Supporting information

Sr-Doping Engineering for Enabling Long-Term Stable FAPb_{1-x}Sr_xI₃ Quantum Dots with 100% Photoluminescence Quantum Yield

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Experimental section

Synthesis of FAPb_{1-x}Sr_xI₃ perovskite quantum dots (PQDs) by hot-injection

The hot-injection synthesis of $FAPb_{1-x}Sr_xI_3$ perovskite quantum dots (PQDs) was carried out by mixing formamidinium oleate (FA-oleate), lead halide and strontium halide precursor solutions stoichiometrically. Reagents were used as purchased without additional purification processes. For preparing the FA-oleate solution, 0.521 g FA-acetate (F15803, 99 %, Sigma-Aldrich) and 10 mL oleic acid (OA, 364525, 90 %, Sigma-Aldrich) were mixed into a 50 mL-three neck flask under vacuum at 60 °C for 30 min. Then, the mixture was heated at 120 °C under a N₂-purge until FA-acetate was completely dissolved. The resultant solution was kept at 85 °C into a N₂ atmosphere ready for injection.

For synthesizing pure FAPbI₃ and FAPb_{1-x}Sr_xI₃ PQDs, 0.75 mmol PbI₂, (AB111058, 99.999 %, ABCR) and the corresponding PbI₂/SrI₂ (466336, anhydrous, 99.99 % Sigma-Aldrich) combinations to obtain nominal Sr-to-Pb molar ratios of x = 0.3, 0.5, 0.6 and 0.7 were mixed with 20 mL 1-octadecene (O806, 90 %, Sigma-Aldrich) into a 100 mL-three neck flask. The mixture was degasified under vigorous stirring at 120 °C for 1 h. Then 3 mL of each preheated OA and oleylamine (OLA, HT-OA100, 98 %, Sigma-Aldrich) was added to the flask, cooling down the temperature to reach 80 °C under N₂ flow. Simultaneously, 5 mL of preheated FA-oleate was rapidly injected, obtaining black FAPbI₃ and red-emitting FAPb_{1-x}Sr_xI₃ PQDs colloidal solutions. The flask was introduced into an ice/water bath for 5 s to quench the reaction mixture. For isolating process, the as-prepared PQDs were centrifugated at 4700 for 10 min. PQDs were recovered and then redispersed in hexane (CHROMASOLV, 34859, 99.7 %, Honeywell) to concentrate at 50 mg mL⁻¹ for further analysis.

Characterization of Sr-doping-induced morphology, structure, optical properties and chemical environment of the $FAPb_{1-x}Sr_xI_3$ PQDs

High-resolution transmission electron microscopy (HRTEM) images of PQDs were achieved by a field emission gun TECNAI G2 F20 microscope operated at 200 kV. The average particle size of PQDs were obtained from the TEM images with ImageJ software. X-ray diffraction (XRD) profiles of the PQDs solutions were obtained by using a D4 Endeavor diffractometer from Bruker-AXS, using a Cu Ka radiation source ($\lambda = 1.54056$ Å). UV-Vis absorption spectra of FAPb_{1-x}Sr_xI₃ perovskite quantum dots solutions were acquired by using a UV-Vis absorption spectrophotometer (Varian, Cary 300). The wavelength range for the measurements was 400-850 nm. Steady state- and time-resolved photoluminescence (PL) measurements were conducted through photoluminescence spectrophotometer (Fluorolog 3-11, Horiba). An excitation wavelength of 450 nm was used to perform the steady state PL. The concentration of the samples was fixed to 2 mgmL⁻¹ in hexane, using a quartz cuvette of 10 x 10 mm. Time-resolved PL measurements were performed at 405 nm pulsed laser (1 MHz frequency, NanoLED-405L, <100 ps of pulse width). The absolute photoluminescence quantum yield (PLQY) of the PQDs solutions was determined with a Hamamatsu PLQY Absolute QY Measurement System C9920-02, equipped with an integrating sphere, at an excitation wavelength of 400 nm. Here, absorbance was adjusted in a interval range around 0.6-0.9 to conduct the measurements, being these values suitable to achieve the maximum PLQY in the samples. Chemical composition and electronic state of PQDs were determined by X-ray Photoelectron Spectroscopy (XPS, ESCA-2R, Scienta-Omicron). Spectra were recorded using monochromatic Al K α = 1486.6 eV. The following sequence of spectra were recorded: survey spectra, C 1s, Pb 4f, I 3d, Sr 3p_{3/2}, I 3d, O 1s, N 1s, VB and C 1s again to verify the stability of the load compensation

in function of time. The survey and high-resolution spectra were recorded at a pass energy of 150 and 20 eV, respectively. Binding energy scale was referenced to adventitious carbon (284.8 eV). The data analysis was performed with the CasaXPS processing software (Casa software Ltd) and the quantitative analysis was made using sensitivity factors provided by the manufacturer.



Figure S1. Histograms for determining the average particle size of (a) FAPbI₃ and FAPb_{1-x}Sr_xI₃ perovskite quantum dots (PQDs) from colloidal solutions, with (b) 4 at. %, Sr (c) 7 at. % Sr, (d) 12 at. % Sr and (e) 6 at. % Sr. (f) UV-vis absorbance spectra of the FAPb_{1-x}Sr_xI₃ PQDs from colloidal solutions by varying the Sr fraction.

Perovskite sample	Absorption edge (nm)	Emission peak position (nm)	Band gap (eV)
FAPbI ₃	750	780	1.59
x = 0.3	743	772	1.61
x = 0.5	726	761	1.63
x = 0.6	712	742	1.67
x = 0.7	707	735	1.68

Table S1. Particle size and optical properties of FAPb_{1-x}Sr_xI₃ PQDs.



Figure S2. SAED measurements obtained for estimating the interplanar spacing and their corresponding diffraction planes of a) FAPbI₃ and FAPb_{1-x}Sr_xI₃ PQDs from colloidal solutions, with (b) 4 at. %, Sr (c) 7 at. % Sr, (d) 12 at. % Sr and (e) 6 at. % Sr by varying the Sr fraction.



Figure S3. Synthesis of a FAPb_{0.93}Sr_{0.07}I₃ PQDs, in (a) presence and (b) absence of the Sr fraction.



Figure S4. Low-wavelength (a) UV-Vis absorbance and (b) photoluminescence (PL) spectra of $FAPb_{1-x}Sr_xI_3$ PQDs from colloidal solutions by varying the Sr fraction.



Figure S5. (a) Images of the separated $FAPb_{1-x}Sr_xI_3$ PQDs colloidal solutions and their corresponding redispersed precipitates. Histograms of the typical lateral dimensions [(b,c) L=length, (b',c') W=width)], (d) UV-vis absorbance and (e) PL spectra of the (b,b') FAPb_{0.88}Sr_{0.12}I_3 and (c,c') FAPb_{0.94}Sr_{0.06}I_3 NPLs from the redispersed precipitates.



Figure S6. Determination of the periodic (*d*) spacing for $FAPb_{0.88}Sr_{0.12}I_3$ and $FAPb_{0.94}Sr_{0.06}I_3$ NPLs from the redispersed precipitates in hexane. First, the peak periodicity was estimated from the XRD patterns of each sample to be 2.04 and 2.25 °, respectively. Through the Bragg equation, *d* (defined as the distance between [PbI₆]⁴⁻ octahedra layers, separated by the alkylammonium capping ligand) was obtained to be 4.3 and 4.0 nm, respectively. Considering that the length of oleylammonium cation is ~ 2.8 nm,¹ the thickness of the FAPb_{0.88}Sr_{0.12}I₃ and FAPb_{0.94}Sr_{0.06}I₃ NPLs was determined to be 1.5 and 1.2 nm, respectively. Accordingly, the samples exhibit a Ruddlesden-popper (OLAm)₂FAPb₂I₇ perovskite phase, n =2.



Figure S7. (a,b) XPS survey spectra and (c,d) high resolution XPS Sr $3p_{3/2}$ spectra of the FAPb_{1-x}Sr_xI₃ PQDs (a,c) colloidal solutions and their corresponding (b,d) redispersed precipitates.



Figure S8. High resolution XPS I 3d spectra of the (a) $FAPb_{1-x}Sr_xI_3$ PQDs colloidal solutions and (b) their corresponding redispersed precipitates.

Effect of the Sr-doping-induced Pb deficiency on the growth of perovskite quantum dots and nanoplatelets

The mixture of 2D/3D perovskites is enabled when the Pb deficiency into the mixture reaction is excessive to be compensated by Sr. Thus, the absence of Pb alters the relation between the quantity of precursors taking place into the reaction to produce PQDs and NPLs. This fact could explain the shift in the Pb 4f doublets from NPLs to lower BEs, as a response from a different perovskite structure than 3D. The precursor distribution can be detailed, for instance, in Table S4, where the OLAm/surface ratios of PQDs and NPLs are compared. Clearly, the OLAm/surface ratio of PQDs is lower than that of NPLs, as their particle size is smaller (assuming that 100 % capping ligand is available to cover the PQDs surface). Because of this fact, larger amount of OLAm cations will be available to participate in the NPLs growth (higher OLAm/surface ratio). Furthermore, the co-existence of PQDs and NPLs promotes the decrease of their respective I/Pb²⁺ atomic ratio (See Tables S2 and S3). This fact strongly suggests that the iodide fraction into the mixture reaction is also distributed to mediate the growth of PQDs and NPLs, generating

iodide defects, and in turn, an excessive density of Pb vacancies. This fact can be the main reason to decrease the amount of substitutional Sr^{2+} into PQDs, decreasing the available iodide to passivate the Schottky defects. In this line, the Pb⁰/(Sr+Pb_{total}) ratio obtained for PQDs (Table S2) and Pb⁰/Pb_{total} ratio estimated from NPLs (Table S3) start to rise simultaneously. These results validate that such a distribution does not satisfy the chemical composition of the materials, favoring the creation of defective structures.

Perovskite sample	Sr ²⁺ (at.%)	I (at.%)	Pb ²⁺ (at.%)	Pb ⁰ (at.%)	Pb deficiency 1-[(Pb ²⁺ + Sr ²⁺ /25.1) *100 (%)	I/Pb ²⁺ atomic ratio	$Pb^{0/}$ (Sr ²⁺ + Pb _{total})
FAPbI ₃	-	72.73	25.10	2.17	0	2.90	0.08
x = 0.3	-	76.18	21.56	2.26	14	3.53	0.09
x = 0.5	5.66	73.65	18.72	1.96	3	3.93	0.07
x = 0.6	4.44	73.41	19.16	2.99	6	3.83	0.11
x = 0.7	-	67.20	21.68	11.12	14	3.10	0.34

Table S2. Surface chemical atomic composition of FAPb_{1-x}Sr_xI₃ PQDs colloidal solutions.

Table S3. Surface chemical atomic composition of FAPb_{1-x}Sr_xI₃ redispersed solids

Perovskite sample	I (at.%)	Pb ²⁺ (at.%)	Pb ⁰ (at.%)	I/Pb ²⁺ atomic ratio	Pb ⁰ /(Pb _{total})
x = 0.3	68.21	29.97	1.84	2.28	0.06
x = 0.5	72.54	25.73	1.73	2.82	0.06
x = 0.6 NPLs	74.28	23.56	2.17	3.15	0.08
x = 0.7 NPLs	73.10	24.44	2.45	2.99	0.09

Table S4. Summary of the calculation of OLAm/surface ratios for $FAPb_{1-x}Sr_xI_3$ PQDs from colloidal solutions and NPLs from redispersed precipitates. Considering the corresponding size of the FAPb_{1-x}Sr_xI₃ PQDs, L, reported in Figures 1, S1, and the cubic shape, see Figure 1, the surface-to-volume (S-V) ratio is calculated as $6L^2/L^3$. In the case of NPLs with characteristic dimensions presented in Figures 1 and 2 (length, L; width, W and thickness, H), we estimated their S-V as [2(LW+LH+WH)]/[LWH]. The total mass of QDs and NPLs obtained after the synthesis is limited by the amount of FA-oleate (5 mmol). Consequently, 5 mmol of material are produced after the synthesis. Attending that the Molecular Weight (MW) of FAPbI₃ and (OLAm)₂FAPb₂I₇ (632.97 and 1884.76 g/mol, respectively) and the corresponding density of the cubic and Ruddlesden-popper perovskite phase (n=2) (4.10 and 3.16 g/cm⁻³, respectively),². ³ the total volume is obtained. Then, from the surface/volume ratio, the total surface that has to be covered by capping ligand is determined. Finally, given the number of mmol of OLA added during the PQDs synthesis and the total surface, we obtained the OLAm/surface ratio.

Derovalvita	Surface/volume	Total	Total	OLAm*/Surface
reiovskite	ratio	volume	surface	ratio
sample	$(10^{6} \cdot \text{cm}^{-1})$	(cm^3)	$(10^{6} \cdot cm^{2})$	$(10^{-6} \cdot \text{mmol} \cdot \text{cm}^{-2})$
FAPbI ₃	4.00	0.77	3.08	2.96
x = 0.3	5.26	0.77	4.05	2.25
x = 0.5	6.06	0.77	4.66	1.96
x = 0.6	6.67	0.77	5.14	1.77
x = 0.7	7.14	0.77	5.49	1.66
x = 0.6 NPLs	14.29	2.98	42.58	21.41
x = 0.7 NPLs	18.73	2.98	55.81	16.34

*Total number of moles of OLA = OLAm (mmol): 9.12



Figure S9. (a) PLQY and (b) time-resolved PL decay measurements for $FAPb_{1-x}Sr_xI_3$ PQDs colloidal solutions.

Table S5. Determination of radiative and non-radiative recombination decay rate constants, k_r and k_{nr} , respectively by fitting the time-resolved PL decays of the FAPb_{1-x}Sr_xI₃ PQDs colloidal solutions (Figure S9b) to a bi-exponential function: $y = y_0 + A_1 e^{-x/\tau 1} + A_2 e^{-x/\tau 2}$. The values of τ_{avg} , k_r and k_{nr} are obtained from their respective definitions: $\tau_{avg} = (\Sigma A_i \tau_i^2 / \Sigma A_i \tau_i)$, $4 \tau_{avg} = 1/(k_r + k_{nr})$ and $k_r = (PLQY/\tau_{avg})$, 4.5. PLQY values were used in the 0-1 range.

Perovskite	A_1	τ_1	A_2	τ_2	DI OV	$ au_{ m avg}$	k _r	k _{nr}	1c /1c
sample	(%)	(ns)	(%)	(ns)	FLQI	(ns)	(10^7s^{-1})	(10^7 s^{-1})	$\mathbf{K}_{nr}/\mathbf{K}_{r}$
FAPbI ₃	25.2	42.4	74.8	152.6	0.959	124.8	0.76	0.0329	0.043
x = 0.3	34.1	36.0	65.9	126.2	0.987	95.4	1.03	0.0136	0.013
x = 0.5	38.3	19.2	61.7	71.6	0.999	51.5	1.94	0.00194	0.001
x = 0.6	41.8	45.9	58.2	15.2	0.876	28.0	3.13	0.442	0.142
x = 0.7	32.6	35.1	67.4	13.8	0.630	20.7	3.04	1.78	0.587

Nominal	Calculated				Time (d	ays)		
composition	composition/ doping, EDS	0	1	4	7	11	15	30
FAPbI ₃	FAPbI ₃	0.959	0.805	0.480	0.207	0.081	0.016	0.000 (no detected)
x = 0.3	x = 0.04	0.987	0.909	0.695	0.647	0.640	0.674	0.609
x = 0.5	x = 0.07	0.999	0.982	0.719	0.763	0.755	0.757*	0.776
x = 0.6	x = 0.12	0.876	0.864	0.521	0.541	0.582	0.571	0.480
x = 0.7	x = 0.06	0.630	0.492	0.173	0.183	0.167	0.134	0.021

Table S6. Absolute PLQY values obtained for $FAPb_{1-x}Sr_xI_3$ PQDs under dark at room conditions, relative humidity 40-50%, in function of aging time (days) (λ_{exc} = 400 nm).

*PLQY after photobrightening (PQDs aged for 15 days): 1.356

Table S7. Stability of PLQY of FAPb_{0.93}Sr_{0.07}I₃ PQDs under dark conditions, 4 °C in function of time (months) (λ_{exc} = 400 nm).

Nominal	Calculated		Ti	me (Mont	:hs)	
composition	composition/ doping, EDS	0	1	3	5	8
x = 0.5	x = 0.07	0.999	0.961	0.945	0.857	0.729

Table S8. Chromaticity coordinates of $FAPb_{1-x}Sr_xI_3$ PQDs at different temperatures and red color in Rec. 2020 standard.

Perovskite sample	Х	У
x = 0.3	0.68	0.32
x = 0.5	0.69	0.31
x = 0.6	0.59	0.40
x = 0.7	0.56	0.44
Rec. 2020		
standard for red	0.708	0.292
color		



Figure S10. XPS valence band spectra of FAPbI₃ and FAPb_{0.93}Sr_{0.07}I₃ PQDs.

Theoretical calculations

The theoretical investigation of bulk FAPb_{1-x}Sr_xI₃ perovskites in the cubic phase relies on density functional theory calculations performed with the Quantum Espresso code.⁶ We studied unit cells with an increasing content of substitutional Sr, namely 0, 3, 6, 9 12.5, 25, 37.5, 50, 62.5, 75, 87.5, and 100 at. %, see Figure S11. In the case of FAPbI₃ and FASrI₃ compounds, the supercell contained 12 atoms; for 3, 6 and 9 at.% Sr content, the supercells were formed by 4x4x2 unit cells and contained 384 atoms; for 12.5, 25, 37.5, 50, 62.5, 75, and 87.5 at.% Sr, the supercells were formed by 2x2x2 unit cells and contained 96 atoms. The atomic relaxation of these structures was computed with pseudopotentials generated with the PBEsol exchange-correlation functional in the GGA approximation.⁷ Furthermore, the first Brillouin zone was sampled with a Γ -centered Monkhorst-Pack grid of 8x8x8 k points for bulk FAPbI₃ and FASrI₃ materials, with a single k point, the Γ point, for cells with 3, 6, and 9 at. % Sr, and with a Γ -centered Monkhorst-Pack grid of 0.01 Ry/a₀, where a₀ is the Bohr radius. It is worth to note that the reported total energies and band gaps extracted from the densities of states, do not account for spin-orbit interactions.



Figure S11. Atomic representation of (a) FASrI₃ and (b) FAPbI₃ unit cells, (c) supercell with 2x2x2 unit cells (50 at. % Sr), and (d) supercell with 4x4x2 unit cells (6 at. % Sr).

Formation Energies

By calculating the difference in total energies between perovskite and precursors, we have quantified the formation energies of FAPbI₃ and FASrI₃; ⁸ they are reported in Tables S9 and S10. We used the precursors PbI₂ and FA-I in the case of FAPbI₃, and the precursors SrI₂ and FA-I for FASrI₃, see Figure S12. The atomic relaxation was computed with the pseudopotentials mentioned above until forces were less than 0.001 Ry/a₀, and the first Brillouin zone was sampled with a Γ -centered Monkhorst-pack grid of 6x8x8 k points for SrI₂, 8x8x6 k points for PbI₂, 8x8x8 k points in the case of FAPbI₃ and FASrI₃, and a single k point, Γ , for FA-I. We included the effect of spin-orbit coupling with pseudopotentials generated by the fully relativistic PBEsol exchange-correlation functional in the GGA approximation,⁷ keeping the same grid of k points. To relax the SrI₂ and PbI₂ structures we started from the experimentally reported unit cells, ICSD 15101 and ICSD 68819, respectively, and we obtained the following cell parameters (in Angstrom):

- SrI₂, orthorhombic: a = 15.12; b = 8.18; c = 7.82; $\alpha = 90^{\circ}$; $\beta = 90^{\circ}$; $\gamma = 90^{\circ}$.
- PbI₂, pseudo-trigonal: a = 4.54; b = 4.53; c = 7.05; $\alpha = 90^{\circ}$; $\beta = 90^{\circ}$; $\gamma = 120^{\circ}$.



Figure S12. Atomic representation of (a) FA-I system and (b) PbI₂ and (c) SrI₂ unit cells.

Table S9. DFT total energies of FAPbI₃, FASrI₃ and their corresponding metal precursors (PbI₂ and SrI₂, respectively).

Compound	Total Energy (Ry)
FA-I (molecular form with 9 atoms)	-453.658
FASrI ₃ (bulk crystal, 12-atoms unit cell)	-1458.874
FAPbI ₃ (bulk crystal, 12-atoms unit cell)	-2068.791
SrI ₂ (bulk crystal, 24-atoms unit cell)	-8041.169
PbI ₂ (bulk crystal, 3-atoms unit cell)	-1615.061

Table S10. Formation energies as obtained from precursors FA-I, PbI₂ and SrI₂.

Perovskite compound	Expression ⁸	Formation energy
FAPbI ₃	E(FAPbI ₃) - E(FA-I) - E(PbI ₂)	- 0.072 Ry (-94.52 kJ/mol)
FASrI ₃	$E(FASrI_3) - E(FA-I) - E(SrI_2)/8$	-0.069 Ry (-90.58 kJ/mol)

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