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Supplementary Information

Simple and Sustainable Synthesis of Perovskite-based Optoelectronic Material: $CsPbBr_3$ Nanocrystals via Laser Ablation in Alcohol

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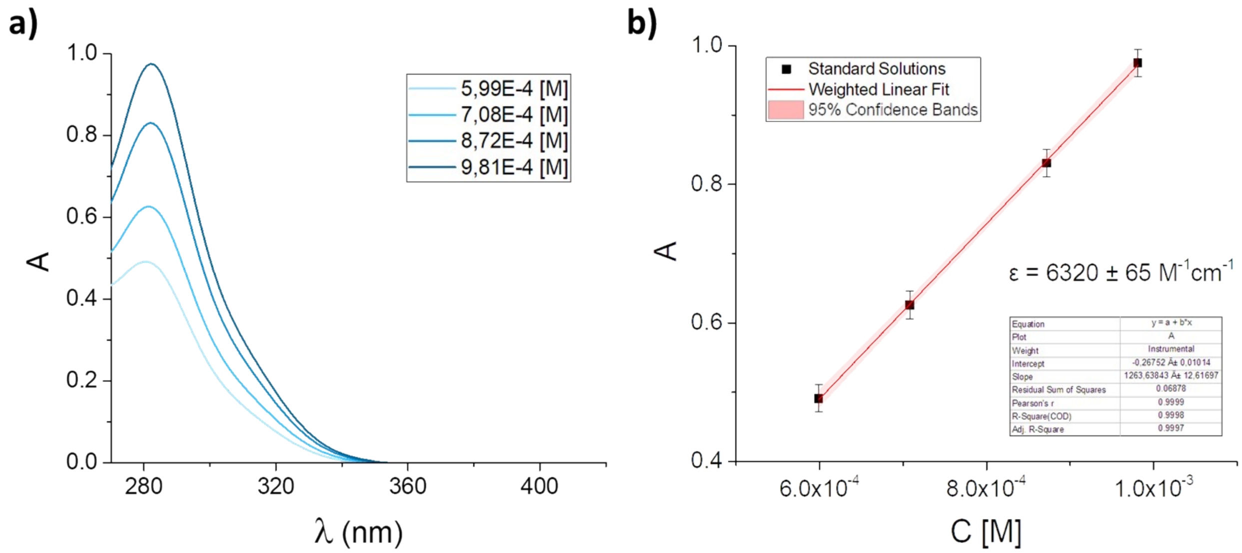

Figure S1. Evaluation of $PbBr_2$ molar extinction coefficient (ε_{PbBr2}). a) UV-Vis spectra of standard solutions prepared by dissolving $PbBr_2$ powders in N,N-dimethylformamide (DMF). b) Weighted linear fit made by evaluating the Abs peak at 282 nm as a function of concentration. By the Lambert-Beer law, ε_{PbBr2} is proportional to the angular coefficient of the calibration line. The concentration of $PbBr_2$ NCs colloidal solutions was determined by centrifugating the solutions for 15 min at 30000 RCF, digesting the precipitate in DMF and then evaluating the Abs peak at 282 nm.[1]

	SAFETY & HEALTH			INK PROCESSABILITY			INTERACTION w. PEROVSKITE			
SOLVENT	BP (ºC)	FP (ºC)	TLV (ppm)	η (mPa·s, 25°C)	P_V (kPa, 25°C)	σ (dyn/cm, 20°C)	Relative polarity	ε (20°C)	D_N (kcal/mol)	USED IN THIS WORK
Acetonitrile	82	6	20	0.36	11.83	29.1	0.460	38.0	14.1	
γ-Butyrolactone	204	98	20	1.75	0.06	44.6	0.420	41.0	17.8	
N,N-Dimethylformammide	153	58	10	0.79	0.52	36.4	0.386	36.1	26.6	
N,N-Dimethylpropyleneurea	246	120	20	3.41	0.20	41.0	0.350	36.1	33.0	
1,3-dimethyl-2-imidazolidinone	222	114	20	1.43	<0.1	41.0	0.352	37.6	27.7	
Dimethyl sulfoxide	189	95	50	1.98	0.08	43.5	0.444	45.0	29.8	
N-metil-2-pirrolidone	202	91	20	1.65	0.05	40.7	0.355	32.8	27.3	
Anisole	154	43	10	0.79	0.47	35.0	0.198	4.3	9.0	
Chlorobenzene	132	23	10	0.81	1.60	33.5	0.188	5.6	10.0	
Chloroform	61	/	10	0.54	26.27	27.2	0.259	4.8	4.0	
Ethyl acetate	77	- 4	400	0.43	12.43	23.8	0.228	6.0	17.1	
Butyl acetate	126	22	200	0.74	1.53	25.1	0.178	5.1	15.0	
Diethyl ether	35	- 45	400	0.22	70.92	17.0	0.120	4.3	19.2	
Toluene	111	4	20	1.17	3.79	28.4	0.099	2.4	0.1	
Methanol	65	12	200	0.54	16.93	22.5	0.762	32.6	19.0	x
Ethanol	78	13	1000	1.07	7.91	22.4	0.654	24.5	19.2	x
Isopropanol	82	12	400	2.04	6.05	21.8	0.546	19.9	21.1	x
tert-Butanol	82	11	100	3.77	5.43	20.7	0.389	10.9	21.9	x
tert-Pentanol	102	20	200	3.79	2.22	23.6	0.318	5.8	>22	x
Triethylcarbinol	143	38	100	>3.85	0.24	26.9	0.290	3.2	>23	x
Water	100	/	/	0.89	3.17	72.8	1.000	81.0	33.0	

Figure S2. Solvent evaluation based on environmental, health and safety (EHS) guidelines reported in literature.[2,3] The table reports the main physicochemical properties of commonly used perovskite solvents (red) and antisolvents (blue), as well as those of alcohols used in this work (green). Solvent properties were classified based on their impact on safety and health, ink processability and their interaction with metal halide perovskite materials (boiling point BP, flash point FP, threshold limit value TLV,[4,5] viscosity η, vapor pressure P_V, surface tension σ, dielectric constant ε, donor number D_N [6,7]). Ranges of values were reported when no reference parameters have been identified in the literature

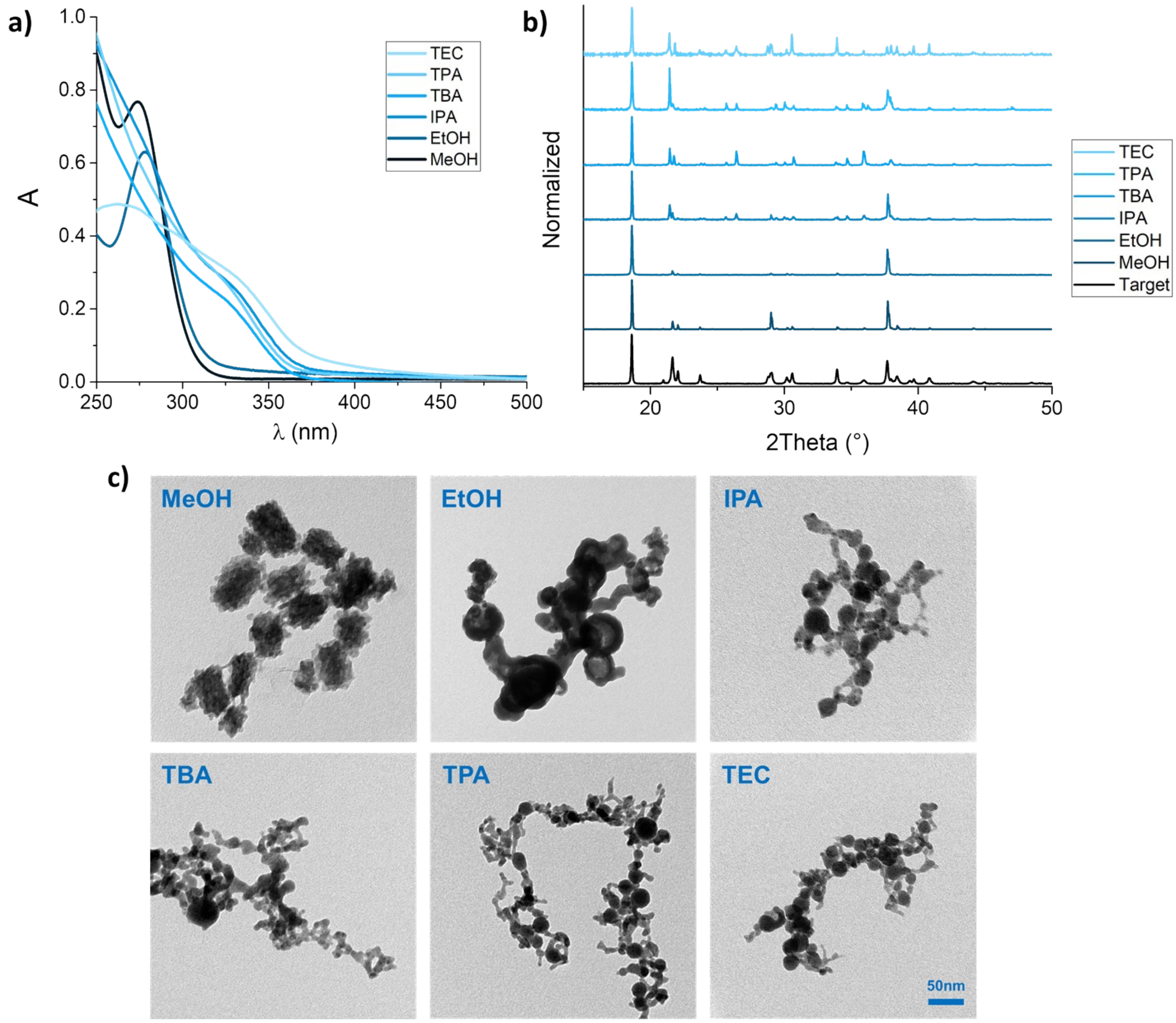

Figure S3. Optical and morphological characterization of $PbBr_2$ NCs precursor solutions synthesized by LASiS in alcohols. a) The typical lead bromide absorption edge at 350 nm can be observed in UV-Vis spectra,[8] while peaks around 275 nm in MeOH and EtOH spectra were attributed to bromo-plumbate complexes in solution.[1] b) The different relative intensities of reflections in XRD patterns can be ascribed to preferential orientation of the NCs onto the substrate and/or to different NCs morphologies, as noticed in c) by TEM images.

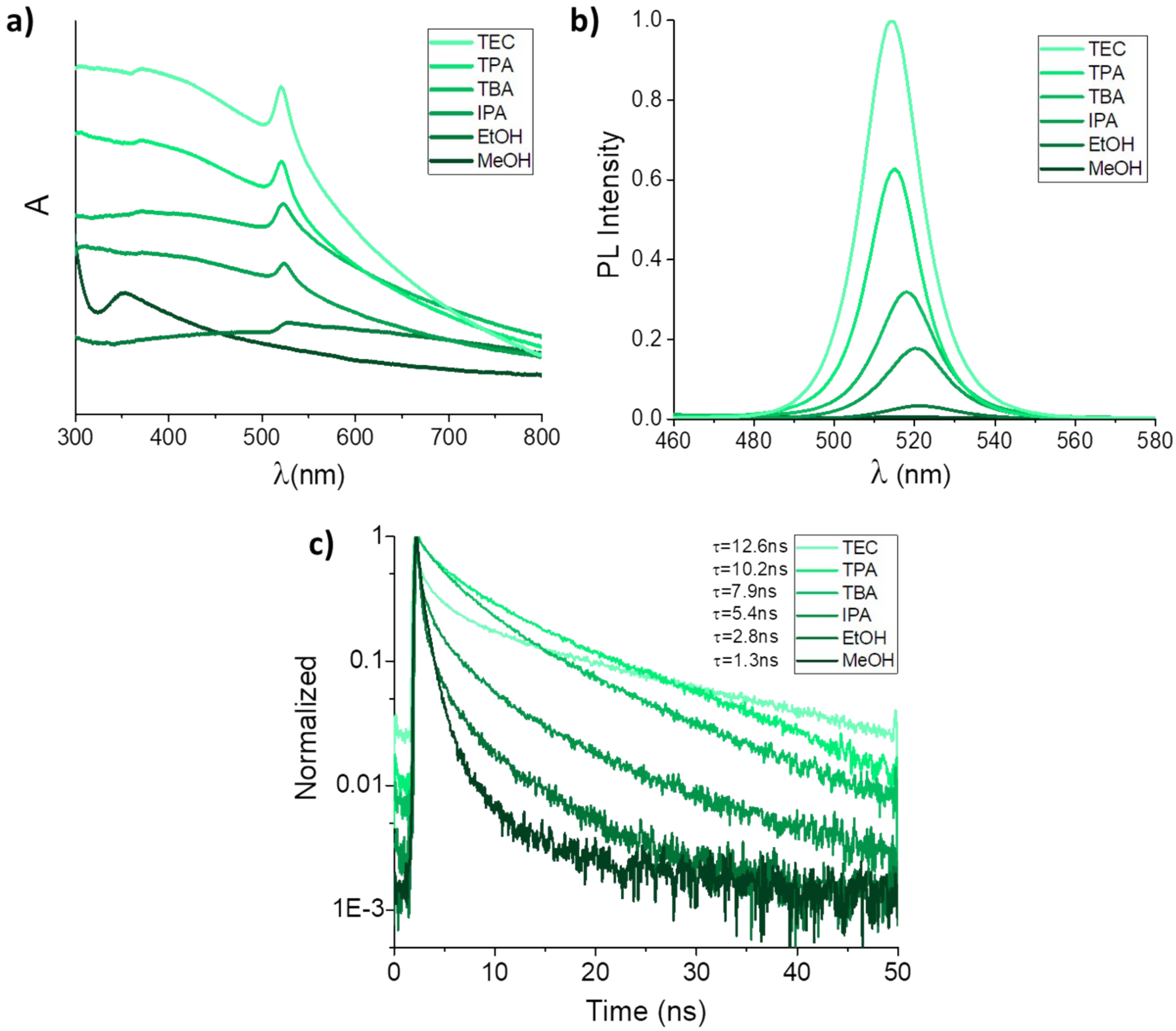

Figure S4. a) UV-Vis spectra, b) steady-state PL measurements, and c) time-resolved PL decays of $CsPbBr_3$ NCs synthesized by 2-step conversion in different alcohols. PL profiles are normalized to the intensity of the respective absorption peak. The intensity-averaged lifetimes were estimated by three-exponential fit.[9,10]

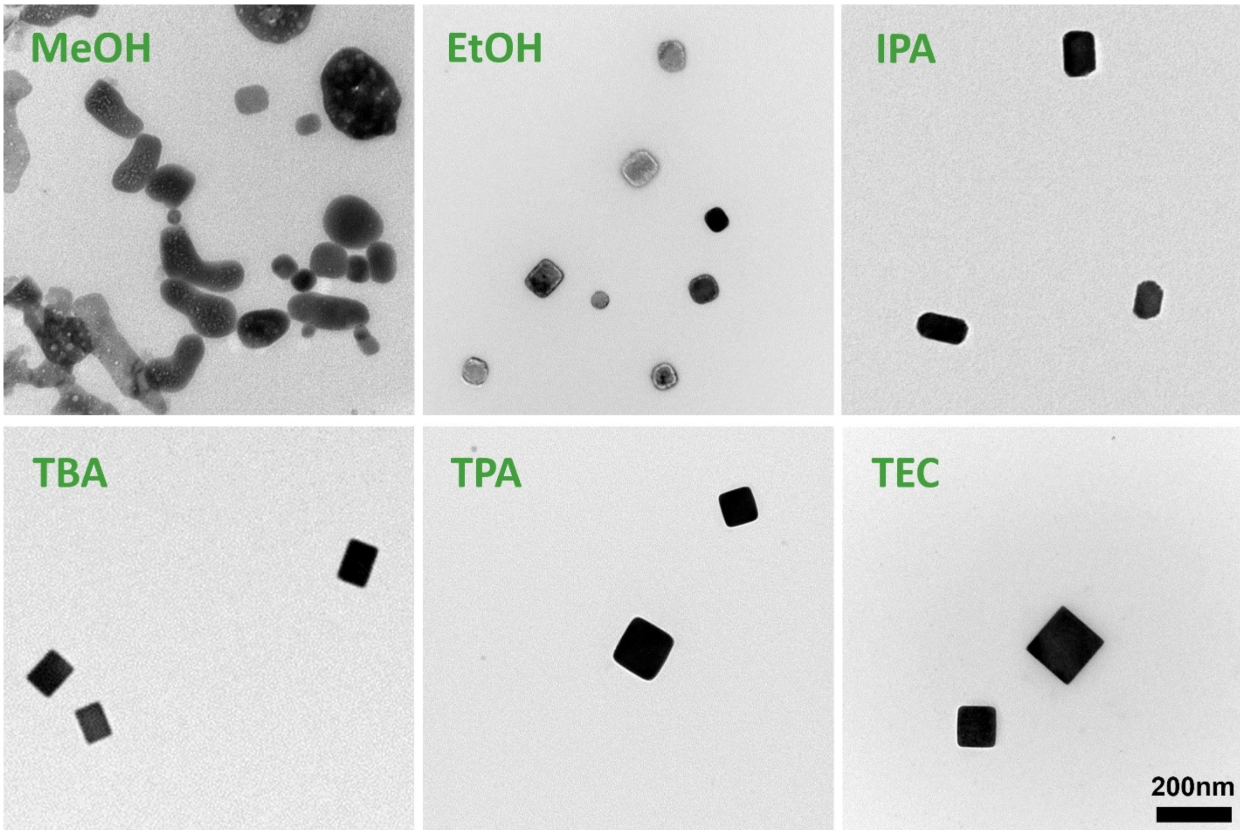

Figure S5. TEM images of $CsPbBr_3$ NCs synthesized by 2-step conversion in different alcohols. Nanoparticles with more amorphous shapes are observed in alcohols with higher polarity and dielectric constants (i.e. methanol and ethanol), while cubic-shaped nanocrystals are obtained in alcohols with a more antisolvent-like behavior (i.e. tert-pentanol and triethyl carbinol).

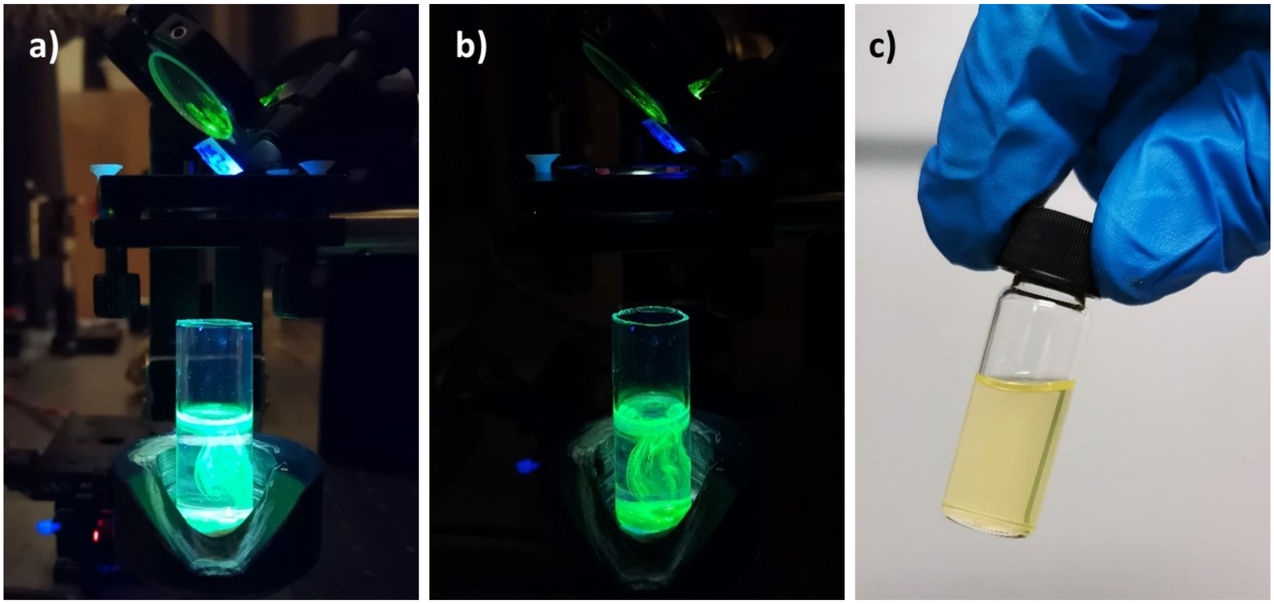

Figure S6. 1-step in-situ synthesis of $CsPbBr_3$ NCs during laser ablation in triethyl carbinol a) under low-intensity visible light and b) in the dark. c) $CsPbBr_3$ NCs colloidal solution.

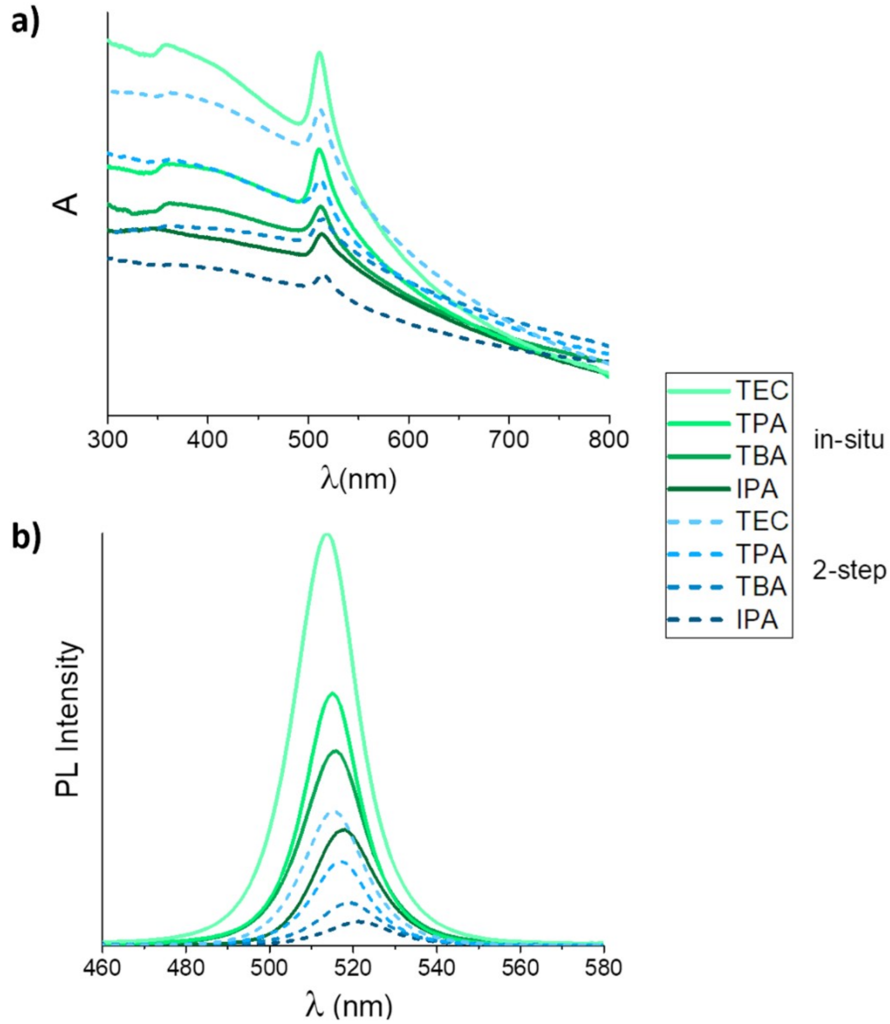

Figure S7. Comparison of a) UV-Vis spectra and b) steady-state PL emissions of $CsPbBr_3$ NCs synthesized by 2-step conversion (dashed lines) and 1-step in-situ (solid lines) synthesis in different alcohols. PL profiles are normalized to the intensity of the respective absorption peak.

SOLVENT	Z Pot (2-step)	Z Pot (in-situ)
IPA	11.8 mV	16.3 mV
TBA	13.5 mV	15.9 mV
TPA	13.2 mV	17.7 mV
TEC	14.1 mV	18.2 mV

Figure S8. Table reporting the z-potential values obtained for $CsPbBr_3$ NCs colloidal solutions by the 2-step conversion and the 1-step (in-situ) synthesis protocols. All measurements were performed with a Malvern Instrument Zetasizer Nano operating with a 633 nm He−Ne laser, placing the solutions in a sonication bath for 5 minutes before each measurement.

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