Electronic Supplementary Information for

A new route for the shape differentiation of cesium lead bromide perovskite nanocrystals with near-unity photoluminescence quantum yield

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Table S1. Summary of the experimental conditions and optical properties of perovskite NCs synthesized in the presence of oleylamine.

Sample	Cs/Pb	Br/Pb	PL peak (nm)	2D[a]	0D[b]	fwhm (meV)	PLQY (%)
NP1	1/4	3/1	513	no	no	92	23
NP2	1/4	4/1	511	yes	no	111	44
NP3	1/4	5/1	507	yes	no	108	14
NP4	1/4	6/1	508	yes	no	100	34
NP5	1/3	3/1	510	yes	no	136	67
NP6	**1/3**	**4/1**	**512**	**no**	**no**	**89**	**~100**
NP7	1/3	5/1	512	no	no	90	42
NP8	1/3	6/1	508	no	no	110	45
NP9	1/2	3/1	508	no	yes	130	39
NP10	1/2	4/1	510	no	no	130	65
NP11	1/2	5/1	512	no	no	90	81
NP12	1/2	6/1	507	yes	no	100	79
NP13	1/1	3/1	511	no	yes	104	12
NP14	1/1	4/1	511	no	yes	103	13
NP15	1/1	5/1	514	no	yes	86	87
NP16	1/1	6/1	513	no	yes	87	~100

[a]Intended as presence/absence of nanoplatelets, nanosheets or $[(RNH_3)_2PbBr_4]_n$ monolayers. [b]Presence/absence of the 0D phase (Cs_4PbBr_6). Conditions yielding near-unity PLQY are highlighted in bold.

Table S2. Summary of the experimental conditions and optical properties of perovskite NCs synthesized in the presence of decylamine.

Sample	Cs/Pb	Br/Pb	PL peak (nm)	2D[a]	0D[b]	fwhm (meV)	PLQY (%)
NP17	1/4	6/1	513	yes	no	89	33
NP18	1/3	6/1	513	yes	no	83	29
NP19	1/2	6/1	515	yes	no	95	44
NP20	**1/1**	**6/1**	**510**	**no**	**no**	**92**	**~100**

[a]Intended as presence/absence of nanoplatelets, nanosheets or $[(RNH_3)_2PbBr_4]_n$ monolayers. [b]Presence/absence of the 0D phase (Cs_4PbBr_6). Conditions yielding near-unity PLQY are highlighted in bold.

Table S3. Summary of the experimental conditions and optical properties of perovskite NCs synthesized in the presence of hexylamine.

Sample	Cs/Pb	Br/Pb	PL peak (nm)	2D[a]	0D[b]	fwhm (meV)	PLQY (%)
NP21	**1/4**	**6/1**	**–**	**no**	**yes**	**–**	**–**
NP22	**1/3**	**6/1**	**515**	**no**	**no**	**81**	**95**
NP23	1/2	6/1	516	no	yes	78	35
NP24	1/1	6/1	517	no	yes	86	4

[a]Intended as presence/absence of nanoplatelets, nanosheets or $[(RNH_3)_2PbBr_4]_n$ monolayers. [b]Presence/absence of the 0D phase (Cs_4PbBr_6). Conditions yielding near-unity PLQY are highlighted in bold.

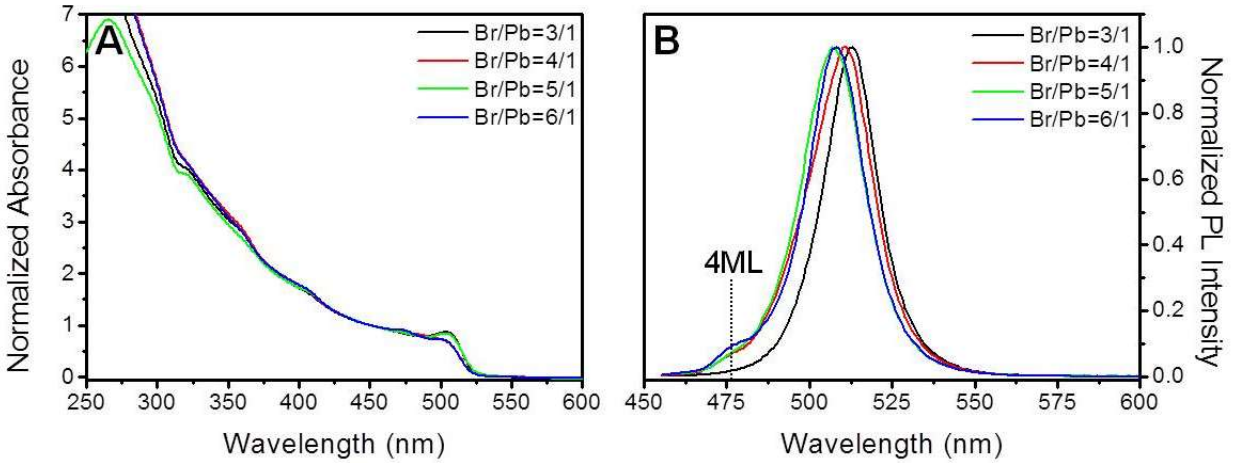

Figure S1. (A) Absorption spectra (normalized at λ = 450 nm, hexane) of the perovskite nanocrystals obtained using a Cs/Pb=1/4 at different Br/Pb ratios (**NP1-4** of Table S1). (B) Normalized emission spectra of the same nanocrystals (λ_{ex} = 450 nm, hexane), evidencing the emission of nanoplatelets (four-layer thickness, 4ML, λ_{em} = 476 nm) in the case of **NP2-4**.

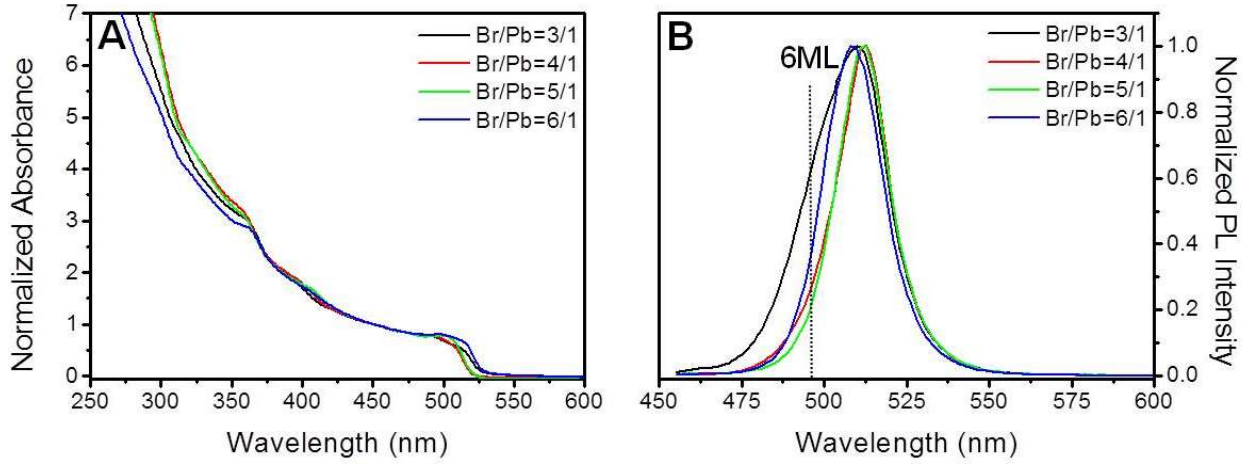

Figure S2. (A) Absorption spectra (normalized at λ = 450 nm, hexane) of the perovskite nanocrystals obtained by using a Cs/Pb=1/3 at different Br/Pb ratios (**NP5-8** of Table S1). (B) Normalized emission spectra of the same nanocrystals (λ_{ex} = 450 nm, hexane), evidencing the emission of nanoplatelets (six-layer thickness, 6ML, λ_{em} = 492 nm) in the case of **NP5**.

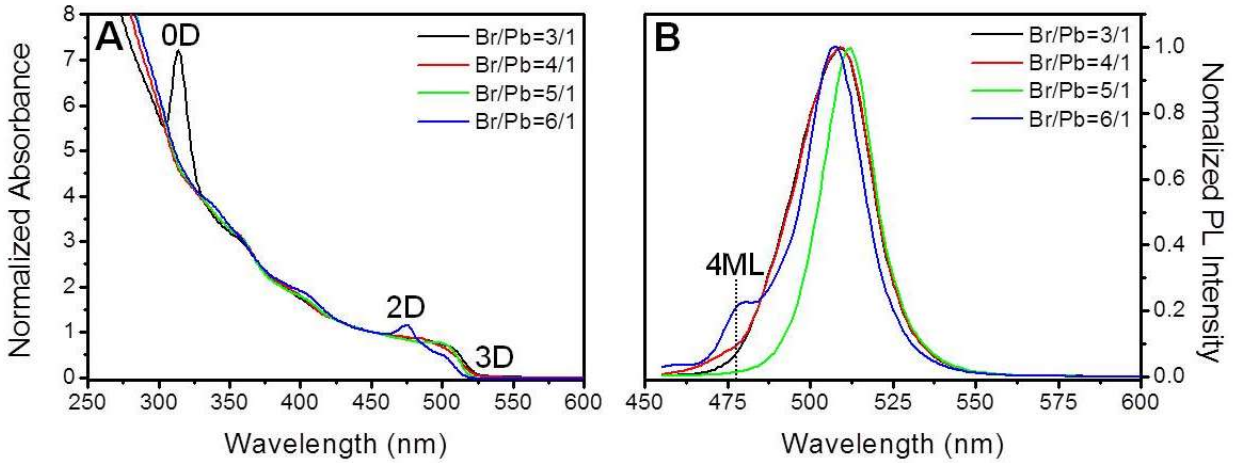

Figure S3. (A) Absorption spectra (normalized at λ = 450 nm, hexane) of the perovskite nanocrystals obtained by using a Cs/Pb=1/2 at different Br/Pb ratio (**NP9-12** of Table S1), evidencing the formation of 0D phases (λ_{abs} = 314 nm) in the case of **NP9** as well as of 2D phases (λ_{abs} = 487 nm) in the case of **NP12**. (B) Normalized emission spectra of the same nanocrystals (λ_{ex} = 450 nm, hexane), evidencing the emission of nanoplatelets (four-layer thickness, 4ML, λ_{em} = 478 nm) in the case of **NP12**.

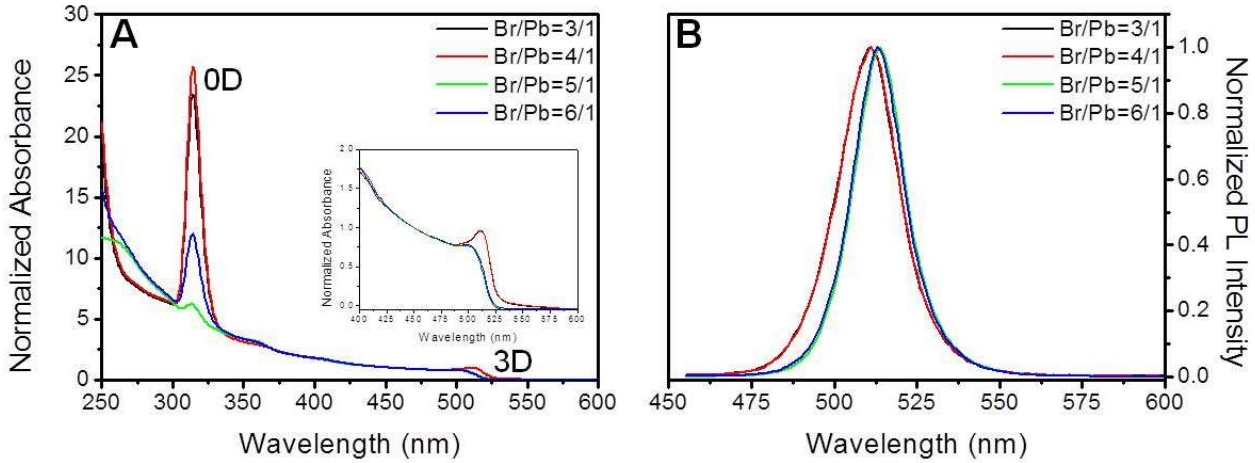

Figure S4. (A) Absorption spectra (normalized at λ = 450 nm, hexane) of the perovskite nanocrystals obtained by using a Cs/Pb=1/1 at different Br/Pb ratios (**NP13-16** of Table S1), evidencing the formation of 0D phases (λ_{abs} = 314 nm). Inset: excitonic peaks of 3D phases present in the same sample. (B) Normalized emission spectra of the same nanocrystals (λ_{ex} = 450 nm, hexane).

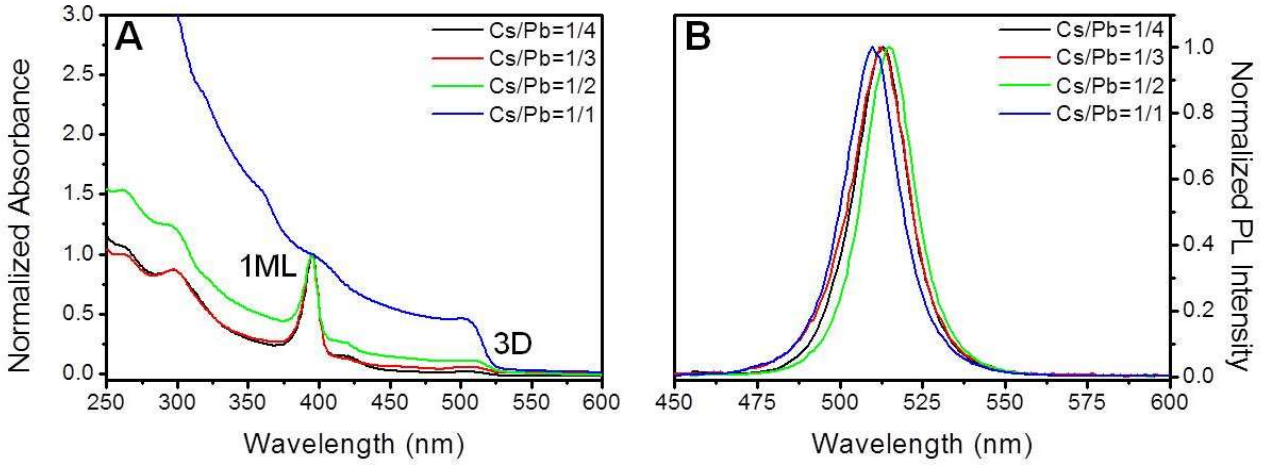

Figure S5. (A) Absorption spectra (normalized at λ = 395 nm, hexane) of the perovskite nanocrystals obtained by using a Br/Pb=6/1 at different Cs/Pb molar ratios (**NP17-20** of Table S2), evidencing the presence of $[(RNH_3)_2PbBr_4]_n$ monolayers (where R = $C_{10}H_{21}$, 1ML, λ_{abs} = 395 nm). (B) Normalized emission spectra of the same nanocrystals (λ_{ex} = 450 nm, hexane).

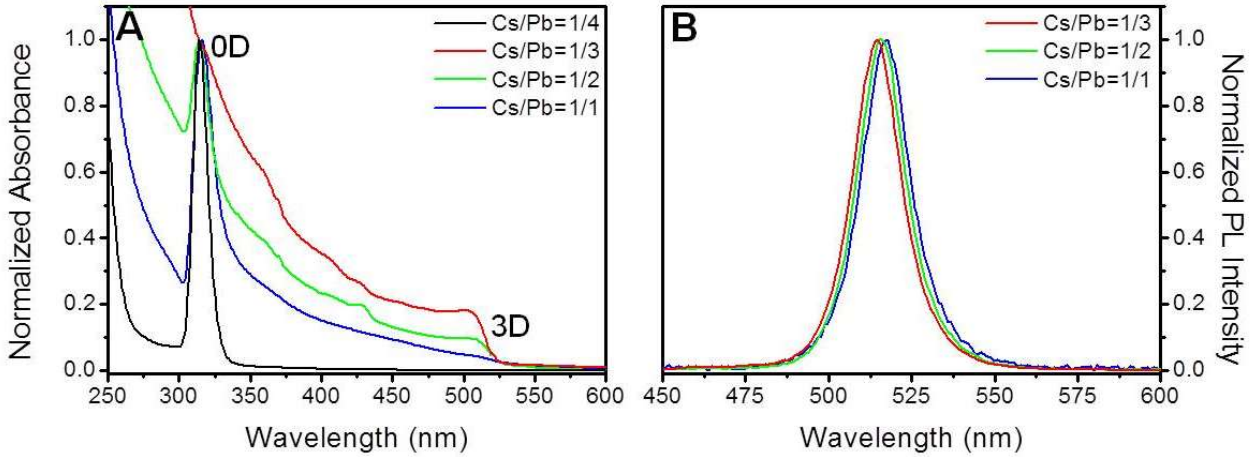

Figure S6. (A) Absorption spectra (normalized at λ = 314 nm, hexane) of the perovskite nanocrystals obtained by using a Br/Pb=6/1 at different Cs/Pb molar ratio (**NP21-24** of Table S3), evidencing the absence of 0D phases (λ_{abs} = 314 nm) only in the case of **NP22**. (B) Normalized emission spectra of **NP22-24** (λ_{ex} = 450 nm, hexane), while **NP21** is not emissive.

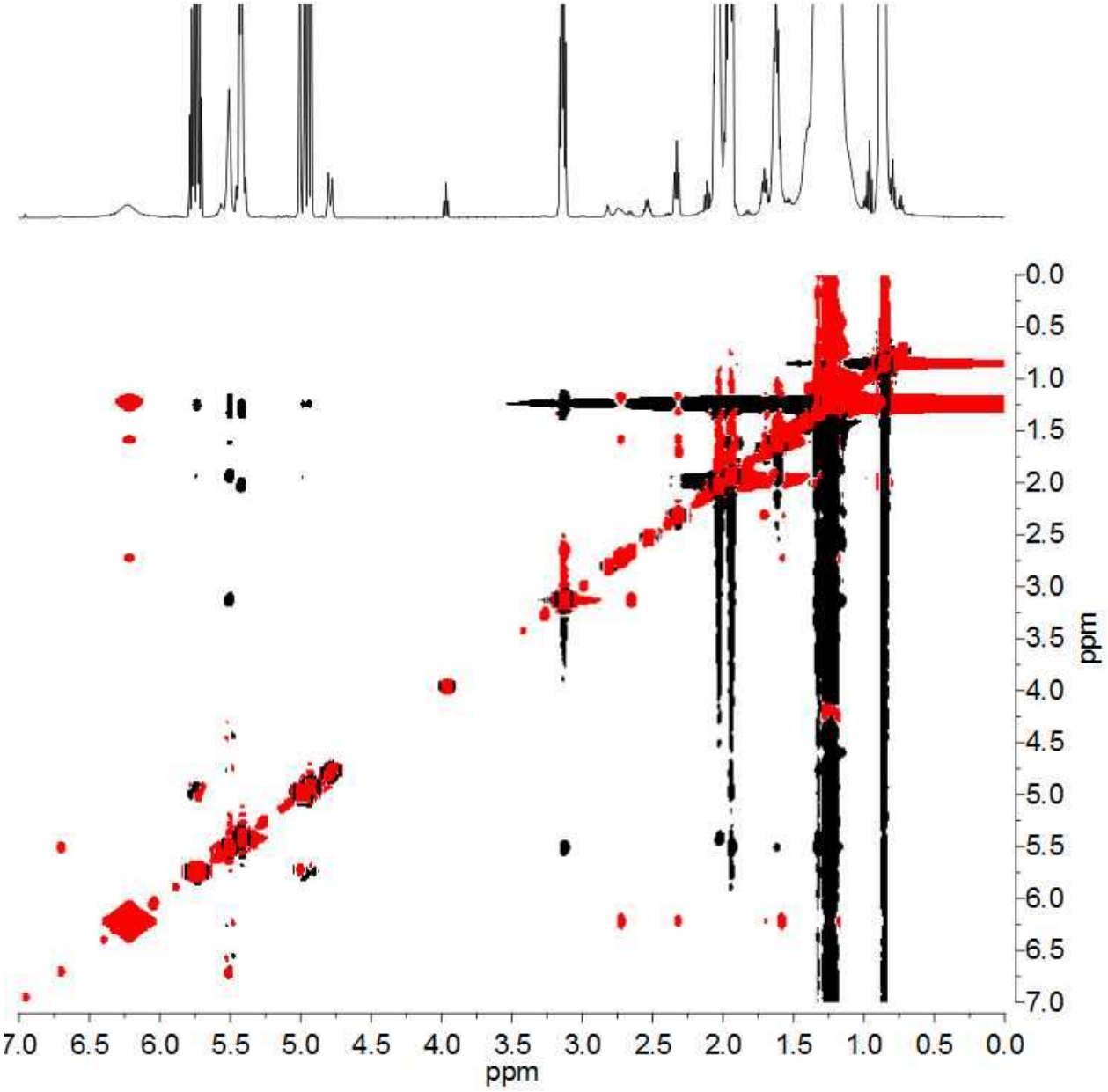

Figure S7. NOESY spectrum of **NP20** recorded in C_6D_6 . Negative (red) cross-peaks confirm passivation of the NC surface of decylamine (δ = 2.7 ppm) and oleic acid (δ = 2.3 ppm).

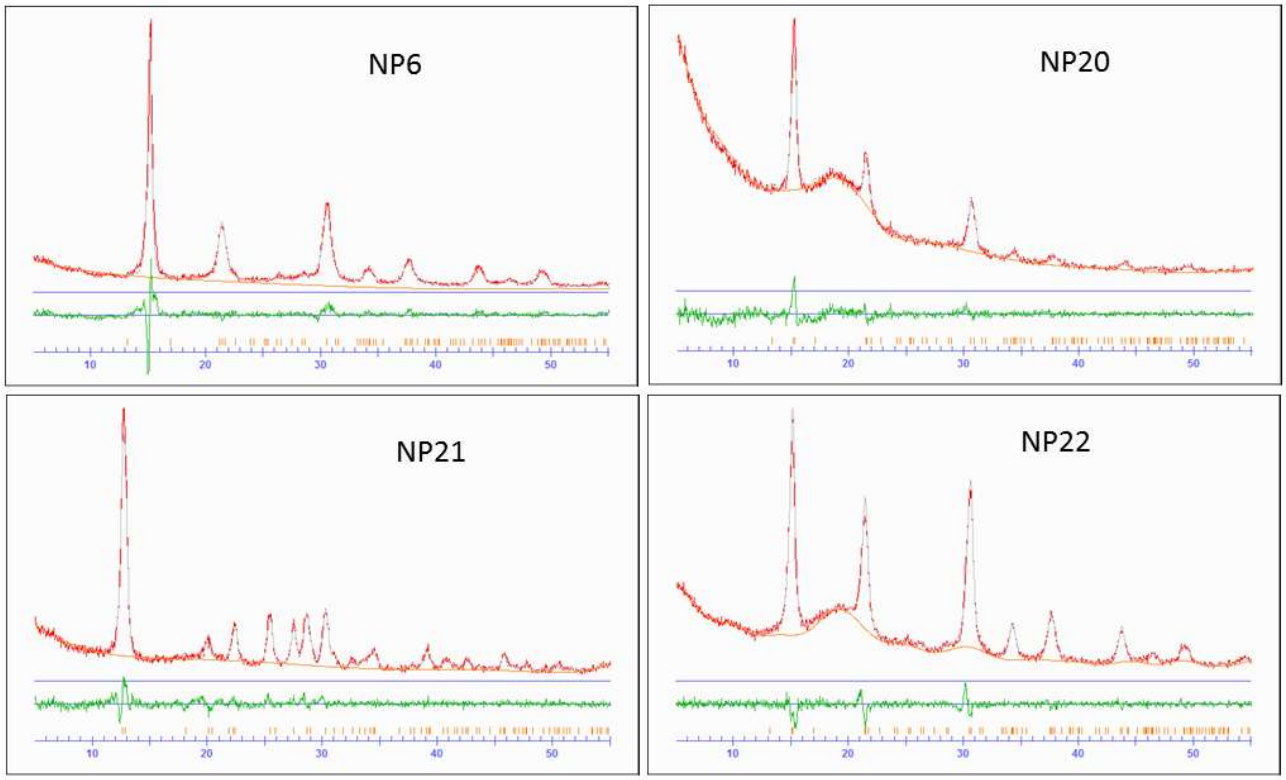

Figure S8. XRD (detector scan, with 5° incidence angle) experimental (red) and calculated (grey) patterns of $CsPbBr_3$ (ICSD n. 97851) for **NP6**, **NP20**, **NP22** samples, and Cs_4PbBr_6 (ICSD n. 25124) for sample **NP21**. The background (orange trace) and difference (green trace) profiles are also reported. The reference markers for the expected crystalline phase with the refined unit cell returned by the fit (orange bars) are reported at the bottom of each graph.

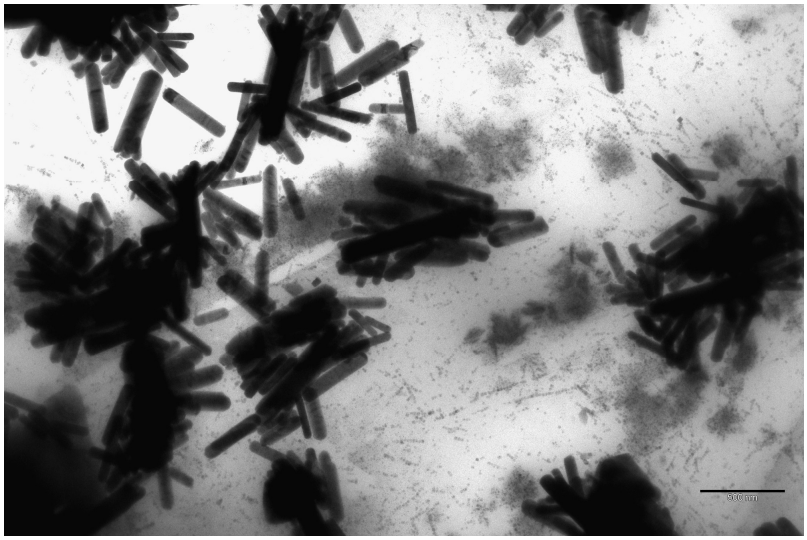

Figure S9. TEM image of **NP19**.

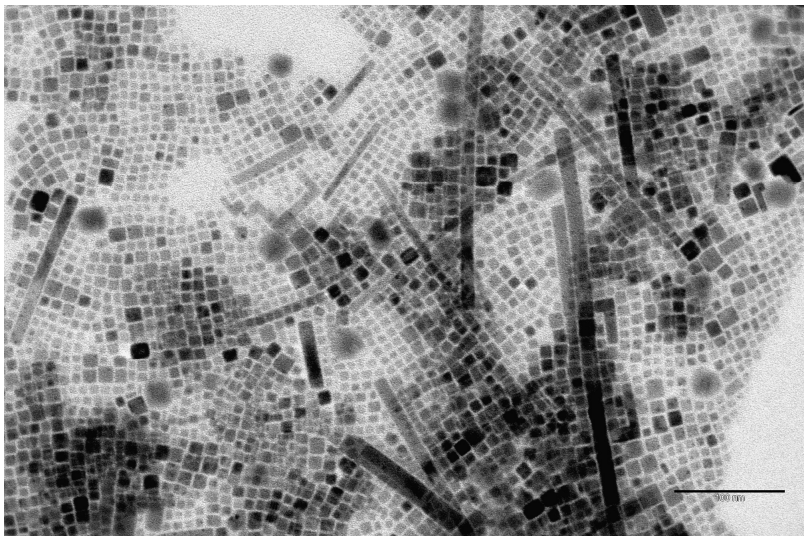

Figure S10. TEM image of **NP8**.