Chemi-structural stabilization of formamidinium lead iodide perovskite by using embedded quantum dots for high-performance solar cells

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Abstract

The extraordinary low non-radiative recombination and band gap versatility of halide perovskites have led to considerable development in optoelectronic devices. However, this versatility is limited by the stability of the perovskite phase, related to the relative size of the different cations and anions. The most emblematic case is that of formamidinium lead iodine (FAPbI₃) black phase, which has the lowest band gap among all 3D lead halide perovskites, but quickly transforms into the non-perovskite yellow phase at room temperature. Efforts to optimize perovskite solar cells have largely focused on the stabilization of FAPbI₃ based perovskite structures, often introducing alternative anions and cations. However, these approaches commonly result in a blue-shift of the band gap, which limits the maximum photo-conversion efficiency. Here, we report the use of PbS colloidal quantum dots (QDs) as stabilizing agent for the FAPbI₃ perovskite black phase. The surface chemistry of PbS plays a pivotal role, by developing strong bonds with the black phase but weak ones with the yellow phase. As a result, stable FAPbI₃ black phase can be formed at temperatures as low as 85°C in just 10 minutes, setting a record of concomitantly fast and low temperature formation for FAPbI₃, with important consequences for industrialization. FAPbI₃ thin films obtained through this procedure preserve the original low band gap of 1.5 eV, reach a record open circuit potential (V_{oc}) of 1.105 V -91% of the maximum theoretical V_{oc} - and preserve high efficiency for more than 700 hours. These findings reveal the potential of strategies

exploiting the chemi-structural properties of external additives to relax the tolerance factor and optimize the optoelectronic performance of perovskite materials.

Production expenses and photoconversion efficiency (PCE) are critical factors impacting on the final cost of the solar energy technologies. Perovskite solar cells (PSCs) bring promise for affordable and efficient devices, with PCE recently reaching 25.2%.¹ Beyond excellent optoelectronic properties, this newcomer family of materials has a great composition versatility, that enables the synthesis of perovskites with tunable bandgap,² producing a broad range of possibilities for light emitting systems. For the development of photovoltaic systems, however, the range of material choice is confined to cations suitable for 3D perovskites with good charge transport properties, namely methylammonium (MA), formamidinium (FA) and Cs.³ Moreover, for a single layer absorber, a band gap as close as possible to 1.4 eV is required, as then the Shockley-Queisser model predicts a maximum theoretical efficiency of 33%.⁴ FAPI perovskite phase has the lowest band gap,⁵ 1.48 eV,⁶ with a maximal theoretical PCE (PCE_{max}) of 32.3%.⁷ With the further advantage of higher thermal stability in comparison to MA-based PSCs, FAPI perovskite crystals fulfill an ideal compromise between a fully inorganic and a hybrid perovskite in terms of both thermal stability⁸ and band gap.⁶

The structural stability is however an issue. FAPI has a Goldschmidt tolerance factor close to unity, but its polymorphism limits the stability of the black phase -which includes cubic (α) and tetragonal (β and γ) phases-^{3,9-12} in favor of the yellow -hexagonal (δ)- phase,¹³ which is photoinactive with a band gap of 2.43 eV.¹⁴ Consequently, the black phase is the most stable phase for temperatures over 165 °C only.⁹ This implies it must be synthesized at high temperatures (the annealing range is 150-185 °C for 30 min),¹⁵⁻¹⁷ and after cooling down to room temperature it constitutes a metastable phase that transforms into the yellow phase in a relatively short time, especially in humid environments.¹⁸ Cation alloying is a standard technique to decrease the Goldschmidt effective tolerance factor.⁹ Different studies report the addition of methylammonium (MA^+),¹⁹ cesium (Cs^+),^{11,20,21} potassium (K^+),²² rubidium (Rb^+),²³ or large organic cations forming 2D perovskites²⁴⁻²⁶ to stabilize the mixed cation perovskite α -phase.^{27,28} with the double advantage of a higher reproducibility and the formation of the α -phase at lower temperature (100-150 °C). Yet, in the case of Pb-perovskites, smaller A-site cation causes

octahedral tilting resulting in an increased band gap.^{29,30} This is an undesired side-effect, as it shifts the gap energy away from the optimal value in terms of PCE_{max} .^{4,7} For example, the extensibility used $Cs_{0.05}MA_{0.16}FA_{0.79}Pb(I_{0.83}Br_{0.17})_3$ presents a band gap of 1.63 eV,¹¹ limiting PCE_{max} to 29.8%.⁷ Recent research efforts are trying to reduce the perovskite band gap by removing Br.^{19,31} This strategy has yielded the current PCE published record of 23.3%¹⁹ with the reduction of band gap limited to 1.55 eV, as 8% of MA must be added to stabilize FAPI black phase. The use of Cs instead of MA to stabilize the α -phase in $RbCsFAPbI_3$ succeeded in further reducing the band gap to 1.53 eV, where Rb has the additional role of increasing the reproducibility.³¹

In this work, we propose to stabilize FAPI perovskite not through the introduction of alternative cations or anions to FA^+ and I^- , but by taking benefit of the synergistic interaction of halide perovskites with colloidal PbS quantum dots (QDs).³² MA-based halide perovskite thin films with embedded QDs^{33,34} have been employed for the development of LEDs,³⁵ photodetectors³⁶ and solar cells.³⁷ Inorganic $CsPb(I_{1-x}Br_x)_3$ perovskites with embedded PbS QDs, due to the zero-mismatch, increase the stability (photoluminescence (PL) reduction of just 10% after an annealing of one hour while for samples without embedded QDs the PL was reduced in a 50 %), especially for Br rich perovskite with the same lattice parameter than PbS.³⁸ We show that the use of embedded PbS QDs presents multiple advantages over alloying, since it stabilizes the black phase in ambient conditions, while preserving the narrow band gap of pure FAPI. Also, the synthetic conditions become milder, with temperatures as low as 85 °C, annealing times of only 10 minutes and no deleterious effect on the thermal stability of the resulting film. PSCs prepared out of FAPI films stabilized with PbS QDs demonstrated higher performance and reproducibility than their counterparts without QDs, as well as a record open circuit potential, V_{oc} , of 1.105 V for pure FAPI. PSCs with embedded PbS QDs further exhibited a significant improvement in long term stability, with only 16% decrease of the initial PCE after 720 hours, as compared to QD free samples, which presented a reduction in efficiency of 30% after a single day since preparation, and no performance at all after 500 hours. To elucidate the physical processes involved in the superior stabilization of FAPI by means PbS QDs, we combined systematic studies on the effect of QD size and concentration with a two-level theoretical analysis based on Density Functional Theory (DFT) and linear elastic theory of continuous media. The PbS-FAPI interface is

found reduce the thermodynamic preference for the yellow phase, by creating stronger chemical bonds with the black one, and to propagate strain fields over long distances, which favor the formation of large grain sizes. These factors point to surface chemistry engineering as a less invasive and yet efficient methodology to stabilize halide perovskite materials.

The first step carried out for the incorporation of the inorganic PbS QDs into the FAPI perovskite matrix is to make both materials chemically compatible in solution for the spin coating deposition. The finest method is to replace the organic ligand, specifically the oleic acid (OA), coming from the synthesis of the QDs, with a new one. In this case, the ligand has to anchor itself to the surface of the PbS, avoiding their aggregation in solution, but at the same time it has to be polar, to guarantee the solubility of the quantum dots in the perovskite solvent, namely dimethylsulfoxide (DMSO) or dimethylformamide (DMF). The ligand exchange procedure used is similar to previously reported in literature,^{33,34,39} substituting the organic capping of PbS QDs by a FAPI shell, see details in the Experimental Section. After the ligand exchange PbS/FAPI core/shell QDs are soluble in DMF solution, see Figure 1a. A Fourier-Transform Infrared Spectroscopy (FTIR) measurement before the ligand exchange exhibits the signals related to the oleic acid, the stretching modes of the O-H at $3,446\text{ cm}^{-1}$, of the C-H at $3,020\text{--}2,800\text{ cm}^{-1}$ and of the carboxyl C=O at $1,527\text{ cm}^{-1}$. These modes are totally absent after ligand exchange, see Figure 1b, pointing the success of the ligand exchange procedure. Furthermore, the solutions of the PbS/FAPI in DMSO or DMF are stable until the concentration of 50 mg/ml, indicating the universality and robustness of the method, which in fact preserves the features of the as synthesized PbS QDs, Figure 1c, after the ligand exchange, see Figure 1d.

Transmission Electron Microscopy (TEM) images reveal an increase of the average size of QDs comparing the as-synthesized OA capped PbS QDs (PbS/OA) and PbS/FAPI core/shell QDs, see Figure 1 c,d. The statistic distribution is plotted in Figure S1 in good agreement with the estimated QDs size from PL spectra, see Figure 2a, around $3.8 \pm 1.8\text{ nm}$ and $4.7 \pm 1.5\text{ nm}$ for the PbS/OA and the PbS/FAPI, respectively.⁴⁰ As synthesized PbS/OA QDs present cubic rock salt structure, see Figure 1e. After ligand exchange a shell of FAPI is formed with majority black phase, despite a small contribution from yellow phase is visible in the X-Ray Diffraction (XRD) pattern, see Figure 1f.

Figure 1 | PbS quantum dots ligand exchange characterization. **a**, Pictures (left) before the ligand exchange with the PbS QDs capped with oleic acid in octane solution and FAPI precursors (PbI₂ and FAI) in DMF and (right) after the ligand exchange with PbS/FAPI core/shell QDs in DMF solution. **b**, FTIR of the PbS QDs before and after the ligand exchange. TEM images of 10 mg/ml PbS QDs solutions before and after ligand exchange; **c**, with the oleic acid and **d**, with FAPI shell, respectively; **e**, XRD of the oleic acid capped PbS QDs spin coated on glass from octane solution and **f**, XRD of PbS/FAPI QDs spin coated from DMF solution.

Ligand exchange produces a change in the photoluminescence (PL) emission peak (Figure 2a) and in the absorbance of the PbS QDs (Figure 2b). QDs PL exhibits a red shift when QDs in solution are deposited on glass forming thin films. In agreement with the absorption red shift (Figure 2b), after ligand exchange, PbS/FAPI QDs PL presents a red shift with respect to PbS/OA QDs for both solution and thin film. To shed light the PL red shift ($\Delta\lambda_{\text{(solution)}} = 132 \text{ nm}$ and $\Delta\lambda_{\text{(thin film)}} = 211 \text{ nm}$) we carry out k-p theory calculations of exciton emission. Electron and hole states are computed within a multi-band Dimmock Hamiltonian, including mutual Coulomb interaction via self-consistent process and dielectric mismatch effects, see section 2 in Supporting Information. In Figure 2a we show the experimental PL emission of PbS QDs surrounded by OA or FAPI, either in solution or in film, and compare with theoretical estimates.

Figure 2|Optoelectronic characterization and theoretical fitting of PbS/OA and PbS/FAPI core/shell in solution and in film (3.8 nm diameter). **a**, PL steady state spectra of the PbS QDs in solution (scatter plots) and in thin film (line) with OA (black) and FAPI (blue) as ligands: overlapped to the experimental spectra is the fitting from theoretical calculation with the k·p model (green and cyan lines). **b**, IR Absorbance of PbS/OA and PbS/FAPI QDs in solution (octane and DMF respectively). The position of the peak maximum is indicated for both PL and absorption.

Excellent agreement is obtained when the k·p model adopts QD diameters of 3.8 nm (OA, solution), 3.96 nm (FAPI, solution), 3.98 nm (OA, film) and 4.42 nm (FAPI, film), with Gaussian-shaped bands to account for size inhomogeneity. The mean size of emitting QDs surrounded by FAPI is slightly larger than that in OA, which is consistent with TEM measurements. Also, the size in films is larger than that in solution, possibly because enhanced tunneling facilitates photo-excited carrier relaxation into larger dots prior to electron-hole recombination. Our theoretical k·p analysis further provides complete information on exciton binding energies, dielectric mismatch effects, band offset distribution and size-dependent absorption in PbS/FAPI QDs, see Supporting Information section 3 and Figure S2-S6.

The properties of FAPI thin films with embedded PbS QDs have been analyzed as function of the QDs concentration and size. The QDs concentration in the perovskite solution is tuned from 0 mg/ml (reference sample) to 7.5 mg/ml, resulting in FAPI thin films with different volume percentage of QDs from 0.18 vol % to 0.55 vol % (see Supporting Information section 4 for more details about the calculation of the QD percentage). The first beneficial effect of the PbS addition is observed for the crystallization of FAPI film from solution after spin coating. As mentioned

above, to produce the black phase of FAPI perovskite an annealing after spin coating at 165-185 °C is needed, but the addition of PbS reduces dramatically the annealing temperature to obtain the black phase of FAPI, to values as low as 85 °C for a concentration of PbS/FAPI QDs in solution of 5mg/ml, see Supporting Video 1, and annealing times as short as 10 minutes. The presence of PbS accelerates⁴¹ the FAPI black phase crystallization, not just for FAPI but for reported halide perovskites, reducing radically both the self-assembly time and temperature.¹⁵⁻¹⁷

The annealing time for the crystallization of the FAPI black phase presents a dependence on the QDs concentration. An optimal response is obtained at 5 mg/ml, with complete conversion into black phase in 10 min. If the concentration is lower or higher, for instance 2.5 mg/ml or 7.5 mg/ml, the formation is slowed down to 20 min and 40 min, respectively, but it still occurs at 85°C, see Figure S7a. We observe this phenomenon not only with pure DMSO but also with a co-solvent DMF:DMSO (9:1). For the mixture of solvents, the required annealing temperature can be decreased only to 140 °C (Figure S8a), and the films have a lot of pin-holes on the surface as revealed by Scanning Electron Microscopy (SEM), Figure S8b, compared to the uniform and smooth surfaces of the films obtained from the pure DMSO solution (Figures 3c-f). This observation is in agreement with previous works pointing out that DMSO accelerates the crystallization of the perovskite, leading to bigger grains, passing from the intermediate adduct with the precursors.⁴²⁻⁴⁴ However, in this study there is a third component, namely PbS QDs, having a prominent role, as the FAPI black phase crystallizes in DMSO and DMF:DMSO (9:1) at 165 °C or 185 °C, respectively, without the presence of PbS, see Supporting Video 2, with annealing time longer than 30 minutes to completely convert the precursors in the final product. Summing up, a proper concentration of PbS QDs results in an impressive shift ($\Delta T = 45^\circ\text{C}$ if the solvent is DMF and $\Delta T = 80^\circ\text{C}$ if the solvent is the DMSO) of the perovskite starting formation temperature, while reducing the conversion time of the precursors into the black phase. This result has the potential to severely reduce production expenses in an eventual industrialization stage.

We have verified that below 85 °C (i.e. 80 °C) an incomplete perovskite formation occurs, as the signatures of PbI_2 and of the FAPI yellow phase are observed in the XRD spectra, see Figure S9. On the contrary, the XRD measurements confirm the complete conversion of the perovskite

precursors, FAI and PbI_2 , to black FAPI perovskite upon annealing at 85 °C, independently of the PbS concentration, see Figure 3a. Only the peaks corresponding to the FTO substrate and the FAPI black α -phase at 14.03° (001), 24.33° (111), 28.23° (002), 31.66° (012) and 40.25° (022) are observed after thin film preparation, see Figure 3a.⁴⁵ No peaks pointing the presence of PbI_2 or FAPI δ -phase are observed after samples preparation. The degradation of these layers was followed at ambient condition with a relative humidity of almost 45%. After 30 days, the degradation of the reference sample is evident with bare eyes, see Figure 3b, and from absorbance measurements, see Figure S10. For some of the samples with embedded QDs it can be also observed, but not for others. In details, the XRD measurement after 30 days revealed that the FAPI film prepared with a concentration of PbS QDs of 5mg/ml is stable and the black phase is preserved.

Figure 3 | XRD pattern and SEM images of the FAPI-PbS thin films. Aging test performed on the perovskite thin films without and with 3.8 nm size PbS QDs at different concentrations; X-Ray diffraction patterns of **a**, the fresh samples and **b**, after 30 days, stored in ambient conditions; top-view SEM images of the FAPI thin films **c**, without PbS QDs and with PbS QDs **d**, 2.5 mg/ml, **e**, 5 mg/ml and **f**, 7.5 mg/ml. The annealing temperature and time for the samples without PbS QDs are 180 °C for 30 min, and for the samples with the three different PbS QDs concentrations are 85 °C for 10 min.

On the other hand, the perovskite without PbS QDs and with the highest concentration embedded, are totally converted into the δ -phase, as indicated by the diffraction peak at 11.8° and the disappearance of black phase peaks, see Figure 3b. In the case of the sample with the lowest QD concentration, it presents a mixture of the FAPI black and yellow phases, see Figure 3b. Likewise, the FAPI perovskite grain size increases with the increase of the concentration, but at 7.5 mg/ml the grain size decreases again, as the SEM images display, see Figure 3 c-f. The black dots observed in the top-view SEM image of the FAPI with no QDs and with PbS QDs 7.5 mg/ml are yet another evidence of the fast degradation of such films when exposed to ambient air or to stress conditions, like the SEM beam. No such signs are observed for the sample with 5 mg/ml QDs.

The size of the PbS QDs also has a significant effect on the stabilization of FAPI black phase. To illustrate this point, we keep the concentration in solution constant, at 5mg/ml, and vary the PbS QDs size. PbS QDs with diameter size of 2.9 nm, 3.8 nm and 8.2 nm are studied. PL, TEM images and XRD of the corresponding PbS QDs are plotted in Figure S11. An optimal response is obtained for the mid-sized QD diameter, 3.8 nm. The trends of annealing time and black phase stability when varying the size from this value are analogous to those observed when varying the concentration from its optimal value, see Figure S7. Namely, the annealing time is shortened from the system with PbS QDs of 2.9 nm to the system with 3.8 nm and increases again for PbS QDs of 8.2 nm. In the same way, the stability improves from 2.9 nm to 3.8 nm, but it decreases for the largest size.

One of the most significant advantages of the FA-based perovskite compared with the MA-based perovskite, in addition to the lower band gap, is the thermal stability beyond 150°C , as it can be expected from the higher formation energy. Despite the introduction of PbS QDs reduces significantly the annealing temperature for the synthesis of FAPI black phase, the presence of QDs does not affect the thermal stability of the FAPI layer, as it has been verified by thermogravimetric analysis (TGA). TGA was measured from room temperature to $1,000^\circ\text{C}$ under nitrogen, Figure S12, observing no significant differences for samples prepared with and without QDs.

In order to understand the physical origin of the phase stability of FAPI in the presence of embedded PbS QDs, density functional theory (DFT) calculations including spin-orbit coupling are carried out (see Supporting Information, section 5, Figure S13-S16). We compare the energetic stability of black and yellow phases in different conditions. As shown in panel (i) of Figure 4a, in the bulk the energy of black (cubic) phase exceeds that of the yellow one by $\Delta E_{by} = E_b - E_y = 0.27$ eV per FAPbI_3 unit. This fact explains the well-known thermodynamic preference for the yellow phase in the absence of PbS QDs.⁸ Upon inclusion of the QDs, however, several changes take place in the host FAPI matrix: (i) the smaller lattice constant of PbS generates strain, (ii) crystal surfaces arise on the interface with the QD and (iii) chemical bonds form between the two materials. We study the individual effect of each factor to determine their presumable role in stabilizing the black phase.

First, we investigate the effect of strain. Previous studies have suggested strain may favor the black phase stability in CsPbI_3 and $(\text{Cs,FA})\text{PbI}_3$ perovskites with different substrates.⁴⁶⁻⁴⁸ We calculate the strain arising from the lattice mismatch between spherical PbS QDs and cubic FAPI using linear elastic theory (see details in section 2 of Supporting Information). Figure 4b shows the strain parallel ($\parallel$) and normal ($\perp$) to the (100) crystal direction for QDs of different sizes. We find most of the strain occurs in the FAPI matrix, as it stays well under 1 % inside the QDs, but it becomes strong (up to 4-6 %) outside. This is consistent with the rigid (soft) bonds of PbS (FAPI). A strongly compressive strain $\epsilon_{\perp}$ builds up in FAPI near the interface with PbS (dashed lines), which facilitates lattice matching. In response, a tensile strain $\epsilon_{\parallel}$ (solid lines) develops in the orthogonal direction, which propagates several nanometers away from the interface. This behavior implies a long-ranged tetragonal distortion of the FAPI lattice, as sketched in Figure 4c. The energetic impact of such a strain is determined by DFT calculations. The isolated effect of the strain on the bulk is evaluated by forcing that the bulk perovskite matches with the PbS lattice: black (cubic) and yellow (hexagonal) bulk phases are forced to match the lattice constant of PbS on (100) and (111) surfaces, respectively, which are the most compatible crystallographic planes in each case. The in-plane (out-of-plane) lattice parameters are compressed (tensiled) by 7 % on axis a and b (12 % on c axis) for the black phase -which becomes tetragonal- and by 13 % on a axis and 2 % on b axis (8 % on c axis) for the yellow phase. The resulting energies show that strain

destabilizes both phases, but the effect is more pronounced in the yellow one. Thus, the energy splitting decreases from $\Delta E_{by}=0.27$ eV to $\Delta E_{by}=0.18$ eV, as shown in Figure 4a, cf. panels (i) and (ii). A similar energetic trend has been recently reported in Ref.⁴⁶ for CsPbI₃ thin films depending on the strain induced by the substrate. However, the small reduction is unlikely to explain the drastic stabilization of the black phase revealed in our experiments. We have tested biaxial and uniaxial strain on bulk crystals, both tensile and compressive, and confirmed that the black phase is systematically less stable than the yellow one, i.e. $\Delta E_{by}>0$, see Figure S17.

We next study the effect of surface formation. PbS QDs of small size present an octahedral shape exposing (111) planes, while QDs with diameters over ~ 3.5 nm PbS QDs adopt a cubooctahedral shape with increasing area covered by (100) planes, see Figure 4d.⁴⁹ FAPI black phase is prone to use (100) planes to bind with PbS, while the yellow phase prefers (111) planes, each with a preferred ionic termination. A quantitative comparison of the corresponding surface energies is however prevented by the lack of reflection symmetry in the unit cell of the yellow phase, its inherent polarity, and the wide uncertainty range of FAPI chemical potential. We then carry out a semi-quantitative analysis of surface energies by directly comparing the total electronic energy of strained slabs in black and yellow phases. The slabs, as plotted in panel (iii) of Figure 4a, are chosen to have similar thicknesses and hence similar quantum confinement. As expected, the presence of surfaces increases the energy per FAPbI₃ unit with respect to strained bulk. The increase is small for the black phase but large for the yellow one, which then becomes less stable than the black phase by $\Delta E_{by}=-0.76$ eV. This result is consistent with recent studies on CsPbI₃, where large (small) surface energies were reported for the δ (α) phase.⁴⁸ It follows that the presence of surfaces between FAPI and PbS QDs is an important factor destabilizing the yellow phase relative to the black one.⁴⁶

The last factor to be considered is the chemical binding of FAPI to PbS. For a semi-quantitative estimate, we attach slabs of FAPI and PbS, as illustrated in panel (iv) of Figure 4a. The resulting energy per FAPbI₃ unit decreases for both phases as compared to that of bare slabs, which confirms that stable bonds are formed between the two materials. Remarkably, the stabilization is much stronger for the black phase than for the yellow one, the energy difference increasing from $\Delta E_{by}=-0.76$ eV in the free-standing slabs to $\Delta E_{by}=-1.06$ eV in the heterostructure.

Altogether, the energetic trends revealed by our DFT calculations (see SI for more details), make clear that the origin of thermodynamically favored black FAPI upon inclusion of PbS QDs is due mainly to two distinct, but both needed, mechanisms: *in primis* the structure stabilization, that destabilizes the yellow phase due to its large surface energy and *in secundis* the crucial chemical stabilization, by chemical bonds between the PbS and FAPI, that stabilizes the black one phase. The latter is also likely related to the mild annealing conditions observed in our experiments. The low annealing temperature indicates PbS QDs are acting as catalyzers,⁴¹ regardless of the size and concentration, which reduce the activation energy required to attain the metastable black phase. It is then plausible that the strong PbS-black FAPI bonds are stabilizing the transition state of the reaction path. Strain, on the other hand, plays a secondary role in energetic stabilization. Still, the long-ranged tetrahedral distortion reported in Figure 4b suggests PbS QDs could further contribute to stabilize by stimulating the formation of large FAPI grains black phase FAPI. It has been recently claimed that the strain enables the formation of large grain sizes through the coherent propagation of its field over crystal regions with otherwise random orientation of domains,⁴⁶ which is beneficial for the stability of the synthesized phase.⁸

The results above clearly explain the experimental observation that small size PbS QDs and small concentrations of QDs fail to stabilize the FAPI black phase, because of the lack of (100) surfaces and the reduced number of surfaces and chemical bonds, respectively. In order to understand the lower stability for high QDs concentration and higher QD size other arguments are needed. A possible explanation is that the presence of QDs rich regions can produce a large increase of the strain, see Figure S18, especially in the case of large QDs size. This significant strain enhancement produces in turn an important increase of the energy per formula unit, see Figure S17, which could induce the observed destabilization of the thin film.

Figure 4 | Theoretical insight into the effect of PbS QDs on FAPI. **a**, Total energy DFT calculation of (i) black and yellow bulk FAPI phases represented by red and blue colors respectively, (ii) the effect of strain on the bulk when matching the PbS lattice, (iii) the presence of surfaces in the slabs, and (iv) the role of chemical binding to the PbS substrate in the heterojunctions. The insets depict the atomic structures under study, which are 3D in (i) and (ii), and 2D in (iii) and (iv). **b**, Strain tensor elements parallel and perpendicular to (100) axis, for three different QD diameters. The (100) direction is normal to the FAPI-PbS interface. **c**, Sketch of the effect of strain in the lattice, as inferred from b). A tetragonal distortion is observed, which penetrates several nm inside FAPI. **d**, Atomic representation of PbS quantum dots showing facets (111) and (100). The small dot in panel (i) is 3 nm size and the larger one in panel (ii) is 4.2 nm size.

To investigate the effects of the PbS QDs incorporation in photovoltaic devices, we fabricated PSCs with planar configuration,⁵⁰ FTO/SnO₂/FAPbI₃/spiro-OMeTAD/Au, see Figure 5a, with and without embedded QDs. We employed the optimized PbS QDs solution concentration

of 5mg/ml and QD size of 3.8 nm. The average of the results is summarized in Figure S19 and Table S3 and the curves of the best devices are shown in Figure 5b. We highlight that the presence of PbS QDs not only increases the maximum and average performance of the solar cells but also the reproducibility of the devices, see Figure S19d, due to the augmentation of the open-circuit voltage, V_{oc} , and the fill factor, FF, see Figure S19b and S19c, respectively, for average values and Figure 5b for champion devices. Significantly, the champion device has a photo-conversion efficiency of 18%, see Table S3 and Figure 5b, with a V_{oc} of 1,105 mV, a photocurrent, J_{sc} of 21.5 mA/cm^2 and a FF of 75.7%, with typical negligible hysteresis, in accordance with previous reports.⁵¹ However, the solar cells optimization is not exhausted, as the theoretical limit of 27 mA/cm^2 suggests,⁵¹ and further optimization can be expected in the near future. An increase of the layer thickness (higher than 220 nm) optimizing the deposition process, keeping the FF as high as in this study, will allow to take benefit of the lower band gap of FAPI, see Figure 5e, to increase the device J_{sc} .

Figure 5| Photovoltaic device J/V characterization. a, Sketch of the architecture used in this study; b, Current/Voltage curves of the best performance perovskite solar cells recorded at reverse and forward scan; c, and d, SEM cross sections of the devices with the two different active layers FAPI and FAPI-PbS; e, Tauc plot of the FAPI and FAPI with 5 mg/ml; the estimated band gap is 1.50 eV; f, Stability of the perovskite solar cells during the days.

Figure S20 shows the incident photon-to-current efficiency (IPCE %) and the integrated current J_{sc} , corresponding to the value collected with the J/V curves measurements. The value of the integrated current of the control device, because of the fast degradation of the film, is lower than the initial value, while there is a good agreement with the measured J_{sc} in the case of samples with QDs. On the other hand, the $\text{SnO}_2/\text{FAPbI}_2$ interface is more compact if compared to the layer without PbS QDs, see Figure 5c-d, thus confirming that the PbS QDs also positively affect the morphology enhancing the device performance, in particular the V_{oc} . The obtained V_{oc} in fact increases reaching a promising record value of 1,105 mV, 91% of the maximum theoretical V_{oc} of 1,215 mV for pure FAPbI₂ perovskite with a band gap of 1.5 eV,⁷ see Figure 5e. To our knowledge, this is the highest V_{oc} reported for pure FAPbI₂ PSCs. Beyond the improvement of the PCE, PbS QDs provide a drastic enhancement of long term stability, see Figure 5f. Devices prepared with QDs preserve 85% of their performance after 720 hours, while samples without QDs decrease their performance by 30% after a single day since fabrication, and show no performance at all after 500 hours.

In conclusion, we have shown that pure FAPbI₂ perovskite, preserving its excellent optical properties for solar cell devices, can be stabilized by embedding a small fraction of PbS QDs. As compared to previous strategies, mostly based on ion alloying, the present method avoids blue shifting of the band gap –thus paving the way for higher PCE– and reduces dramatically both synthesis temperature and time –thus reducing production expenses –. The stabilization is based on the double contribution of the PbS-FAPbI₂ interface, chemical and structural, which selectively favors black phase against yellow one. This work opens venue for crystalline phase stabilization of metastable polymorphs through surface chemistry engineering, not just in very thin films under the effect of a substrate, but in bulky systems by the intentional creation of surfaces and chemical bonds with embedded QDs.

Methods

Methods, including materials, ligand exchange, solar cell fabrication, characterization, theoretical $k \cdot p$ model, Density Functional Theory and strain calculations are available in the Supplementary Information.

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Author Contributions

S.M. and I.M.-S. conceived the project. S.M. and S.K.P.M. optimized the ligand exchange and T.T.N synthesized and characterized by PL of the PbS QDs. S.M prepared the solar cells and characterized them. P.M. prepared the samples and performed the SEM. E. F. L performed the absorbance and Tauc plot. C.E.A developed the DFT simulations and J.I.C., J.P. and D.F.M.P. the strain theoretical calculations and the k·p model analysis. S.M. coordinated the experimental work. J.I.C. coordinated the theoretical work. I.M.-S. coordinated the whole project. S.M, J.I.C. and I.M.-S. wrote the manuscript. All the authors contributed to the discussions.

SUPPLEMENTARY INFORMATION

Chemi-structural stabilization of formamidinium lead iodide perovskite by using embedded quantum dots for high-performance solar cells

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1. EXPERIMENTAL SECTION

1.1 Materials

All materials are reagent grade and are used as received. Lead iodide (PbI_2 , > 98%, from TCI), formamidinium iodide (FAI, 98%, from GreatCell solar), 2-propanol (99.7% from Carlo Erba), ethanol (96%) and acetone (99.25%) from PanReac, hydrochloric acid (HCl 37%), dimethyl sulfoxide (DMSO anhydrous 99.9%), chlorobenzene (CB anhydrous 99.8%), acetonitrile (MeCN anhydrous 99.8%), 4-tert-butylpyridine (TBP 96%), zinc powder (99.995%) and lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI 99.95%) from Sigma Aldrich, while 2,20,7,70-tetrakis [N,N-di(4-methoxyphenyl)amino]-9,90-spirobifluorene (spiro-OMeTAD 99% from Feiming chemical limited), toluene (TOL anhydrous 99.8%) from VWR and SnO_2 colloid precursor from Alfa Aesar (15% in H_2O colloidal dispersion). Fluorine doped tin oxide (FTO) coated glass substrates (Pilkington TEC15, $\sim 15 \Omega \text{ sq}^{-1}$).

1.2 Ligand exchange

PbS QDs are synthesized according a modified procedure previously reported.¹ The FAPI solution (0.25 M in DMF) and the QDs solution (10 mg/ml in octane) are mixed in a volume ratio of 1:1 and stirred for 40 min. During the stirring the QDs are transferred from the top octane phase to the bottom DMF phase. When all the QDs are dispersed in DMF the supernatant octane is removed and the QD solution is washed

three times with fresh octane to remove the organic residue. Then, the QDs are precipitated by the addition of toluene, and centrifuged at 3,500 rpm for 5 minutes. QDs are dried under vacuum for 3 hours.²

1.3 FAPI-PbS solution and film preparation. 1.5 M FAPI solution is prepared by dissolving 691 mg of PbI_2 and 256 mg of FAI in dimethyl sulfoxide (DMSO) at 70 °C. Dried PbS QDs are dispersed in 0.2 ml of 1.5 M FAPI solution. Considering no losses, therefore their concentration in 0.2 ml of FAPI solution is 50 mg/ml, which is used as mother solution. The FAPI-PbS mother solution is in fact further diluted with 1.5 M FAPI solution to obtain the PbS QDs concentration of 2.5 mg/ml, 5 mg/ml and 7.5 mg/ml. The FAPI and FAPI-PbS films are prepared by spin-coating 1.5 M FAPI solution without and with PbS QDs at 4,000 rpm for 30 seconds. At the 25th second of the spinning, toluene is dropped on the films. FAPI-PbS and FAPI films are annealed at 85 °C or 180 °C, respectively, for 30 minutes. All the solutions and film depositions are prepared inside a glove box in inert atmosphere.

1.4 Fabrication of solar cells

FTO (fluorine doped SnO_2) substrates are etched with zinc powder and HCl 2 M and cleaned with deionized water, isopropanol, and a mixture of acetone and ethanol (50-50 %) in an ultrasonic cleaner for 15 min for each solvent. Then, the substrates are put in an ultraviolet–ozone (UV- O_3) environment for 15 min to remove organic residues. The electron transport layer (SnO_2 2.5 wt %) is spin-coated of at 3,000 rpm for 30 s, and heated at 150 °C for 30 min.³ Before the perovskite deposition, FTO/ SnO_2 substrate are treated with UV- O_3 for 60 min. The perovskite precursor solution (FAPI or FAPI-PbS) is spin-coated at 4,000 rpm for 30 s, and toluene is dropped onto the perovskite film at the last 5th second during the spin coating, in a glove box with nitrogen atmosphere at 22 °C and annealed for 10 min at 85 °C (FAPI-PbS) or 180 °C (FAPI) for 30 minutes. The spiro-OMeTAD solution (72.3 mg/mL in chlorobenzene), doped with 28.8 μL of TBP and with 17.5 μL of a Li-TFSI solution (520 mg/mL of in acetonitrile), is spin-coated at 4,000 rpm for 30 s onto the top of the perovskite layers as hole transport material. Finally, the Au electrode with a thickness of 100 nm was deposited by thermal evaporation.

1.5 Structural characterization

The morphologies of the samples (FTO/ SnO_2 /FAPI with and without PbS) are carried out with a field emission scanning electron microscope (FEG-SEM) JEOL 3100F) operated at 5 kV.

The X-ray diffraction (XRD) patterns of the FAPI films are recorded using an X-ray diffractometer (D8 Advance, Bruker AXS) ($\text{Cu K}\alpha$, wavelength of $\lambda = 1.5406 \text{ \AA}$) within the range of 10–60 °.

Transmission electron microscopy (TEM) images are taken on W JEOL JEM 1010 transmission electron microscope, using an accelerating voltage of 100 kV, with a resolution of 0.4 nm.

The thermogravimetric analysis (TGA) are measured with the TGA/SDTA851e/LF/1600 instruments, working from ambient temperature to 1,600 °C.

The FTIR spectra of the PbS QDs are collected with a FTIR Equinox 55 (Bruker) with an ATR Pro (Jasco) equipped with a diamond crystal, in standard conditions (in the range 600-4,000 cm^{-1}).

1.6 Optoelectronic characterization

Solar cell characterization. The current–voltage (J-V) curves are measured using a Keithley 2612 source meter under AM 1.5 G (100 mWcm^{-2}) provided by a Solar Simulator ORIEL-Newport model 91192A-1000, Xenon short arc lamp Ushio 150 watts, in air at a temperature around 20 °C and a relative humidity around 30%, without encapsulation. Each curve is generated using 123 data points from a starting potential of 1.2 V to a final potential of -0.02 V (reverse scan; *viceversa* for the forward scan) using a scan rate of 10 mVs⁻¹. The area of the photovoltaic devices is 2.5 cm^2 , with 5 pixels, each one of 1 cm x 0.4 cm. The active area of the cell is 0.121 cm^2 , determined with a metallic external mask (a microscope is used to define the real active area). Photovoltaic performance of the aged devices are measured in ambient conditions.

The incident photons to current efficiency (IPCE) measurements are performed with a QEPVSI-b Oriel measurement system.

The steady state *absorption* spectra of the perovskite films are achieved by using a UV/Vis absorption spectrophotometer (Varian, Cary 300) and the emission measurements are collected by a Horiba Fluorolog.

The photoluminescence (PL) is collected at a wavelength of 800 nm after excitation at 532 nm. To protect the perovskite films from the ambient air, 10 mg/mL of poly-methyl methacrylate (PMMA, 182230, Mn 120,000, Sigma-Aldrich) in anhydrous chlorobenzene is also spin-coated (2,000 rpm for 60 s) on the top of the perovskite layers. And the PL of different PbS/OA QDs sizes in solution (presented in Figure S11a) was carried out using a CCD detector (InGaAsAndor-iDUS DU490A-2.2) coupled with an adaptive focus imaging spectrograph (Kymera KY-193i-B2). A commercial continuous laser (532 nm, GL532RM-150) was used as an excitation source. The long-pass filter 20CGA-590 was used in order to block the excitation source.

2. THEORETICAL $\mathbf{k \cdot p}$ MODEL AND MATERIAL PARAMETERS

The lead salts have rock-salt crystal structure and had direct gaps at four equivalent L points in the Brillouin zone.⁴ The valence band (VB) edge Bloch function is s-like (L_6^+ symmetry), while the conduction band (CB) edge Bloch function is p_z-like (L_6^- symmetry), where z denotes the $\langle 111 \rangle$ direction of the cubic lattice. Due to high atomic number of some of the atoms present in the system, it is essential to include the spin-orbit effects. The simplest $k \cdot p$ Hamiltonian including the CB-VB interaction, the present anisotropies and spin-orbit effects is the Dimmock Hamiltonian.⁵ Basically, this Hamiltonian is the expansion of the $k \cdot p$ Hamiltonian,

$$H_{k \cdot p} = \frac{-\hbar^2 k^2}{2m} + \frac{\hbar k}{m} \cdot \hat{p} + \frac{\hbar^2}{4m^2 c^2} (\sigma \times \nabla V) \cdot k, \quad [1]$$

in the abovementioned conduction and valence basis set. The inclusion of the remote bands interaction by means of perturbation theory introduces the anisotropies. For example, the mass m is not isotropic anymore, yielding different longitudinal $m_{\parallel} = m_z$ and transverse $m_{\perp} = m_{xy}$ masses. Altogether, it yields the following Hamiltonian operator,⁴ written in a.u.,

$$\begin{pmatrix} -\frac{1}{2} \left(\frac{\partial}{\partial z} \frac{1}{m_z^*} \frac{\partial}{\partial z} + \nabla_{\perp} \frac{1}{m_{\perp}^*} \nabla_{\perp} \right) + V_c & 0 & \frac{-i}{2} \left(p_{\parallel} \frac{\partial}{\partial z} + \frac{\partial}{\partial z} p_{\parallel} \right) & \frac{-1}{2} \left(p_{\perp} \left[i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \right] + \left[i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \right] p_{\perp} \right) \\ 0 & -\frac{1}{2} \left(\frac{\partial}{\partial z} \frac{1}{m_z^*} \frac{\partial}{\partial z} + \nabla_{\perp} \frac{1}{m_{\perp}^*} \nabla_{\perp} \right) + V_c & \frac{-1}{2} \left(p_{\perp} \left[i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right] + \left[i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right] p_{\perp} \right) & \frac{i}{2} \left(p_{\parallel} \frac{\partial}{\partial z} + \frac{\partial}{\partial z} p_{\parallel} \right) \\ \frac{-i}{2} \left(p_{\parallel} \frac{\partial}{\partial z} + \frac{\partial}{\partial z} p_{\parallel} \right) & \frac{-1}{2} \left(p_{\perp} \left[i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \right] + \left[i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \right] p_{\perp} \right) & \frac{1}{2} \left(\frac{\partial}{\partial z} \frac{1}{m_z^*} \frac{\partial}{\partial z} + \nabla_{\perp} \frac{1}{m_{\perp}^*} \nabla_{\perp} \right) + V_v & 0 \\ \frac{-1}{2} \left(p_{\perp} \left[i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right] + \left[i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right] p_{\perp} \right) & \frac{i}{2} \left(p_{\parallel} \frac{\partial}{\partial z} + \frac{\partial}{\partial z} p_{\parallel} \right) & 0 & \frac{1}{2} \left(\frac{\partial}{\partial z} \frac{1}{m_z^*} \frac{\partial}{\partial z} + \nabla_{\perp} \frac{1}{m_{\perp}^*} \nabla_{\perp} \right) + V_v \end{pmatrix} \quad [2]$$

where V_c/V_v includes conduction/valence spatial confinement and the self-polarization potential⁶ due to the dielectric mismatch between the spherical PbS quantum dot and the perovskite environment. It is calculated according to the procedure developed in ref.⁷

The neutral exciton system has, in addition, Coulomb interactions. Interacting electron-hole states are obtained by iteratively solving the Schrödinger-Poisson equation in a self-consistent manner. We initially assume an independent particle electron-hole Hartree-product wave function. Then, the Coulomb potential, including polarization due dielectric mismatch effects, is calculated using the Poisson equation, that reads (a.u.),

$$\nabla \cdot [\epsilon(r) \nabla V(r)] = -4\pi \rho^{(k)}$$

The polarization image effects are incorporated in this equation by means of the spatial dependence of the dielectric constant $\epsilon(r)$. $V(r)$ is the potential produced by the density $\rho^{(k)} = \sum_v \varphi_v^{(k)}(r)^2 -$

$\sum_c \varphi_c^{(k)}(r)^2$, with $\varphi_j^{(k)}$ the j -th component (v refers to valence and c to conduction) of the wave function¹. Finally, k refers to iteration cycle. The self-consistent process starts, e.g. with the free electron wave-function $\varphi_e^{(0)}(r)$. From it, we calculate the associated Coulomb potential $V(r)$ by means of the Poisson equation. Then, we diagonalize the Hamiltonian matrix [2] after the addition of the calculated Coulomb potential to the diagonal conduction/valence potential according to $V_{v/c} \rightarrow V_{v/c} - V(r)$.² Once the diagonalization of the Hamiltonian is carried out, we select the hole ground state $\varphi_h^{(1)}(r)$. Its associated density is then injected to the Poisson equation to find the associated potential $V(r)$ that is used, in turn, to modify the Hamiltonian diagonal conduction/valence potential. The diagonalization of this Hamiltonian yields $\varphi_e^{(1)}(r)$. The process is repeated until energy and wave-function convergence. Absorption spectra intensities are taken proportional to the electron-hole overlap squared, which is calculated as in Ref.⁴. The bandwidth is described with a Gaussian function, whose width is fitted to experiments. Strain calculations are carried out in the linear elastic anisotropic continuum model, which has been widely used to describe epitaxial and colloidal hetero-nanostructures.⁸⁻¹⁰ The elastic energy is minimized using Comsol Multiphysics 4.2.

The following table summarizes the material parameters employed in our calculations.

Table S1. PbS (rock salt), oleic acid (OA) and FAPI parameters used in the calculations. OA Kane energy was adapted from eq. (4) in ref¹¹

Description	Symbol	PbS	FAPbI ₃	OA	Units	PbS Ref.	FAPbI ₃ Ref.	OA Ref.
Elastic modulus tensor	C ₁₁	124·10 ⁹	11.1·10 ⁹	--	Pa	¹²	¹³	--
Elastic modulus tensor	C ₁₂	33·10 ⁹	-5.5·10 ⁹	--	Pa	¹²	¹³	--
Elastic modulus tensor	C ₄₄	23·10 ⁹	2.7·10 ⁹	--	Pa	¹²	¹³	--

¹ Electron and hole wave-functions contain both conduction and valence components. We call electron/hole to the eigenvector whose conduction/valence weight is larger and, in general, its energy is positive/negative.

² We have defined the density in a way that it turns to be positive when the contribution of the valence band to the wave function is larger than the conduction band contribution. Therefore, it has the appropriate sign as required by the Poisson equation. Then, attraction/repulsion should decrease/increase the conduction band energy (stabilization/destabilization). All the same, it should increase/decrease the valence band one (again corresponding to stabilization/destabilization). This is the reason of introducing a minus sign in $V_{v/c} \rightarrow V_{v/c} - V(r)$.

Lattice constant	A	5.935	6.362	--	Å	14	13,15	--
Dielectric constant	ϵ	17.2	11.4	2.5	ϵ_0	12	11	16
Electron effective mass	m^*	0.4	0.159	1	m_0	4	11	--
Hole effective mass	m^*	0.33	0.2345	1	m_0	4	11	--
Band gap	E_{gap}	0.41	1.521	6.6	eV	4	11	17
Kane energy	$2P^2/m_0$	2.5	8	3.3	eV	4	11	11

Here ϵ_0, m_0 are the vacuum permittivity and the free electron mass, respectively. P is the momentum matrix element coupling conduction and valence wave functions.

Figure S1. Statistical distribution PbS QDs sizes.

3. ADDITIONAL THEORETICAL CALCULATION

For a more complete characterization of the photo-physics of PbS/FAPI QDs embedded in FAPI, in this section we analyze the influence of different factors in their elastic and optoelectronic response. In Figure S2 we show absorption peak corresponding to the exciton ground state in QDs with varying size. For the calculations, we have chosen the CB and VB offsets to distribute symmetrically the band gap of FAPI (the effect of asymmetric distribution is discussed below).

The figure shows that varying the QD size within the experimental range of dimensions, one can shift the absorption maximum in the range of 750-2,000 nm approximately, covering most of the near

infrared spectrum. These energies are slightly lower than those of QDs embedded in oleic acid (620-1,900 nm, for the same sizes), because the PbS/FAPbI₃ band-offset is smaller.

Figure S2. Exciton absorption spectrum vs QD radius in a PbS/FAPbI₃ system.

The figure also shows that the absorption intensity increases for small dots. This is a (non-trivial) consequence of CB-VB mixing. The main component of the electron and hole wave functions of the exciton have near-unity overlap for all sizes, because the effective masses and band offsets seen for the carriers are similar. However, the eigenvectors of Hamiltonian (2) contain admixture of different components (e.g. the electron ground state has small but finite projection onto the valence band). Minor components barely contribute to the optical recombination because of symmetry restrictions.⁴ We find that, as the quantum dot size decreases, band mixing is gradually suppressed and the overall electron-hole recombination probability increases. This is because off-diagonal terms of the Dimmock Hamiltonian, Eq.(2), which induce band mixing are linear in the momentum, while the diagonal terms splitting energetically electrons from holes are quadratic (kinetic energy). Therefore, with decreasing size the effect of latter prevail over the former, and admixture is quenched. This is illustrated in Figure S3, which shows the evolution of the main component of the electron/hole state in the exciton ground state.

Figure S3. Band purity of the electron (red) and hole (blue) function in the exciton ground state as a function of the PbS QD size. 100% means full CB (for electron) or VB (for hole) component.

To our knowledge, at present no study has determined what the values of conduction and valence band offset between PbS and FAPI are. The fundamental band gap of PbS (L point) is 0.42 eV, and that of FAPI 1.521 eV, but the band alignment between the two materials is not clear. Here we address this issue from a theoretical point of view. The band gap energy of FAPI is decomposed as $E_{\text{gap}} = \Delta E_{\text{CB}} + \Delta E_{\text{VB}}$, where ΔE_j is the energy splitting between the edge of the band j and the mid-gap energy of PbS (see ΔE_{CB} in the schematic in the inset of Figure S4). We vary the value of ΔE_{CB} from 0 to E_{gap} (then, $\Delta E_{\text{VB}} = E_{\text{gap}} - \Delta E_{\text{CB}}$). Figure S4 shows that the highest exciton energy is obtained for a symmetric band gap partition ($\Delta E_{\text{CB}} = E_{\text{gap}}/2$). Away from that point, the energy redshifts and the recombination probability decreases. This is because one of the two carriers (electron or hole) starts leaking into the matrix FAPI, gradually evolving towards a type-II system.

Figure S4. Exciton absorption in a PbS/FAPbI₃ QD with diameter 4.0 nm, as a function of the band alignment (see inset).

Experimentally, the size distribution of PbS/FAPbI₃ QD is found to be 4.7 ± 1.5 nm. The corresponding emission energy in solution is 1,227 nm -see Figure 2a of the main text-. We can fit such an energy assuming the central emission comes from smaller-than-average QDs (~ 4 nm) and symmetric band offset distribution. An asymmetric distribution would require even smaller QD sizes to match experimental results, which is difficult to justify. Therefore, our analysis suggest nearly symmetric band offset distribution as the most likely scenario.

Dielectric mismatch effects are known to be important for colloidal QDs surrounded by molecular ligands. The different dielectric constant in the inorganic QD and the organic environment usually translates into polarization enhancement of the exciton Coulomb interaction, as well as repulsive self-interaction potentials.^{6,7} However, for spherical dots with strong quantum confinement the two effects tend to cancel out and the exciton energy is only weakly affected.¹⁸ We next study how dielectric mismatch effects influence PbS/FAPbI₃ QDs.

In PbS QDs, the relative dielectric constant is large (17.2, high frequency value). In FAPbI₃, an effective relative constant of 11.4 has been proposed,¹¹ which we use in most of our simulations. However, the lattice polarization varies strongly with the external field, and smaller values may be expected if the high-frequency regime is achieved.¹⁹ Moreover, the relatively low band offset between

PbS and FAPI (0.555 eV for symmetric distribution of band offsets) may reduce the compensation between Coulomb polarization and self-potential energy effects. In Figure S5 we analyze the exciton absorption dependence on the outer dielectric constant. As can be seen, both absorption intensity and wavelength are only weakly sensitive to changes in the dielectric confinement, which confirms we are close to the usual case of colloidal spherical QDs,¹⁸ with approximate compensation of attractive and repulsive terms.

Figure S5. Exciton absorption in a PbS/FAPI QD with diameter 4 nm, as a function of the relative dielectric constant of the outer medium, which we let vary between its approximate high frequency value (5-6) and approximate PbS value (18). An effective constant of 11.4 has been proposed¹¹ and used in the rest of calculations of this paper.

In Figure S6 we plot the exciton binding energy in PbS/FAPI QDs, taken as the difference between the converged exciton energy and the single-particle (electron plus hole) energies. A maximum binding energy of ~70 meV is obtained for QDs with radius $R \approx 1.5$ nm. For larger sizes, the binding energy decreases because Coulomb potential is $1/r$ potential term (neglecting dielectric mismatch effects). For smaller sizes, confinement energy exceeds the band-offset potential energy and then carriers start leaking into the matrix, which again reduces the interaction.

Figure S6. Binding energy of an exciton in a PbS/FAPI QD with varying radius.

4. PERCENTAGE OF VOLUME OF QDs IN THE FAPI FILMS WITH EMBEDDED QDs AND CALCULATION OF THE AVERAGE DISTANCE BETWEEN QDs IN THE THIN FILM

To calculate the PbS-PbS distance we assume that the weight concentration of PbS (10 mg/mL) has taken as the constant value before and after the ligand exchange process (this is done by omitting the layer thickness and weight of oleic acid ligands on PbS surface before the ligand exchange and in the same way for the FAPI layer after the post ligand exchange).

FAPI solution was prepared by mixing 1:1.5 ratio of PbI_2 :FAI; the total solute weight of 1,464 mg was dissolved in 2 mL of DMSO (solution **A**). The ligand exchanged PbS quantum dots (10 mg) were dissolved in 0.2 mL of FAPI solution (solution **B**). The 2.5 mg/mL, 5 mg/mL, and 7.5 mg/mL solutions were prepared by mixing 10 μL , 20 μL , and 30 μL of solution **B** with constant amount of 200 μL of solution **A**.

- **Calculation of PbS volume percentage (vol %) contribution respect to the total volume of the FAPI matrix**

$$\text{vol\%} = V_{\text{PbS}} / V_{\text{FAPI}}$$

- a) PbS volume calculation (V_{PbS})

Volume (V) = Mass (m)/density (d)

$$d_{\text{PbS}} = 7.6 \text{ g/cm}^3 \text{ or } 7600 \text{ kg/m}^3$$

The mass of the PbS in the solution **B** is:

$$m_{\text{PbS}} = 10 \text{ mg} (= 10 \times 10^{-6} \text{ kg})$$

So, the volume of PbS in the solution B is:

$$V_{\text{PbS}} = 10^{-5} \text{ Kg}/7600 \text{ kg/m}^3 = \mathbf{1.3157 \times 10^{-9} \text{ m}^3}$$

b) FAPI volume calculation (V_{FAPI})

In order to calculate the volume of the FAPI (V_{FAPI}) we calculate first the unit cell FAPI density ($d_{\text{FAPI UNIT CELL}}$).

According to the literature¹⁵ the total number of atoms/unit cell contributions are

- Number of lead (Pb) = $(1/8) \times 8 = 1$ atom/ unit cell; it is occupied in corner.
- Number of iodide (I) = $(1/4) \times 12 = 3$ atoms/unit cell; it is occupied in cell edges.
- Number of carbon (C) = 1 atom/unit cell; contribution from formamidinium cation.
- Number of nitrogen (N) = 2 atoms/unit cell; contribution from formamidinium cation.
- Number of hydrogen (H) = 5 atoms/unit cell; contribution from formamidinium cation.

So, the unit cell molecular weight is:

$$\text{Atomic weight sum} = (1 \times \text{Pb} + 3 \times \text{I} + 1 \times \text{C} + 2 \times \text{N} + 5 \times \text{H}) = 632.89 \text{ g/mol}$$

$$m_{\text{FAPI unit cell}} = \text{Unit cell molecular weight} / \text{Avogadro's Number } (N_A) = 632.89 \text{ g/mol} / 6.023 \times 10^{23} \text{ mol}^{-1} = 105.07 \times 10^{-23} \text{ g}$$

$$V_{\text{FAPI unit cell}} = 257 \text{ \AA}^3 = 257 \times 10^{-24} \text{ cm}^3 \text{ [15]}$$

$$d_{\text{FAPI unit cell}} = 105.07 \times 10^{-23} \text{ g} / 257 \times 10^{-24} \text{ cm}^3 = 4.088 \text{ g/cm}^3 \text{ or } 4088 \text{ kg/m}^3.$$

Contribution of the FAPI Volume to the solution **B** (total volume 200 μl):

The FAPI mass in 200 μl is proportional to the mass of FAPI in the solution **A** (with a total volume of 2 ml):

$$2,000 \mu\text{l} : 1,464 \text{ mg} = 200 \mu\text{l} : m_{\text{FAPI}}$$

$$m_{\text{FAPI}} = 146.4 \text{ mg} = 1.464 \times 10^{-4} \text{ kg};$$

$$d_{\text{FAPI unit cell}} = 4088 \text{ kg/m}^3$$

$$V_{(\text{FAPISolution B})} = 1.464 \times 10^{-4} \text{ kg} / 4088 \text{ kg/m}^3 = 3.581 \times 10^{-8} \text{ m}^3$$

From the $V_{\text{PbS}} = 1.3157 \times 10^{-9} \text{ m}^3$ (corresponding to the PbS mass in the solution **B** calculated before) it is possible to calculate the PbS volume contribution in the three different concentrations considering that the 2.5 mg/mL, 5 mg/mL, and 7.5 mg/mL solutions were prepared by mixing 10 μL , 20 μL , and 30 μL of solution **B** with constant amount of 200 μL of solution **A**.

$$V_{\text{PbS } 2.5 \text{ mg/mL}} = (1.3157 \times 10^{-9} \text{ m}^3) / (200 \mu\text{L} / 10 \mu\text{L}) = 6.5785 \times 10^{-11} \text{ m}^3$$

$$V_{\text{PbS } 5 \text{ mg/mL}} = (1.3157 \times 10^{-9} \text{ m}^3) / (200 \mu\text{L} / 20 \mu\text{L}) = 1.3157 \times 10^{-10} \text{ m}^3$$

$$V_{\text{PbS } 7.5 \text{ mg/mL}} = (1.3157 \times 10^{-9} \text{ m}^3) / (200 \mu\text{L} / 30 \mu\text{L}) = 1.9934 \times 10^{-10} \text{ m}^3$$

Thus, the volume percentages are:

$$\text{Vol \% PbS } 2.5 \text{ mg/mL} = V_{\text{PbS } 2.5 \text{ mg/mL}} / V_{\text{FAPISolution B}} = (6.5785 \times 10^{-11} \text{ m}^3) / (3.581 \times 10^{-8} \text{ m}^3) \times 100 = \mathbf{0.18\%}$$

$$\text{Vol \% PbS } 5 \text{ mg/mL} = V_{\text{PbS } 5 \text{ mg/mL}} / V_{\text{FAPISolution B}} = (1.3157 \times 10^{-10} \text{ m}^3) / (3.581 \times 10^{-8} \text{ m}^3) \times 100 = \mathbf{0.37\%}$$

$$\text{Vol \% PbS } 7.5 \text{ mg/mL} = V_{\text{PbS } 7.5 \text{ mg/mL}} / V_{\text{FAPISolution B}} = (1.9934 \times 10^{-10} \text{ m}^3) / (3.581 \times 10^{-8} \text{ m}^3) \times 100 = \mathbf{0.55\%}$$

- **Calculation of PbS-PbS particle distance**

We assume that PbS quantum dots (4 nm in diameter) are equally distributed in the FAPI perovskite matrix in a cuboidal geometry. The edge length of cube gives the distance between the PbS-PbS centres. The volume of the cube gives the ratio of one PbS quantum dot volume to the volume percentage distribution of PbS in the film. (NB: the factor in the numerator is the effective contribution of individual parts in a cube which give rise to the volume of one PbS quantum dot). The volume of PbS quantum dot is approximated to the volume of the sphere $(4/3)\pi r^3$.

$$V = l^3 = (\text{Volume of one PbS quantum dot}) / (\text{volume percentage})$$

$$l = [(\text{Volume of PbS quantum dot}) / (\text{volume percentage of PbS in the film})]^{1/3}$$

a) PbS diameter 2 nm

$$V_{\text{PbS QDs}} = (4/3)\pi r^3 = (4/3) \cdot \pi \cdot (1 \times 10^{-9})^3 = 4.19 \times 10^{-27} \text{ m}^3$$

The centre to centre distance is related to the volume percentage of PbS in the film:

- For 2.5 mg/mL (the volume percentage of 0.18%)

$$l_{\text{PbS } 2 \text{ nm}} = [(4.19 \times 10^{-27} \text{ m}^3 / 0.0018)]^{1/3} = \mathbf{13.25 \text{ nm}}$$

ie, the border to border distance is = 13.25 nm – 2 nm = 11.25 nm

- For 5 mg/mL (the volume percentage of 0.37%)

$$l_{\text{PbS } 2 \text{ nm}} = [(4.19 \times 10^{-27} \text{ m}^3 / 0.0037)]^{1/3} = \mathbf{10.42 \text{ nm}}$$

ie, the border to border distance is = 10.42 nm – 2 nm = 8.42 nm

- For 7.5 mg/mL (the volume percentage of 0.55%)

$$l_{\text{PbS } 2 \text{ nm}} = [(4.19 \times 10^{-27} \text{ m}^3 / 0.0055)]^{1/3} = \mathbf{9.13 \text{ nm}}$$

ie, the border to border distance is = 9.13 nm – 2 nm = 7.13 nm

b) PbS diameter 4 nm

$$V_{\text{PbS QDs}} = (4/3)\pi r^3 = (4/3)\pi(2 \times 10^{-9})^3 = 33.5 \times 10^{-27} \text{ m}^3$$

The centre to centre distance is related to the volume percentage of PbS in the film:

- For 2.5 mg/mL (the volume percentage of 0.18%)

$$l_{\text{PbS } 4 \text{ nm}} = [(33.5 \times 10^{-27} \text{ m}^3 / 0.0018)]^{1/3} = \mathbf{26.5 \text{ nm}}$$

ie, the border to border distance is = 26.5 nm – 4 nm = 22.5 nm

- For 5 mg/mL (the volume percentage of 0.37%)

$$l_{\text{PbS } 4 \text{ nm}} = [(33.5 \times 10^{-27} \text{ m}^3 / 0.0037)]^{1/3} = \mathbf{20.8 \text{ nm}}$$

ie, the border to border distance is = 20.8 nm – 4 nm = 16.8 nm

- For 7.5 mg/mL (the volume percentage of 0.55%)

$$l_{\text{PbS } 4 \text{ nm}} = [(33.5 \times 10^{-27} \text{ m}^3 / 0.0055)]^{1/3} = \mathbf{18.3 \text{ nm}}$$

ie, the border to border distance is = 18.3 nm – 4 nm = 14.3 nm

c) PbS diameter 8 nm

$$V_{\text{PbS QDs}} = (4/3)\pi r^3 = (4/3)\pi(4 \times 10^{-9})^3 = 267.94 \times 10^{-27} \text{ m}^3$$

The centre to centre distance is related to the volume percentage of PbS in the film:

- For 2.5 mg/mL (the volume percentage of 0.18%)

$$l_{\text{PbS } 8 \text{ nm}} = [(267.94 \times 10^{-27} \text{ m}^3 / 0.0018)]^{1/3} = \mathbf{52.99 \text{ nm}}$$

ie, the border to border distance is = 52.99 nm – 8 nm = 44.99 nm

- For 5 mg/mL (the volume percentage of 0.37%)

$$l_{\text{PbS } 8 \text{ nm}} = [(267.94 \times 10^{-27} \text{ m}^3 / 0.0037)]^{1/3} = \mathbf{41.68 \text{ nm}}$$

ie, the border to border distance is = 41.68 nm – 8 nm = 33.68 nm

- For 7.5 mg/mL (the volume percentage of 0.55%)

$$l_{\text{PbS } 8 \text{ nm}} = [(267.94 \times 10^{-27} \text{ m}^3 / 0.0055)]^{1/3} = \mathbf{36.52 \text{ nm}}$$

ie, the border to border distance is = 36.52 nm – 8 nm = 28.52 nm

Table S2. Distances between PbS QDs for different QDs size and concentrations.			
QDs diameter (nm)	2.5 mg/ml (0.18 vol%)	5mg/ml (0.37 vol%)	7.5 mg/ml (0.55 vol%)
2	13.25 nm	10.42 nm	9.13 nm
4	26.5 nm	20.8 nm	18.3 nm
8	52.99 nm	41.68 nm	36.52 nm

Figure S7. a) Trend of the annealing time for the formation of the black phase in function of the concentration of the PbS QDs 3.8 nm and in function of the size of the PbS QDs. The picture shows that at 85 °C the fast conversion into FAPI black phase after solution spin coating occurs for the samples with PbS 3.8 nm 5mg/ml embedded, while with the other two concentrations and sizes become dark more slowly. **b)** Trend of the time for the preservation of the black phase in function of the concentration of the PbS QDs 3.8 nm and in function of the size of the PbS QDs. Note that for samples with PbS QDs 3.8 nm prepared with a concentration of 5 mg/ml the black phase is stable for more than 30 days. The picture shows that after 15 days the film with PbS QDs of 2.9 nm and 3.8 nm are more stable.

Figure S8. a) Photography of the FAPI with different concentrations of the PbS QDs (3.8 nm diameter), during the annealing at 140 °C. **b)** Top view SEM images of the FAPI spin-coated from DMF:DMSO (9:1) at low and high magnification.

Figure S9. XRD patterns of the FAPI films spin coated from DMSO with and without PbS QDs (3.8 nm diameter), annealed at 80 °C for 30 minutes.

Figure S10. Uv-vis absorbance spectra of the FAPI thin film without and with PbS QDs **a)** fresh made and **b)** after 30 days. The slight shift of the FAPI with 2.5 mg/ml PbS QDs is due to the formation of the δ -phase.²⁰

Figure S11. a) Steady state PL and b) TEM images of the PbS QDs with different sizes. The scale bar is 20 nm; c) XRD patterns of the film without and with PbS QDs embedded, with different sizes, fresh made and after 15 days.

Figure S12. TGA curves FAPI and FAPI-PbS 5mg/ml in DMSO, from room temperature to 1,000 °C, under nitrogen. This figure shows the sequentially loss of the solvents, the decomposition of the FAI in HI and FA and the decomposition of the PbI₂ octahedra and that the PbS QDs preserve the thermal stability until 300 °C, meaning that do not change the acidity of the formamidinium, indeed higher is the acidity lower the degradation temperature.²¹

5. DENSITY FUNCTIONAL THEORY (DFT) CALCULATIONS

We performed DFT calculations with the Quantum Espresso code²² on slabs and bulk systems using pseudopotentials generated with the PBEsol exchange-correlation functional, spin-orbit interactions and, in the case of slabs of PbS, FAPI, and FAPI-PbS, dipolar corrections and a void space of 12 Å. The atomic structures were relaxed until the forces on the individual nuclei were smaller than 0.001 Ry/a₀ for bulk systems, 0.002 Ry/a₀ for PbS slabs, and 0.004 Ry/a₀ for FAPI slabs and FAPI-PbS heterojunctions, where a₀ is the Bohr radius. The first Brillouin zone was sampled based on a Monkhorst-Pack grid centered on the Gamma point with: 8.8.8 k points for PbS bulk and for free and strained α bulks; 6.6.6 k points for the rest of α bulks; 4.4.4 k points for FAPI bulks in the δ phase; 4.4.1 k points for α slabs and PbS (100) substrates; 3.3.1 k points for δ slabs and PbS (111) substrates; and with 3.3.1 and 2.2.1 k points for FAPI-PbS heterojunctions in the α - and δ -phase, respectively.

Results

1. PbS bulk. The relaxed lattice parameter is 5.90 Å.

2. α -phase

The computed bulk unit cell is a fully optimized pseudo-cubic structure¹⁵ with a single formula unit of 12 atoms and lattice constants $a = 6.41$ Å, $b = 6.25$ Å, and $c = 6.36$ Å, see Fig. S13a). This cell is comparable, in volume, to a cube of 6.34 Å size. The calculated total energy is $E_{\text{freebulk}} = -2068.7912$ Ry. Moreover, the α bulk strained by the (100) surface of PbS has lattice parameters $a = b = 5.90$ Å and $c = 7.10$ Å, Fig. S13b). The total energy is $E_{\text{strbulk}} = -2068.7802$ Ry.

Figure S13. Atomic description of **(a)** free and **(b)** strained unit cells of FAPI in alpha phase.

We calculated as well a FAPI slab (~ 19 Å width), a PbS substrate showing the (100) face (~ 12 Å), and a FAPI-PbS heterojunction (~ 33 Å), Fig. S14. Their respective total energies are $E_{\text{slab}} = -6206.2985$ Ry, $E_{\text{subs}} = -9318.7964$ Ry, and $E_{\text{hj}} = -15525.1922$ Ry.

Figure S14. Atomic representation of **(a)** FAPI slab in α -phase, **(b)** PbS (100) substrate, and **(c)** FAPI-PbS heterojunction.

Surface and interaction energies

The previous total energies allow us to estimate the mean surface energy (of top and bottom faces) as $E_{\text{surf}} = (E_{\text{slab}} - 3 \cdot E_{\text{strbulk}}) / 2 = (-6206.2985 - 3 \cdot (-2068.7802)) / 2 = 0.021$ Ry = 0.29 eV. Based on this value, the interaction energy is approximated as $E_{\text{inter}} = E_{\text{hj}} - E_{\text{subs}} - E_{\text{surf}} - 3 \cdot E_{\text{strbulk}} = -15525.1922 + 9318.7964 - 0.021 + 3 \cdot 2068.7802 = -0.0762$ Ry = -1.04 eV.

3. δ -phase

The free δ bulk unit cell is a fully optimized structure with two formula units (fu) and 24 atoms, Fig S15a), with lattice parameters $a = 9.55$, $b = 8.55$ Å, $c = 7.87$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 124^\circ$; the experimental values are $a = b = 8.66$ Å, $c = 7.90$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$.²³ The calculated total energy is $E_{\text{freebulk}} = -4137.6222$ Ry, thus -2068.8111 Ry/fu. The strained δ bulk on the (111) surface of PbS has lattice parameters $a = b = 8.34$ Å and $c = 8.51$ Å with angles $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$, Fig. S15b). The total energy is $E_{\text{strbulk}} = -4137.5864$ Ry.

Figure S15. Atomic description of (a) free and (b) strained unit cells of FAPI in δ phase.

We calculated as well a FAPI slab (~ 16 Å width), a PbS substrate showing the (111) face (~ 9 Å), and a FAPI-PbS heterojunction (~ 20 Å), Fig. S16. Their respective total energies are $E_{\text{slab}} = -8274.8412$ Ry, $E_{\text{subs}} = -11182.2827$ Ry, and $E_{\text{hj}} = -15319.7236$ Ry.

Figure S16. Atomic representation of (a) FAPI slab in δ -phase, (b) PbS (111) substrate, and (c) FAPI-PbS heterojunction.

Surface and interaction energies

From the previous total energies we calculate the mean surface energy as $E_{\text{surf}} = (E_{\text{slab}} - 2 \cdot E_{\text{strbulk}}) / 2 = (-8274.8412 - 2 \cdot (-4137.5864)) / 2 = 0.1658 \text{ Ry} = 2.25 \text{ eV}$. Based on this value, the interaction energy is approximated as $E_{\text{inter}} = E_{\text{hj}} - E_{\text{subs}} - E_{\text{surf}} - E_{\text{strbulk}} = -15319.7236 - (-11182.2827) - 0.1658 + 4137.5864 = -0.0203 \text{ Ry} = -0.28 \text{ eV}$.

The estimated surface energy of 2.25 eV for the δ phase is significantly larger than 0.29 eV for the α phase, and the interaction energy of -0.28 eV is significantly smaller than -1.04 eV. These energy values provide physical insight into the origin of the reported larger stability of the alpha phase on the PbS substrate.

4. Uniaxial and biaxial tensile and compressive strain

In order to assess the effect of strain in the stability of α and δ phases, we have calculated the total energies of bulk crystals with tensile and compressive strain on one and two axis, Fig. S17: uniaxial in the direction of the formamidinium molecule, **c** axis, and biaxial on the perpendicular plane, axis **a** and **b**. We have considered deformations between -7 % and +6 % on cubic ($a = 6.34 \text{ \AA}$) and hexagonal bulk crystals in α and δ phases, respectively. The reported data suggest that the relative stabilities of α and δ phases cannot be switched only through strain, and would confirm the role of the PbS substrate in stabilizing the α -phase.

Figure S17. Energy vs. strain for biaxial strain on axis **a** and **b** (with circles) and uniaxial strain on **c** axis (with triangles) on alpha (cubic, black) and delta (hexagonal, yellow) bulk crystals, with indication of the unit-cell volume in the inset graph. The -7% corresponds to the compression on PbS (100) surface (5.9/6.34).

6. Strain and Displacement calculations

In Figure S18a we calculate the strain in a system formed by two PbS QDs inside a FAPI matrix. The dots are split along the (100) crystallographic axis, and the strain tensor component we plot is parallel to this direction. One can see that strain accumulates in the region in between QDs, for short enough distances. Figure S18b shows the associated total displacement.

Figure S18. a) Strain between two QDS with 5 nm (green), 10 nm (blue), 16.8 nm (orange) and 33.7 nm (red) edge to edge separations. QDs have 4 nm (8 nm) diameter in left (right) panels. The dots are separated along the (100) direction of the crystal and the strain component is that parallel to that direction. **b)** Total displacement for different distances between two QDs (4 nm diameter) surrounded by FAPI.

Figure S19. Statistical analysis of of **a)** J_{sc} , **b)** V_{oc} , **c)** FF, **d)** PCE of the perovskite solar cells fabricated with bare FAPI or with FAPI-PbS QDs in the concentration of 5 mg/ml as active layers. The data from 20 cells were statistically analyzed.

Table S3. Figures of merits, J_{sc} , FF, V_{oc} , PCE, expressed as mean and standard deviation, in forward and reverse scan for the solar cells based on FAPI or FAPI-PbS QDs 5mg/ml.

	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	PCE %	Best PCE %
FAPI-PbS rev	21.8 ± 0.7	1060 ± 20	70 ± 5	16.2 ± 2	18.0
FAPI-PbS fw	20.8 ± 0.5	1054 ± 25	69 ± 6	15.1 ± 2	16.1
FAPI rev	22.3 ± 0.6	1020 ± 59	58 ± 13	13.1 ± 3	16.4
FAPI fw	21.2 ± 0.4	1018 ± 40	57 ± 20	12.3 ± 2	15.9

Figure S20. IPCE spectra and integrated photocurrent of the champion devices.

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