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Electronic Supplementary Information

Surface Matrix Curing of Inorganic CsPbI₃ Perovskite Quantum Dots for Solar Cells with Efficiency over 16%

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Experimental Section

Chemicals

1-Octadecene (ODE, >90.0% (GC)), cesium carbonate (Cs₂CO₃, 99.99% metals basis), oleic acid (OA, technical grade 90%), oleylamine (OAm, technical grade 80-90%), methyl acetate (MeOAc, anhydrous 99.5%), ethyl acetate (EtOAc, spectrographic grade 99.5%), trioctylphosphine (TOP, 90%), n-hexane (>99% (GC)), n-octane (>99% (GC)), glycine (C₂H₅NO₂, 98%) were purchased from Aladdin and used without additional purification. Tert-Butyl iodide (TBI, 95%, with copper powder as stabilizer), chlorobenzene (anhydrous, 99.8%) and SnO₂ (15% in H₂O colloidal dispersion) were purchased from Alfa Aesar. Lead iodide (PbI2, 99%) and 2,2',7,7'-tetrakis (N,N-dip-methoxyphenylamine)-9,9'spirobifluorene (Spiro-OMeTAD, ≥99.5%) were purchased from Xi'an Polymer Technology Corp. 4-tert-butylpyridine 96%). Light (4-TBP, lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI), and acetonitrile (anhydrous, 99.8%) were purchased from Sigma-Aldrich.

Preparation of the Cs-OA Precursor

 $0.407 \text{ g } \text{Cs}_2\text{CO}_3$ was dissolved into 20 mL ODE and 1.25 mL OA, the mixture was stirred under vacuum at 120 °C for 1 h. Then, the temperature was raised to 150 °C in an N₂ atmosphere, which was maintained until Cs₂CO₃ reacted sufficiently with OA. The as-synthesized Cs-OA solution was stored in an N₂ atmosphere.

"Surface Matrix Curing" of CsPbI₃ PQDs

CsPbI₃ PQDs were synthesized with some changes based on the previous report of Protesescu et al.¹ Briefly, 0.922 g PbI₂ and 50 ml ODE were loaded in a 250 ml 3-neck flask and degassed under vacuum at 120 °C for 1 h. Then, a continuous stream of N₂ gas was introduced and the preheated OA and OAm (5 ml each) were added to the reaction flask, the temperature was maintained until all the lead precursors were completely dissolved. The reaction system was then heated to 180 °C under the N₂ protection. When the reaction temperature was reached, 4 ml of Cs-OA was rapidly injected into the reaction flask, and the flask was quickly moved into an ice bath within 5-7 s.

For the first step purification process, a triple volume of antisolvent MeOAc was added to the as-synthesized CsPbI₃ PQD solution, followed by centrifuging at 8000 rpm for 5 min. The precipitate

in each centrifuge tube was redispersed in hexane and fresh TBI TOP solution with 50 mg/ml, respectively. For conventional purification and surface matrix curing (SMC) treatment, each solution was sufficiently oscillated to dissolve the PQDs. The TBI TOP solution was prepared in an N₂ glovebox by dissolving 0.01% vol. of TOP into the hexane solution containing 5% vol. of TBI, which was filtered by a 0.45 µm nylon filter membrane before use to wipe out the effect of copper. It is worth noting that the fresh TBI TOP solution is necessary to be used to dissolve the PQD precipitate, otherwise the effect of SMC will be worse if using the aged TBI-TOP solution to dissolve the precipitate. The detailed discussion about the freshness of TBI-TOP solution on the effect of SMC is described in Note S1. The once-purified PQD intermediate solution w/wo SMC treatment was precipitated again by adding MeOAc with an equal volume and centrifuged at 4000 rpm for 5 min. Then, the twice-purified PQD precipitate was dispersed in hexane and stored in the refrigerator overnight to precipitate excess impurities. The purification processes and SMC treatment of PQDs were carried out under ambient conditions. It is worth noting that for the preparation of SMC-based PQDs, during the entire purification process, the PQDs were always dissolved in the SMC solution until finally being dissolved in hexane, so the SMC treatment would continuously effective during the purification process. Before use, the hexane was dried under vacuum and the dried CsPbI₃ PQD pellets were dispersed in octane with a concentration of ~85 mg/mL.

Device Fabrication

The etched ITO glass substrate was sequentially sonicated in acetone, deionized water and ethanol for 30 min and dried for later use. The substrates were further treated with ultraviolet ozone for 20 min to improve surface wettability and remove organic pollutants. The SnO₂ nanoparticle solution (2.67%, diluted with deionized water) was spin-coated on the ITO substrates at 4000 rpm for 30 s and annealed at 150 °C for 30 min. The glycine solution for ligand exchange was obtained by dissolving glycine in MeOAc at a concentration of 1 mg/ml, followed by ultrasonic for 20 min and centrifugation to remove excess salt. The PQD solution (~85 mg/mL in octane) was spin-coated on the top of the SnO₂ film at 1000 rpm for 10 s and 2000 rpm for 20 s. Then the PQD film was quickly dipped in the ligand solution for 3-5 s followed by rinsing with MeOAc. The above procedure was repeated 4-5 times to achieve a suitable thickness of PQD solid films. After the PQD layers were deposited to the desired thickness using the layer-by-layer spin-coating process, a

chlorobenzene solution of Spiro-OMeTAD with a concentration of 72.3 mg/mL that added with 28.8 μ L of 4-TBP, 17.5 μ L of Li-TFSI and 10 μ L of FK 209 was spin-coated on the PQD layer at 4000 rpm for 30 s.² All the spin-coating procedure mentioned above were carried out under the ambient condition with controlled humidity lower than 40%. Finally, the Ag electrode with a thickness of 100 nm was thermally evaporated onto the Spiro-OMeTAD layer.

Computational method

The density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP) code.^{3,4} The generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) functionals were used to treat the exchange-correlation functions of electrons.⁵ Projector augmented wave (PAW) method was used to solve the ion-electron interactions in the periodic boundary conditions.⁶ The surface slab model was constructed based on cubic phase CsPbI₃ {001} surface slab containing 8 atomic layers in a 2×2 supercell, and the slab was separated by a vacuum layer of about 30 Å to avoid interaction between periodic structures. A kinetic energy cut-off of 400.0 eV and a Monkhorst-Pack K-point mesh of 6×6×1 was used for the calculation of SMC of PQDs. For calculating the S_N1 reaction of TOP and TBI molecules, a kinetic energy cut-off of 450.0 eV and a Monkhorst-Pack K-point mesh of 4×4×4 was used. Each system followed the cutoff energy and K-point mesh convergence criteria of 0.001 eV/atom, and the effect of dispersive force was described using the DFT-D3 approach. The TBI TOP model and the top four layers of CsPbI₃ {001} surface slab w/wo passivation were fully relaxed with the quasi-Newton algorithm, in which the energy difference between two successive ionic steps and the Hellmann-Feynman force of each atom was converged to 10⁻⁴ eV and 0.02 eV/Å, respectively. The binding energy ($E_{binding}$) was defined as $E_{binding} = E_{total} - E_{addivive}$ - $E_{surface}$, where E_{total} represents the total energy of the system after structure optimization, $E_{addivive}$ and $E_{surface}$ are energies of the added molecule or ion and the surface slab, respectively.

Material Characterization

The UV-visible spectroscopy was obtained using a UV-vis spectrophotometer (UV-3600, Shimadzu, Japan). The steady-state photoluminescence (PL) spectra were recorded through a

spectrofluorometer with an excitation of 490 nm (LLS-490, Ocean Optical, USA). PL mapping images were captured by an optic spectrometer (NOVA, Ideaoptics Technology Ltd., China) with an automatically controlled microscopic platform. The PL quantum yields (PLQYs) of the PQD solutions were calculated by measuring the absorption and PL spectra of the reference rhodamine 6G (dissolved in ethanol) dye and PQD solutions. Time-resolved PL (TRPL) decay was tested using a picosecond diode laser (FLS980) with an excitation light of 470 nm and a cut-off filter (570 nm) was used to avoid the scattered excitation light during the measurement. The morphology of PQDs was characterized using a transmission electron microscope (JEM-2100, JEOL, Japan) at an accelerating voltage of 200 kV. The crystal structure characteristic of PQDs was detected using a diffractometer (D/MAX-2500, Rigaku, Japan) with Cu K α radiation (λ =1.54 Å). The scanning range of the diffraction angle was from 10° to 60°. ³¹P nuclear magnetic resonance (NMR) spectra were collected on a Bruker AVANCE III 600M using CDCl₃ as solvent at room temperature. Fourier transform infrared (FT-IR) was carried out using the Nicolet 6700 Fourier Transform Infrared Spectrometer in the transmittance mode. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were performed using the Thermo ESCALAB 250Xi Ultraviolet photoelectron spectrometer with a He I (21.22 eV) UV-light source as the excitation source. And the final data acquisition and signal handling were acquired through Thermo Vantage software. The PLQYs of the films were obtained by using a fluorescence spectrometer with an integrated sphere (C9920-02, Hamamatsu Photonics Co., Ltd.) excited at the wavelength of 397 nm.

Solar Cell Characterization

Under the one sun illumination (AM1.5G, 100 mW cm⁻²) provided by a solar simulator (Enli Technology Co., Ltd. SS-F5-3A), the current density-voltage (*J-V*) curves of devices were recorded using the Keithley 2400 digital source meter. The devices were tested in an N₂ filled holder under ambient conditions, and the working area of the devices was 0.06 cm², which was defined using a black metallic mask. The light intensity was calibrated using a certified reference silicon solar cell (Fraunhofer ISE) before the *J-V* measurement. The voltage sweep rate is 20 mV with a delay of 20 ms for the forward and backward sweeping direction. The incident photon-to-electron conversion efficiency (IPCE) spectra of devices were obtained by an Enli Technology QE-R system, which was composed of four parts, including a xenon lamp (Spectral Products QE-LD), a Czerny-Turner

monochromator (Spectral Products QE-M110), an optical imaging system and a light intensity detection system (Spectral Products QE-M1). The setup was calibrated using a certified reference silicon solar cell (Fraunhofer ISE) before the measurement. For the stabilized power output (SPO) measurement, the devices were measured by holding the device at the maximum power point and monitoring the photocurrent variation under AM1.5G illumination. The space charge limiting current (SCLC) was obtained by using Keithley 2400 to record the *I-V* curve of the electron-only device under dark conditions. Transient photovoltage (TPV) measurement was recorded by a compositive electrochemical workstation (Zahner Zennium CIMPS-pro), which can obtain the time constants that related to the charge carrier recombination in the devices.

Supplementary Figures



Scheme S1. S_N 1 reaction of the TBI and TOP.



Fig. S1. Photograph of the TBI·TOP with different ratios of TOP/TBI dissolved in hexane. (a) Pristine TBI·TOP solution. (b) TBI·TOP solution stored in N₂ atmosphere for 5 days. (c) ³¹P NMR spectra of the I₂·TOP, TBI·TOP with a TOP/TBI ratio of 1:1 and the aged TBI·TOP with the TOP/TBI ratio of 1:500. (d) Light absorption spectra of the TBI and the aged TBI·TOP dissolved in hexane.

Supplementary Notes:

Note S1. Exploration of the optimal conditions for TBI·TOP solution conducting SMC treatment.

To study the optimal conditions of TBI TOP solution using for the SMC treatment, hexane solutions of TBI TOP with different ratios of TOP/TBI were prepared, as summarized in Fig. S1a. It can be observed that when TOP is added to the hexane solution of TBI with ratios from 1:1 to 1:600, all the solutions change from brown to colorless in a short time, indicating a tiny amount of TOP is sufficient for completely reacting with TBI. As shown in Fig. S1b, after aging above solutions for 5 days, the TBI TOP solutions with TOP/TBI ratios greater than 1:50 remain colorless, however, when TOP was added to the hexane solution of TBI with ratios less than 1:500, the solution would change from colorless to yellow in a short time. Meanwhile, with the decreased content of the added TOP, the degree and speed of yellowing of the TBI TOP solution increase during the aging process. To study the effect of TOP/TBI ratio on the TBI·TOP solution, we performed ³¹P Nuclear magnetic resonance (NMR) tests on the TBI TOP solutions with TOP/TBI ratios of 1:1 and 1:500, respectively. The NMR spectra of I_2 TOP and pure TOP were also tested for reference, in which the I_2 TOP was prepared by dissolving I₂ into the TOP followed by gathering the white solid according to the previous report.⁷ The results are shown in Fig. 1b and Fig. S1c. The characteristic peaks of pure TOP are located at ~-30.97, ~34.20, ~47.80, and ~57.02 ppm, respectively. When TOP is added to the TBI with a ratio of 1:500, the peaks of TOP are fully disappeared and a new peak at ~12.04 ppm is observed, corresponding to the feature of the [TB-TOP]⁺I⁻ complex in an ionic form. However, when TOP is added to the TBI with a ratio as large as 1:1, there remain pure TOP characteristics at ~-30.97 and ~47.72 ppm, indicating that TOP might be very excessive. In addition, we found that the peaks at ~37.57, ~32.56 and ~9.65 ppm of the TBI TOP correspond to the characteristics of I_2 TOP. Besides, two unique weak peaks at ~33.80 and ~35.50 ppm might be the feature of I_x-TOP complex.⁸ Therefore, we believe that when the ratio of TOP in the TBI TOP solution becomes larger, the dissociated iodide ions from the S_N1 reaction can be readily complexed by the excess TOP, resulting in the decreased amount of free iodide ions in the solution, thereby weakening the SMC effect of PQDs. However, when the ratio of TOP/TBI is lower than 1:500, TOP could be rapidly consumed, and the dissociated iodide ions would soon be re-complexed by the [TB-TOP]⁺ cationic species,

leading to an unstable state of the TBI TOP solution. Moreover, we also fabricated the PQDSC devices based on the PQDs treated with different ratios of TOP/TBI, in which, the best performing PQDSC was obtained at a TOP/TBI ratio of 1:500 (Table S3). Therefore, we believe that the TOP/TBI ratio of 1:500 is an ideal ratio for the SMC of PQDs. Moreover, to study the effect of the freshness of the TBI TOP solution on SMC of PQDs, we prepared fresh (colorless) and aged (yellow) TBI TOP with a TOP/TBI ratio of 1:500 and tested their ³¹P NMR and light absorption spectra. We found that the characteristic peak at ~12.04 ppm of the fresh TBI TOP disappears (Fig. 1b), which is replaced by the two characteristic peaks at ~80.41 and ~8.36 ppm of the aged TBI TOP (Fig. S1c). In addition, as shown in the light absorption spectra in Fig. S1d, the peak at ~310 nm of the TBI solution corresponds to the intrinsic absorption of TBI, whereas the peak at ~508 nm may be the feature of the TBI-I₂ complex (also known as TBI₃ complex) generated from the reaction of TBI and the dissociated iodine component due to the low photostability of TBI.⁹ There is no light absorption property of the fresh TBI TOP solution due to its colorlessness, and an absorption peak at 378 nm is observed after aging the TBI TOP solution for 5 days. The results of the NMR and the light absorption spectra indicate that when the S_N1 reaction of TBI and TOP is finished, the dissociated iodide ions may further be re-complexed by the [TB-TOP]⁺ cationic species to form a new TBI_x-TOP complex in a molecular form, instead of reversibly forming the original reactant.¹⁰ It is notable that the formation of the TBI_x-TOP complex is unfavorable for the SMC of PQDs due to fewer iodide ions remaining in the solution. Therefore, the fresh TBI TOP with a TOP/TBI ratio of 1:500 is preferred to be used for the SMC of PQDs.



Fig. S2. TEM images of (a) pristine PQDs and (b) TBI·TOP-based PQDs. It is obvious that after the TBI·TOP treatment, PQD surface matrix becomes more complete, and there is less agglomeration between PQDs.



Fig. S3. Comparisons of (a) normalized light absorption and (b) PL spectra of pristine and TBI·TOPbased PQDs.



Fig. S4. Emission comparisons of the PQDs treated with different nucleophiles and iodide sources. (a) Photograph of pristine, TBI·TOP and TBI·tributylphosphine (TBUP)-based PQDs under ultraviolet illumination. (b) PL spectra of the pristine, TBI·TOP and TBI·TBUP-based PQDs. (c) PL spectra of as-prepared TBI·TBUP-based PQDs and aged TBI·TBUP-based PQDs for 48h. The PL intensity and stability of TBI·TBUP-based PQDs is lower than that of TBI·TOP-based PQDs, which may be due to the TBUP with stronger polarity and reducibility could lead to the dissolution of oleate components from the PQD surface. (d) Photograph of pristine, TBI·TOP, 2-iodopropane (2-IPrA)·TOP and iodoethane (IEA)·TOP-based PQDs under ultraviolet illumination. (e) PL spectra of pristine, TBI·TOP, 2-IPrA·TOP and IEA·TOP-based PQDs. The PL intensities of 2-IPrA·TOP and IEA·TOP-based PQDs based on the S_N2 reaction are lower than that of the TBI·TOP-based PQDs based on the S_N1 reaction, which may be due to the S_N1 reaction is independent of the concentration of the nucleophile and electrophile, while the S_N1 reaction is independent of the concentration of the sweakens the SMC effect.



Fig. S5. I/Cs ratio statistical histogram of pristine, TBI, TOP and TBI TOP-based PQD solid films.



Fig. S6. FT-IR spectra of pristine, TBI, TOP and TBI TOP-based PQD solid films.



Fig. S7. UPS plots of pristine and TBI·TOP-based PQD solid films. (a) and (b) correspond to the secondary electron cut-off region. (c) and (d) correspond to the spectra close to the Fermi edge.



Fig. S8. Cross-sectional SEM image of full TBI TOP-based PQDSC.



Fig. S9. *J-V* curves of (a) conventional and (b) TBI·TOP-based PQDSCs under reverse and forward voltage scanning directions.



Fig. S10. J-V curve of TOP-based PQDSC.



Fig. S11. J-V curves of TBI TOP-based PQDSCs with different ratios of TOP/TBI.



Fig. S12. Statistics of (a) V_{OC} , (b) J_{SC} , and (c) FF of conventional, TBI and TBI TOP-based PQDSCs. 21 devices fabricated from different branches were applied for statistics.



Fig. S13. IPCE spectra and integrated J_{SC} curves of conventional and TBI-based PQDSCs.



Fig. S14. Stabilized current densities and power outputs of (a) conventional and (b) TBI-based PQDSCs.



Fig. S15. Photographs of pristine, TBI, TOP and TBI·TOP-based PQD solid films stored with time. The films were aged under ambient conditions (RH of 25~35%) at room temperature.



Fig. S16. Light absorption spectra of (a) pristine, (b) TBI, (c) TOP, and (d) TBI·TOP-based PQD solid films. The films were aged under ambient conditions (RH of 25~35%) at room temperature.



Fig. S17. *J-V* curves of TBI-TOP-based PQDSC aging under ambient conditions with an RH of $\sim 10\%$.



Fig. S18. Stability test of un-encapsulated conventional and TBI·TOP-based PQDSCs. The devices were stored in an N_2 glovebox.



Fig. S19. Stability test of un-encapsulated conventional and TBI-TOP-based PQDSCs under continuous one sun equivalent illumination, which was provided using a white LED light.



Fig. S20. Steady-state PL spectra of pristine and TBI·TOP-based PQD solid films. The insets show the corresponding photographs of PQD solid films under ultraviolet illumination and the PLQY values were also included.



Fig. S21. Light intensity-dependent J_{SC} curves of conventional and TBI·TOP-based PQDSCs.



Fig. S22. ELF displays of (a) TBI·TOP, (b) TBI/PQD, (c) I/PQD and (d) OA/PQD systems.



Fig. S23. (a) The constructed PQDSC model for SCAPS simulations. The simulated performance including (b) PCE, (c) V_{OC} , (d) J_{SC} , and (e) FF of PQDSCs with different carrier mobilities (x-axis) and shallow-level (0.05 eV below the conduction band) defect densities (y-axis). The parameters for SCAPS simulations were summarized in Table S5.



Fig. S24. PL spectra of pristine and TBBr·TOP-based CsPbBr₃ PQDs. The inset shows the photograph of the corresponding PQD solution under ultraviolet illumination.



Fig. S25. Anion exchange of CsPbBr₃ PQDs using TBI TOP. The PL spectrum of CsPbBr_xI_{3-x} PQDs was gradually changed with the reaction time. The insets show the photographs of PQD solution under ultraviolet illumination at different periods, which was obtained from **Video S1**.

Supplementary Tables:

Table S1. Fitted parameters of TRPL decay of pristine, TBI, TOP and TBI·TOP-based PQDs. The bi-exponential function was used to fit the results.

PQD solid film	A_{l}	$ au_1(\mathbf{ns})$	A_2	$ au_2$ (ns)	$ au_{ave}(\mathbf{ns})$
Control	0.767	1.95	0.265	9.03	6.31
TBI	0.808	3.23	0.244	15.54	10.52
ТОР	0.786	3.37	0.257	17.45	12.22
TBI·TOP	0.986	3.91	0.208	31.23	21.05

The PL decay curve was fitted using the following equation,²

$$I(t) = A \cdot exp\left(-\frac{t}{\tau_1}\right) + B \cdot exp\left(-\frac{t}{\tau_2}\right) + C$$
(Eq. 1)

where A, B, and C are constants, t is PL decay time, τ_1 and τ_2 are fitted lifetimes.

The average lifetime, τ_{ave} , was calculated using the following equation,

$$\tau_{ave} = \frac{A\tau_1^2 + B\tau_2^2}{A\tau_1 + B\tau_2}$$
(Eq. 2)

Cell stack	PCE (%)	$V_{oc}(\mathbf{V})$	J _{SC} (mA cm ⁻ ²)	FF	Ref.
FTO/TiO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/MoO _x /Al	10.77	1.23	13.47	0.65	11
FTO/TiO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/MoO _x /Al	13.43	1.16	15.24	0.76	12
FTO/TiO2/µGR-CsPbI3 PQDs/PTAA/Au	11.64	1.18	13.59	0.72	13
FTO/TiO ₂ /CsPbI ₃ PQDs/PTB7/MoO _x /Ag	12.55	1.27	12.89	0.80	14
FTO/TiO ₂ / CsPbI ₃ PQDs/Spiro-OMeTAD/MoO _x /Al	13.47	1.18	15.50	0.73	15
FTO/TiO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/Au	12.15	1.11	14.80	0.74	16
FTO/TiO ₂ /Yb:CsPbI ₃ PQDs/PTB7/MoO _x /Ag	13.12	1.25	14.18	0.74	17
FTO/TiO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/Au	11.87	1.04	16.98	0.67	18
FTO/TiO ₂ /Sb:CsPbI ₃ PQDs/Spiro-OMeTAD/Au	9.4	1.04	13.15	0.69	19
ITO/PTAA/CsPbI ₃ PQDs/C60/BCP/Graphene	6.8	1.09	10.90	0.57	20
FTO/TiO ₂ /CsPbI ₃ PQDs/PTAA/MoO _x /Ag	14.1	1.25	14.96	0.76	21
FTO/TiO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/Au	11.2	1.11	14.40	0.70	22
FTO/TiO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/MoO _x /Ag	13.3	1.18	15.21	0.74	23
FTO/c-TiO ₂ /m-TiO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/Au	14.32	1.06	17.77	0.75	24
FTO/TiO ₂ /CsPbI ₃ PQDs/PTAA/MoO _x /Ag	13.8	1.22	15.10	0.75	25
ITO/SnO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/Ag	13.66	1.22	17.66	0.63	2
FTO/TiO ₂ /CsPbI ₃ PQDs/PTAA/MoO _x /Ag	15.21	1.25	15.85	0.77	26
ITO/TiO ₂ /CsPbI ₃ PQDs/Spiro-OMeTAD/MoO _x /Ag	14.1	1.23	15.30	0.75	27
FTO/TiO ₂ /Zn:CsPbI ₃ PQDs/Spiro-OMeTAD/Ag	14.8	1.19	16.4	0.76	28
FTO/TiO ₂ /CsPbI ₃ PQDs/PTAA/MoO _x /Ag	14.9	1.24	15.84	0.75	29
FTO/TiO ₂ /CsPbI ₃ PQDs/PTAA/MoO _x /Ag	14.25	1.25	14.32	0.79	30
FTO/TiO ₂ /Zn:CsPbI ₃ PQDs/Spiro-OMeTAD/MoO _x /Ag	16.07	1.23	17.58	0.74	31
FTO/TiO ₂ /CsPbI ₃ PQDs/PTAA/MoO _x /Ag	14.62	1.23	15.23	0.78	32
FTO/TiO ₂ /CsPbI ₃ :PbSe QDs/Spiro-OMeTAD /Ag	12.0	1.21	16.91	0.69	33
ITO/SnO ₂ /PCBM/PCBM:CsPbI ₃ hybrid	15.9	1.21	15.2	0.08	34
QDs/PTB7/MoO _x /Ag	13.1	1.20	13.2	0.78	5.
$FTO/TiO_2/Y6:CsPbI_3\ hybrid\ QDs/PTAA\ /MoO_x/Ag$	15.05	1.26	15.81	0.75	35
ITO/SnO2/CsPbI3 PQDs/Spiro-OMeTAD/Ag	16.21	1.27	17.71	0.72	This work

Table S2. Summary of device architectures and photovoltaic performance of reported efficientinorganic CsPbI3 PQDSCs.

TOP/TBI ratio	V_{oc} (V)	<i>J_{SC}</i> (mA cm ⁻²)	FF	PCE (%)
1:1	1.08	14.60	0.57	8.91
1:2	1.10	14.79	0.58	9.38
1:5	1.12	15.73	0.57	9.97
1:10	1.14	16.25	0.56	10.41
1:20	1.16	16.70	0.57	11.08
1:50	1.18	16.85	0.58	11.49
1:100	1.20	17.35	0.59	12.19
1:250	1.24	17.62	0.62	13.59
1:500	1.27	17.71	0.72	16.21
1:600	1.29	17.69	0.67	15.35

Table S3. Photovoltaic parameters of TBI·TOP-based PQDSCs with different ratios of TOP/TBI. The parameters were measured under AM1.5G 100 mW/cm² illumination.

Control	TBI·TOP		
0.55	0.42		
0.14	0.33		
0.24	0.48		
1.30	3.06		
1.07	2.82		
	Control 0.55 0.14 0.24 1.30 1.07		

Table S4. Fitted parameters of TPV curves of conventional and TBI TOP-based PQDSCs.

The V_{OC} decay was fitted using the following equation,²

$$V_{OC} = A \cdot exp\left(-\frac{t}{\tau_1}\right) + B \cdot exp\left(-\frac{t}{\tau_2}\right) + C$$
(Eq. 3)

where A, B, and C are constants, t is V_{OC} decay time, τ_1 and τ_2 are fitted lifetimes.

The average lifetime, τ_{ave} , was calculated using the following equation,

$$\tau_{ave} = \frac{A_1 \tau_1^2 + B_1 \tau_2^2}{A_1 \tau_1 + B_1 \tau_2}$$
(Eq. 4)

Table S5. Parameters for SCAPS simulations.

Name	ΙΤΟ	SnO ₂	PQD	Spiro-
				OMeTAD
Thickness (nm)	200	40	300	150
Bandgap edge (eV)	3.65	3.5	1.74	2.94
Electron affinity (eV)	4.7	4.1	3.7	2.28
Permittivity (er)	3.3	9	6.3	3
CB DOS (cm ⁻³)	4E+18	4.36E+18	3E+19	2.2E+18
VB DOS (cm ⁻³)	1E+18	2.52E+19	5E+20	1.8E+19
Electron mobility (cm ² /Vs)	1E+2	6E-3	1E-2~1E+0	1E-3
Hole mobility (cm ² /Vs)	1E+2	6E-3	2.3E-1	1E-3
Ndonor (cm ⁻³)	4.8E+20	1E+18	1E+15	0
Nacceptor (cm ⁻³)	0	0	0	2E+18
Defect type	Neutral	Neutral	Neutral	Neutral
Capture cross section (cm ²)	1E-15	1E-15	5E-16	1E-15
Position below Ec (eV)				
Position above Ev (eV)	0.6	0.6	1.7	0.6
Density (cm ⁻³)	1E+15	1E+15	1E+14~1E+17	1E+15
SnO ₂ /PQD interface defects type	Oxygen vacancies of SnO ₂ (Donor)		Physical contact loss (Neutral)	
Capture cross section (cm ²)	1	E-19	1E-19	
Position above E _v (eV)	().17	0.6	
Density (cm ⁻³)	11	E+11	1E+11	

References:

1. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.

- 2. D. Jia, J. Chen, M. Yu, J. Liu, E. M. J. Johansson, A. Hagfeldt and X. Zhang, Small, 2020, 16, 2001772.
- 3. G. Kresse and J. Hafner, Phys Rev. B Condens. Matter., 1993, 47, 558-561.
- 4. G. Kresse and J. Furthmüller, Comp. Mater. Sci., 1996, 6, 15-50.
- 5. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
- 6. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys.*, 1992, 64, 1045-1097.
- 7. F. Krieg, S. T. Ochsenbein, S. Yakunin, S. Ten Brinck, P. Aellen, A. Suess, B. Clerc, D. Guggisberg, O. Nazarenko,
- Y. Shynkarenko, S. Kumar, C. J. Shih, I. Infante and M. V. Kovalenko, ACS Energy Lett., 2018, 3, 641-646.
- 8. R. Nunez, F. Teixidor, R. Kivekas, R. Sillanpaa and C. Vinas, *Dalton Trans.*, 2008, DOI: 10.1039/B716217K, 1471-1480.
- 9. J. E. Bujake and R. M. Noyes, J. Am. Chem. Soc., 1961, 83, 1555-1559.
- 10. S. S. Chitnis and N. Burford, Dalton Trans., 2015, 44, 17-29.
- 11. A. Swarnkar, A. R. Marshall, E. M. Sanehira, B. D. Chernomordik, D. T. Moore, J. A. Christians, T. Chakrabarti and J. M. Luther, *Science*, 2016, **354**, 92-95.
- 12. E. M. Sanehira, A. R. Marshall, J. A. Christians, S. P. Harvey, P. N. Ciesielski, L. M. Wheeler, P. Schulz, L. Y. Lin, M. C. Beard and J. M. Luther, *Sci. Adv.*, 2017, **3**, eaao4204.
- 13. Q. Wang, Z. Jin, D. Chen, D. Bai, H. Bian, J. Sun, G. Zhu, G. Wang and S. F. Liu, *Adv. Energy Mater.*, 2018, **8**, 1800007.
- 14. J. Yuan, X. Ling, D. Yang, F. Li, S. Zhou, J. Shi, Y. Qian, J. Hu, Y. Sun, Y. Yang, X. Gao, S. Duhm, Q. Zhang and W. Ma, *Joule*, 2018, **2**, 2450-2463.
- 15. A. Hazarika, Q. Zhao, E. A. Gaulding, J. A. Christians, B. Dou, A. R. Marshall, T. Moot, J. J. Berry, J. C. Johnson and J. M. Luther, *ACS Nano*, 2018, **12**, 10327-10337.
- 16. F. Liu, C. Ding, Y. Zhang, T. Kamisaka, Q. Zhao, J. M. Luther, T. Toyoda, S. Hayase, T. Minemoto, K. Yoshino, B. Zhang, S. Dai, J. Jiang, S. Tao and Q. Shen, *Chem. Mater.*, 2019, **31**, 798-807.
- 17. J. Shi, F. Li, J. Yuan, X. Ling, S. Zhou, Y. Qian and W. Ma, J. Mater. Chem. A, 2019, 7, 20936-20944.
- 18. K. Chen, Q. Zhong, W. Chen, B. Sang, Y. Wang, T. Yang, Y. Liu, Y. Zhang and H. Zhang, *Adv. Funct. Mater.*, 2019, **29**, 1900991.
- 19. S. Bera, D. Ghosh, A. Dutta, S. Bhattacharyya, S. Chakraborty and N. Pradhan, *ACS Energy Lett.*, 2019, **4**, 1364-1369.
- 20. M. M. Tavakoli, M. Nasilowski, J. Y. Zhao, M. G. Bawendi and J. Kong, Small Methods, 2019, 3, 1900449.
- 21. X. Ling, S. Zhou, J. Yuan, J. Shi, Y. Qian, B. W. Larson, Q. Zhao, C. Qin, F. Li, G. Shi, C. Stewart, J. Hu, X. Zhang, J. M. Luther, S. Duhm and W. Ma, *Adv. Energy Mater.*, 2019, **9**, 1900721.
- 22. J. Yuan, C. Bi, S. Wang, R. Guo, T. Shen, L. Zhang and J. Tian, Adv. Funct. Mater., 2019, 29, 1906615.
- 23. J. Kim, B. Koo, W. H. Kim, J. Choi, C. Choi, S. J. Lim, J. S. Lee, D. H. Kim, M. J. Ko and Y. Kim, *Nano Energy*, 2019, **66**, 104130.
- 24. K. Chen, W. Jin, Y. Zhang, T. Yang, P. Reiss, Q. Zhong, U. Bach, Q. Li, Y. Wang, H. Zhang, Q. Bao and Y. Liu, *J. Am. Chem. Soc.*, 2020, **142**, 3775-3783.
- 25. K. Ji, J. Yuan, F. Li, Y. Shi, X. Ling, X. Zhang, Y. Zhang, H. Lu, J. Yuan and W. Ma, *J. Mater. Chem. A*, 2020, **8**, 8104-8112.
- X. Ling, J. Yuan, X. Zhang, Y. Qian, S. M. Zakeeruddin, B. W. Larson, Q. Zhao, J. Shi, J. Yang, K. Ji, Y. Zhang, Y. Wang, C. Zhang, S. Duhm, J. M. Luther, M. Gratzel and W. Ma, *Adv. Mater.*, 2020, **32**, 2001906.
- 27. J. Kim, S. Cho, F. Dinic, J. Choi, C. Choi, S. M. Jeong, J. S. Lee, O. Voznyy, M. J. Ko and Y. Kim, Nano Energy,

2020, 75, 104985.

28. C. Bi, X. Sun, X. Huang, S. Wang, J. Yuan, J. X. Wang, T. Pullerits and J. Tian, *Chem. Mater.*, 2020, **32**, 6105-6113.

29. Y. Wang, J. Yuan, X. Zhang, X. Ling, B. W. Larson, Q. Zhao, Y. Yang, Y. Shi, J. M. Luther and W. Ma, *Adv. Mater.*, 2020, **32**, 2000449.

30. J. Khan, X. Zhang, J. Yuan, Y. Wang, G. Shi, R. Patterson, J. Shi, X. Ling, L. Hu, T. Wu, S. Dai and W. Ma, ACS *Energy Lett.*, 2020, **5**, 3322-3329.

31. L. Zhang, C. Kang, G. Zhang, Z. Pan, Z. Huang, S. Xu, H. Rao, H. Liu, S. Wu, X. Wu, X. Li, Z. Zhu, X. Zhong and A. K. Y. Jen, *Adv. Funct. Mater.*, 2020, **31**, 2005930.

32. J. Shi, F. Li, Y. Jin, C. Liu, B. Cohen-Kleinstein, S. Yuan, Y. Li, Z. K. Wang, J. Yuan and W. Ma, *Angew. Chem. Int. Ed.*, 2020, **59**, 22230-22237.

33. S. Wang, C. Bi, A. Portniagin, J. Yuan, J. Ning, X. Xiao, X. Zhang, Y. Y. Li, S. V. Kershaw, J. Tian and A. L. Rogach, *ACS Energy Lett.*, 2020, **5**, 2401-2410.

34. L. Hu, Q. Zhao, S. Huang, J. Zheng, X. Guan, R. Patterson, J. Kim, L. Shi, C. H. Lin, Q. Lei, D. Chu, W. Tao, S. Cheong, R. D. Tilley, A. W. Y. Ho-Baillie, J. M. Luther, J. Yuan and T. Wu, *Nat. Commun.*, 2021, **12**, 466.

35. J. Yuan, X. Zhang, J. Sun, R. Patterson, H. Yao, D. Xue, Y. Wang, K. Ji, L. Hu, S. Huang, D. Chu, T. Wu, J. Hou and J. Yuan, *Adv. Funct. Mater.*, 2021, 2101272. https://doi.org/10.1002/adfm.202101272