28.7	16.4
5.1±0.5	**496**	6904	3.4	3096	8.3	4.9
4.1±0.7	**481**	6249	1.7	3751	4.6	2.8
3.4±0.5	**473**	7382	1.6	2618	5.2	2.5

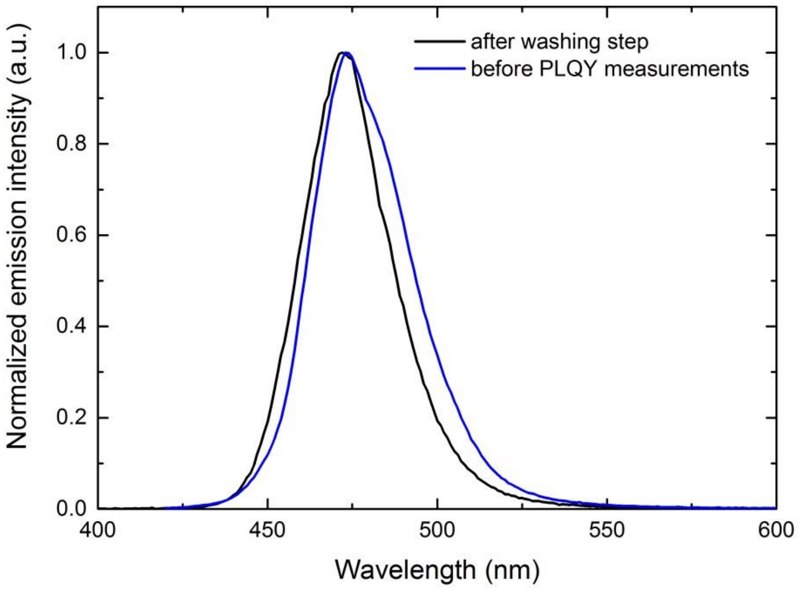

Figure S10: PL spectra of the 4.1 nm NWs sample in toluene solution, recorded directly after washing (black solid line) and then recorded again a few minutes later, just before performing PLQY and time-resolved measurements (blue solid line, within 15 minutes from the first spectrum).

Supplementary References:

(1) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites ($CsPbX_3$, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* 2015, 15, 3692