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Lattice Anchoring Stabilizes Solution-Processed Semiconductors

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The stability of solution-processed semiconductors remains an important area for improvement on their path to wider deployment. Inorganic cesium lead halide perovskites have a bandgap well-suited to tandem solar cells¹; but suffer from an undesired phase transition in the vicinity of room temperature². Colloidal quantum dots (CQDs) are structurally robust materials prized for their size-tunable bandgap³; yet they too require further advances in stability, for they are prone to aggregation and surface oxidization at high temperatures as a consequence of incomplete surface passivation^{4,5}. Here we report lattice-anchored materials that combine cesium lead halide perovskites with lead chalcogenide CQDs and achieve as a result stability exceeding that of the constituent materials. We find that CQDs keep the perovskite in its desired black phase, suppressing the transition to the undesired, lattice-mismatched, phases. We achieve an order of magnitude enhancement in air stability for the perovskite, reporting greater than six months' stability at room ambient condition (25 °C, 30±5% humidity); and also document more than five hours at 200°C in air. The perovskite prevents oxidation of the CQD surfaces and reduces the nanoparticles' agglomeration under 100°C by a factor of five compared to CQD controls. The matrix-protected CQDs exhibit 30% photoluminescence quantum efficiency for a CQD solid emitting at infrared wavelengths. The lattice-anchored CQD:perovskite solid exhibits a doubling in charge carrier mobility as a result of a reduced energy barrier for carrier hopping compared to the pure CQD solid. These benefits indicate the potential of this new materials platform in solution-processed optoelectronic devices.

Solution-processed semiconductors combine ease of processing, scalable fabrication, and compatibility with flexible substrates – compelling properties for next-generation optoelectronic devices⁶. Given solution-processed materials' steadily-increasing performance in sensing⁷, light-emission^{8,9} and photovoltaics^{3,10}, their limited stability is an increasingly urgent and important challenge. Much progress has been made toward the goal for the long-term stability in printable semiconductors^{11,12}; however, their lifetime in room ambient and at elevated temperatures and humidity has not yet fulfilled the multi-thousand-hour stringent requirement for industrial applications.

Hybrid organic-inorganic perovskites – solution-processed, structurally soft materials¹³ – have attracted intense interest especially as a result of their remarkable photovoltaic performance¹⁴. The best certified power conversion efficiency (PCE) of perovskite solar cells has rapidly advanced to 23.7%¹⁵. However, the limited environmental and thermal stability of perovskites remains an important challenge that – until it is addressed – threatens to hamper their widespread deployment in optoelectronics and energy harvesting. This instability stems from the volatility of perovskites' organic components, aggravated by external stress such as heat and light¹⁶.

These issues can potentially be addressed using all-inorganic perovskites, of which cesium lead halide perovskite CsPbX_3 (X=halide) is a candidate of interest. The cubic phase (α -phase) CsPbI_3 has a bandgap suited to tandem solar cells¹. Unfortunately, it transforms readily into the transparent orthorhombic phase (δ -phase) under ambient conditions at room temperature². This is associated with the low formation energy of the δ -phase at room temperature and the high flexibility of the perovskite lattice¹⁷. Substituting iodine with bromine improves the stability of α -phase; however, mixed-halide perovskites undergo

phase segregation when annealed at high temperature in air ambient. Approaches to stabilizing the α -phase CsPbX_3 perovskite are of urgent interest.

CQDs – also solution-processed and widely studied for optoelectronic applications – have a bandgap that is tuned via the quantum size effect across the wide solar spectrum³. Advanced materials processing strategies and device architectures have contributed to improved solar cell performance^{10,11}; however, incomplete surface passivation leads to CQD aggregation and surface oxidation⁴, particularly when operated at high temperatures. These militate against device performance and lifetime.

Previously investigated methods to improve the stability of inorganic solution-processed materials have advanced each material system considerably. For α -phase CsPbX_3 perovskites, decreasing grain size and doping were proven useful for phase stabilization^{2,18–20}. However, the stability is still not satisfactory; and a large number of surface trap states are detrimental to their electronic properties²¹. Moreover, stability under demanding accelerated lifetime conditions, such as 200°C in air ambient, remains to be addressed.

For CQDs, improved air stability has been achieved using strongly-bound surface ligands^{3,11}. Unfortunately, the oxidation of sulfur-rich facets in lead sulfide CQDs occurs at temperatures as low as 50°C and deteriorates device performance^{5,22}. Recent studies revealed that a monolayer of perovskite provided surface passivation of CQDs, a promising insight on the path to longer-term stability^{23–26}; however, these perovskites failed to prevent oxidation and aggregation of the CQDs at high temperatures.

In sum, ever more effective stabilization strategies are needed both in perovskites and CQDs.

We sought herein an approach that would block the phase transition of CsPbX₃. We would prevent atomic site adjustment and lattice deformation by incorporating inclusions – CQDs – that lattice-matched to the desired, but otherwise unstable, α -solid; while being appreciably mismatched with the δ -phase.

The new hybrid material demonstrates a significant improvement in stability relative to the individual stability of each component. CQDs promote the epitaxial growth of α -phase perovskite and anchor the atoms of the perovskite to the CQD surfaces. This leads to improved ambient lifetime, which reaches greater than six months for the newly-stabilized CsPbX₃ perovskite. It also leads to significantly enhanced thermal stability in air – materials do not degrade following exposure to 200°C for five hours. This is fully an order of magnitude longer than for the pure perovskite absent the CQDs.

The CQD:perovskite lattice-anchored hybrid materials system is depicted in Figure 1a. Lead chalcogenides – PbS and PbSe – with their rock salt structure have a Pb-Pb distance of 5.94 and 6.12 Å²⁷, respectively, close to that of the α -phase CsPbBr_xI_{3-x} perovskite (5.85 Å to 6.21 Å)¹. By tuning the Br to I ratio in matrix composition, we achieve near-zero lattice mismatch (ϵ) for PbS CQDs at Br content ~ 66% ($\epsilon < 0.2\%$), enabling the strain-free epitaxial growth of perovskite (Figure 1b).

We prepared the hybrid films using CsPbBr_xI_{3-x} matrix solutions combined with pre-exchanged CQDs (Figure S1). By controlling the weight ratio of CQD to perovskite, we tuned the amount of perovskite matrix and the expected average dot-to-dot distance²⁴. The hybrid ink was deposited by spin-coating to achieve an optimized thickness, followed by an annealing process to crystallize the matrix and remove solvent residue. Elemental mapping from energy dispersive X-ray spectroscopy (EDX) in scanning electron

microscopy (SEM) indicates a uniform elemental distribution in the hybrid films (Figure S1c-f, S2).

We carried out synchrotron high-resolution X-ray diffraction (XRD) measurements to elucidate the composition and crystal structure of the hybrid films (Figure 1c, S3). In this study, we used CQD films with CsPbBrI₂ and CsPbBr₂I matrix. XRD demonstrates that as-synthesized perovskite and CQDs are each in the cubic phase: CsPbBrI₂ shows a 1% lattice mismatch with PbS CQDs; in contrast, CsPbBr₂I and PbS show complete agreement in lattice planes (Figure S3b).

We then used high-resolution transmission electron microscopy (HRTEM) to ascertain further the crystal structure and identify the orientation of perovskites and CQDs relative to one another (Figure 1d, 1e, S4a, S4b). The real space images show that a perovskite shell forms at high CQD concentration and inherits the crystalline orientation of its associated dot (Figure 1d). No spacing differences between core CQD and perovskite shell were observed from HRTEM images, indicating epitaxial orientational alignment at two dominant facets. Lattice fringes of 3.4 ± 0.1 Å and 3.0 ± 0.1 Å spacing are ascribed to (1 $\bar{1}$ 1) and (200) planes, respectively, both for the CQDs and for the matrix, in agreement with Fast Fourier Transform (FFT) images (Figure S4a, S4b). As the amount of perovskite increases, the shell grows thicker and forms a continuous matrix with dots embedded inside (Figure 1e). The incorporation of CQDs is further confirmed via elemental distribution analysis using electron energy-loss spectroscopy mapping (Figure S4c, S4d).

We then investigated the effect of embedded dots on perovskite lifetime. In pristine CsPbBr_xI_{3-x} films, phase transition and phase segregation are detrimental to their stability. An α -phase (dark) to δ -phase (transparent) transition occurs, particularly in films with low

Br content, at low temperatures (e.g. room atmosphere), leading to a loss in the amplitude of film absorption. Phase segregation occurs when mixed-halide perovskite films are annealed in air at high temperatures, a result of the increased ion migration triggered by oxygen and heat. This results in separated Br-rich phases and I-rich phases (Figure 2a), leading to a blueshift in the absorption edge. Film degradation is thus readily witnessed via an intensity loss and bandedge shift in absorption spectra (Figure 2b).

We used a volume fraction lower than 15% of CQDs in order to ensure uniform coverage and maintain the original grain size of perovskites (Figure S1c-f). The films were stored in air at room-ambient condition, under $30\pm 5\%$ relative humidity at 25 °C, unencapsulated. Our findings reveal that the incorporation of CQDs improves the stability of perovskite films by an order of magnitude (Figure S5a). We associate the improved stability with the high formation energy of the α/δ -phase interface. For CsPbBrI₂ perovskite, room-ambient stability is enhanced from three days to more than six months when 13 vol% CQDs are incorporated (Figure 2c). XRD measurements confirm that the crystal structure remains unchanged after six months storage. This strategy is also compatible with previously-reported methods² and allows for greater than six months' stability in lattice-anchored CsPbI₃ (Figure S5b).

We then proceeded to explore the thermal stability of perovskites in air. The absorption spectra of films were recorded before and after annealing in air at 200°C for five hours (Figure 2d and 2e). Phase segregation occurs in pristine perovskite films within 30 min. However, this is largely suppressed when CQDs are integrated at a concentration above 6%: no film degradation is observed following five hours of annealing in air.

We found the extent of improvement in film stability to depend strongly on the lattice mismatch between CQDs and perovskite. For CQD:CsPbBr₂I samples in which ~ zero lattice mismatch is achieved, reduced intensity loss and bandedge shift in absorption spectra are detected with increasing CQD concentrations, showing a gradual improvement in film stability. When lattice mismatch increases as we decrease the Br ratio, a larger strain is generated at interfaces. The stability vs. increasing CQD concentration follows a V-shaped trend, first declining and then improving. We explain this by invoking interfacial strain between perovskites and CQDs: an unstrained CQD/perovskite interface is the most energetically favourable; and a certain amount of elastic strain can be accommodated without generating dislocations or defects²⁸.

In a lattice-mismatched system, a lower CQD concentration results in more perovskite layers between neighbouring CQDs and consequently increases the effects of strain. At low CQD loading, the interfacial strain is large enough to generate atomic dislocations. In this case, CQD surfaces act as defect centers, and the increasing concentration thus leads to a decreased lifetime of the perovskite. When the dot-to-dot distance is small enough to keep the strain energy below the formation energy of dislocations²⁹, the stability is increased. As a result, a perovskite matrix with the larger lattice mismatch demands a higher CQD concentration to anchor the atoms and achieve improved lifetime (Figure 2d, 2e). This result is consistent with the observed phase stability measured at room temperature (Figure S5a).

We then turned to investigate the thermal stability of CQDs when a perovskite matrix is added. Our hypothesis was that passivation provided by the perovskite matrix could inhibit oxidation and aggregation of CQDs.

We carried out in-situ grazing incident small-angle X-ray scattering (GISAXS) measurements to track changes in CQD packing density and uniformity at elevated temperatures (Figure 3). Before annealing, pure and hybrid films each present a hexagonal diffraction pattern, indicating an orientational ordering of CQDs (Figure S6). Azimuthal integration of the diffraction pattern (Figure 3b, 3d) reveals changes at elevated temperatures. It reveals that pure CQD films begin to show aggregation at relatively low temperatures (40°C), and lose packing uniformity rapidly as temperature increases. By contrast, no degradation is observed below 100°C in the matrix-protected films. Following annealing, the hexagonal pattern is no longer observable in pure CQD films; whereas it is sustained in hybrid films (Figure 3a, 3c).

Photoluminescence (PL) studies affirm this finding: we recorded the PL intensity of films following annealing under 100°C for different periods of time (Figure 3e). The pure CQD film shows a rapid PL quenching and loses half of the intensity after an hour, which is consistent with a previous report⁵. In contrast, matrix-protected films maintain 90% of the initial value following annealing.

In addition to evincing improved stability, the hybrid materials also show improved optoelectronic properties. The quantum dots used in this study, which have bandgaps ranging from 1.1 eV and 1.3 eV, were predicted to experience both hole and electron confinement by the CsPbBr_xI_{3-x} matrix, i.e. to the lower-bandgap inclusions within a type-I heterostructure (Figure 4a, S7a). When the perovskite matrix is excited using light having a photon energy that exceeds its bandgap, photocarriers are generated in the perovskite and transfer from matrix to the CQDs. This contributes to an enhanced near-infrared PL emission compared to the situation in which excitons are generated in CQDs only. At high

CQD loading, the carrier transfer efficiency²⁴ exceeds $87\pm 3\%$ (Figure 4d, Table S1). A complete quenching of the perovskite signal is also observed, consistent with efficient carrier transfer (Figure S7b).

The PL increases as the concentration of CQDs is reduced, and reaches its maximum in films with 7 vol% CQDs (Figure S7c). We studied the photoluminescence quantum efficiency (PLQE) of films having different matrix compositions to verify the effect of an epitaxially grown matrix on interface passivation (Figure 4e). The PLQE of CQDs increases with a higher bromine ratio in the matrix and peaks at 67% bromine concentration, the value at which lowest lattice mismatch is achieved ($\epsilon < 0.2\%$). The lattice-matched matrix augments surface passivation of CQD solids and leads to a film PLQE of $30\pm 3\%$ at the infrared wavelength, equivalent to the PLQE of CQD solution. The film retains its initial value of PLQE after it is stored in air for one week. By contrast, the film PLQE is below 15% when the lattice mismatch is above 0.5%.

We investigated whether the inorganic matrix – with its modest conduction band (CB) and valence band (VB) offsets relative to the dots – could improve carrier mobility relative to prior CQD solids. Pure CQD films exhibit random close packing with a theoretical maximum volume fraction of about 64%³⁰. This corresponds to about 30% of film volume that – in the absence of matrix – can be occupied by high-barrier vacuum (Figure 4c). We posited that, when the perovskite matrix was added at a level sufficient to fill substantially these voids, this could ease transport via barrier lowering (Figure 4b).

We obtained carrier mobility using transient absorption spectroscopy (TAS) studies, and observed a doubling in mobility in the matrix-infiltrated CQDs with 15 vol% CsPbBr₂I compared to pristine CQD films (Figure 4e, S8).

We then pursued the realization of CQD solar cells with the best matrix-infiltrated active layer. We relied on a previously-reported photovoltaic device architecture³ (Figure S9a). The matrix-protected CQDs demonstrate improved photovoltaic properties compared to controls, generating higher current density and open-circuit voltage (Figure S9b, S9c). When we used 15 vol% CsPbBr₂I matrix, the devices show a reproducibly increased performance relative to controls, and a champion PCE of 12.6%. They also exhibit significantly enhanced photostability, retaining 95% of their initial PCE following two hours of continuous AM1.5G illumination, unencapsulated (Figure S9d). The matrix-free controls, on the other hand, degrade to 70% of their initial PCE value within an hour. This result supports the contention that the lattice-matching perovskite matrix provides improved surface passivation and lowers the energy barrier for carrier hopping.

This work reports a lattice anchoring strategy that provides solution-processed semiconductor materials exhibiting increased stability relative to either constituent phase. We incorporated CQDs in CsPbBr_xI_{3-x} perovskites and suppressed thereby the formation of the undesired δ -phase configuration. This significantly increased the lifetime of α -phase cesium lead halide perovskite including under 200°C multi-hour thermal stress. The epitaxially-oriented perovskite matrix also provides excellent passivation to CQD surfaces, inhibiting attack from oxygen and preventing CQD fusion at elevated temperatures. In addition, the perovskite matrix lowers the energetic barrier to carrier transport, contributing to a doubling in carrier mobility. This study suggests avenues to stabilize further structures such as cesium-based and formamidinium-based perovskites; to improve the thermal stability of CQDs; and to enhance the performance of solution-processed optoelectronic materials and devices.

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Author Contributions

M.L. conceived the idea of this study. M.L. developed the hybrid materials system, fabricated solar cell devices, and performed synchrotron X-ray diffraction measurements and materials stability test. Y.C., B.S. and B.S. assisted in the fabrication of quantum dot in matrix samples. C.-S.T. performed TEM imaging. R.Q.-B. contributed to XPS measurements. A.H.P. carried out transient absorption measurements. R.M. and A.A. carried out *in-situ* GISAXS measurements. H.T. contributed to GIWAXS measurements. G.W. contributed to photoluminescence measurements. A.P.T.K. carried out the mobility measurements. M.-J. C. performed SEM imaging and EDX analysis. O.V., F.P.G.A., S.O.K., and E.H.S. supervised the project. All authors discussed the results and assisted in the preparation of the manuscript.

Competing interests

The authors declare no competing interests.

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Figure 1. Epitaxial alignment between cesium lead halide perovskite and colloidal quantum dots. **a**, Schematics that depicts the atomistic model of CQD:perovskite lattice-anchored hybrid materials system. **b**, The lattice constant of lead chalcogenide CQDs and cesium lead halide perovskites of different stoichiometry. **c**, Synchrotron X-ray diffractions of the CQDs with perovskite matrix showing the successful incorporation of CQD and perovskite components in the hybrid materials. **d and e**, HRTEM images of the lattice-anchored CQD:perovskite hybrid materials at high (d) and low (e) CQD concentration. The shell has a lower contrast compared to CQDs, since the perovskite has a lower density than PbS. These confirm the crystal structure and demonstrate the epitaxial orientational alignment at different facets.

Figure 2. Stability of CQD-anchored cesium lead halide perovskites. **a**, Schematic of phase transition and separation in cesium lead halide perovskites. The cubic to orthorhombic phase transition occurs at room temperature by exposure to moisture and air. Mixed halide perovskite samples, when heated to a high temperature in air, segregate into Br-rich and I-rich phases. **b**, The absorbance spectra of pristine CsPbBrI₂ film before and after annealing at 200°C for five hours. The high annealing temperature leads to a notable phase degradation and segregation, which is verified by the changes in absorbance and the shift of absorption edge, respectively. **c**, Stability of the lattice-anchored CsPbBrI₂ perovskite with different ratio of CQDs. The film stability is improved from three days to more than six months when 13 vol% CQDs are incorporated. Inset figure shows the X-ray diffraction of CsPbBrI₂ films with and without CQDs after stored in air for six months. **d and e**, The intensity loss in absorbance (d) and the shift in absorption edge (e) after five-hour annealing in air.

Figure 3. Changes in CQD packing density and uniformity at elevated temperatures. **a and c**, GISAXS 2D pattern of the matrix-protected CQD film (a) and pristine film (c) measured at 70°C. Dark color represents the lower intensity and bright color represents the higher intensity. The in-situ GISAXS scans were taken from room temperature to 100 °C. **b and d**, Azimuthally-integrated GISAXS intensities of the matrix-protected CQD (b) and pristine CQD film (d) showing the distribution of inter-dot spacing at elevated temperatures. **e**, Changes in PL intensity when different annealing time is applied.

Figure 4. Carrier transfer and energetics within lattice-anchored CQD-in-perovskite hybrid solids. **a-c**, Schematics of carrier transport in the case of low CQD loading (a), high CQD loading (b), and pure CQDs (c). The conduction and valence band of CQD solids reside within the bandgap of CsPbBr_xI_{3-x} matrix, forming a type I heterojunction. At low CQD loading, the photocarriers generated in perovskite matrix transfer to embedded CQD solids. At high CQD loading, the carriers tunnel through the perovskite matrix by overcoming an energy barrier. **d**, PL excitation spectra of CQDs. In the perovskite absorption region, the PL excitation intensity increases as matrix concentration increases, showing an efficient carrier transfer from matrix to CQDs. **e**, PL and PLQE of CQDs with different perovskite matrix. **f**, Carrier mobility measured by transient absorption spectroscopy. Matrix-infiltrated CQD films show a doubling in carrier mobility compared to pristine CQD films.

Methods

1) CQD synthesis and solution ligand exchange. CQDs were synthesized and washed using previously published methods³¹. A ligand-exchange process was carried out in the solution phase in an air ambient. The exchange solution was prepared by dissolving perovskite precursors (lead iodide 0.05 M, lead bromide 0.05 M, cesium iodide 0.1 M) and ammonium acetate (0.01 M) in N,N-dimethylformamide (DMF). CQD solution in octane (5-6 mg/mL) was added to the exchange solution in a 1:1 volume ratio. The mixed solution was vortexed vigorously for 3 min until CQDs completely transferred to DMF phase. The DMF solution was then washed three times using octane. After the exchange process, CQDs were precipitated via the addition of toluene, and then separated by centrifugation. This was followed by a drying process.

2) Film fabrication. The amount of perovskite matrix, and thus the average dot-to-dot distance, are tuned through the ratio of CQD to perovskite. For perovskite-dominant films with less than 15 vol% CQDs, the exchanged CQDs were redispersed in 0.4 M CsPbBr_xI_{3-x} perovskite precursor solution in a mixed solvent of 4:1 dimethyl sulfoxide (DMSO) to DMF. The CsPbI₃ matrix solution was prepared following a reported method². For CQD-dominant films with CQD loading above 30 vol%, matrix solution was added first to the exchanged CQDs, resulting in a partially dispersed CQD paste. Butylamine, a solvent widely used in CQD film fabrication, was then added to increase the solubility and disperse the dots completely. The hybrid ink was deposited by spin-coating at 2000 rpm for 60 s to achieve an optimized thickness. This was followed by an annealing process to crystallize

the matrix and remove solvent residues. This method can be extended to a larger scale via spray coating and blade coating.

3) High-Energy X-Ray Diffraction measurements. CQD/perovskite samples were made using the abovementioned spin-coating process. High-energy X-ray diffraction experiments were conducted at the 6-ID-D beamline at Argonne National Laboratory, USA. The energy of the x-ray incident beam was 100.329 keV. The two-dimensional (2D) setup was applied for data collection with a Perkin Elmer model 1621 x-ray area detector. The results of the diffraction patterns were calculated using the Fit2D software.

4) X-ray scattering measurements. Grazing-incidence small-angle X-ray scattering (GISAXS) measurements were performed at the D1 beamline, Cornell High Energy Synchrotron Source (CHESS). The wavelength of the employed X-ray beam was 1.155 Å. A wide bandpass (1.47%) double-bounce multilayer monochromator was used. The scattering patterns were obtained at a photon-incident angle of 0.5 degrees with respect to the sample plane. A heating stage was set up for temperature-dependent in situ studies. The GISAXS scans were taken from 40 °C to 100 °C. The annealing temperature was increased by 30 °C at a time, and kept at each temperature for 20 min.

Grazing-incidence wide-angle x-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Wavelength of the employed X-ray beam was 1.24 Å. The scattering patterns were obtained at a photon-incident angle of 0.25 degrees with respect to the sample plane. Samples were scanned in a He environment to reduce air scattering. Exposure times were

30 s. The scattering patterns were recorded using a Pilatus 2M detector at a fixed distance of 277.674 mm. Calibration of the lengths in reciprocal space was done by using silver behenate.

Samples for GISAXS and GIWAXS were spin-coated on glass substrates following the same spin coating and annealing procedures as were used in film fabrication.

5) HRTEM and EELS measurements. HRTEM samples were prepared by spin-coating the CQDs in perovskite precursor solution onto an ultrathin-carbon film (Ted Pella 01800-F). The samples were baked at 80 °C for 20 min and stored under high vacuum overnight. The HRTEM images and EELS elemental maps were then taken on a Hitachi HF-3300 instrument with 300 kV accelerating voltage observation condition.

6) SEM and EDX measurements. The morphologies and elemental maps of the prepared films were investigated using SEM and EDX on a Hitachi SU8230 apparatus.

7) PL, PLQE and the calculation of carrier transfer efficiency. PL measurements were carried out using a Horiba Fluorolog system. Steady-state PL and was acquired with a time-correlated single-photon-counting detector and a monochromatized xenon lamp excitation source. The film was placed at an incident angle of 30° away from the detector to avoid reflections of the incident beam. The PLQE is measured using an integrating sphere and calculated following a reported method³².

The carrier transfer efficiency (η) was defined as:

$$\eta = \frac{n_{transfer}}{n_{total}}$$

where $n_{transfer}$ is the number of charge carriers that are transferred into the CQDs from the perovskite, and n_{total} is the total number of carriers photogenerated in the perovskite. The transfer efficiency η is extracted from PLQE measurement using a reported method²⁴.

We measured the photoluminescence from CQDs in lattice-anchored matrix using two excitation wavelengths: a short wavelength that excites both CQDs and perovskite, and a long wavelength that only excites CQDs. The photoluminescence (PL) of CQDs in these two scenarios are

$$PL_{CQDs,short} = (A_{CQDs,short} + \eta A_{p,short}) \times PLQE_{CQDs} \times I_{ex,short} \quad (1)$$

$$PL_{CQDs,long} = A_{CQDs,long} \times PLQE_{CQDs} \times I_{ex,short} \quad (2)$$

PL_{CQDs} and I_{ex} represent the photoluminescence yield from the CQDs (in photons per second) and the photon intensity of the excitation source (in photons per second), respectively. A_{CQDs} and A_p are the absorption of CQDs and perovskite component, respectively. From equations (1) and (2), we determine

$$\eta_{total} = \left[\left(\frac{PL_{CQDs,short} \times I_{ex,long}}{PL_{CQDs,long} \times I_{ex,short}} \right) \times A_{CQDs,long} - A_{CQDs,short} \right] \frac{1}{A_{p,short}} \quad (3)$$

The measured values of PL_{CQDs}/I_{ex} and absorption results are presented in Table S1.

8) Extraction of Mobility from transient absorption spectroscopy (TAS). Charge carrier mobilities were obtained with the aid of ultrafast and nanosecond transient absorption spectroscopy³³. The amplitude of the bandedge bleach signal in TAS is representative of the bandedge carrier population³⁴. When small-bandgap carrier-acceptor CQDs were added to large-bandgap carrier-donor CQDs at given concentrations (N_t), the

change in donor CQD lifetime (τ) with varying N_t of acceptor CQDs provides the diffusion coefficient (D) and mobility (μ).

$$D = \frac{d}{6\sigma \left(\tau / N_t^{-1} \right)}$$

σ is the capture cross section, which for the 3D model is assumed to be $1/4 \pi d^2$ ³⁵. Population transfer can be monitored directly by tracking the decay in the donor CQD bleach signals (Figure S9, S10). When N_t^{-1} is plotted against τ , the resulted slope is proportional to mobilities of carriers (Figure 4f). The matrix-infiltrated CQD film shows a two-fold improvement in carrier mobility compared to pristine CQD films.

Transient absorption spectra were recorded using a femtosecond pump-probe spectroscopy. Femtosecond laser pulses were produced by a regeneratively amplified Yb:KGW laser at a 5 kHz repetition rate (Light Conversion, Pharos). By passing a portion of the 1030 nm fundamental through an optical parametric amplifier (Light Conversion, Orpheus) the pump pulse was generated. The second harmonic of the signal pulse was selected for 750 nm light. Both the pump pulse and probe (fundamental) were directed into an optical bench (Ultrafast, Helios), where a white-light continuum was generated by focusing the 1030 nm fundamental through a sapphire crystal. Low excitation fluence of $\langle N \rangle = 0.001$ was used to avoid the Auger recombination. The time delay (time resolution ~ 350 fs) was adjusted by optically delaying the probe pulse, with time steps increasingly exponentially. A chopper was used to block every other pump pulse. Each probe pulse was measured by a CCD after dispersion by a grating spectrograph (Ultrafast, Helios). Samples were prepared on glass substrate and translated at 1 mm/s during the measurement. Pump fluences were kept at $8 \mu\text{J}/\text{cm}^2$. Kinetic traces were fit to the convolution of the instrument

response and a sum of exponential decays. Time zero was allowed to vary with wavelength to account for the chirp of the probe.

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Data Availability

The data that support the findings of this study are available from the corresponding authors on reasonable request.

Extended Data for

Lattice Anchoring Stabilizes Solution-Processed Semiconductors

Figure S1. Morphology of CQD:perovskite hybrid films. (a) Photographs of as-prepared CsPbBr₂I films with 0, 10 and 20 vol% of CQDs, from left to right, respectively. (b) Photographs of as-prepared CsPbBrI₂ films with 0, 10 and 20 vol% of CQDs, from left to right, respectively. (c-f) SEM images of the pure CsPbBr₂I film (c) and CQD:CsPbBr₂I hybrid films with 10 vol% (d), 20 vol% (e), 33 vol% CQDs (f). At low CQD loading (10 vol%), no significant changes were observed in grain size. This argues against a main role for grain size on stability. When CQD loading is higher than 20 vol%, a smaller grain size is observed, which is consistent with the XRD peak broadening shown in Figure 1c.

Figure S2. EDX mapping and elemental analysis of CQD:CsPbBr₂I hybrid films. (a-c) EDX mapping of CsPbBr₂I films with 10 vol% (a), 20 vol% (b) and 33 vol% (c) CQDs. (d-f) Elemental analysis of films in (a-c), respectively. An aluminum specimen holder was used for the measurement, resulting to a strong Al signal in EDX analysis. The energy peak of Al_{K α} (1.486 keV) overlaps with Br_{L α} (1.480 keV) in EDX spectrum. To avoid sample damage, an accelerating voltage of 10 keV was used, which is unable to detect the signal from Br_{K α} (11.922 keV). As a result, we cannot ascertain the elemental ratio of Br in the film. The values from experiments and calculations are both presented in the inset table. The elemental ratios are normalized to Pb.

Figure S3. X-ray diffractions of the CQD:CsPbBr₂I films. (a) Two-dimensional grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns of CQD:CsPbBr₂I films. (b) Azimuthal integrated line profile along the q_z -axis.

Figure S4. Morphological and structural characterization of CQD:perovskite hybrid structures. (a,b) The HRTEM (a) and FFT (b) images of PbS quantum dots with thin CsPbBr₂ perovskite shell. The shell has a lower contrast compared to CQDs, since CsPbX₃ has a lower density than PbS. (c,d) Scanning TEM images and EELS elemental mapping of CQD/CsPbBr₂ core-shell structure (c) and CQD-in-CsPbBr₂-matrix (d).

Figure S5. Stability studies of lattice-anchored and control materials system. (a) Stability of the lattice-anchored perovskite with mixed halides. The film stability is improved from couple of days to several months. For Br content higher than 33%, the perovskite film could be stabilized in room ambient for more than six months without any degradation. (b) Stability of the lattice-anchored α -phase CsPbI₃. The fabrication of CsPbI₃ films follows a reported method (ref.2), which exhibits one-thousand-hour air stability for the pure perovskite matrix. CQDs further enhanced the stability to greater than six months, showing the compatibility of this strategy with other previous-built methods. (c,d) Thermal stability studies of MAPbI₃ films with and without CQDs. Absorption spectra of pure MAPbI₃ (c) and MAPbI₃ with 10 vol% CQDs (d) before and after annealing at air ambient. The degradation of MAPbI₃ perovskite arises due to the volatility of organic components. The CQD:MAPbI₃ film does not show any improvement in thermal stability compared to

pure MAPbI₃. The reduced and broadened excitonic peak of PbS shows an increase in CQD aggregation.

Figure S6. GISAXS 2D pattern of the matrix-protected CQD films (a) and pristine films (b) measured at room temperature.

Figure S7. Photophysical studies of CQD-in-matrix hybrid films. (a) The absorption spectra of CsPbBrI₂ film with and without CQDs embedded. **(b)** The PL quenching at perovskite emission range. When CQDs are embedded, the PL signal from perovskite is completely quenched, showing an efficient carrier transfer from matrix to CQDs. **(c)** PL quantum yield of CQD-in-matrix films at different CQD ratios.

Figure S8. Mobility studies of the matrix-protected CQD films (a,b) and pristine CQDs (c,d) from the dependence of carrier lifetime on trap percentage. (a,c) Time traces at the exciton bleach peak of 960 nm bandgap CQD donor films with a range of acceptor CQD concentrations, increasing from top (0%) to bottom (5%). **(b,d)** Data with fits after subtracting Auger dynamics from the pure donor film, with fitted values for lifetime and offset.

Figure S9. CQD solar cell devices. (a) Device architecture. **(b-d)** Solar cell performance. Dark blue curves represent the matrix-infiltrated CQD samples, and the light blue curves represent the pure CQD samples. **(b)** J-V curves. **(c)** EQE. **(d)** Stability test with continuous AM1.5G illumination unencapsulated.

Table S1. Photophysical parameters of lattice-anchored hybrid material.

$PL_{CQDs,short}/I_{ex,short}$	$PL_{CQDs,long}/I_{ex,long}$	$AC_{QDs,short}$	$AC_{QDs,long}$	$A_p,short$
5135476	813487	0.11	0.07	0.38

PL_{CQDs} and I_{ex} represent the photoluminescence yield from the CQDs (in photons per second) and the photon intensity of the excitation source (in photons per second), respectively. AC_{QDs} and A_p are the absorption of CQDs and perovskite component, respectively.