

Enriching Conductive Capping by Alkaline Treatment of Perovskite Quantum Dots towards Certified 18.3%-Efficient Solar Cells

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this manuscript, the authors developed a PQD fabrication method by modifying both the ligand exchange solvent and the post-treatment process. They employ methyl benzoate as the main ligand exchange solvent and alkaline medium to accelerate its hydrolysis, achieving an PCE of 18.3%. To validate this concept, authors evaluate various device characteristics along with chemical and theoretical analyses across different solvent pools and device structures. However, the overall direction of the manuscript is complex, making it difficult to compare target and control samples. The manuscript should be simplified to enhance clarity and reliability. Furthermore, the chemical analyses are unreliable due to a high noise ratio and insufficient details regarding experimental conditions—such as the NMR sampling solvent, reference peaks, and thickness values used for conductivity or other related factors on measurements. Overall, while the intuitive concept—that an alkaline environment promotes methyl benzoate hydrolysis and thereby facilitates ligand exchange—is appealing, the reliability of the analytical data is insufficient. Therefore I recommend a major revision based on the following comments.

[Major]

1. Further confirmation of methyl benzoate hydrolysis:

The manuscript's main claim is that an alkaline environment accelerates the hydrolysis of methyl benzoate. However, the current analysis does not adequately quantify or demonstrate the extent of this hydrolysis. More detailed evidence or characterization is needed to support this key claim.

2. Reliability of NMR sampling condition and analysis:

The NMR analysis raises concerns regarding the solvent used and the identification of PQD-related peaks. Although CDCl_3 is referenced, it is unclear whether a film that has undergone significant ligand removal via solvent treatment is fully dissolved and properly represented in the NMR spectrum. This may lead to concentration discrepancies that undermine meaningful peak comparisons.

Notably, the expected peaks in the 7–9 ppm region—corresponding to FA amidinium or OAm ammonium—are either weak or obscured, while the peaks attributed to incorporated benzoate are minimal. The authors should specify the solvent used, provide full spectral details, and consider using an internal standard (e.g., FA) to account for concentration differences inherent in the ligand exchange process.

3. Detailed FT-IR sampling condition and PQD state:

In Fig 1d and supplementary fig 4, The authors present FT-IR spectra for neat antisolvent treatment, stating that the peaks associated with the carbon chain (C-H_2 , C-Hx) decrease while those for FA and OAm remain largely unchanged.

Although the carbon chain peaks between $2780\text{--}2980\text{ cm}^{-1}$ and the FA peaks around $3200\text{--}3450\text{ cm}^{-1}$ are distinct, the OAm $\nu(\text{N-H})$ stretch near 3138 cm^{-1} is obscured. Instead, the N-H bending peak (approximately $1600\text{--}1680\text{ cm}^{-1}$) shows an increase around 1610 cm^{-1} in the solvent-treated film compared to the as-cast film.

The authors should clarify whether the enhanced N-H peak is a direct effect of solvent treatment or if it could be attributed to variations in film thickness or baseline discrepancies.

4. FT-IR result after Post treatment:

Supplementary Fig. 23 shows FT-IR data after post-treatment. Given that the post-treatment involves a reagent containing both benzylamidinium cations and iodide anions, one would generally expect a decrease in the COO^- peak. However, the data indicate a significant increase in the COO^- peak intensity after post-treatment. In contrast, Figure 2b shows only a slight

peak shift under KOH treatment relative to methyl benzoate treatment. This discrepancy requires further explanation.

5. Doubt on PL Blue Shift Interpretation:

The PL spectra of PQD films after antisolvent coating show that films treated with EtCa exhibit a blue shift compared to as-cast films. Attributing this shift solely to enhanced electronic coupling is questionable since the hydrocarbon chain of EtCa, although longer than that of acetate, remains significantly shorter than that of oleic acid.

It is more likely that the observed blue shift results from cation compositional changes due to differences in cation solubility (J. Am. Chem. Soc. 2022, 144, 27, 12102–12115) or a mixed-phase state (alpha- and delta-phase or different phase of CsPbI₃, Chem. Sci. 2017, 8, 800–805). The yellowish appearance of the EtCa-treated film further suggests compositional or phase changes.

6. Consideration of External Factors Affecting Analysis:

The vertical conductivity measurements are strongly influenced by film thickness. Solvent treatments, particularly with nonpolar solvents like methyl benzoate, may partially dissolve QDs, resulting in thinner films. Moreover, reduced interdot distances can further affect film thickness. Given that even a 10 nm difference can significantly impact conductivity in thin films, precise thickness measurements must be provided.

[Minor]

1. On page 2 (line 31), the manuscript states that strain induced by the quantum confinement effect stabilizes the perovskite core in the black alpha phase. A more appropriate reference supporting the correlation between confinement and phase stability is needed.

2. On page 2 (line 36), when discussing the performance of PQD solar cells, it is advisable to specify exact performance figures. The highest reported efficiency is 19.1% according to the NREL chart. Stating "exceeding 18%" without this context seems arbitrary and should be revised.

3. The vertical conductivity measurements are strongly influenced by film thickness. Solvent treatments, particularly with nonpolar solvents like methyl benzoate, may partially dissolve QDs, resulting in thinner films. Moreover, reduced interdot distances can further affect film thickness. Given that even a 10 nm difference can significantly impact conductivity in thin films, precise thickness measurements must be provided.

4. If the primary objective of adding an alkaline additive is to promote methyl benzoate hydrolysis, it may be more straightforward to directly add a K⁺ benzoate- compound. The authors should justify why they need to create an alkaline environment—with its potential adverse effects on PQDs—rather than using K⁺ benzoate- molecule directly.

5. The manuscript compares XRD data at a 0.2° incident angle to assess alignment. However, the data reliability is questionable. The minimal differences observed around 0.8° suggest that the variations might be due to a high noise-to-signal ratio rather than genuine differences between the surface and bulk regions.

6. In line 38, "post-synthetic" seems to be a typo and should be "post-synthetic."

7. In Figure 5d, the illustration appears to be incorrect.

In the processing of the Neat MeBz-based PQDSC, the MeBz treatment is depicted as an ester treatment, which could be misleading. It should either be redrawn to show MeBz treatment correctly or the final device name should be changed from "Neat MeBz" to "Neat ester" for consistency.

8. In SI Table 2, the efficiency of the Neat MeBz device is listed as 16.15%, while the Neat MeOAc device is 15.80%. However, in SI Table 5 and SI Table 7, the Neat MeBz efficiency is reported as 15.80% and 15.82%, respectively. These values indicate that the efficiency of Neat MeBz and Neat MeOAc is actually quite similar.

9. Additional device efficiencies based on the data in the paper are as follows:

Neat MeOAc: 15.8% (SI Table 2)

Neat MeBz: 16.15% (SI Table 2)

MeOAc + KOH: 17.51% (SI Fig. 28)

MeBz + KOH: 17.25% (SI Table 7)

EtOAc + KOH: 17.78% (SI Fig. 28)

MeBz + KOH + PhADI PT: 18.21% (SI Table 6), 18.372% (Fig. 3)

Based on this data, the efficiencies for MeOAc + KOH + PhADI PT and EtOAc + KOH + PhADI conditions are not explicitly stated in the paper. If there was a mistake in labeling MeOAc + KOH and EtOAc + KOH, it should be explicitly clarified to avoid confusion.

Reviewer #2

(Remarks to the Author)

In this work, the authors fabricate CsPbI₃ perovskite nanocrystal solar cells. The key conceptual advance is the use of alkalis to hydrolyze ester anti solvents, which then are proposed to bind to the surface of the nanocrystals, leading to enhanced passivation and performance. The champion devices reach a certified efficiency of 18.3%. This is close to the highest reported for quantum dot solar cells (19.6% certified according to the NREL chart). The devices also demonstrate decent stability. This work is a good fit for Nature Communications. However, the following points need to be addressed.

Major:

The authors, from the beginning, lean in to the explanation stated above. The authors should explore alternative explanations that the hydroxide anions could be playing. The authors should provide experiments and evidence showing whether or not these play any other role

The authors show well that the benzoate ligands covalently bond to Pb²⁺ species at I vacancies to form a Lewis acid-base adduct. However, can the authors also show whether this passivation leads to a reduction in the trap energy or concentration

of defects associated with I vacancies?

The PLQY and TRPL measurements are missing fluency-dependence. At present, we cannot conclusively say which treatment works better because changes in PLQY and PL lifetime can simply be due to changes in recombination regime. These fluence dependent measurements need to be added.

The biexponential model used to fit the PL decay are likely phenomenological rather than physically relevant. This should be clarified.

Beyond the efficiency from certification, the stabilized power output from maximum power point tracking needs to be shown more prominently. The abstract should also state the device area and the median device efficiency, along with how many samples the median value is for.

Minor:

Fig. 1 has a typo in title "Easter"

Fig. 2a. Many XRD peaks not accounted for. Reference pattern and refinement need to be given.

The stability tests need to be described better. Did the authors follow the ISOS protocols?

For XPS, the survey spectrum needs to be given

Suppl. Fig. 14 cannot be correct. These Tauc plots are constructed for indirect bandgap materials, whereas the bandgap should be direct. Did authors account for excitonic peak? Fig. 1b cannot give bandgap since this is simply taking the tangents of the absorption onset, and not Tauc plots.

The English needs to be improved throughout. The abstract should be rewritten to be more specific. Some words incorrect, such as "complementation". What are the authors trying to say?

It should be diffraction pattern and not spectra (no change in energy in XRD)

The authors make arguments on ligand binding to Pb based on changes in binding energy from XPS. This can also be due to a change in Fermi level. The authors need to discuss whether they can rule this out.

The authors attribute changes in diode ideality factor to changes in the recombination regime of the device. This can also change because of space charge regions in the device and other regions. The authors should not draw too many conclusions simply from the fitted ideality factor

Reviewer #3

(Remarks to the Author)

Jia et al. reported a method that promotes rapid substitution of the original insulating oleic acid ligand by modulating the alkaline environment and selective ester solvents during ligand exchange in the solid film of perovskite quantum dots (PQDs). By mixing potassium hydroxide (KOH) with methyl benzoate (MeBz) antisolvent for interlayer washing of PQD solid, a conductive PQD film with uniform orientation, minimal agglomeration of particles and less trap state can be obtained, and the application efficiency in solar cells reaches a certified 18.3%. The manuscript presents many new insights into PQD solar cells, but some issues need to be addressed before it can be published in Nature Communications.

1. The manuscript emphasizes the role of alkaline-generated hydroxide ions (OH⁻) in ester hydrolysis that drives ligand exchange on the surface of PQDs. But this reaction still takes place under humidity conditions, so is this change due to the hydrolysis of the alkali itself or some reaction with the water in the air? Or the reaction could be attempted in nitrogen instead of humidity.

2. The photoluminescence (PL) spectrum presented in Fig. 3g exhibits an unexpected splitting of the emission peak (e.g., dual peaks at ~700 nm and ~740 nm), which raises concerns about the material homogeneity or phase purity of the PQDs. Such splitting is atypical for well-passivated, monodisperse PQDs and may indicate one or more of the following issues: phase segregation (The coexistence of multiple crystal phases (e.g., CsPbI₃ and FAPbI₃) due to incomplete stabilization of the perovskite lattice under alkaline conditions); defect-Mediated emission (emergence of trap states or surface defects that introduce additional radiative recombination pathways, potentially linked to incomplete surface capping or ligand desorption during the alkaline treatment). To resolve these ambiguities, the authors should provide X-ray diffraction (XRD) data or high-resolution transmission electron microscopy (HR-TEM) to confirm phase purity and crystallographic uniformity.

3. The authors' choice of FA_{0.47}Cs_{0.53}PbI₃ PQDs for solar cell fabrication warrants clarification, given that recent studies, such as the work published in Advanced Materials (e.g., Adv. Mater. 2023, 35, 2212160), report superior device performance with FA_{0.36}Cs_{0.64}PbI₃ PQDs, achieving efficiencies exceeding 17%. In addition, the current efficient PQD devices are

almost based on pure FAPbI₃ PQDs. Is the method proposed in the manuscript also applicable to FAPbI₃ PQD solar cell fabrication?

4. There are identified errors in Fig. 3h of the steady-state output measurements.

5. This manuscript describes the use of ester hydrolysis and alkaline environmental treatment to modify the surface of PQD films; However, key morphological evidence supporting the effects of these treatments is absent. Specifically, the authors should provide scanning electron microscopy (SEM) images of PQD films treated with different ester antisolvents as well as different alkaline environments to assess surface uniformity and grain boundary integrity.

6. The manuscript does not adequately address the critical role of carrier dynamics in validating the proposed alkali-mediated surface capping mechanism. To confirm the claims of enhanced charge transport and reduced non-radiative recombination, the authors needed to provide time-resolved photoluminescence (TRPL) or transient absorption (TA) spectral data for both untreated and treated PQD films.

7. The manuscript employed multiple antisolvent treatments (washing sequentially with MeBz, 2-PeOH) to purify the PQD film and remove the remaining ligands. While this method can enhance surface passivation, it introduces significant process complexity that undermines the usefulness of the method in scalable manufacturing. Is it possible to reduce the number of antisolvent uses by adjusting the polarity of anti-solvent uses?

8. Capacitance-voltage (C-V) and transient photovoltage (TPV) analyses are suggested to perform for validating the proposed alkaline surface capping mechanism and its impact on charge storage, transport, and recombination dynamics.

9. The manuscript reports a certification efficiency of 18.3% for small area perovskite quantum dot (PQD) solar cells (presumably $\leq 0.1 \text{ cm}^2$), but it ignores the key challenge of addressing scalability for commercial viability. To assess the actual potential of the proposed alkaline surface capping strategy, it is recommended that the authors provide data for large-area devices ($\geq 1 \text{ cm}^2$).

10. The manuscript would benefit from referencing recent advancements in high-efficiency PQD solar cells to provide context and highlight the novelty of this work.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The revised manuscript provides clearer experimental details and improves the characterization of the MeBz/KOH treatment, bringing the work substantially closer to meeting publication standards. However, the following issues require attention:

1. O 1s Deconvolution and Pb–OH Assignment:

The claim that MeBz without alkaline treatment yields higher trap density and lower stability—due to increased Pb–OH formation—is supported solely by deconvoluted O 1s XPS peaks. These fitted peaks in Supplementary Fig.8 and 14, however, bear little resemblance to the raw data, even accounting for O 1s contamination. The current CO–O[–]/OH[–] fitting appears arbitrary and undermines confidence.

Please replot the raw O 1s spectrum in a darker or thicker line to clearly show the original signal. Increase the number of XPS scans to improve the signal-to-noise ratio, then reattempt deconvolution on the higher-quality data.

If significant ambiguity remains, remove the COO[–]/OH[–] ratio analysis (Fig. 2d, Supplementary Fig. 8h) and the related discussion (p. 12, lines 253–255), or provide an alternative, more reliable indicator of hydroxyl content.

2. Work-Function Discrepancy:

KPFM and UPS should report comparable work-function shifts, yet the manuscript shows a 0.13 V shift by KPFM versus only ~0.02 eV by UPS when comparing MeBz and MeBz/KOH films. This discrepancy suggests either some reproducibility issue in fabrication or inconsistent measurement conditions.

Please provide the KPFM tip information (model, calibration results, illumination condition) and report the corresponding work function value of each sample. If necessary, repeat KPFM or UPS measurements under the same conditions to ensure consistency.

3. Minor text correction:

A duplicate sentence remains on page 20 (lines 430–434).

Reviewer #2

(Remarks to the Author)

This paper is now much improved, and I recommend publication after correcting for the following minor comments:

1) The English in this paper still needs to be improved. The title is cumbersome and not grammatically correct. Grammatical errors remain throughout the rest of the paper

2) The authors refer to alkalinity in a qualitative way. Can they be more quantitative in their descriptions?

3) The authors need to provide more details on their XPS fitting. What were the profiles that they fit? Sum Lorentian and Gaussian? Something else? What profile did they use to fit the background. The authors should justify all points

Reviewer #3

(Remarks to the Author)

In the revised manuscript, the author has made lots of changes and most of my previous concerns have been addressed, I would recommend the current version for publication in Nat. Commun. after updating some recent reports of high-efficiency PQD solar cells, e.g. 17.5% CsPbI₃ PQD (DOI: 10.1039/d4ee04628e); 18.21% FAPbI₃ PQD solar cells (DOI: 10.1002/adma.202417346) and latest review article on PQD solar cells towards 20% (DOI: 10.1039/d4cs01107d).

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The revised manuscript demonstrates that alkaline hydrolysis of methyl benzoate accelerates ligand exchange, increases COO⁻ formation, and enhances surface passivation. The arguments are now clearly presented and supported by solid evidence, and the reported high-PCE devices confirm that the work meets the high standard of Nature Communications. I recommend acceptance of this manuscript.

Reviewer #2

(Remarks to the Author)

I am mostly satisfied with the changes made. The title still does not quite make sense. Here is a suggestion: "Alkaline treatment of perovskite nanocrystals to achieve certified 18.3%-efficient solar cells"

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Reviewer #1:

In this manuscript, the authors developed a PQD fabrication method by modifying both the ligand exchange solvent and the post-treatment process. They employ methyl benzoate as the main ligand exchange solvent and alkaline medium to accelerate its hydrolysis, achieving an PCE of 18.3%. To validate this concept, authors evaluate various device characteristics along with chemical and theoretical analyses across different solvent pools and device structures.

However, the overall direction of the manuscript is complex, making it difficult to compare target and control samples. The manuscript should be simplified to enhance clarity and reliability. Furthermore, the chemical analyses are unreliable due to a high noise ratio and insufficient details regarding experimental conditions-such as the NMR sampling solvent, reference peaks, and thickness values used for conductivity or other related factors on measurements.

Overall, while the intuitive concept-that an alkaline environment promotes methyl benzoate hydrolysis and thereby facilitates ligand exchange-is appealing, the reliability of the analytical data is insufficient. Therefore, I recommend a major revision based on the following comments.

***Response:** We sincerely thank the reviewer for recognizing the value of our work and for the constructive suggestions on improving the clarity and conciseness of the manuscript. Therefore, we strictly followed the reviewer's suggestions and carried out point-to-point modifications, as detailed below.*

[Major]

1. Further confirmation of methyl benzoate hydrolysis:

The manuscript's main claim is that an alkaline environment accelerates the hydrolysis of methyl benzoate. However, the current analysis does not adequately quantify or demonstrate the extent of this hydrolysis. More detailed evidence or characterization is needed to support this key claim.

Response:

We appreciate the reviewer's valuable comments. To evaluate the extent of ester hydrolysis under different alkaline conditions, we designed and performed a comparative experiment using ¹H Nuclear magnetic resonance (NMR) spectroscopy, the experimental details and results discussions are as follows,

Four reaction systems were prepared by mixing 2 mmol (250 μ L) of methyl benzoate (MeBz) with 2 mL of D_2O , either in the absence or presence of 0.1 mmol of an alkaline additive (K_2CO_3 , Me_3SiOK , or KOH). After standing at room temperature for 1 hour, the mixtures were analyzed by 1H NMR spectra.

As shown in **Supplementary Fig. 11**, the control sample (MeBz only) displayed broad singlets at 7.50, 6.83, and 3.26 ppm, indicating a uniform chemical environment. In contrast, samples treated with alkalis showed signal splitting at these positions, suggesting altered proton environments due to the hydrolysis of MeBz. The original MeBz signals decreased, accompanied by new aromatic peaks at 7.68 and 7.29 ppm, corresponding to the hydrolysis product BZA^- .

To enable quantitative comparison, all spectra were normalized to the D_2O peak at 4.63 ppm. Among the alkaline additives tested, KOH led to the most pronounced hydrolysis effect, as evidenced by the strongest BZA^- signal and the most diminished original MeBz signals, followed by K_2CO_3 and Me_3SiOK . These results correlate well with the relative alkalinity of the additives. **Notably, the amount of BZA^- generated in the presence of KOH was twice that produced with K_2CO_3 , further confirming that stronger alkalinity enhances both the rate and extent of ester hydrolysis.**

In summary, the above experimental results supported our central claim that alkaline environments could promote MeBz hydrolysis.

Modifications:

According to the reviewer's suggestion, we added the additional experimental details, the corresponding analysis, and NMR spectra into the revised manuscript and Supplementary Information, as follows,

“After identifying the available alkaline additives, we confirmed that their ability to promote MeBz hydrolysis increases with their alkalinity by designing hydrolysis experiments, detailed experimental procedure and analysis are shown in **Supplementary Fig. 11** and **Supplementary Note 2**.” On page 10 of the manuscript.

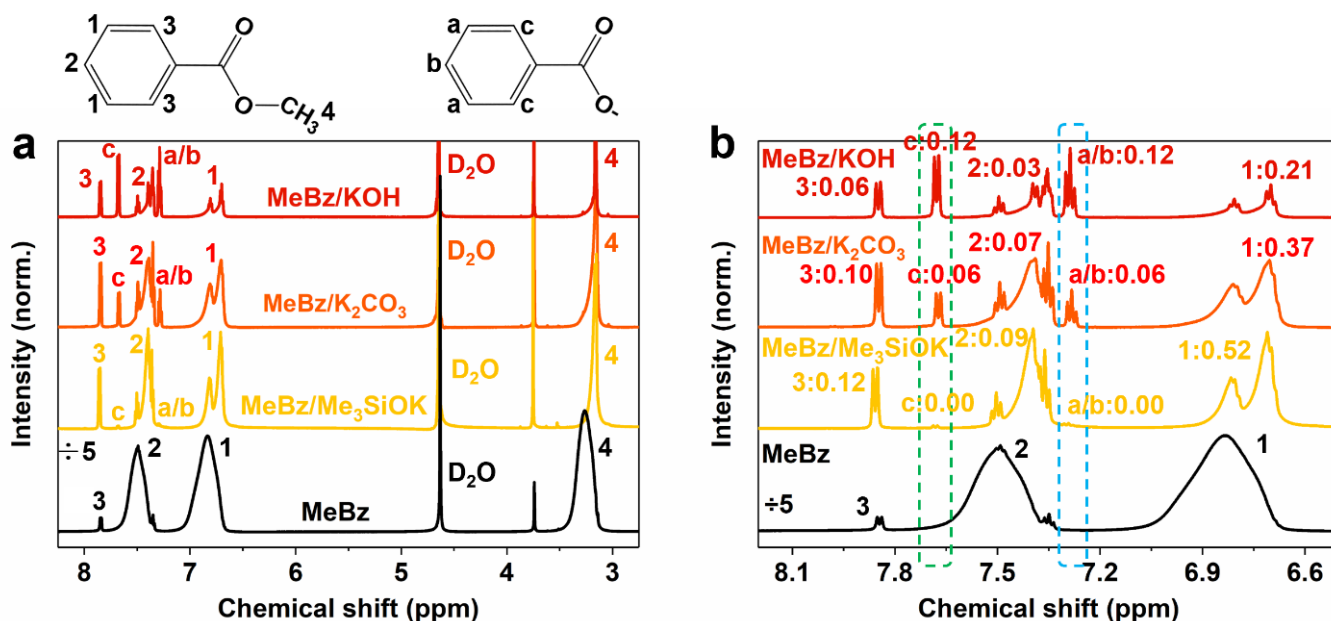
“Supplementary Note 2. Experimental evidence for alkali-augmented MeBz hydrolysis.

To verify the effectiveness of alkaline environments in augmenting the hydrolysis of ester antisolvent, we carried out a series of comparative 1H NMR experiments.

Specifically, four samples were prepared: Each reaction system contained 2 mmol (250 μ L) of MeBz, and 2 mL of heavy water (D_2O) with and without dissolved 0.1 mmol of the alkaline additives, including K_2CO_3 , Me_3SiOK and KOH . After thoroughly mixing and incubating at room temperature for 1 hour, all samples were subjected to 1H NMR analysis.

As shown in **Supplementary Fig. 11**, the neat MeBz control sample exhibited characteristic aromatic signals centered at 7.50 and 6.83 ppm, and a methyl peak at 3.26 ppm, all appearing as broad singlets without splitting, confirming the uniform chemical environment for hydrogen atoms of MeBz in the absence of alkalis. In contrast, all three alkali-containing samples showed splitting of the peaks at the same positions, indicating changes in the chemical environment for hydrogen atoms of the hydrolyzed MeBz. Furthermore, each ^1H NMR peak was normalized to the area of the D_2O proton resonance ($\delta = 4.63$ ppm) for quantitative analysis of the variation of MeBz during the hydrolysis reaction. It can be observed that the area of original MeBz signal at 7.50, 6.83, and 3.26 ppm significantly decreased, accompanied by the emergence of new, well-resolved aromatic signals at 7.68 and 7.29 ppm. These new peaks are attributed to the formation of BZA^- ligands, whose resonance patterns reflect altered chemical environments for hydrogen atoms on the aromatic ring.

Among the three alkaline conditions, KOH treatment resulted in the most pronounced hydrolysis, as evidenced by the largest BZA^- and smallest MeBz areas, followed by K_2CO_3 , while Me_3SiOK exhibited the weakest hydrolysis ability, correlating well with the relative pH values of MeBz/alkali solutions. Notably, the most effective additive KOH could facilitate the hydrolysis of MeBz into twice the amount of BZA^- compared to the suboptimal K_2CO_3 , highlighting the conclusion that higher alkalinity leads to faster and more complete ester hydrolysis. ” on page 16 of the *Supplementary Information*.



Supplementary Fig. 11 (a) ^1H nuclear magnetic resonance (NMR) spectra of neat MeBz in D_2O , and MeBz in D_2O with added K_2CO_3 , Me_3SiOK and KOH. (b) Magnified ^1H NMR spectra in the range of 6.5-8.2 ppm.

2. Reliability of NMR sampling condition and analysis:

The NMR analysis raises concerns regarding the solvent used and the identification of PQD-related peaks. Although CDCl_3 is referenced, it is unclear whether a film that has undergone significant ligand removal via solvent treatment is fully dissolved and properly represented in the NMR spectrum. This may lead to concentration discrepancies that undermine meaningful peak comparisons.

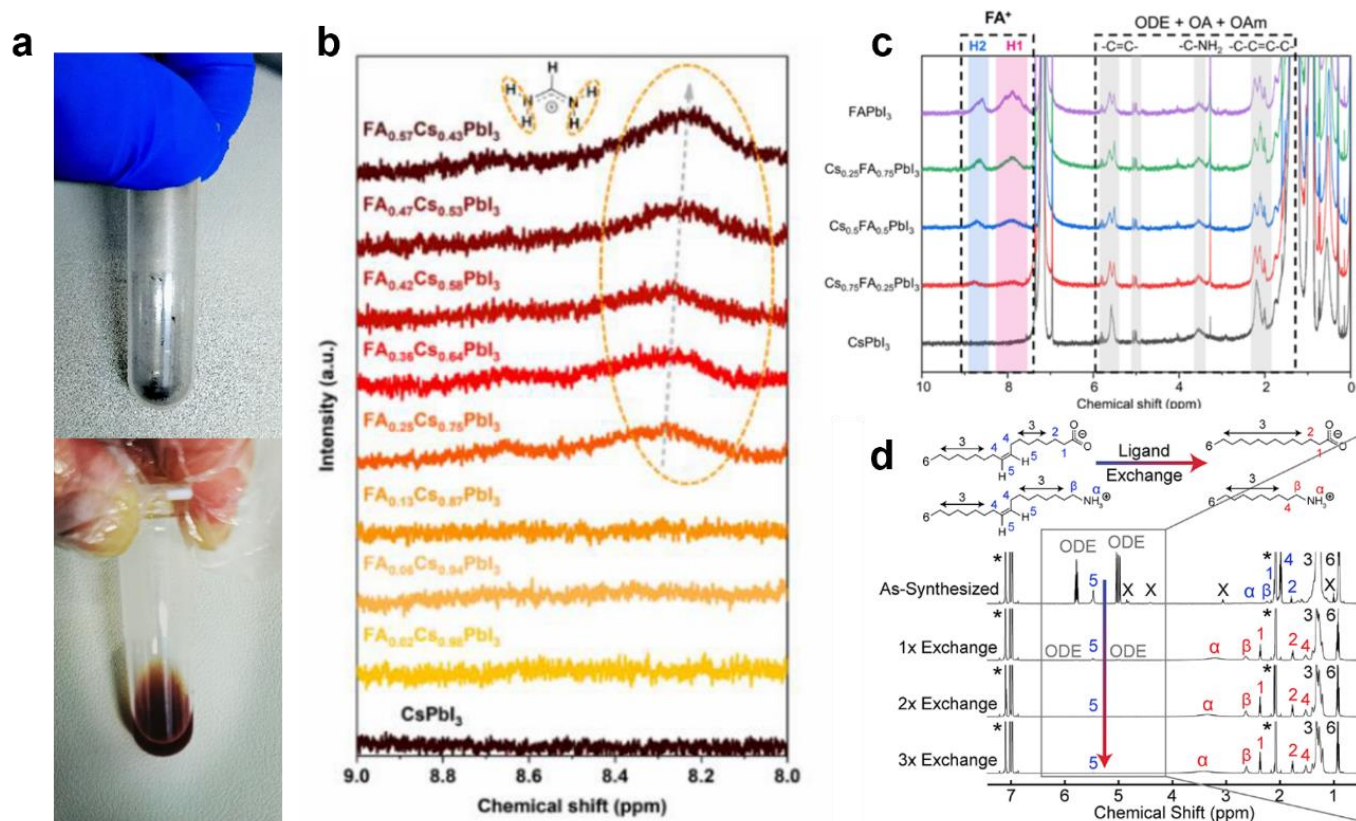
Notably, the expected peaks in the 7-9 ppm region-corresponding to FA amidinium or OAm ammonium-are either weak or obscured, while the peaks attributed to incorporated benzoate are minimal. The authors should specify the solvent used, provide full spectral details, and consider using an internal standard (e.g., FA) to account for concentration differences inherent in the ligand exchange process.

Response:

Firstly, concerning the solubility issue of ligand-removed perovskite quantum dots (PQD) in CDCl_3 . Samples for ^1H NMR measurements were prepared by scraping the powders from ester antisolvent rinsed PQD solids, which were layer-by-layer deposited on Si wafers, and fully dissolved in CDCl_3 (99.8atom%D, Sigma-Aldrich)) at a concentration of 2 mg mL^{-1} . The complete dissolution of these PQD powders can be attributed to the fact that they were only subjected to X-site ligand exchange via ester antisolvent rinsing. As a result, the pristine long-chain OAm^+ ligands remained on the surface A-site, which are known to impart high solubility in nonpolar solvents. Similar ^1H NMR reports using CDCl_3 solvent have also been shown in previous studies on ligand exchange of PQD solids (ACS Energ. Lett., 2024, 9, 2807-2815, Adv; Funct. Mater., 2022, 32, 2200454). **Therefore, our manipulations did not lead to concentration differences that would affect meaningful peak comparisons.**

Secondly, regarding the ambiguous attribution of the 7-9 ppm region in the ^1H NMR spectra of samples. We would like to clarify that in this work, we chose CsPbI_3 -PQDs as the sample for NMR measurement, instead of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ -PQDs. According to our previous study (Jia et al. Adv. Mater., 2023, 35, 2212160), we observed a broad resonance signal around 8.3 ppm, corresponding to the protons on the amidinium group of FA^+ cation. Unfortunately, this region overlapped with the expected chemical shift of the aromatic group from benzoate anionic ligands (BZA^-), potentially interfering with the accurate quantification of exchanged BZA^- ligands. To avoid this complication, we used pure CsPbI_3 PQDs, which do not contain FA^+ ions, thereby ensuring that the 7-9 ppm region was free of overlapping signals. Supporting this, as shown in **Supplementary Fig. 13b**, the ^1H NMR spectrum of neat MeOAc-based CsPbI_3 PQDs displayed no signal at $\sim 8.3 \text{ ppm}$, indicating the absence of FA^+ . Furthermore, the AAAH strategy was similarly effective for fabricating high-performing CsPbI_3 PQDSCs (**Supplementary Fig. 35e, f**), validating that the CsPbI_3 system was also representative and appropriate for evaluating ligand exchange behavior. **To prevent confusion, we included a statement in the manuscript for using CsPbI_3 - instead of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ -PQDs as samples for the NMR test.**

Moreover, as shown in the following figures, given that the ^1H NMR signal of ammonium groups in oleylammonium (OAm^+) is too weak to be quantified accurately. Instead, a well-established approach is to track the vinyl protons at ~ 5.1 ppm according to previous reports (Nat. Commun., 2023, 14, 2216; J. Am. Chem. Soc., 2020, 142, 6117-6127), which serves as a reliable quantitative indicator for the oleyl-based ligands on the PQD surface. Therefore, the ^1H NMR peaks at 7-9 ppm of these samples were similarly not attributed to the OAm^+ .

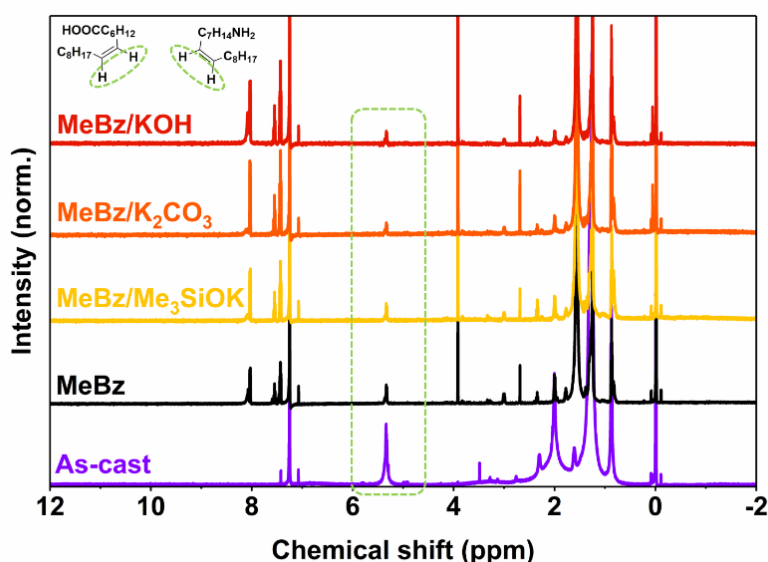


(a) Photograph of the scraped MeBz-based PQD powders before (top) and after (bottom) dissolved in chloroform. ^1H NMR spectra of (b, c) $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ -PQDs and (d) CsPbBr_3 -PQDs. (b: Adv. Mater., 2023, 35, 2212160; c: Nat. Commun., 2023, 14, 2216; d: J. Am. Chem. Soc., 2020, 142, 6117-6127)

Modifications:

According to the reviewer's suggestions, we included the sample preparation details and the full NMR spectra in the revised manuscript, as follows,

"The ^1H nuclear magnetic resonance (NMR) spectra detailed the status of ligands on the PQD surface, as depicted in Fig. 2c and Supplementary Fig. 13a. To avoid the proton signal overlapping between the amidinium group of FA^+ cation and the aromatic group of MeBz, we chose CsPbI_3 PQDs as the sample for NMR measurement, instead of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ PQDs. Samples were prepared by scraping PQD powders from Si wafers and dissolving them completely in deuterated chloroform ($d\text{-CDCl}_3$) at a concentration of 2 mg mL^{-1} ." On page 11 of the manuscript.



Supplementary Fig. 13 (a) Full ^1H NMR of as-cast, MeBz-, MeBz/ K_2CO_3 -, MeBz/ Me_3SiOK -, and MeBz/KOH-based CsPbI_3 -PQDs. It can be observed that after MeBz antisolvent rinsing, the content of pristine long-chain oleyl-based ligands on the PQD surface was significantly reduced, and distinctive signals of BZA ligands appeared.

3. Detailed FT-IR sampling condition and PQD state:

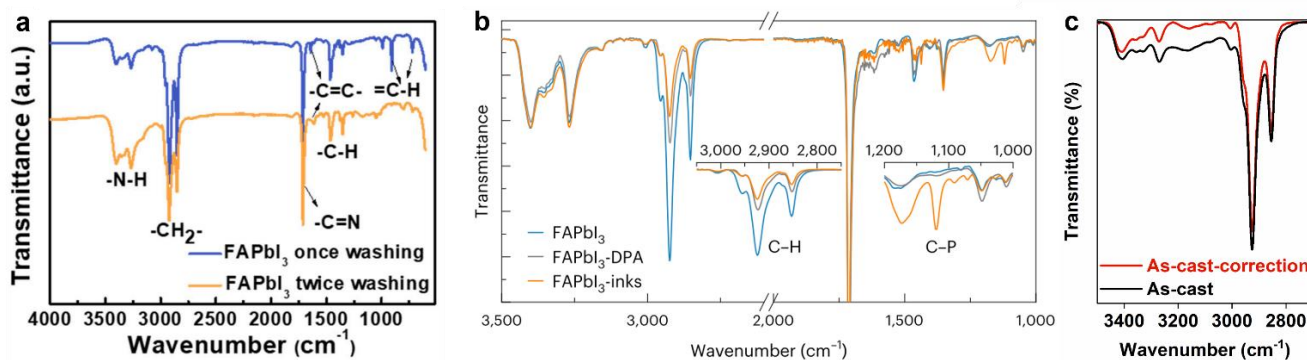
In Fig 1d and supplementary fig 4, The authors present FT-IR spectra for neat antisolvent treatment, stating that the peaks associated with the carbon chain (C-H_2 , C-H_x) decrease while those for FA and OAm remain largely unchanged.

Although the carbon chain peaks between $2780\text{--}2980\text{ cm}^{-1}$ and the FA peaks around $3200\text{--}3450\text{ cm}^{-1}$ are distinct, the OAm $\nu(\text{N-H})$ stretch near 3138 cm^{-1} is obscured. Instead, the N-H bending peak (approximately $1600\text{--}1680\text{ cm}^{-1}$) shows an increase around 1610 cm^{-1} in the solvent-treated film compared to the as-cast film.

The authors should clarify whether the enhanced N-H peak is a direct effect of solvent treatment or if it could be attributed to variations in film thickness or baseline discrepancies.

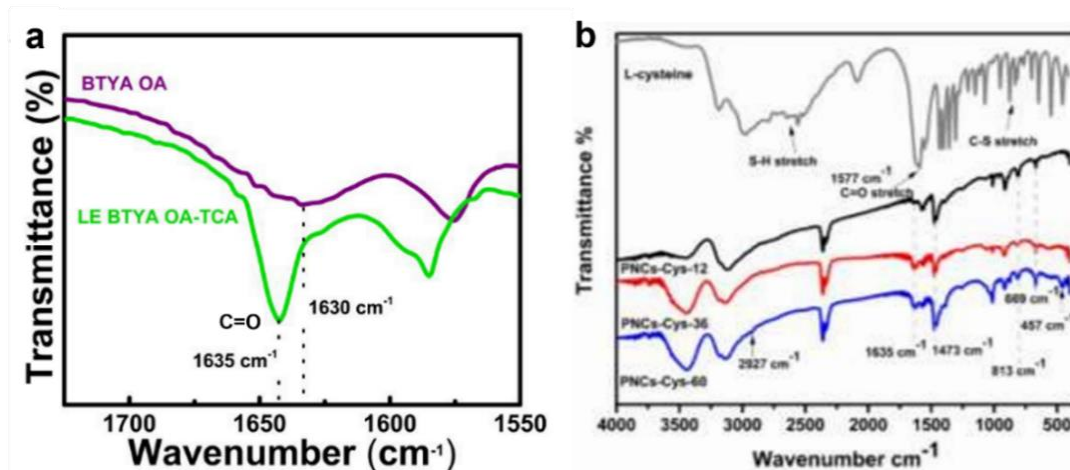
Response:

Firstly, regarding the obscured $\nu(\text{N-H})$ signal of OAm^+ at $\sim 3138\text{ cm}^{-1}$ in our presented FT-IR spectra. This vibrational mode was intrinsically weak due to the low dipole moment change during stretching, as previously discussed in the literature (Adv. Mater., 2021, 33, 2006722). In some reports, this signal appears more prominent when it overlaps with stronger neighboring peaks such as the $\nu(\text{C=N-H}_2^+)$ mode from FA^+ , giving the impression of a more distinct $\nu(\text{N-H})$ feature (Nat. Energy, 2020, 5, 79-88; Nat. Energy, 2024, 9, 1378-1387). **The reason for the obscured $\nu(\text{N-H})$ signal of OAm^+ in Supplementary Fig. 4d was that we applied a flat and consistent baseline correction across the $3000\text{--}3500\text{ cm}^{-1}$ range to isolate changes in these functional groups more clearly, which may diminish the apparent intensity of the $\nu(\text{N-H})$ signal.** For clarity, we included baseline-free spectra in the **following figure** to demonstrate the underlying signal prior to correction.



Reported FT-IR spectra of (a, b) FAPbI₃-PQDs. (a: Nat. Energy, 2020, 5, 79-88; b: Nat. Energy, 2024, 9, 1378-1387) (c) Comparison of FT-IR spectra for as-cast PQRs before and after baseline correction.

Secondly, regarding the enhanced vibration signal observed in the region of 1600-1680 cm^{-1} (previously attributed to N-H bending) for ester antisolvent-rinsed PQD solids. Upon delicate investigation of FT-IR spectra, we found that the observed signal actually corresponds more accurately to the C=O stretching vibration ($\nu(\text{C}=\text{O})$) of carboxylate species bound to the PQD surface. Besides, this signal was more pronounced on PQDs rinsed by ester antisolvents with added alkalis (**Fig. 2b**). Similar spectral features in this region have been clearly identified in previous reports (ACS Energy Lett., 2020, 5, 817-825; J. Mater. Chem. C, 2018, 6, 10994-11001), as shown in the following figures. **Therefore, the enhanced vibrational signal in the 1600-1680 cm^{-1} region of antisolvent-rinsed PQDs was ascribed to the increased binding of short carboxyl ligands hydrolyzed from ester antisolvents to the PQD surface.** This observation provides evidence supporting the presence of X-site ligand exchange during ester antisolvents rinsing of PQD solids.



Reported FT-IR spectra of (a, b) PQDs. (a: ACS Energy Lett., 2020, 5, 817-825; b: J. Mater. Chem. C, 2018, 6, 10994-11001)

Modifications:

According to the reviewer's suggestion, we revised both the label in **Fig. 1d** and the main text. Moreover, to further support this interpretation, we extended the range of presented wavenumbers in **Fig. 2b** to explicitly highlight the spectral region associated with the C=O stretching vibration, as follows,

“Notably, all PQDs rinsed with ester antisolvents exhibited stronger C=O stretching vibration centered at 1636 cm^{-1} compared to the as-cast sample.⁴⁰ These observations suggest changes in the chemical environment of carboxylate groups on the PQD surface after being rinsed by esters, probably resulting from the substitution of pristine OA^- ligands with other species containing carboxylate groups.” *On page 7 of the manuscript.*

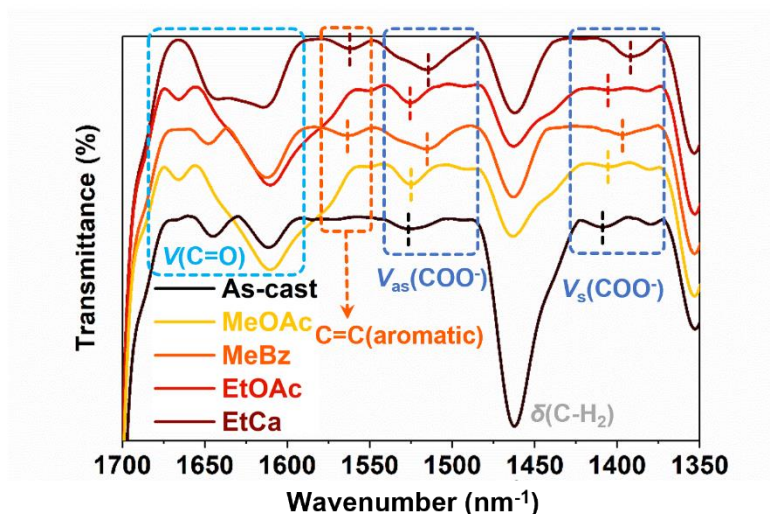


Fig. 1d FT-IR spectra of as-cast, MeOAc-, MeBz-, EtOAc-, and EtCa-based PQD solid films.

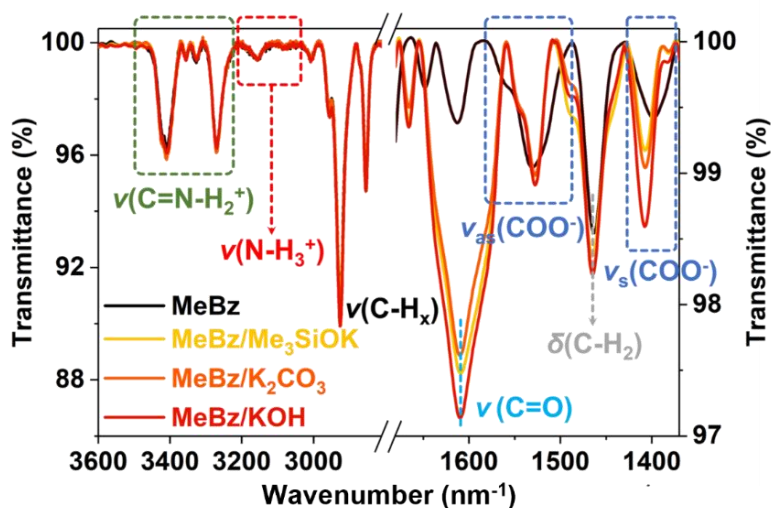


Fig. 2b FT-IR spectra of MeBz-, MeBz/ K_2CO_3 -, MeBz/ Me_3SiOK -, and MeBz/ KOH -based PQD solid films. Note that in (b), spectral ordinates on the left and right sides of the dividing line correspond to their respective transmittance ranges.

4. FT-IR result after Post treatment:

Supplementary Fig. 23 shows FT-IR data after post-treatment. Given that the post-treatment involves a reagent containing both benzylamidinium cations and iodide anions, one would generally expect a decrease in the COO^- peak. However, the data indicate a significant increase in the COO^- peak intensity after post-treatment. In contrast, Figure 2b shows only a slight peak shift under KOH treatment relative to methyl benzoate treatment. This discrepancy requires further explanation.

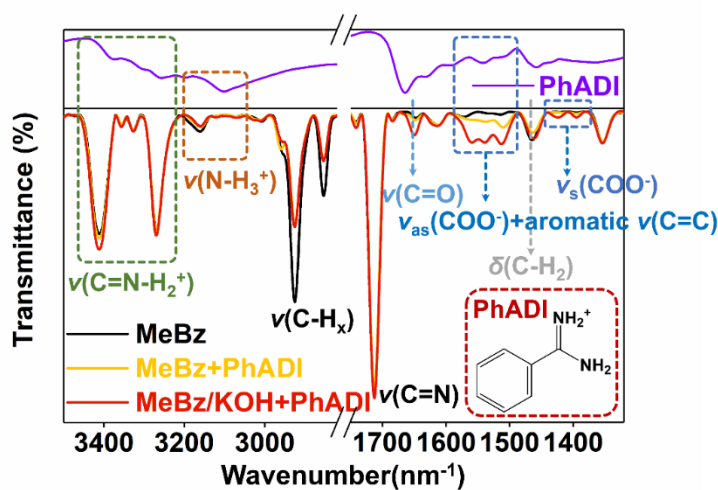
Response:

Regarding the increased COO^- peak intensity for PQDs after post-treatment with the 2-pentanol solution of benzamidinium cations (2-PeOH/PhAD⁺). We additionally measured the FT-IR spectrum of PhADI powder, as shown in **Supplementary Fig. 29**. It can be observed a strong aromatic C=C stretching vibration ($\nu(\text{C}=\text{C})$) centered at 1541.6 cm^{-1} . Therefore, when measuring the FT-IR spectra of 2-PeOH/PhAD⁺ post-treated PQDs, this $\nu(\text{C}=\text{C})$ peak would overlap with the $\nu_{\text{as}}(\text{COO}^-)$ signal of PQDs, making the original interpretation of the $1510\text{-}1550\text{ cm}^{-1}$ region less straightforward. In contrast, the region centered at 1408 cm^{-1} merely corresponds to the $\nu_{\text{s}}(\text{COO}^-)$ signal. After comparing **Fig. 2b** and **Supplementary Fig. 29**, this peak was essentially unchanged in neat MeBz-based samples, regardless of whether conducting 2-PeOH/PhAD⁺ post-treatment. However, in the MeBz/KOH-based sample, a marked increase in signal intensity at this position was detected, consistent with our proposed mechanism that alkaline environments facilitated the MeBz hydrolysis into more BZA⁻ ligands bound to the PQD surface.

Therefore, the increase in signal intensity around 1540 cm^{-1} of PQDs after 2-PeOH/PhAD⁺ post-treatment was primarily attributed to the aromatic $\nu(\text{C}=\text{C})$ peaks of newly bound PhAD⁺ ligands overlapped with the $\nu_{\text{as}}(\text{COO}^-)$ signal of X-site carboxyl ligands, rather than an anomalous increase in COO^- content. Particularly, the significant intensity increase of this signal in the MeBz/KOH-based sample likely further arose from the reduced particle aggregation during post-treatment that offered better surface accessibility of PhAD⁺ ligands, as confirmed by PL lifetime mapping results (**Figs. 4j** and **4k**). This interpretation is further supported by the stronger C=N vibrations at $1670\text{-}1740\text{ cm}^{-1}$ and $3300\text{-}3500\text{ cm}^{-1}$ of the MeBz/KOH-based sample.

Modifications:

According to the reviewer's suggestion, we updated the FT-IR spectra in **Supplementary Fig. 29** and added an interpretation in the figure legend, as follows,



Supplementary Fig. 29 FT-IR spectra of 2-PeOH/PhAD⁺ post-treated MeBz- and MeBz/KOH-based PQD solid films. FT-IR spectrum of MeBz-based PQD solid film without post-treatment was included for comparison. The inset shows the FT-IR spectra and chemical structure of PhAD⁺. Note that the broad signal centered at $\sim 1540\text{ cm}^{-1}$ includes contributions from both $\nu_{\text{as}}(\text{COO}^-)$ mode of X-site BZA⁻ ligands and aromatic $\nu(\text{C}=\text{C})$ mode of A-site PhAD⁺ ligands. The significantly enhanced intensity of this signal in the MeBz/KOH-based sample likely reflects improved binding of PhAD⁺ ligands during post-treatment due to the reduced PQD aggregation through employing AAAH-based X-site ligand exchange.

5. Doubt on PL Blue Shift Interpretation:

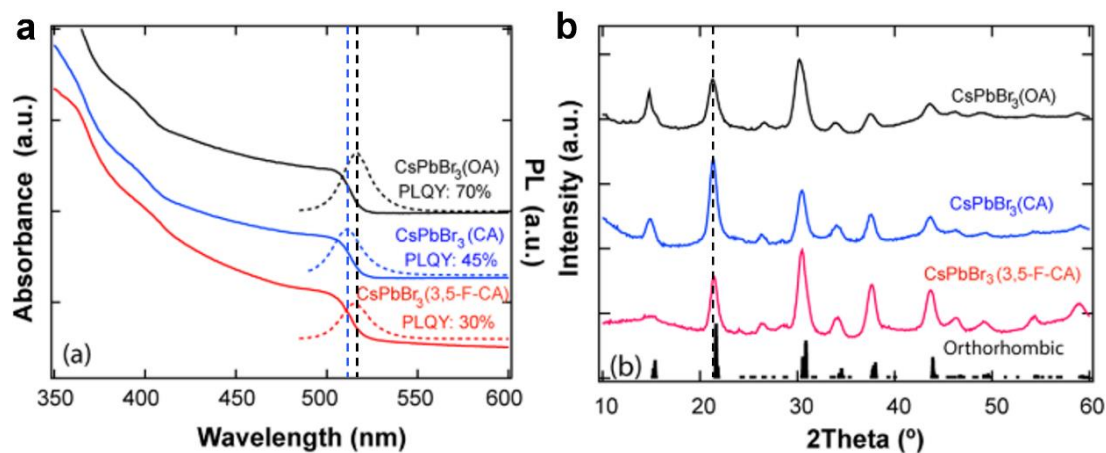
The PL spectra of PQD films after antisolvent coating show that films treated with EtCa exhibit a blue shift compared to as-cast films. Attributing this shift solely to enhanced electronic coupling is questionable since the hydrocarbon chain of EtCa, although longer than that of acetate, remains significantly shorter than that of oleic acid.

It is more likely that the observed blue shift results from cation compositional changes due to differences in cation solubility (J. Am. Chem. Soc. 2022, 144, 27, 12102-12115) or a mixed-phase state (alpha- and delta-phase or different phase of CsPbI₃, Chem. Sci. 2017, 8, 800-805). The yellowish appearance of the EtCa-treated film further suggests compositional or phase changes.

Response:

Regarding the blue-shifted emission of EtCa-treated PQDs than the as-cast sample, we carefully considered the reviewer's suggestions on possible cation composition changes or phase transitions in EtCa-treated films and studied the recommended references. **We also conducted additional XRD measurements to compare patterns between ester antisolvent-rinsed PQDs and their as-cast states.** As shown in **Supplementary Figs. 4b and 4c**, no detectable peak shifts between these samples, indicating that the crystal structure and composition of PQDs remained unchanged after ester antisolvents rinsing. However, in comparison to as-cast and other ester antisolvent-rinsed PQDs, a distinct reduction in the (001)/(011) peak intensity ratio could be observed in EtCa-based PQDs, suggesting that the pristine (001) preferential orientation of PQDs was significantly weakened after using cinnamate anionic ligands to substitute pristine OA⁻ ligands.

To gain further insights into the PL blue shift, we refer to prior work (J. Chem. Phys., 2019, 151, 204305), which showed that PQDs capped with cinnamate anionic ligands exhibited blue-shifted absorption and PL relative to oleate (OA⁻) ligands capped PQDs, with XRD changes limited to crystal orientation rather than phase transition, as shown in the **following figures**. This phenomenon was probably attributed to the rigid and bulky structure of cinnamate (featuring both conjugated benzene ring and alkenyl group), which could not fold and entangle like the pristine soft OA⁻ ligands. As a result, the original crystallographic orientations of PQDs were disrupted by the surface strain imposed by the hydrolyzed cinnamate anionic ligands, leading to altered electronic coupling, and thus blue-shifted emission.



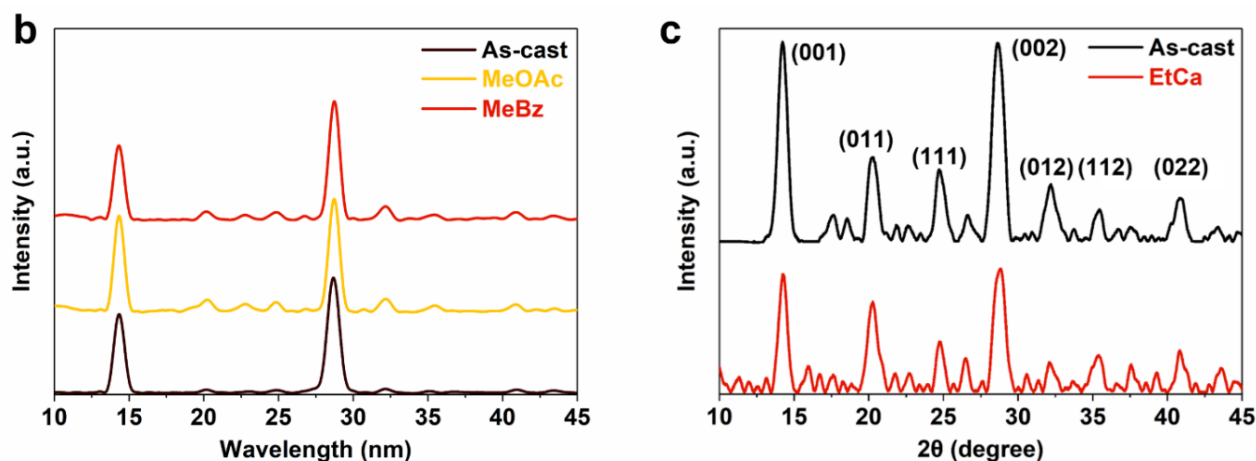
Reported (a) absorption and PL spectra and (b) XRD patterns of CsPbBr₃-PQDs capped with OA⁻ and cinnamate anionic ligands. (*J. Chem. Phys.*, 2019, 151, 204305)

Based on these insights, we concluded that the blue-shifted emission observed in PQDs rinsed with EtCa likely did not arise from cation solubility effects or phase segregation, but instead stemmed from changes in surface chemistry and interparticle interactions associated with the incorporation of more rigid ligands.

Modifications:

According to the reviewer's suggestion, we added XRD patterns of PQDs before and after ester antisolvent rinsing in the Supplementary Information and revised the manuscript, as follows,

“In contrast, PQD solid film treated by EtCa exhibited slight blue-shifted emission compared to the as-cast sample. This is likely attributed to the disrupted pristine crystallographic orientation caused by surface strain, which arises from the hydrolyzed cinnamate anionic ligands with rigid and bulky conjugated benzene rings and alkenyl groups (**Supplementary Figs. 4b and 4c**).³⁹” On page 7 of the manuscript.



Supplementary Fig. 4 (b) XRD pattern of as-cast, MeOAc- and MeBz-based PQDs. (c) Magnified XRD pattern of as-cast and EtCa-based PQDs.

6. Consideration of External Factors Affecting Analysis:

The vertical conductivity measurements are strongly influenced by film thickness. Solvent treatments, particularly with nonpolar solvents like methyl benzoate, may partially dissolve QDs, resulting in thinner films. Moreover, reduced interdot distances can further affect film thickness. Given that even a 10 nm difference can significantly impact conductivity in thin films, precise thickness measurements must be provided.

Response:

*We fully agree with the reviewer that film thickness is a crucial parameter that can significantly influence vertical conductivity measurements. **Therefore, we measured the thickness of PQD solids using a step profiler (Dektak XT, Bruker) as recommended.***

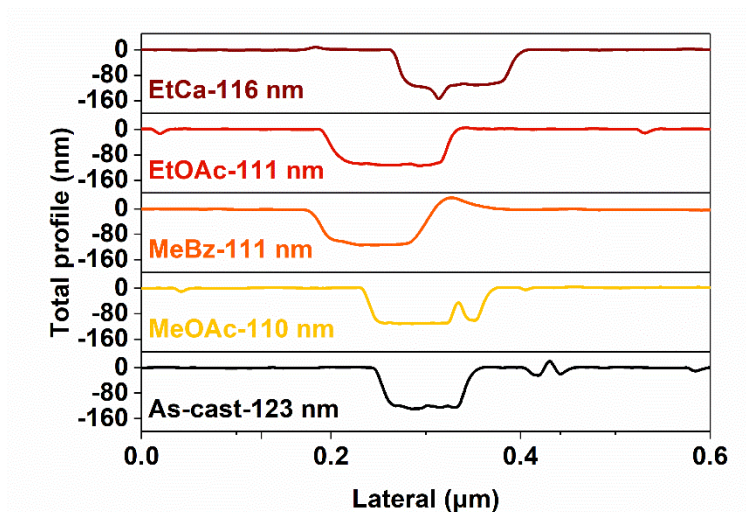
*As shown in **Supplementary Fig. 5**, the thickness of the as-cast sample was measured to be 123 nm. At this stage, PQDs capped with pristine long-chain ligands, were in a loosely packed configuration. After rinsing films with ester antisolvents, their thickness decreased uniformly, which could be attributed to the removal of pristine long-chain ligands, leading to a denser packing of PQDs. The thicknesses of MeOAc-, MeBz-, and EtOAc-treated films were essentially the same (110-111 nm), while the EtCa-treated sample showed a slightly larger thickness of 116 nm. This could be attributed to the lower polarity of EtCa and the longer chain length of the cinnamate group.*

*These thickness measurements not only validated the reliability of our vertical conductivity data but also aligned well with the steady-state PL results (**Fig. 1c**). **The increase in assembly compactness of PQDs after antisolvent rinsing was consistent with the red-shifted emission peaks observed in the PL spectra, facilitating more efficient charge transfer between PQDs.***

Modifications:

According to the reviewer's suggestion, we revised the manuscript, and included the thickness measurement results as well as the associated analysis in the Supplementary Information, as follows,

*"We proceeded to study the resistance of PQD solid films, vertical conductivity combined with film thickness measurements (**Fig. 1e** and **Supplementary Fig. 5**) revealed improved conductivity in all the ester antisolvents treated PQDs compared to as-cast PQDs with surfaces densely covered by pristine long-chain insulating ligands.³² Among these, the MeBz-based PQDs possessed the highest conductivity, ~1.5 times higher than that of conventional MeOAc- and EtOAc-rinsed PQDs, whereas the conductivity of PQDs rinsed by EtCa with a longer hydrocarbon chain was weaker, at only ~53% of MeBz-based PQDs." On page 7 of the manuscript.*



Supplementary Fig. 5 Film thickness of as-cast, MeOAc-, MeBz-, EtOAc-, and Etca-based PQD solids measured by a step profiler.

“Vertical conductivity (σ) is classically given by the following equation,

$$\sigma = \frac{(t \cdot I)}{A \cdot U} \quad (1)$$

where t is the thickness of PQD solid film, A is electrode area (0.036 cm^2) and I is current, U is voltage. As measured from **Fig. 1e** and **Supplementary Fig. 5**, the electrical conductivity of MeBz-based PQD solid ($\sigma = 2.64 \times 10^{-5} \text{ S cm}^{-1}$) is ~ 1.5 times higher than that of conventional MeOAc- and EtOAc-based sample ($\sigma = 1.74 \times 10^{-5} \text{ S cm}^{-1}$) and ~ 1.9 times higher than that of the EtCa-based sample ($\sigma = 1.39 \times 10^{-5} \text{ S cm}^{-1}$).” On page 9 of the Supplementary Information.

[Minor]

Q1: On page 2 (line 31), the manuscript states that strain induced by the quantum confinement effect stabilizes the perovskite core in the black alpha phase. A more appropriate reference supporting the correlation between confinement and phase stability is needed.

Response:

We thank the reviewer for this valuable suggestion. To better support our claim, we included a reference published by Zhao et al. (ACS Energy Lett., 2019, 5, 238-247). As stated in their report: **“However, at the nanoscale, it has been shown that the NCs stabilize in a perovskite structure. It is believed that the surface-to-volume ratio is so high that surface tension can cause enough tensile strain for the crystal to remain in the perovskite structure at room temperature.”**

Modifications:

The above explanation supported the idea that the surface strain played a significant role in stabilizing the photoactive black phase of nanoscale PQDs with a large surface-to-volume ratio. However, we realized

that this size-limit effect was not equivalent to quantum confinement. Therefore, according to the reviewer's suggestion, we revised the manuscript and added this reference, as follows,

“Compared to bulk counterparts, the enhanced surface strain of PQDs with a large surface-to-volume ratio stabilizes their perovskite core lattices in the photoactive black phase.¹²” On page 2 of the manuscript.

Q2: On page 2 (line 36), when discussing the performance of PQD solar cells, it is advisable to specify exact performance figures. The highest reported efficiency is 19.1% according to the NREL chart. Stating “exceeding 18%” without this context seems arbitrary and should be revised.

Response and modifications: We recognized upon being reminded that the statement "exceeding 18%" in the original manuscript lacked context and precision. According to the reviewer's valuable feedback, we revised this statement in the manuscript, as follows,

“Continued advances in surface ligand chemistry, A-site composition regulation, and homo-/hetero-junction light-absorbing layer architecture design have significantly improved the power conversion efficiency (PCE) of PQD solar cells (PQDSC) from 10.7% to currently National Renewable Energy Laboratory (NREL) certified 19.1%.¹⁶⁻²⁰” On page 2 of the manuscript.

Q3: The vertical conductivity measurements are strongly influenced by film thickness. Solvent treatments, particularly with nonpolar solvents like methyl benzoate, may partially dissolve QDs, resulting in thinner films. Moreover, reduced interdot distances can further affect film thickness. Given that even a 10 nm difference can significantly impact conductivity in thin films, precise thickness measurements must be provided.

Response: According to the reviewer's suggestion, we measured the thickness of PQD solids using a step profiler (Dektak XT, Bruker) and reanalyzed the conductivity values of these samples based on the measured data, as detailed in the answer to major Q6 of reviewer 1.

Modifications

We included the thickness measurement method in the revised manuscript, as follows,

“The thickness of PQD solid films was measured by step profiler (Dektak XT, Bruker).” On page 29 of the manuscript.

Q4: If the primary objective of adding an alkaline additive is to promote methyl benzoate hydrolysis, it may be more straightforward to directly add a K⁺ benzoate-compound. The authors should justify why they need to create an alkaline environment-with its potential adverse effects on PQDs-rather than using K⁺ benzoate-molecule directly.

Response:

The reason we did not directly apply potassium benzoate as ligands for surface treatment was associated with the limited solubility and reactivity in our system. Specifically, the vulnerable nature of the ionic PQD

lattice imposes stringent constraints on antisolvent selection during interlayer rinsing. Although several studies have explored the use of short exogenous ligands dissolved in protic solvents with higher polarity to substitute pristine ligands during post-treatment of the assembled PQD films, aprotic esters with moderate polarity remain the most suitable antisolvents for interlayer rinsing. Antisolvents with higher and lower polarity would result in underlying PQD lattices being destroyed and dissolved during subsequent layer-by-layer deposition processes, respectively (Joule, 2018, 2, 1866-1878).

However, the moderate polarity of esters limits the solubility of ionic ligand salts with strong polarity, such as potassium benzoate, challenging to achieve efficient and controllable ligand exchange. Therefore, to overcome this limitation, we adopted a promising strategy proposed by Luther et al. (Science, 2016, 354, 92-95; J. Am. Chem. Soc., 2018, 140, 10504-10513), in which methyl acetate antisolvents undergone in-situ hydrolysis under ambient conditions during rinsing of PQD solids, generating short acetate ligands capable to exchange the pristine OA^- ligands. Herein, by constructing a suitable alkaline environment to accelerate the ester antisolvent hydrolysis, we doubled the number of exchanged target short ligands compared to the convention approach during the brief antisolvent rinsing process, leading to a more robust and conductive ligand capping on the PQD surface.

In summary, we tailored a desirable alkaline environment to promote ester hydrolysis, thus providing a more controllable and efficient pathway for ligand exchange. **This strategy circumvents the solubility and reactivity challenges associated with directly using potassium benzoate salts and enhances the uniformity and robustness of the PQD surface capping.**

Modifications:

According to the reviewer's suggestion, we included these rationales behind our experimental design in the revised manuscript, as follows,

“Despite the progress achieved in enhancing the photovoltaic efficiency of PQDSCs through regulating A-site cationic ligand salts for post-treatment, the controlled solubilization of highly polar exogenous anionic salts in mild ester antisolvents remains challenging. As a result, relying on ambient hydrolysis of ester antisolvents to generate target anionic ligands has become the standard practice to exchange the X-site pristine OA^- ligands during interlayer rinsing of PQD solids.³² On page 3 of the manuscript.

Q5: The manuscript compares XRD data at a 0.2° incident angle to assess alignment. However, the data reliability is questionable. The minimal differences observed around 0.8° suggest that the variations might be due to a high noise-to-signal ratio rather than genuine differences between the surface and bulk regions.

Response:

Regarding the credibility of grazing-incidence X-ray scattering (GIWAXS) data. **Firstly**, the reason for conducting depth-dependent GIWAXS measurement was inspired by prior studies (Chem. Eng. J., 2022, 448, 137672). Since PQDs assembled in the top layer of the film are the earliest to be exposed to the antisolvent, the surface ligand removal would be most severe at this position. Meanwhile, PQDs assembled in the top layer have higher mobility in the antisolvent environment than those in the bottom. Therefore, when PQD solids are processed by excessive ligand removal through repeated antisolvent rinsing, the top-bottom structural divergence is prone to occur, which would cause delamination between the topmost and deeper layers, severely impairing charge transport. This was evidenced in the shifted q -values between the surface and bulk of the antisolvent-rinsed PQD solids (**Supplementary Figs. 30a-c**). Therefore, to investigate whether the AAAH strategy could alleviate the disparity in crystallographic features between the top and bottom regions of the PQD solid, we employed GIWAXS at incident angles of 0.2° and 0.8° , corresponding to probing depths of ~ 2 and ~ 100 nm, respectively.

Based on the above, as shown in **Fig. 4e**. **After 2-PeOH/PhAD⁺ post-treatment, the MeBz/KOH-based PQD solid exhibited only a slightly stronger azimuthal intensity at 90° than the neat MeBz-based sample under an incidence angle of 0.8° stemming from the more restricted mobility of the underlying PQDs during the ligand exchange process.** In contrast, the azimuthal intensity of MeBz/KOH-based PQD solids perpendicular to the substrate was significantly higher than that of the neat MeBz-based sample at an incidence angle of 0.2° , indicating that the AAAH strategy led to a more homogeneous surface crystallographic orientation than the conventional method. **This improvement was likely attributed to the AAAH-based ligand exchange enhanced BZA⁻ ligand capping that avoided drastic ligand removal and particle agglomeration during post-treatment, which effectively prevented top-bottom structural disruption and the subsequent layer delamination.**

Moreover, considering the lower crystallinity and scattering intensity of PQDs compared to bulk counterparts, primarily due to the presence of non-crystallizable organic ligands, **we have increased the exposure time for each PQD solid from the conventional 60 s to 120 s during GIWAXS measurement to maximize the signal-to-noise ratio.** Meanwhile, we did not embellish the instrumentally measured curves to reflect the practical condition. Therefore, the observed differences in signal intensity between samples were not random fluctuations but correlated well with the underlying ligand treatment protocols.

In summary, we supposed that the GIWAXS analysis at shallow incident angles captured meaningful orientational differences in the topmost PQD layers, and supported our conclusion that the AAAH strategy stabilizes homogeneous crystallographic orientation throughout the depth of the light-absorbing layer.

Modifications:

According to the reviewer's suggestion, we refined the relevant explanations added detailed information on the GIWAXS measurement conditions in the revised manuscript, as follows,

"These results suggested that the AAAH strategy effectively stabilizes homogeneous crystallographic orientations throughout the depth of the light-absorbing layer by forming a more integral surface BZA⁻ ligand capping." On page 20 of the manuscript.

"Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement was performed using a SAXS/WAXS laboratory beamline (Xeuss 3.0, XENOCs) equipped with a Cu K α 2 X-ray source (8.028 keV, 1.54 Å), and the diffraction patterns were collected by a detector (Pilatus3 1M, Dectris). The exposure time for each PQD solid was kept for 120 s during measurement to maximize the signal-to-noise ratio." On page 29 of the manuscript.

Q6: In line 38, "post-syntactic" seems to be a typo and should be "post-synthetic."

Response and modifications: We appreciate the reviewer pointing out this error. It should indeed be "post-synthetic". According to the reviewer's suggestion, we made this correction in the revised manuscript, as follows,

"Hybrid A-site lead iodide PQDs prepared by post-synthetic cation exchange enable solar cell devices exhibiting higher short-circuit current (J_{sc}) and lower open-circuit voltage (V_{oc}) deficits.²¹⁻²³" On page 2 of the manuscript.

Q7: In Figure 5d, the illustration appears to be incorrect.

In the processing of the Neat MeBz-based PQDSC, the MeBz treatment is depicted as an ester treatment, which could be misleading. It should either be redrawn to show MeBz treatment correctly or the final device name should be changed from "Neat MeBz" to "Neat ester" for consistency.

Response and modifications: We agree with the reviewer that the original label "neat MeBz-based" PQDSCs in **Fig. 5d** may lead to confusion. According to the reviewer's suggestion, we revised that to "neat ester-based", the revised figure and caption were updated in the manuscript, as follows,

"In contrast, the AAAH strategy involves interlayer rinsing of PQD solid films utilizing ester antisolvents with incorporated alkalis (especially MeBz with added KOH), allowing sufficient substitution of pristine long-chain OA⁻ ligands with short anionic ligands due to the significantly lowered energy thresholds for ester hydrolysis." On page 25 of the manuscript.

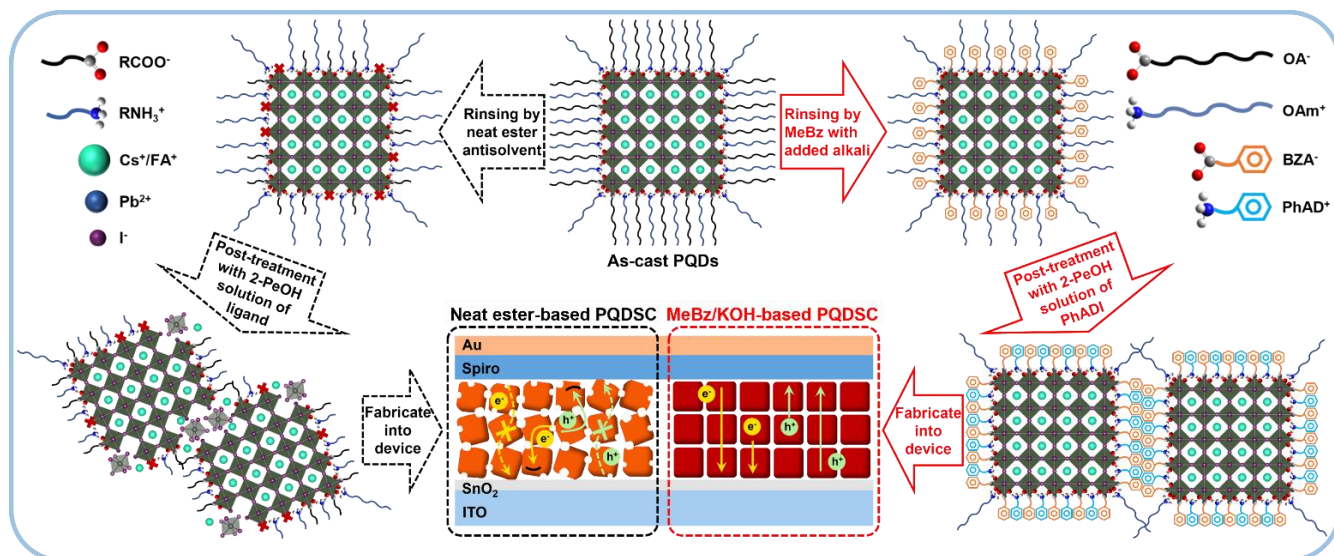


Fig. 5d Schematic diagrams of charge carrier dynamics within PQDSCs fabricated with neat ester antisolvent interlayer rinsing (neat ester-based PQDSCs) and MeBz/KOH-based AAAH interlayer ligand exchange.

Q8: In SI Table 2, the efficiency of the Neat MeBz device is listed as 16.15%, while the Neat MeOAc device is 15.80%. However, in SI Table 5 and SI Table 7, the Neat MeBz efficiency is reported as 15.80% and 15.82%, respectively. These values indicate that the efficiency of Neat MeBz and Neat MeOAc is actually quite similar.

Response:

In this work, the champion and statistical average efficiency values presented in **Supplementary Table 2** were obtained from **multiple batches, with 20 devices counted for each variant, aiming to provide a comprehensive evaluation of the impact of different neat ester antisolvent treatments on PQDSC performance.** In this context, the reported efficiencies of **16.15% (champion)** and **15.56% (average)** for neat MeBz-based PQDSCs were both higher than devices fabricated with other neat ester antisolvents rinsing including MeOAc.

In contrast, the efficiencies reported in **Supplementary Tables 6 and 8** were obtained from individual manufacturing batches, with **8 devices** fabricated under each condition. The purpose of these experiments was to directly compare the influence of different additives on the performance of MeBz-based PQDSCs prepared using PQD colloids synthesized from the same batch. Therefore, we reported the best-performing devices within each batch, instead of reusing the champion efficiency from **Supplementary Table 2**.

It is also worth noting that the efficiencies shown in **Supplementary Tables 6 and 8** were still above the average efficiency reported for the MeBz-based PQDSCs in **Supplementary Table 2**, indicating that they were representative and valid for comparison within the batch context. **Therefore, neat MeBz-based PQDSCs were superior to neat MeOAc-based devices, both in terms of statistical and champion efficiency.**

The device performances presented in these Supplementary Tables were selected to serve different comparative purposes and thus were not in conflict with one another.

Modifications:

According to the reviewer's suggestion, we revised the captions for **Supplementary Tables 6 and 8** to explicitly indicate that the data were obtained from a single batch of devices, as follows,

“Supplementary Table 6. Photovoltaic parameters of the best-performing MeBz-based PQDSCs fabricated with different 2-PeOH/ligand post-treatments extracted from **Supplementary Fig. 17**. For each condition, the reported efficiency corresponds to the highest value obtained from 8 devices. All the devices presented in this table were fabricated using PQDs synthesized from the same batch.” on page 50 of the *Supplementary Information*.

“Supplementary Table 8. Photovoltaic parameters of best-performing MeBz-, MeBz/K₂CO₃-, MeBz/Me₃SiOK- and MeBz/KOH-based PQDSCs fabricated without post-treatment extracted from **Supplementary Fig. 19**. For each condition, the reported efficiency corresponds to the highest value obtained from 8 devices. All the devices presented in this table were fabricated using PQDs synthesized from the same batch.” On page 52 of the *Supplementary Information*.

Q9: Additional device efficiencies based on the data in the paper are as follows:

Neat MeOAc: 15.8% (SI Table 2)

Neat MeBz: 16.15% (SI Table 2)

MeOAc + KOH: 17.51% (SI Fig. 28)

MeBz + KOH: 17.25% (SI Table 7)

EtOAc + KOH: 17.78% (SI Fig. 28)

MeBz + KOH + PhADI PT: 18.21% (SI Table 6), 18.372% (Fig. 3)

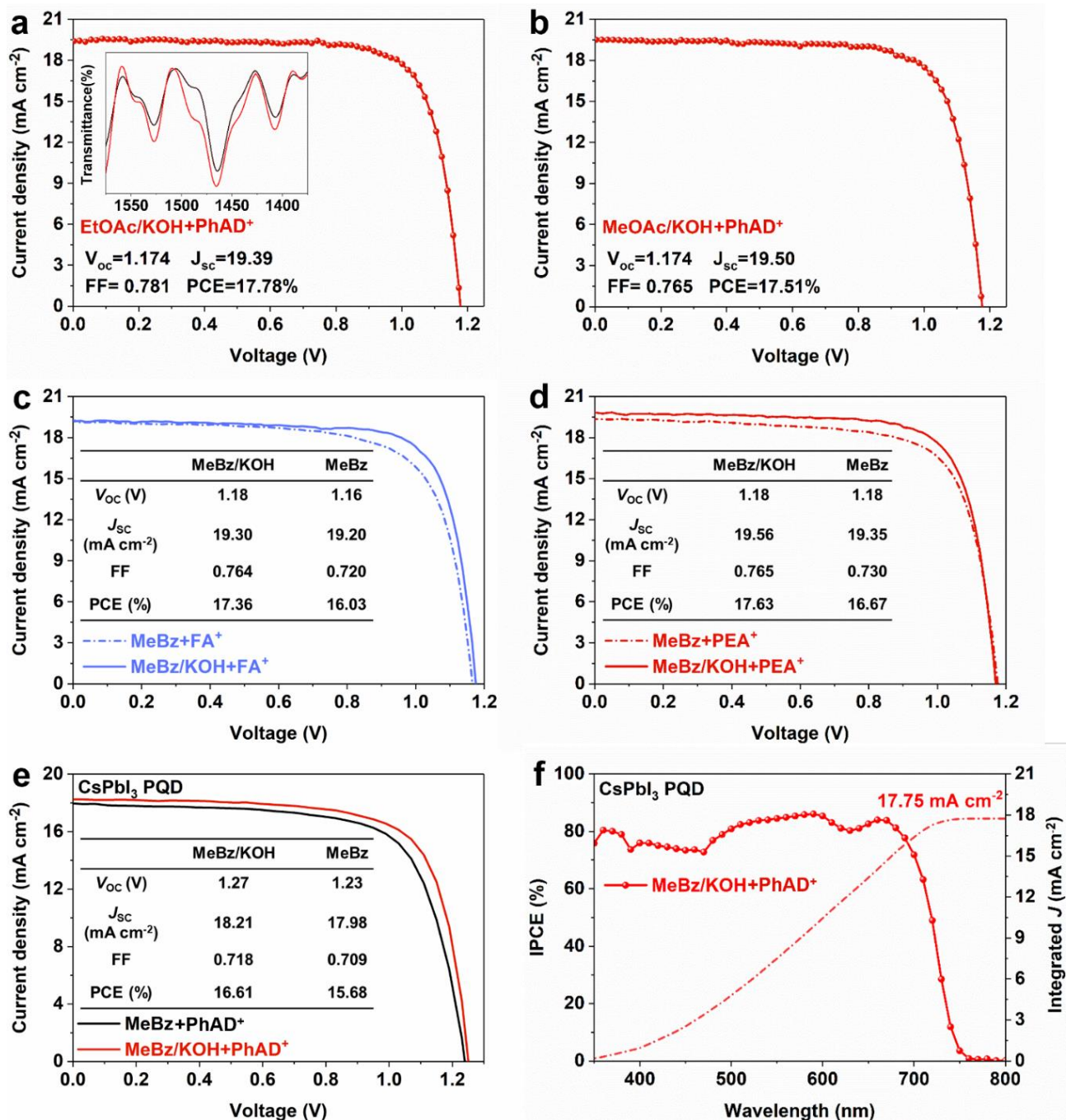
Based on this data, the efficiencies for MeOAc + KOH + PhADI PT and EtOAc + KOH + PhADI conditions are not explicitly stated in the paper. If there was a mistake in labeling MeOAc + KOH and EtOAc + KOH, it should be explicitly clarified to avoid confusion.

Response:

We thank the reviewer for carefully compiling the performance data and pointing out the inconsistency. In **Supplementary Figs. 35a and 35b**, we aimed to demonstrate the versatility of the AAAH strategy using different ester antisolvents beyond MeBz, especially MeOAc and EtOAc. **It should be emphasized that all devices shown in Supplementary Fig. 35, except for those clearly labeled as using other ligand post-treatments, were fabricated with the post-treatment A-site ligand exchange using 2-PeOH/PhAD⁺.** Without A-site post-treatment, devices would not yield such high efficiencies, consistent with results shown in **Supplementary Table 8**, where the performance without post-treatment was lower.

Modifications:

According to the reviewer's suggestion, we revised the legend and caption of **Supplementary Fig. 35** to address the oversight, as follows,



Supplementary Fig. 35 J - V curves of $Cs_{1-x}FA_xPbI_3$ PQDSCs fabricated based on AAAH strategy with (a) EtOAc/KOH and (b) MeOAc/KOH for interlayer rinsing, respectively. The inset in (a) shows the FT-IR spectra of EtOAc and EtOAc/KOH-based PQDs. J - V curves of MeBz- and MeBz/KOH-based $FA_xCs_{1-x}PbI_3$ PQDSCs fabricated with post-treatment (c) FA^+ and (d) PEA^+ ligand exchange. (e) J - V curves of MeBz- and MeBz/KOH-based $CsPbI_3$ PQDSCs. (f) Incident photon-to-electron conversion efficiency (IPCE) spectrum of MeBz/KOH-based $CsPbI_3$ PQDSC. Note that PQD light-absorbing layers presented in **a**, **b**, **e**, and **f** were all subjected to post-treatment A-site ligand exchange with $PhAD^+$.

Reviewer #2:

In this work, the authors fabricate CsPbI₃ perovskite nanocrystal solar cells. The key conceptual advance is the use of alkalis to hydrolyze ester antisolvents, which then are proposed to bind to the surface of the nanocrystals, leading to enhanced passivation and performance. The champion devices reach a certified efficiency of 18.3%. This is close to the highest reported for quantum dot solar cells (19.6% certified according to the NREL chart). The devices also demonstrate decent stability. This work is a good fit for Nature Communications. However, the following points need to be addressed.

Major:

Q1: The authors, from the beginning, lean into the explanation stated above. The authors should explore alternative explanations that the hydroxide anions could be playing. The authors should provide experiments and evidence showing whether or not these play any other role.

Response:

We thank the Reviewer for the valuable comments and suggestions. Regarding the potential multifaceted role of hydroxide anions (OH^-) in our system, we agree that it is essential to consider alternative pathways beyond the proposed ester hydrolysis mechanism. **Therefore, we conducted several experimental and theoretical investigations to clarify this point.**

Firstly, we examined the FT-IR spectra of PQD films treated with MeBz containing various alkaline additives (**Fig. 2b** and **Supplementary Fig. 10**). Interestingly, we found that only MeBz/NaOH-treated PQDs showed a pronounced hydroxyl stretching ($\nu(\text{O-H})$) signal centered at $\sim 3400\text{ cm}^{-1}$, which meanwhile exhibited significant disintegration and decomposition phenomena. In contrast, PQD films rinsed with MeBz/KOH, MeBz/ K_2CO_3 , and MeBz/ Me_3SiOK showed no identifiable hydroxyl peaks and remained morphologically intact. This suggests that OH^- would not be coordinated to the PQD surfaces under proper alkaline conditions, while adopting additives with excessive alkalinity may be detrimental.

Further support came from the deconvolution of O 1s peak in X-ray photoelectron spectroscopy (XPS) measurements (**Fig. 2d** and **Supplementary Fig. 14**). The results showed that with increasing alkalinity, the content of surface hydroxyl decreases while the contribution from carboxylate groups increases. This trend suggested that stronger alkalis could promote more efficient hydrolysis of ester antisolvents (e.g., MeBz), resulting in a higher yield of desired short anionic ligands (e.g. BZA^-) to bind to the PQD surface, thus enhancing conductive capping.

Besides, to directly validate the alkali-promoted ester hydrolysis, we additionally carried out comparative ^1H NMR experiments mixing MeBz with D_2O in the presence and absence of various alkaline additives, including K_2CO_3 , Me_3SiOK , and KOH, *as detailed in the answer to major Q1 of reviewer 1*. As shown in **Supplementary Fig. 11**, the neat MeBz sample exhibited sharp and unsplit signals, indicating uniform chemical environments without detectable hydrolysis. In contrast, all three alkali-containing samples showed clear peak splitting and a substantial decrease in the original MeBz signal, alongside the

emergence of distinct BZA^- peaks at 7.68 and 7.29 ppm. After normalizing these signals to the D_2O proton resonance ($\delta = 4.63$ ppm) for quantitative comparison, the hydrolysis ability of the added alkalis was found to increase with their alkalinity.

Moreover, density functional theory (DFT) calculations revealed that MeBz hydrolysis under neutral conditions was both thermodynamically unfavorable and kinetically hindered due to the high activation energy. In contrast, the presence of OH^- significantly lowered that energy barrier, confirming that alkaline environments effectively accelerated spontaneous ester hydrolysis (**Figs. 2e and 2f**).

In summary, the above comprehensive experimental and theoretical results consistently indicated that the primary role of alkali additives in our system was to facilitate ester antisolvent hydrolysis, thereby rapidly generating a greater quantity of the desired short anionic ligands to passivate PQD surface vacancies.

Modifications:

According to the reviewer's suggestion, we included relative discussions in the revised the manuscript, as follows,

“As illustrated in the FT-IR spectra (**Fig. 2b**), when the alkalinity of the added additive did not exceed that of KOH, rinsing PQD solid films with MeBz/alkali antisolvents would not introduce destructive hydroxyl groups (stretching vibration mode at $3250-3600\text{ cm}^{-1}$) to the PQD surface.” on page 10 of the manuscript.

Q2: The authors show well that the benzoate ligands covalently bond to Pb^{2+} species at I vacancies to form a Lewis acid-base adduct. However, can the authors also show whether this passivation leads to a reduction in the trap energy or concentration of defects associated with I vacancies?

Response:

Firstly, to focus on exploring defects associated with iodide vacancies, we additionally measured the trap density of states (tDOS) using thermal admittance spectroscopy (TAS) on devices fabricated from PQD solids without any ligand post-treatment, as shown in **Supplementary Fig. 28**. The MeBz/KOH-based device exhibited a lower trap density than the neat MeBz-based control sample, particularly for shallow-level region of 0.3-0.37 eV, implying that iodide vacancies on PQD surface were effectively passivated by hydrolyzed BZA^- Lewis base.

Besides, in our original manuscript, we employed the space charge limited current (SCLC) measurement to quantitatively analyze the trap density (N_{trap}) within PQD solids. As presented in **Fig. 5a**, the calculated N_{trap} decreased from $3.26 \times 10^{15}\text{ cm}^{-3}$ in neat MeBz-based devices to $1.9 \times 10^{15}\text{ cm}^{-3}$ in MeBz/KOH-based devices, indicating that the AAAH strategy effectively reduced the concentration of defects in PQD solids.

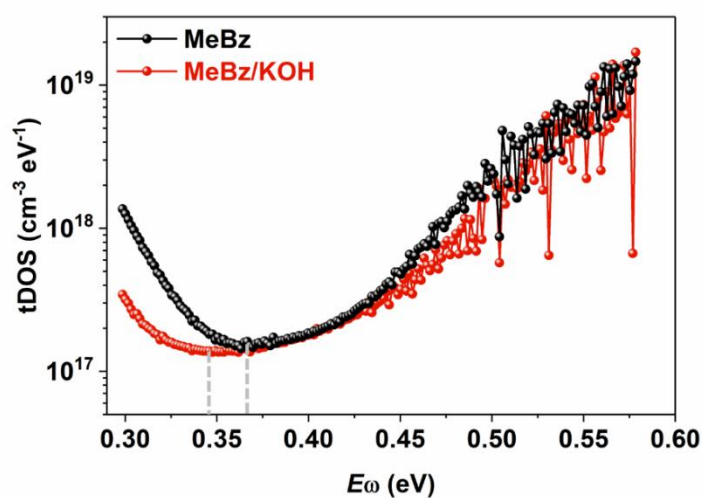
Moreover, Kelvin probe force microscopy (KPFM) measurements exhibited that the surface potential of PQDs decreased from 592 meV in the neat MeBz rinsing condition to 366 meV in the AAAH-based ligand exchange condition using MeBz/KOH (**Figs. 4f and 4g**). This was likely attributed to a greater number of phenyl electron donors effectively coordinated to the PQD surface, demonstrating a reduction in trap energy.

In conclusion, through multiple experimental techniques, including TAS, SCLC, and KPFM, we comprehensively demonstrated that BZA^- ligand passivation effectively decreased the concentration of shallow-level defects associated with iodide vacancies on the PQD surface.

Modifications:

According to the reviewer's suggestion, we added the analysis on tDOS measurement in the revised manuscript, as follows,

“The aforementioned studies have demonstrated that the pristine long-chain OA^- ligands on the PQD surface could be sufficiently substituted with short anionic ligands through the AAAH strategy. Accordingly, we measured the trap density of states (tDOS) using thermal admittance spectroscopy on devices fabricated from PQD solids without post-treatment A-site ligand exchange, as shown in **Supplementary Fig. 28**. The MeBz/KOH-based PQDSCs exhibited a notably lower trap density compared to the neat MeBz-based control device, especially in the shallow trap region of 0.30-0.37 eV. This result indicates that the hydrolyzed BZA^- Lewis base ligands effectively passivate iodide vacancies on the PQD surface, contributing to the suppression of nonradiative recombination pathways in photovoltaic devices.”
on page 19 of the manuscript.



Supplementary Fig. 28 Trap density of states (tDOS) obtained by thermal admittance spectroscopy for MeBz- and MeBz/KOH-based devices fabricated from PQD solids without post-treatment A-site ligand exchange.

Q3: The PLQY and TRPL measurements are missing fluency-dependence. At present, we cannot conclusively say which treatment works better because changes in PLQY and PL lifetime can simply be due to changes in the recombination regime. These fluence-dependent measurements need to be added.

Response:

As suggested by the reviewer, we conducted fluence-dependent time-resolved photoluminescence (TRPL) measurements using a femtosecond pulsed laser (405 nm, 2.5MHz) under a confocal microscope setup. As shown in **Fig. 2g**, despite that the local excitation density under microscopic conditions is significantly higher than that in conventional macro-optical systems, leading to overall shorter absolute PL lifetimes of samples. This setup remains highly effective for comparing the relative lifetimes and trend variations among different samples.

The results show that the PL lifetime of neat MeBz-based PQDs initially increased with excitation fluence, then decreased at higher fluences, suggesting a transition from trap-assisted Shockley-Read-Hall recombination at low fluence to radiative recombination as traps became saturated. In contrast, the MeBz/alkali-based samples exhibited a monotonic decrease in PL lifetime with increasing fluence, indicating bimolecular radiative recombination dominated throughout. Among them, MeBz/KOH-based PQDs consistently showed the longest lifetimes, implying the lowest trap density, followed by MeBz/K₂CO₃ and MeBz/Me₃SiOK samples. The neat MeBz-based PQDs exhibited the shortest lifetime across all fluences.

Therefore, the trend in carrier lifetime variations among these PQD solids was consistent with their PL decay behavior observed under fixed excitation fluence, confirming that nonradiative recombination in MeBz-rinsed PQDs was effectively suppressed by increasing the alkalinity of hydrolysis environments, particularly with KOH demonstrating the most significant effect.

Modifications:

According to the reviewer's suggestion, we included the fluence-dependent TRPL results, discussion, and corresponding figures in the revised manuscript, as follows,

“To in-depth analyze the carrier dynamics within PQD solids, fluence-dependent TRPL measurements were performed under confocal excitation. As shown in **Fig. 2g**, the PL lifetime of the neat MeBz-based PQD solid exhibited an initial increase as the excitation fluence increased from 25 to 80 nJ·cm⁻², followed by a decrease at higher fluences. This suggests a trap-assisted Shockley-Read-Hall recombination dominates at low fluence, which transits to bimolecular radiative recombination once the traps become saturated upon photon filling.⁴⁸ In contrast, all three MeBz/alkali-based samples exhibited monotonic decreases in their carrier lifetimes with increasing fluence, which is consistent with a regime dominated by radiative recombination with lower trap density.³³ Among these samples, MeBz/KOH-based PQDs consistently

showed the longest PL lifetime across all excitation fluences, indicating the lowest trap density, followed by MeBz/K₂CO₃- and MeBz/Me₃SiOK-based samples, while neat MeBz-based PQDs exhibited the shortest lifetime.” On page 13 of the manuscript.

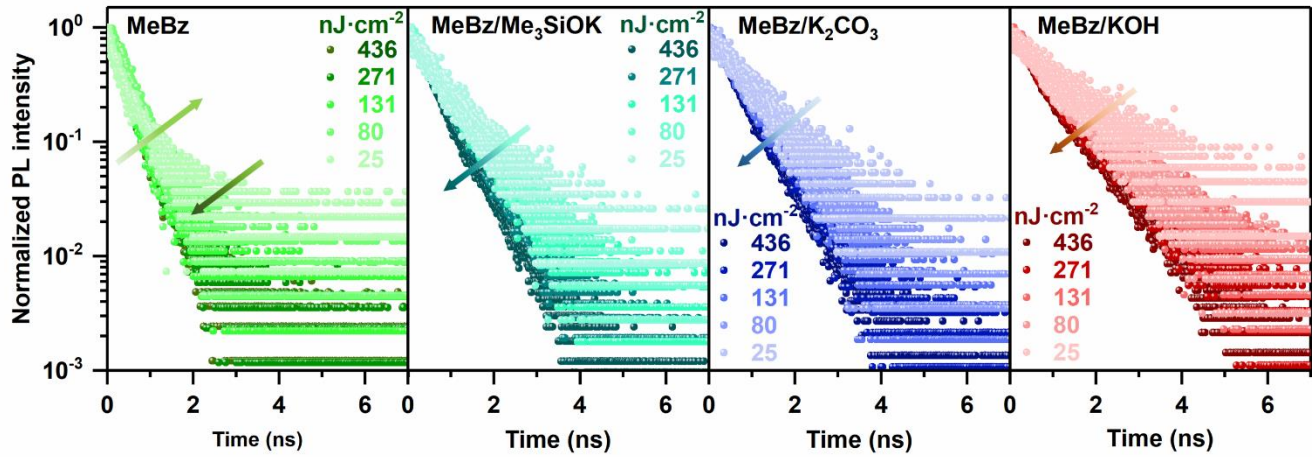


Fig. 2g Fluence-dependent TRPL of MeBz-, MeBz/K₂CO₃-, MeBz/Me₃SiOK-, and MeBz/KOH-based PQD solid films.

Supplementary Table 5. Fitted parameters of fluence-dependent TRPL decay of FA_xCS_{1-x}PbI₃ PQD solids under MeBz rinsing with and without added alkalis.

PQD 25 nJ cm ⁻²	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{ave} (ns)
MeBz	0.59	0.16	0.31	0.62	0.47
MeBz/Me ₃ SiOK	0.84	0.86	--	--	0.86
MeBz/K ₂ CO ₃	0.82	0.99	--	--	0.99
MeBz/KOH	0.77	1.32	--	--	1.32
PQD 80 nJ cm ⁻²	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{ave} (ns)
MeBz	0.37	0.41	0.64	0.58	0.53
MeBz/Me ₃ SiOK	0.97	0.74	--	--	0.74
MeBz/K ₂ CO ₃	0.95	0.82	--	--	0.82
MeBz/KOH	0.90	0.97	--	--	0.97
PQD 131 nJ cm ⁻²	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{ave} (ns)
MeBz	0.65	0.39	0.38	0.54	0.46
MeBz/Me ₃ SiOK	0.99	0.70	--	--	0.70
MeBz/K ₂ CO ₃	0.94	0.71	--	--	0.71
MeBz/KOH	0.97	0.96	--	--	0.96
PQD 271 nJ cm ⁻²	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{ave} (ns)

MeBz	0.89	0.38	0.16	0.54	0.41
MeBz/Me ₃ SiOK	1.06	0.62	--	--	0.62
MeBz/K ₂ CO ₃	0.98	0.66	--	--	0.66
MeBz/KOH	0.96	0.79	--	--	0.79
PQD 436 nJ cm⁻²	A₁	τ_1 (ns)	A₂	τ_2 (ns)	τ_{ave} (ns)
MeBz	1.01	0.38	--	--	0.38
MeBz/Me ₃ SiOK	1.08	0.52	--	--	0.52
MeBz/K ₂ CO ₃	1.01	0.57	--	--	0.57
MeBz/KOH	1.02	0.69	--	--	0.69

Note that the local excitation density under microscopic conditions is significantly higher than that in conventional macro-optical systems, leading to overall shorter absolute PL lifetimes of samples. The PL decay results show that the incorporation of alkali additives into MeBz, especially for KOH, could effectively suppress the fast non-radiative decay component observed in the neat MeBz-based PQD solid.

Q4: The bi-exponential model used to fit the PL decay are likely phenomenological rather than physically relevant. This should be clarified.

Response:

Regarding the use of the bi-exponential model for fitting the PL decay curves. We agree with the reviewer’s concern that this model may be more phenomenological than physically meaningful, and we would like to provide the following clarifications,

To evaluate the suitability of the bi-exponential model, each decay curve was independently fitted using mono-exponential, bi-exponential, and tri-exponential functions, the corresponding confidence values (R^2) are summarized in the **following table**. It can be observed that the tri-exponential fitting failed to converge in most cases, while the bi-exponential fitting yielded consistently higher R^2 values than the mono-exponential model, indicating a better fit to the experimental data.

<i>Comparison of fitting confidence for different exponential models in TRPL analysis</i>				
R^2		Mono-exponential	Bi-exponential	Tri-exponential
PQD				
MeBz		0.989	0.997	--
MeBz/Me ₃ SiOK		0.989	0.997	--
MeBz/K ₂ CO ₃		0.988	0.998	--
MeBz/KOH		0.983	0.998	0.998

Therefore, our TRPL data were fitted using a bi-exponential decay function, which is widely employed in both PQDSC and perovskite solar cell studies (Nat. Energy, 2020, 5, 79–88; Nat. Energy, 2024, 9, 324–

332). ***This function provides a practical and commonly accepted numerical description of the PL decay profile, where the fast decay component is typically attributed to non-radiative recombination, and the slow component is associated with radiative recombination.*** Given that the measurements were conducted under low excitation fluence (in the $\text{nJ}\cdot\text{cm}^{-2}$ range), Auger recombination was highly unlikely. Moreover, the synthesized PQDs with sizes comparable to their Bohr exciton radius, resulting in weakly defined excitonic features. Consequently, distinguishing the dominant physical origin of the intermediate decay component in a tri-exponential model would be ambiguous.

In addition to the TRPL curves, we also conducted PL lifetime mapping for 2-PeOH/PhAD⁺ post-treated PQD solids based on the bi-exponential fitting function (**Figs. 4j and 4k and supplementary Fig. 31**). This allowed us to visualize the spatial distribution of carrier lifetimes corresponding to radiative and nonradiative processes, thereby revealing inhomogeneities in the recombination behavior across the film.

In summary, despite the use of a phenomenological bi-exponential fitting model that requires a clear explanation, this approach still yielded valuable insights into the photophysical properties of our PQD samples.

Modifications:

According to the reviewer's suggestion, we revised the manuscript to clarify the rationale for this selection, as follows,

“**Supplementary Tables 4 and 5** summarize the fitting parameters of TRPL decay curves using phenomenological models. Although these models were not necessarily physically relevant, they primarily provided a numerical description of the PL decay process. It can be found that the variation trends in carrier lifetime closely correlate with the PL intensity order of these PQDs, confirming that the AAAH-based ligand exchange leads to more effective surface ligand capping, with KOH emerging as the most effective additive among those tested.” *On page 13 of the manuscript.*

Q5: Beyond the efficiency from certification, the stabilized power output from maximum power point tracking needs to be shown more prominently. The abstract should also state the device area and the median device efficiency, along with how many samples the median value is for.

Response:

Regarding the stabilized power output from maximum power point tracking shown in **Fig. 3e**, the steady-state PCE of our device was 17.85%, slightly lower than the transient efficiency measured from the J-V curve. This discrepancy remains common in state-of-the-art PQDSCs (Adv. Mater. 2025, 37, 2417346; Energy Environ. Sci. 2024, 17, 2145), while the underlying causes are not yet fully understood. In addition,

the active area of our PQDSCs was 0.036 cm², and the median device efficiency was 17.68%, based on 20 samples, highlighting good device reproducibility.

Modifications:

We understand the importance of highlighting these parameters. According to the reviewer's suggestion, we included these data in the revised abstract, as follows,

“Through tailoring potassium hydroxide coupled with methyl benzoate antisolvent for interlayer rinsing of PQD solids, the assembled light-absorbing layers exhibit fewer trap-states, homogeneous orientations, and minimal particle agglomerations, consequently enabling the fabricated solar cells (0.036 cm²) to achieve 18.3% certified efficiency, the highest value among published PQD solar cell reports. Meanwhile, our PQD solar cells exhibit a steady-state efficiency of 17.85%, with an average efficiency of 17.68% across 20 devices. Moreover, the introduced alkaline environment is compatible with diverse solid-state treatments and PQD compositions, demonstrating universality in modulating PQD surface chemistry.” On page 1 of the manuscript.

Minor:

Q1: Fig. 1 has a typo in the title "Easter"

Response and modifications: We appreciate the reviewer pointing out this error. According to the suggestion, we made this correction in the revised manuscript, as follows,

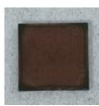
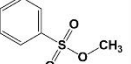
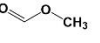
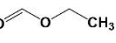
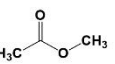
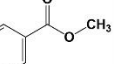
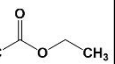
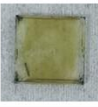
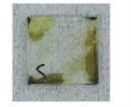
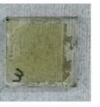
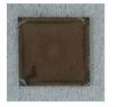
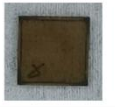
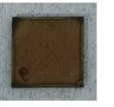
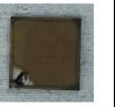
As-cast	Decreased polarity of ester antisolvents →						
	MMS	MeBzSO ₃	MeFo	EtFo	MeOAc	MeBz	EtOAc
							
							

Fig. 1a Molecular structures of the alternative ester antisolvents used in this work.

Q2: Fig. 2a. Many XRD peaks not accounted for. Reference pattern and refinement need to be given.

Response and modifications: After reanalyzing our XRD data following the reference pattern (ACS Nano 2018, 12, 10327), we assigned all diffraction peaks of our PQD samples and incorporated the updated labeling in the revised manuscript, as follows,

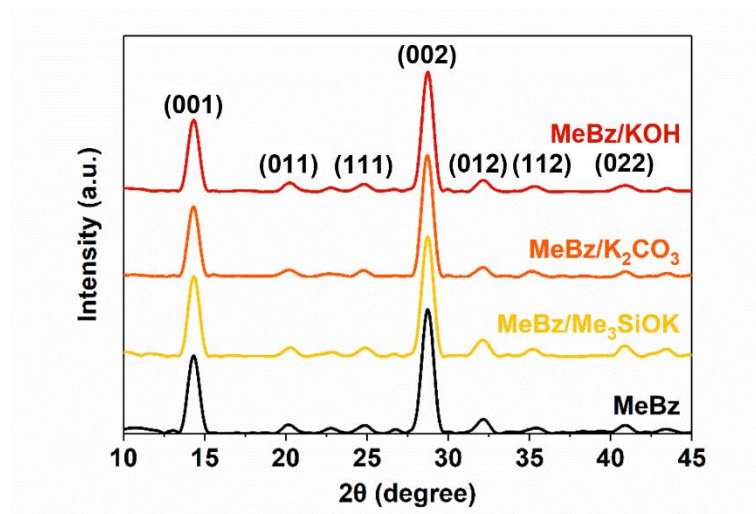


Fig. 2a XRD pattern of MeBz-, MeBz/K₂CO₃-, MeBz/Me₃SiOK-, and MeBz/KOH-based PQD solid films.

Q3: The stability tests need to be described better. Did the authors follow the ISOS protocols?

Response:

Regarding whether we followed the ISOS protocols, we referred to the guidelines outlined in authoritative literature for our stability tests (Nat. Energy 2020, 5, 35-49). Firstly, for the storage stability test of devices shown in **Fig. 3g**, we evaluated their shelf life under ambient conditions with a relative humidity (RH) of $25 \pm 5\%$ and a room temperature of $25 \pm 5^\circ\text{C}$. This setup aligns with the ISOS-D-1 standard, ensuring the reliability of our storage stability data.

However, for the continuous operational stability test of the PQDSCs presented in **Fig. 3h**, we performed maximum power point (MPP) tracking under continuous 100 mW cm^{-2} white LED illumination in an N_2 atmosphere. While this experimental setup allows us to evaluate device performance in a controlled environment, it did not fully comply with the ISOS-L protocol, which requires testing under ambient conditions. Given that current research in the field of PQDSCs primarily focuses on improving device efficiency, even state-of-the-art PQDSC stability tests are typically conducted in an N_2 atmosphere (Nat. Energy 2024, 9, 324-332). We acknowledge this deviation and its implications, in future studies, we will attempt to conduct stability tests that adhere to the ISOS-L protocol, aiming to provide more comprehensive and industry-standard-compliant stability data.

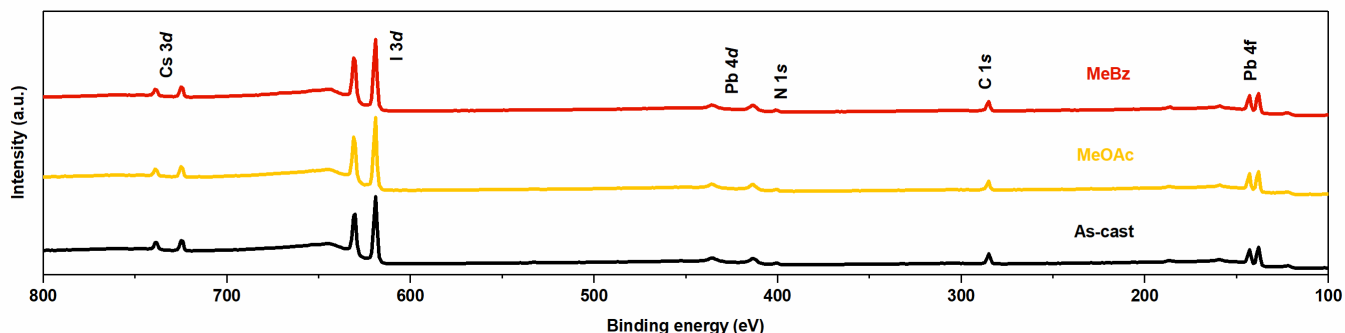
Modifications:

According to the reviewer's suggestion, we revised the manuscript, as follows,

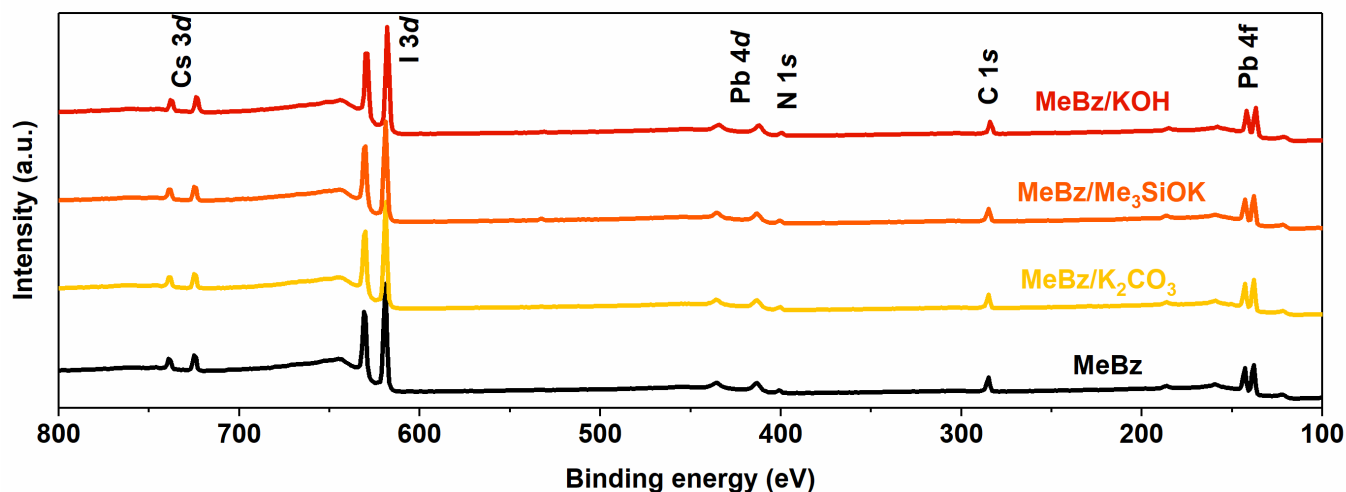
“We first tested the shelf life of unencapsulated PQDSCs under ambient conditions with an RH of 20%-30%, following the ISOS-D-1 protocol.⁵¹” on page 17 of the manuscript.

Q4: For XPS, the survey spectrum needs to be given

Response and modifications: We appreciate the reviewer's attention to the details of our XPS data presentation. Providing the survey spectra is important for a comprehensive XPS analysis. According to the reviewer's suggestion, we included the relevant XPS data in **Supplementary Figs. 8 and 14**, as follows,



Supplementary Fig. 8a Survey spectra of as-cast, MeOAc-, MeBz-based PQD solid film.



Supplementary Fig. 14a Survey spectra of MeBz-, MeBz/K₂CO₃-, MeBz/Me₃SiOK-, and MeBz/KOH-based PQD solid films.

Q5: Suppl. Fig. 14 cannot be correct. These Tauc plots are constructed for indirect bandgap materials, whereas the bandgap should be direct. Did authors account for the excitonic peak? Fig. 1b cannot give bandgap since this is simply taking the tangents of the absorption onset, and not Tauc plots.

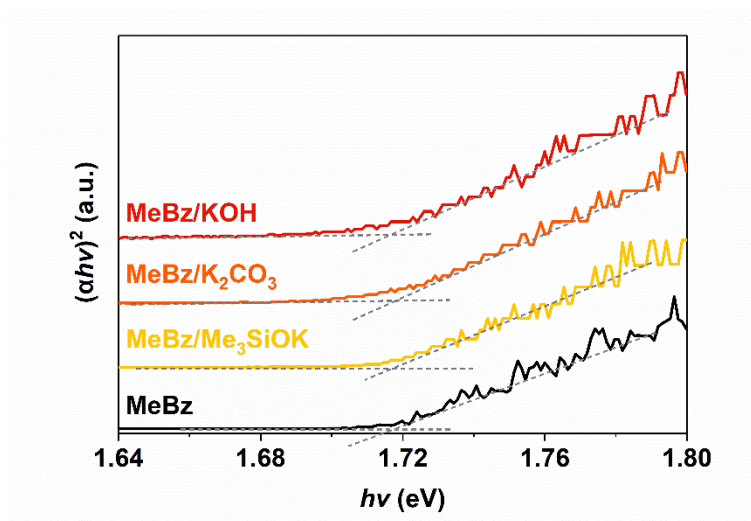
Response:

We thank the reviewer for pointing out the error in the bandgap determination method. **Firstly**, for the Tauc plots in **Supplementary Fig. 16a**, we realized that they were incorrectly constructed using $(\alpha h\nu)^{1/2}$ as the vertical axis, which is suitable for indirect bandgap materials. Therefore, we corrected this by reconstructing the Tauc plots using $(\alpha h\nu)^2$ as the vertical axis, which is more appropriate for direct bandgap semiconductors such as PQDs.

Secondly, we did not observe any distinct exciton-related features in the absorption spectra of our PQD solids. We attributed this to the relatively large size of our synthesized quantum dots, with an average diameter of ~ 12.5 nm, which is comparable to the Bohr exciton radius of CsPbI_3 (~ 12 nm). Under such critical conditions, the PQDs were in a “quasi” quantum confined regime and did not exhibit the strong excitonic absorption typically observed in traditional II-VI quantum dots with smaller dimensions.

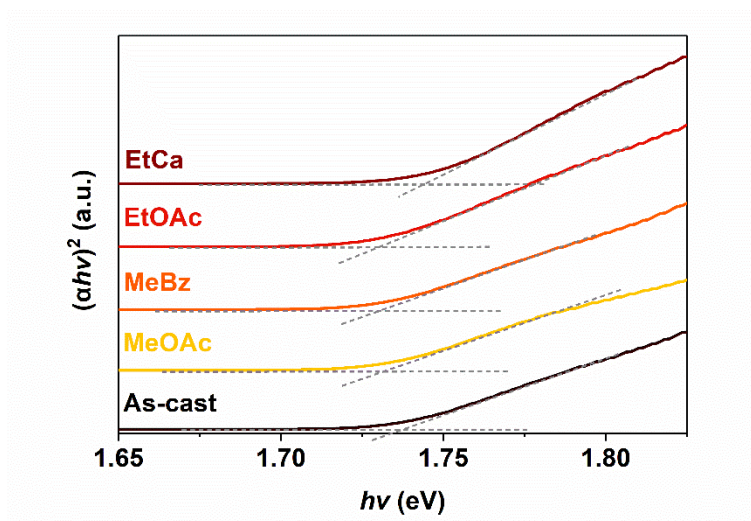
Modifications:

According to the reviewer's suggestion, we revised the Tauc plots in **Supplementary Fig. 16a**, and added the Tauc plots derived from the absorption spectra of **Fig. 1b** in **Supplementary Fig. 4a**, as follows,



Supplementary Fig. 16a Tauc plots of MeBz-, MeBz/ K_2CO_3 -, MeBz/ Me_3SiOK -, and MeBz/KOH-based PQD solid films.

“**Figs. 1b** and **1c** present the light absorption and steady-state photoluminescence (PL) spectra of PQD solid films, and the corresponding Tauc plots are shown in **Supplementary Fig. 4a**.” on page 6 of the manuscript.



Supplementary Fig. 4a Tauc plots of as-cast, MeOAc-, MeBz-, EtOAc-, and EtCa-based PQD solid films.

Q6: The English needs to be improved throughout. The abstract should be rewritten to be more specific. Some words incorrect, such as "complementation". What are the authors trying to say?

Response:

We thank the reviewer for pointing out the language issues in the manuscript and for highlighting the inappropriate use of the word “complementation”. This term appeared in the Introduction part on page 3, in the sentence: “Importantly, inadequate complementation of X-site anionic ligands during interlayer antisolvent rinsing has the potential to induce PQD aggregations after post-treatment A-site cationic ligand exchange.”

Herein, our intended meaning was to emphasize that if the removed pristine X-site ligands were not sufficiently replenished by alternatives during interlayer antisolvent rinsing, vacancy defects would be left on the surface, resulting in the adjacent PQDs being susceptible to aggregate after successive antisolvent treatment.

Modifications:

According to the reviewer’s suggestion, we revised the expression of the sentence mentioned above. We also carefully revised the grammar and clarity of the entire manuscript, as follows,

“Importantly, if the removed pristine X-site anionic ligands are not effectively replenished by the alternatives during the interlayer antisolvent rinsing process, the surfaces of these PQDs would be destabilized. As a result, undesirable aggregation would occur from further shrinkage of inter-particle space during subsequent A-site cationic ligand exchange, which in turn deteriorates charge transport of the assembled light-absorbing layers.” On page 3 of the manuscript.

Q7: It should be diffraction pattern and not spectra (no change in energy in XRD)

Response and modifications: *We appreciate the reviewer's correction. For XRD, "diffraction pattern" is the appropriate term instead of "spectra," since XRD does not involve any change in energy. According to the reviewer’s suggestion, we made the necessary changes throughout the manuscript, as follows,*

“Fig. 2a XRD pattern of MeBz-, MeBz/K₂CO₃-, MeBz/Me₃SiOK-, and MeBz/KOH-based PQD solid films.” On page 14 of the manuscript.

Q8: The authors make arguments on ligand binding to Pb based on changes in binding energy from XPS. This can also be due to a change in the Fermi level. The authors need to discuss whether they can rule this out.

Response:

Regarding the concern that the changes in binding energy observed in XPS could be due to shifts in the Fermi level, we would like to provide the following clarifications,

It is essential to state that all XPS core-level binding energies reported in this study were calibrated using the C 1s internal reference. This calibration ensured that the observed shifts in Pb 4f and O 1s binding energies reflected intrinsic chemical modifications on the PQD surface, instead of measurement errors.

Firstly, we conducted XPS measurements on PQDs in the as-cast state, and those rinsed with neat ester antisolvents (**Supplementary Fig. 8**). It can be observed that after PQDs being rinsed with neat antisolvents, their Pb 4f core level shifted to higher binding energies, indicating decreased electron density. Additionally, by deconvolving the O 1s core level peak of these samples, we found an increase in hydroxyl content on the ester antisolvent rinsed PQD surface. These results indicated that after rinsing PQDs with neat antisolvents, the Lewis base anionic ligands that acted as electron donors were removed from the surface X-site. Conversely, when PQDs were rinsed with ester antisolvents containing alkali additives, the Pb 4f core level shifted back to lower binding energies (**Supplementary Fig. 14**), suggesting an increase in electron density. The O 1s core level peaks deconvolving also showed a decrease in hydroxyl content and an increase in carboxylate amount on these PQD surfaces compared to the samples rinsed with neat ester antisolvent. These results indicated an increase in the carboxyl ligands coordinated to the Pb^{2+} sites exposed on the PQD surface after rinsing solids using ester antisolvents with added alkalis.

In addition to the XPS results, according to the increased COO^- -stretching signal in FT-IR spectra and enhanced phenyl groups resonances in NMR spectra (**Figs. 2b and 2c**), we further determined that the Pb^{2+} exposed on the neat MeBz-based PQD surface was capped by the hydrolyzed BZA^- anionic ligands under the facilitate of alkalis. Moreover, tDOS analysis of devices fabricated from PQD solids without post-treatment A-site ligand exchange (**Supplementary Fig. 28**) showed that MeBz/KOH-treated PQDs exhibited significantly lower trap densities in the shallow region of 0.3-0.37 eV compared to the neat MeBz-based counterparts, indicating X-site vacancy defects were effectively lowered by using the AAAH strategy, [as detailed in the answer to major Q2 of reviewer 2](#).

On the other hand, UPS measurements (**Fig. 5c**) showed that the overall Fermi level of the MeBz/KOH-based sample (-4.98 eV) exhibited only a slight upshift compared to that of the neat MeBz-based PQD solid (-5.00 eV). However, KPFM measurements (**Figs. 4f and 4g**) revealed that the surface potential of MeBz/KOH-based sample (366 meV) was significantly lower than that of the neat MeBz-based sample (592 meV). Therefore, we attributed the minor change in the Fermi level of PQDs to the more sufficient surface capping by BZA^- electron-donor ligands.

In summary, based on the review of previous literature (J. Am. Chem. Soc. 2018, 140, 10504; Nano Energy 2019, 66, 104130) and the above-described collective evidence from multiple tests, we suggest that the ligand binding effect played a major role in the observed XPS variations.

Modifications:

According to the reviewer's suggestion, we included the discussion in the revised manuscript, as follows,

"Therefore, based on the combined results of FT-IR, NMR, and XPS analyses, we conclude that the AAAH strategy effectively compensates for X-site vacancies on the PQD surface by introducing a greater number of short anionic ligands hydrolyzed from ester antisolvents, rather than anions or cations dissociated from the added alkalis." On page 12 of the manuscript.

"Ultraviolet photoelectron spectroscopy (UPS) was employed to assess the energy levels of the functional layers in the PQDSC. As depicted in Fig. 5c, the slight upward shift of Fermi level in MeBz/KOH-based PQD solids is likely attributed to the enhanced surface capping of BZA⁻ electron-donor ligands that reduces surface potential, as measured by KPFM (Figs. 4f and 4g)." On page 24 of the manuscript.

Q9: The authors attribute changes in the diode ideality factor to changes in the recombination regime of the device. This can also change because of space charge regions in the device and other regions. The authors should not draw too many conclusions simply from the fitted ideality factor

Response:

In our study, we initially attributed changes in the diode ideality factor to variations in the recombination regime. **To further validate our conclusions and account for other possible influences, such as changes in space charge region, we conducted additional measurements for PQDSC devices, including capacitance-voltage (C-V) and transient photovoltage (TPV).**

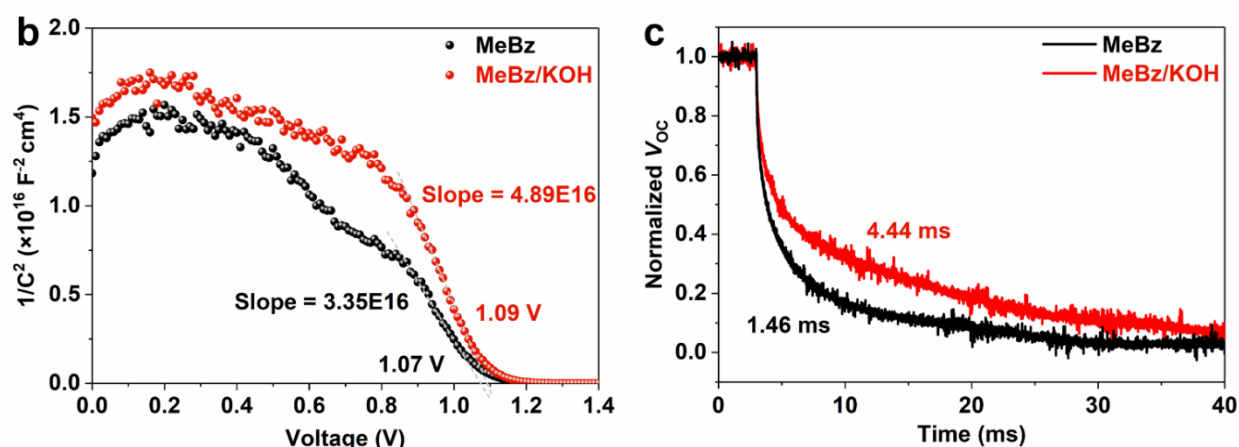
From the C-V tests shown in **Supplementary Fig. 33b**, we analyzed the Mott-Schottky curves and found minor differences in the built-in electric field between MeBz/KOH- and neat MeBz-based PQDSCs (1.09 V vs. 1.07 V), while the interfacial carrier concentration (calculated from the slope in the linear region) was significantly lower for MeBz/KOH-based PQDSCs ($7.28 \times 10^{16} \text{ cm}^{-3}$) than neat MeBz-based counterparts ($1.06 \times 10^{17} \text{ cm}^{-3}$), suggesting that charge accumulation at the interface was effectively suppressed. In addition, as shown in **Supplementary Fig. 33c**, TPV measurements revealed that the carrier lifetime in MeBz/KOH-based PQDSCs (4.44 ms) was significantly longer than that in MeBz-based samples (1.46 ms), demonstrating less carrier recombination within the device.

In summary, by incorporating these additional measurements, we could more confidently assert that the observed decrease in the diode ideality factor was mainly related to improvements in carrier recombination.

Modifications:

According to the reviewer's suggestion, we included these additional measurements and provided a more in-depth discussion in the revised manuscript, as follows,

“As shown in **Supplementary Fig. 33b** and **Supplementary Note 4**, to elucidate the mechanisms behind reduced interfacial charge recombination, Mott-Schottky analysis reveals that compared to the neat MeBz-based devices, MeBz/KOH-based PQDSCs exhibit a higher built-in potential (1.09 V versus 1.07 V) and a significantly lower interfacial carrier density ($7.28 \times 10^{16} \text{ cm}^{-3}$ versus $1.06 \times 10^{17} \text{ cm}^{-3}$). These align well with the higher V_{OC} and FF values for MeBz/KOH-based PQDSCs. Moreover, transient photovoltage (TPV) measurements further show a significantly longer carrier lifetime of 4.44 ms in the MeBz/KOH-based devices compared to that of 1.46 ms in the MeBz-based counterparts (**Supplementary Fig. 33c**). These results further confirm suppressed charge recombination and improved charge extraction within the device fabricated using the AAAH strategy.” *On page 24 of the manuscript.*



Supplementary Fig. 33 (b) Mott-Schottky curves, and (c) TPV curves of MeBz- and MeBz/KOH-based PQDSCs.

Reviewer #3:

Jia et al. reported a method that promotes rapid substitution of the original insulating oleic acid ligand by modulating the alkaline environment and selective ester solvents during ligand exchange in the solid film of perovskite quantum dots (PQDs). By mixing potassium hydroxide (KOH) with methyl benzoate (MeBz) antisolvent for interlayer washing of PQD solid, a conductive PQD film with uniform orientation, minimal agglomeration of particles, and less trap state can be obtained, and the application efficiency in solar cells reaches a certified 18.3%. The manuscript presents many new insights into PQD solar cells, but some issues need to be addressed before it can be published in Nature Communications.

Q1: The manuscript emphasizes the role of alkaline-generated hydroxide ions (OH^-) in ester hydrolysis that drives ligand exchange on the surface of PQDs. But this reaction still takes place under humidity conditions, so is this change due to the hydrolysis of the alkali itself or some reaction with the water in the air? Or the reaction could be attempted in nitrogen instead of humidity.

Response:

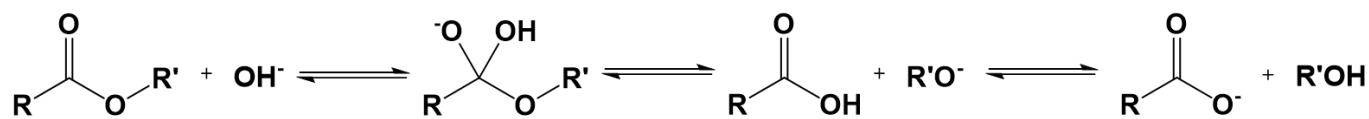
We thank the Reviewer for the valuable comments and suggestions. *Regarding the role of moisture in the ligand exchange process of PQD solids, we first conducted experimental investigations under strictly anhydrous conditions in an N_2 -filled glove box as recommended.*

As shown in **Supplementary Fig. 23**, rinsing PQD films with neat ester antisolvents (EtOAc, MeBz) under anhydrous conditions led to significant delamination and cracking, and the efficiencies of fabricated PQDSCs were quite low. FT-IR results demonstrated that the phenomenon was probably due to the drastic loss of surface ligands without alternative ligand compensation. In contrast, rinsing PQD solids with MeBz/KOH in anhydrous conditions could preserve a complete morphology, and the corresponding PQDSC showed higher efficiency. FT-IR analysis revealed that this phenomenon was likely due to the partial hydrolysis of MeBz promoted by KOH in advance, thus triggering a certain degree of ligand exchange. Nevertheless, despite the introduction of alkaline additives, the extent of ligand exchange via ester hydrolysis under anhydrous conditions remained markedly lower than that observed under ambient conditions (**Fig. 2b**). As a result, the photovoltaic performance of PQDSCs fabricated in anhydrous environments was significantly compromised compared to those processed under ambient conditions.

Moreover, we theoretically studied the mechanism of alkaline hydrolysis of esters. The **following Schematic figure** illustrates the step-by-step changes in the chemical structure of reactants within the reaction process. We found that water molecules, serving as a medium to solvate OH^- , played a crucial role in enabling the transformation of ester antisolvent rinsing into effective anionic ligand exchange for PQD solids. In the absence of water molecules, both the quality of ester antisolvents rinsed solid films and the performance of the resulting PQDSC devices would be compromised significantly.

In summary, the above experimental and theoretical findings collectively underscored the critical role of ambient moisture in facilitating effective ester hydrolysis and subsequent ligand exchange, thus achieving

high-quality PQD solids and optimal device performance.



Schematic diagram of the step-by-step reaction process for ester hydrolysis in an alkaline environment.

Modifications:

According to the reviewer's suggestion, we incorporated these experimental details and explanations in the revised manuscript and Supplementary Information, as follows,

"It is worth noting that although the ester hydrolysis in alkaline environments proceeds via the nucleophilic attack by OH^- ions, the presence of water molecule is essential, as it serves as the medium that enables OH^- dissociation and facilitates the overall hydrolysis process. Without the participation of water, the ester antisolvent rinsing of PQD solids cannot effectively trigger X-site ligand exchange, as demonstrated in **Supplementary Fig. 23** and **Supplementary Note 3**." On page 17 of the manuscript.

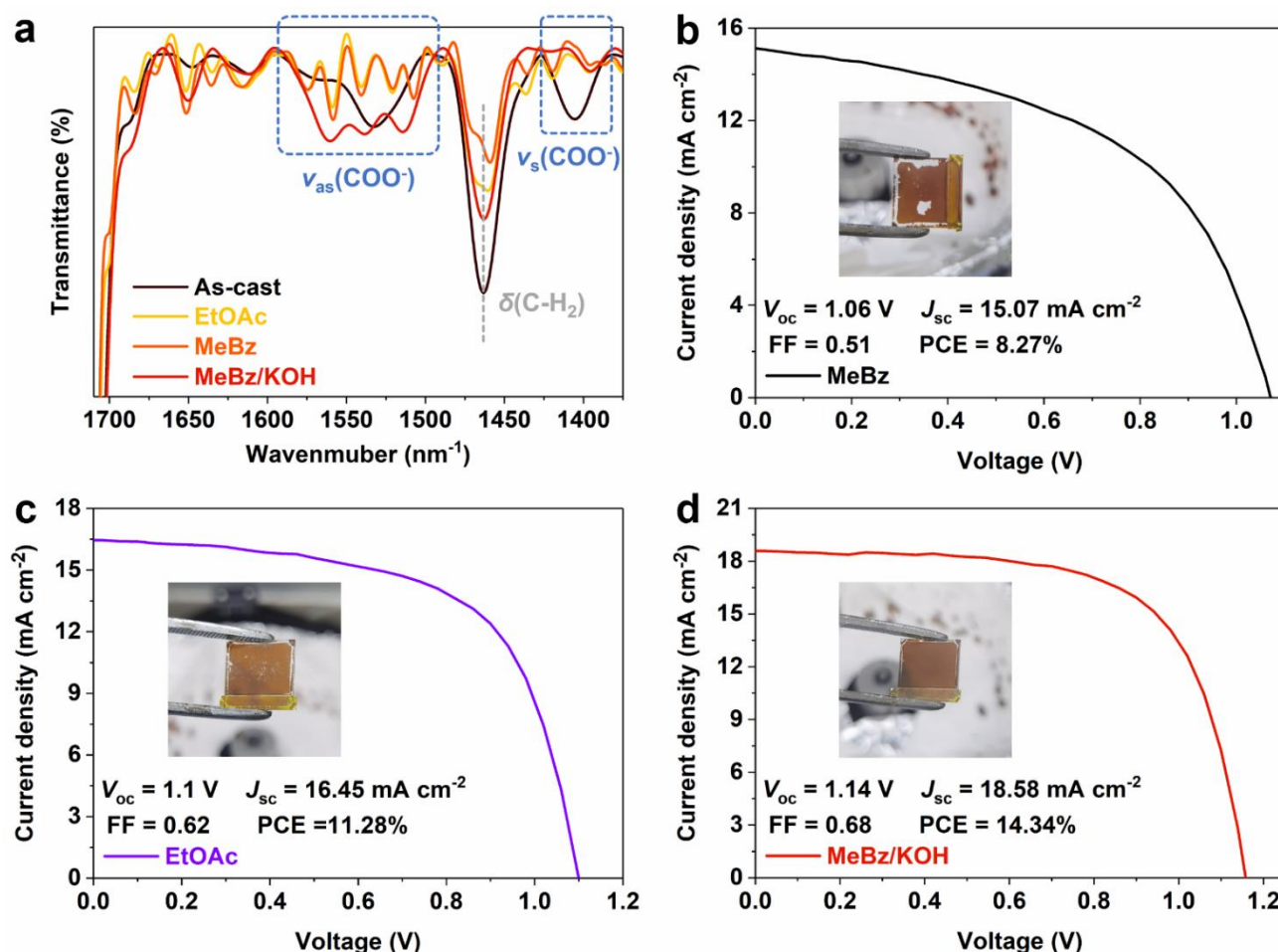
"Supplementary Note 3. The essential role of water in ester antisolvent hydrolysis under alkaline environments."

During the alkaline hydrolysis of esters, hydroxide anions (OH^-) serve as nucleophiles to initiate the cleavage of ester bonds by attacking the carbonyl group ($\text{C}=\text{O}$) of esters, which are typically generated through the dissociation of alkaline additives (e.g., KOH) in the presence of water. Therefore, water not only enables the release of free OH^- ions by solvating alkalis but also acts as the medium to initiate a cascade hydrolysis reaction, ultimately yielding alcohols and carboxylate salts. Particularly, the presence of water enables the rapid neutralization of the carboxylic acid intermediate with excess OH^- , thereby driving the reaction irreversibly toward the formation of stable carboxylate. However, under anhydrous conditions, alkaline additives remain majorly in their solid state without sufficient ionization, preventing the reaction from proceeding efficiently.

To evaluate the necessity of water, we conducted a series of interlayer rinsing experiments in a nitrogen-filled glove box under strictly anhydrous conditions, in which PQD solids were separately rinsed with EtOAc, MeBz, and MeBz/ KOH antisolvents. As shown in **Supplementary Fig. 23a**, in the absence of ambient moisture, neat ester antisolvent rinsing results in the direct removal of pristine long-chain ligands from the PQD surface without available ligand compensation, leading to severe delamination and surface cracking in the resulting PQD solids. In contrast, the morphology of PQD film remains intact after being rinsed with the MeBz with added KOH under anhydrous conditions, likely because KOH has promoted the partial liquid-state hydrolysis of MeBz and generated a few BZA^- ligands in advance, thus triggering ligand

exchange in anhydrous conditions. Nevertheless, a comparison of the FT-IR spectra at 1408 cm^{-1} (**Fig. 2b**) reveals that rinsing the PQD surface with MeBz/KOH under ambient conditions still exhibits significantly greater amounts of hydrolyzed BZA^- ligands.

The photovoltaic performance of solar cell devices further confirms the critical role of water, PQDSCs fabricated with EtOAc, MeBz, and MeBz/KOH interlayer rinsing under anhydrous conditions show efficiencies of 11.28%, 8.27%, and 14.34% (**Supplementary Figs. 23b-d**), respectively. Although these devices fabricated underwent 2-PeOH/PhAD⁺ post-treatment, their performance is far inferior to the corresponding counterparts fabricated in ambient conditions (**Fig. 3b**). Therefore, water is indispensable for effective ester hydrolysis under alkaline environments, without the presence of water, AAAH-based ligand exchange remains insufficient, leading to poor film morphology and significantly deteriorated device performance.” on page 29 of the Supplementary Information.



Supplementary Fig. 23 (a) FT-IR spectra of as-cast, EtOAc-, MeBz-, and MeBz/KOH-based PQD solids prepared under anhydrous conditions. *J-V* curves of (b) EtOAc-, (c) MeBz-, and (d) MeBz/KOH-based PQDSCs and morphology of the corresponding light-absorbing layers assembled in N_2 -filled glovebox. Note that the more pronounced cracking observed in MeBz-based PQD films and the lower efficiency of MeBz-based PQDSCs can be attributed to the higher polarity of the MeBz antisolvent, leading to more intense ligand removal during processing.

Q2: The photoluminescence (PL) spectrum presented in Fig. 3g exhibits an unexpected splitting of the emission peak (e.g., dual peaks at ~700 nm and ~740 nm), which raises concerns about the material homogeneity or phase purity of the PQDs. Such splitting is atypical for well-passivated, monodisperse PQDs and may indicate one or more of the following issues: phase segregation (The coexistence of multiple crystal phases (e.g., CsPbI₃ and FAPbI₃) due to incomplete stabilization of the perovskite lattice under alkaline conditions); defect-Mediated emission (emergence of trap states or surface defects that introduce additional radiative recombination pathways, potentially linked to incomplete surface capping or ligand desorption during the alkaline treatment). To resolve these ambiguities, the authors should provide X-ray diffraction (XRD) data or high-resolution transmission electron microscopy (HR-TEM) to confirm phase purity and crystallographic uniformity.

Response:

We appreciate the reviewer's thoughtful concerns regarding the underlying reasons for the unexpected emission peak splitting of PQD solids observed in **Supplementary Figs. 27a and 27b**. As reported in previous studies (*Nat. Commun.* 2019, 10, 1088; *ACS Energy Lett.* 2019, 4, 54–62), sized-confined PQDs with surfaces fully capped by ligands (typically in the as-cast state) generally exhibited strong resistance to phase segregation due to the absence of ionic migration pathways. However, this resistance to A- or X-site domain formation diminished with increasing grain size and decreasing surface passivation, making such phenomena more common in bulk hybrid perovskites with intrinsic grain boundaries and vacancies.

In our study, for PQD solids subjected to multiple rinses using ester antisolvents with added alkalis (such as MeBz/KOH), the surfaces of these PQDs remained well terminated by the hydrolyzed ligands, thus ion migration was suppressed. In contrast, samples subjected to multiple rinses with neat MeBz experienced substantial ligand removal, leading to the formation of numerous surface vacancies, quasi-grain boundaries, and PQD agglomeration. These structural features potentially acted as channels for ion migration, which accounted for the observed PL peak splitting.

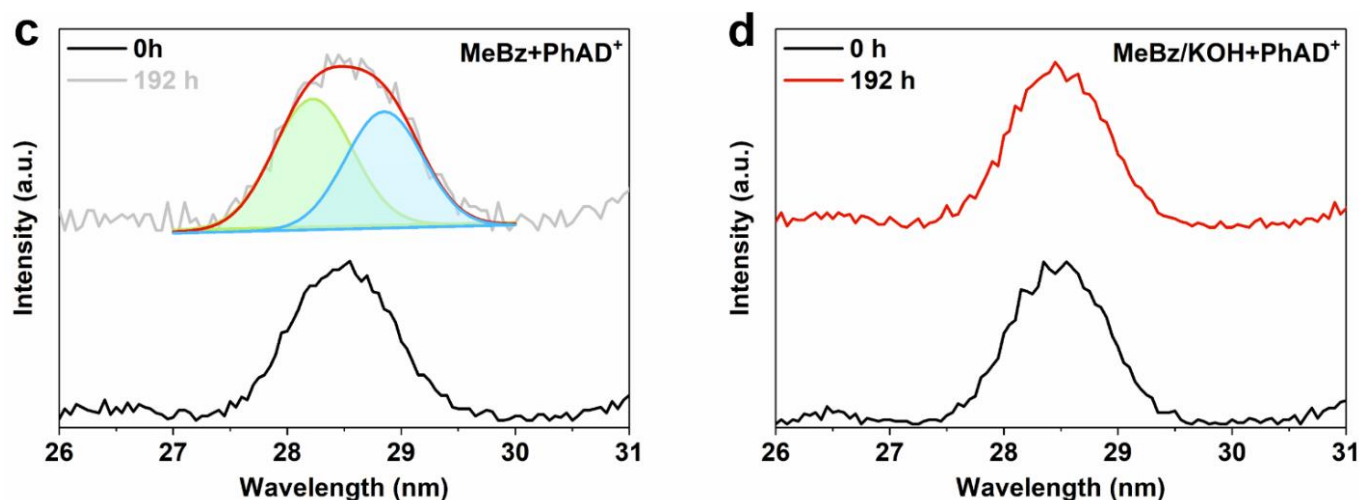
As recommended, we supplemented XRD patterns for 2-PeOH/PhAD⁺ post-treated MeBz- and MeBz/KOH-based PQD solids before and after 192 h of illumination, respectively (Supplementary Figs. 27c and 27d). To rule out other possible factors contributing to the PL peak splitting, we employed a grazing-incidence X-ray diffractometer (*Advance D8, Bruker*) with a fixed incidence angle (Ω) of 0.5°, providing enhanced surface sensitivity. It was observed that the second-order diffraction peak centered at 28.45° in the MeBz/KOH-based sample remained constant after illumination. In contrast, the neat MeBz-based PQD solid exhibited significant peak broadening after light aging. Deconvolution of this broadened peak resolved two distinct components at 28.23° and 28.85°, corresponding to phase separation of Cs-rich (smaller grains, higher angle) and FA-rich (larger grains, lower angle) domains, which was consistent with the splitting of steady-state PL emission.

In summary, we concluded that the reason for the splitting of PL peaks in **Supplementary Figs. 27a** was light-induced phase segregation rather than defect-mediated emission, which was associated with ligand desorption resulting from rinsing PQDs with neat ester antisolvent.

Modifications:

According to the reviewer's suggestion, we included these additional experimental results and analysis in the revised manuscript, as follows,

“The suppressed peak splitting in steady-state PL spectra and grazing-incidence XRD pattern demonstrated that the light-induced phase segregation in neat MeBz-based hybrid $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ PQDs could be significantly inhibited by a more efficient ligand exchange using the AAAH strategy (**Supplementary Fig. 27**).^{35,53}” On page 18 of the manuscript.



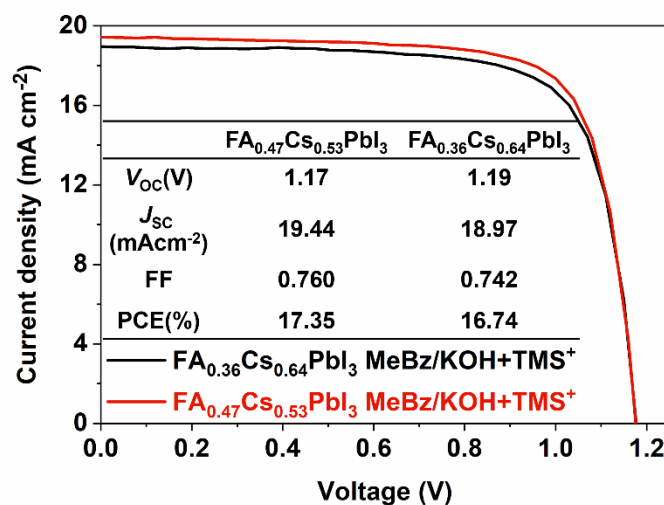
Supplementary Fig. 27 Magnified grazing-incidence X-ray diffraction (GIXRD) patterns from 26 to 31° for 2-PeOH/PhAD⁺ post-treated (c) MeBz- and (d) MeBz/KOH-based PQD solid films during 192 h of illumination under white LED in an N₂ atmosphere. GIXRD was measured at an incidence angle of 0.5°.

Q3: The authors' choice of $\text{FA}_{0.47}\text{Cs}_{0.53}\text{PbI}_3$ PQDs for solar cell fabrication warrants clarification, given that recent studies, such as the work published in *Advanced Materials* (e.g., *Adv. Mater.* 2023, 35, 2212160), report superior device performance with $\text{FA}_{0.36}\text{Cs}_{0.64}\text{PbI}_3$ PQDs, achieving efficiencies exceeding 17%. In addition, the current efficient PQD devices are almost based on pure FAPbI_3 PQDs. Is the method proposed in the manuscript also applicable to FAPbI_3 PQD solar cell fabrication?

Response:

Firstly, Regarding the reason for differences in PQD compositions. The slight difference in the optimal PQD composition between the two studies stemmed from a recent upgrade to our synthesis platform. In our earlier work (*Adv. Mater.* 2023, 35, 2212160), PQDs were synthesized using an oil-bath system, where the temperature sensor measured the oil temperature rather than that of the reaction mixture. We have since replaced this with a heating jacket system, allowing direct monitoring and more accurate control of the

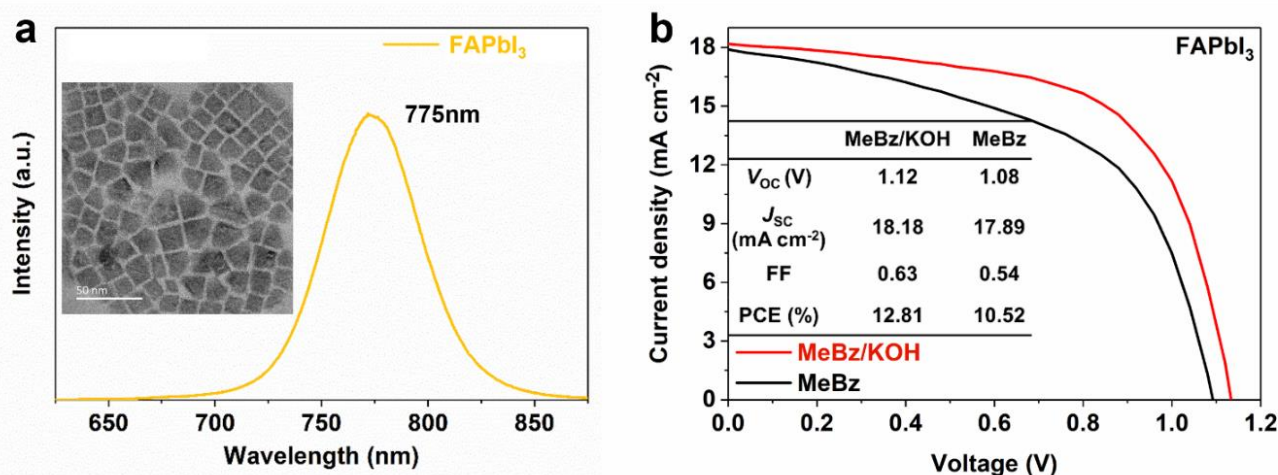
precursor solution temperature during synthesis. As reported in our earlier work, when the FA^+ stoichiometry exceeds 0.5, the excessive substitution would cause a sharp dissociation of OA^- ligands from the PQD surface, leading to pellet agglomeration and poor re-dispersibility of the centrifuged precipitates. A composition with an FA^+ stoichiometry of 0.47 lies just below this threshold, offering a higher tolerance factor and broader solar spectrum utilization. **Therefore, by achieving improved control over the crystallization and growth processes, we obtained $FA_{0.47}Cs_{0.53}PbI_3$ -PQDs with higher quality, leading to PQDSC devices with enhanced efficiency**, as shown in the **following figure**. Moreover, our cationic exchange method and preferred A-site composition have also been adopted in related studies by other research groups (Angew. Chem. Int. Ed. 2024, 64, 202416747).



J-V curves of $FA_{0.36}Cs_{0.64}PbI_3$ - and $FA_{0.47}Cs_{0.53}PbI_3$ -PQDSCs fabricated with MeBz/KOH interlayer rinsing and trimethylsulfonium (TMS^+) post-treatment, according to our previous report (Adv. Mater. 2023, 35, 2212160). Note that these devices were fabricated from the same batch.

Secondly, regarding the feasibility of our AAAH strategy on $FAPbI_3$ -PQDs. In our manuscript, we demonstrated that the AAAH strategy could improve device performance across different PQD compositions, and adopted $CsPbI_3$ -PQDSCs as a representative example to show its universality. According to the reviewer's suggestion, we conducted a comparative study on the performance of MeBz- and MeBz/KOH-based PQDSCs using $FAPbI_3$ -PQDs, as shown in the **following figures**. **The results indicated that solar cells fabricated via the AAAH strategy exhibited superior efficiency compared to the control devices. However, as we have not yet achieved $FAPbI_3$ PQDSCs with sufficiently high efficiencies that could meet the current recognized standards, we did not include these results in the original manuscript.** Given that the content of surface pristine long-chain ligands in $FAPbI_3$ PQDs is typically 5-10 times higher than that in $CsPbI_3$ PQDs (Nat. Energy, 2020, 5, 79-88), we speculated that the current suboptimal performance of fabricated $FAPbI_3$ PQDSCs likely due to the need for further optimization in the methodology of material synthesis and purification.

Furthermore, our hybrid A-site PQDs, prepared via the antisolvent-assisted cation exchange method (Adv. Mater. 2023, 35, 2212160), exhibited device performance comparable to that of advanced FAPbI₃-PQDSCs (Supplementary Table 9). However, since the current efficiency of our FAPbI₃-PQDSCs is still lower than the widely reported values, we could not entirely rule out the possibility that other factors contributed to these results. Moving forward, we will focus on further improving the efficiency of FAPbI₃-PQDSCs.

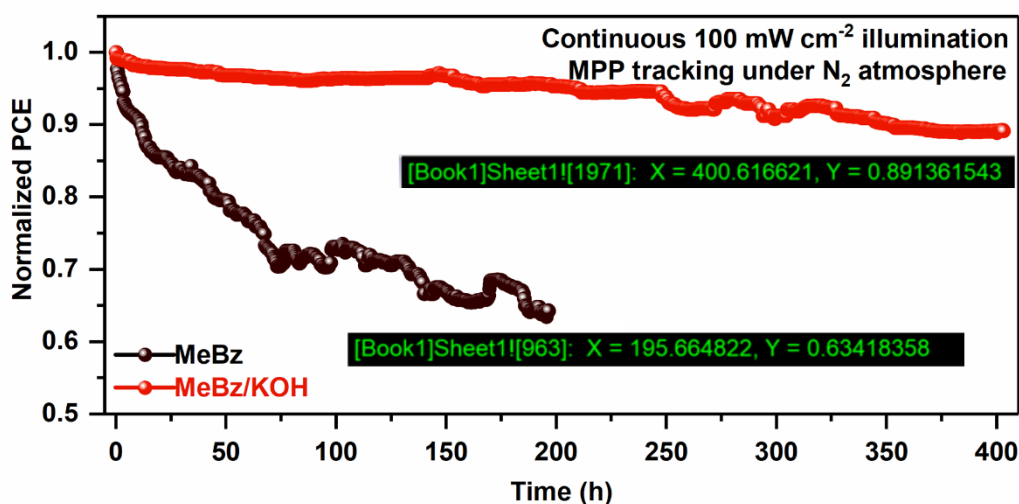


(a) Steady-state PL and TEM image of the as-synthesized FAPbI₃-PQDs. (b) J-V curves of MeBz- and MeBz/KOH-based FAPbI₃ PQDSCs.

Q4: There are identified errors in Fig. 3h of the steady-state output measurements.

Response:

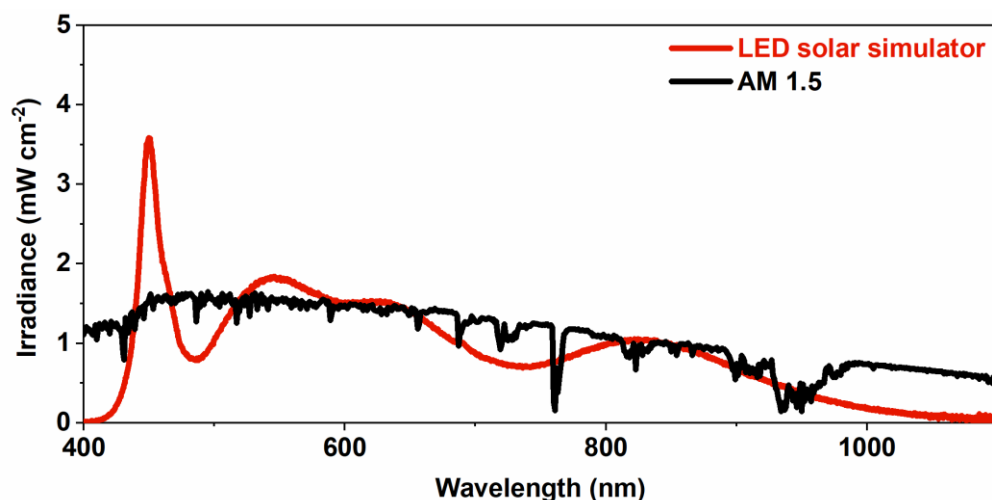
We appreciate the reviewer's attention to the accuracy of our data. After re-examination as recommended, we believe that the data presented in **Fig. 3h** was accurate, as shown in the **following figure**.



Stability of the unencapsulated MeBz- and MeBz/KOH-based PQDSCs under continuous 100 mW cm⁻² white LED illumination in an N₂ atmosphere.

The steady-state output measurements were conducted using a solar cell stability testing system (PV-S-16, Tianjin Meitong Corp., China). The MPP tracking data shown in **Fig. 3h** was obtained by performing continuous I-V measurements under 100 mW cm^{-2} white LED illumination in an N_2 atmosphere.

The emission spectrum of the LED lamp (MT-LED, Tianjin Meitong Corp., China) used in our experiment is shown in the **following figure**, matching well with the AM. 1.5G standard solar spectrum, indicating that the illumination conditions during the stability test effectively simulated actual solar exposure. This ensures the reliability of our test results.



Emission spectrum of the LED lamp used in this work, with the AM 1.5G spectrum shown as a reference.

Modifications:

According to the reviewer's suggestion, we incorporated the testing method of MPP tracking in the revised manuscript, as follows,

"The MPP tracking was carried out in an N_2 atmosphere using a long-term solar cell stability testing system (PV-S-16, Tianjin Meitong Corp., China) under continuous 100 mW cm^{-2} white LED illumination (MT-LED, Tianjin Meitong Corp., China) at $30 \pm 5^\circ\text{C}$, with the results automatically recorded by dedicated aging test software." On page 32 of the manuscript.

Q5: This manuscript describes the use of ester hydrolysis and alkaline environmental treatment to modify the surface of PQD films; However, key morphological evidence supporting the effects of these treatments is absent. Specifically, the authors should provide scanning electron microscopy (SEM) images of PQD films treated with different ester antisolvents as well as different alkaline environments to assess surface uniformity and grain boundary integrity.

Response:

Regarding the morphological evidence, we first performed Top-view scanning electron microscopy (SEM) images of PQD solids rinsed using different ester antisolvents as recommended. As shown in

Supplementary Fig. 3, the as-cast sample exhibited an overall cubic morphology of PQDs. Due to the presence of long-chain OA^-/OAm^+ ligands, the interspacing between adjacent PQDs was large, leading to a low packing density. Upon rinsing with EtFo, which possesses excessive polarity, the PQD solid exhibited obvious cracks even under low magnification, suggesting that the excessive removal of surface ligands induced dramatic shrinkage and stress between neighboring PQDs. In contrast, PQD solids rinsed with MeOAc, MeBz, and EtOAc showed no visible cracking even under high magnification, demonstrating denser packing compared to the as-cast sample. However, the EtCa-based sample displayed a rougher surface with more porous, which was consistent with the XRD pattern observed for EtCa-based PQD solid (**Supplementary Fig. 4c**). This incompact stacking status probably resulted from the strong rigidity of the cinnamate anionic ligands, which disrupted the original orderly arrangement of these nanocrystals on the substrate upon binding to the PQD surface.

Next, considering that the absorption and PL peak positions of PQD solids rinsed with MeBz containing different alkaline additives showed no difference, we suggested that the microscopic changes induced by these additives were difficult to visualize on SEM images. However, this step played a critical role in determining the nanoparticle aggregation behavior during the subsequent 2-PeOH/PhAD⁺ post-treatment process. To further investigate this effect, we performed SEM imaging on MeBz- and MeBz/KOH-based PQD solids with 2-PeOH/PhAD⁺ post-treatment. As shown in **Supplementary Fig. 32**, Both samples exhibited denser particle assembly morphology after post-treatment. Notably, the neat MeBz-based film displayed visible PQD aggregation domains, while the MeBz/KOH-based sample showed a well-defined and uniform morphology. These observations were consistent with the PL lifetime mapping images presented in **Figs. 4j** and **4k**.

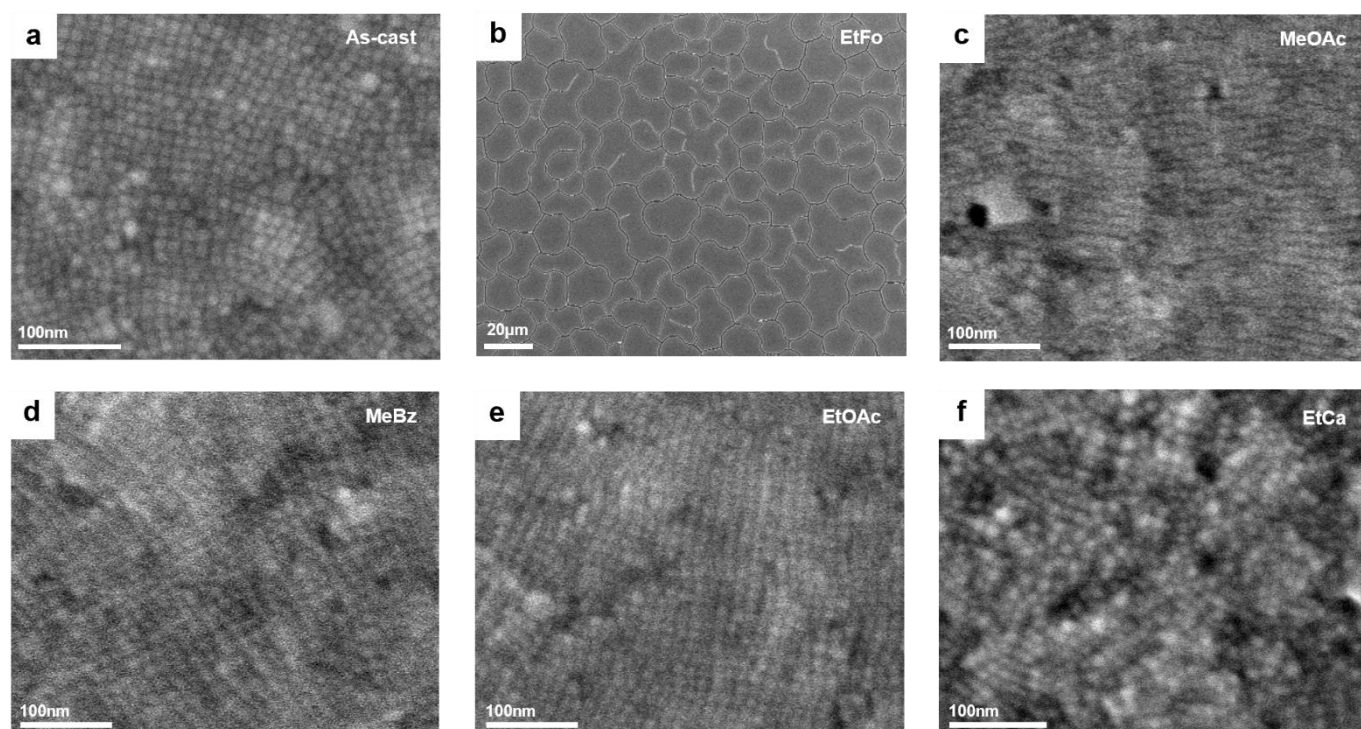
In summary, the above SEM images confirmed that AAAH-based ligand exchange using MeBz could effectively improve the morphology of PQD solids after continuous antisolvent rinsing.

Modifications:

According to the reviewer's suggestion, we included these SEM images and the corresponding analysis in the revised manuscript, as follows,

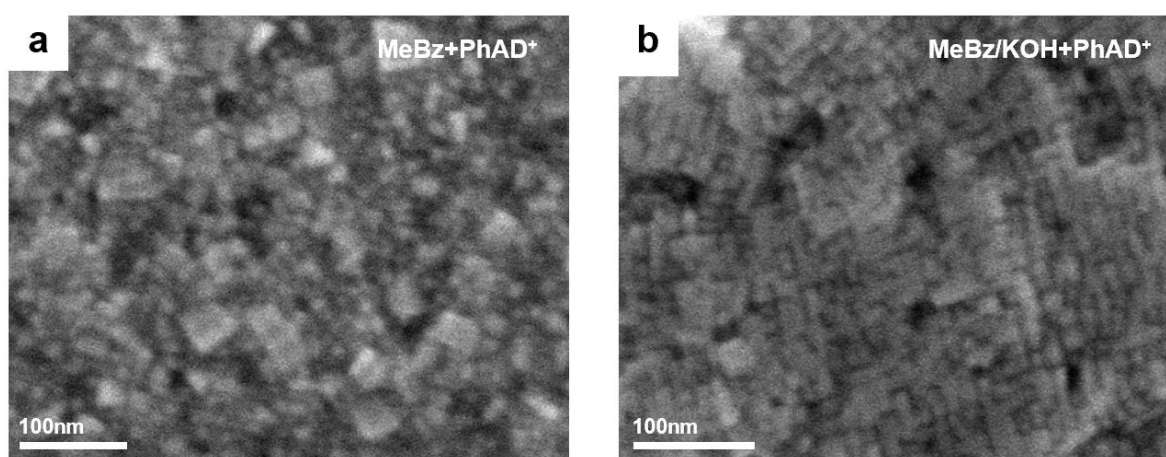
“Meanwhile, as shown in **Supplementary Fig. 3**, among the carboxylate-based esters, the excessive polarity of MeFo and EtFo resulted in degradation and cracking of the assembled PQDs, respectively. In contrast, rinsing with ester antisolvents of moderate polarity, such as MeOAc, MeBz, and EtOAc, preserved the structural integrity of PQD solids, leading to denser packing without the formation of visible cracks. Notably, the EtCa-based PQD solid exhibited a rougher and more porous morphology, accompanied by a

less ordered packing arrangement. Therefore, in the following, we focused on discussing the effect of these available ester antisolvents on the properties of PQDs.” *On page 6 of the manuscript.*



Supplementary Fig. 3 Scanning electron microscope (SEM) images of (a) as-cast, (b) ethyl formate (EtFo)-, (c) methyl acetate (MeOAc)-, (d) methyl benzoate (MeBz), (e) ethyl acetate (EtOAc)-, and (f) ethyl cinnamate (EtCa)-based PQD solid films.

“Furthermore, the more ordered and homogeneous stacking of MeBz/KOH-based PQDs on the substrate than neat MeBz-based counterparts after 2-PeOH/PhAD⁺ post-treatment can also be visualized in the scanning electron microscopy (SEM) images (**Supplementary Fig. 32**)” *On page 21 of the manuscript.*



Supplementary Fig. 32 SEM image of (a) MeBz- and (b) MeBz/KOH-based PQD solid films with 2-PeOH/PhAD⁺ post-treatment.

Q6: The manuscript does not adequately address the critical role of carrier dynamics in validating the proposed alkali-mediated surface capping mechanism. To confirm the claims of enhanced charge transport and reduced non-radiative recombination, the authors needed to provide time-resolved photoluminescence (TRPL) or transient absorption (TA) spectral data for both untreated and treated PQD films.

Response:

As recommended, we performed additional fluence-dependent TRPL measurements on MeBz rinsed PQD solid films with and without added alkalis (i.e, neat MeBz, MeBz/KOH, MeBz/K₂CO₃, and MeBz/Me₃SiOK). As shown in Fig. 2g, the neat MeBz-based control sample exhibited a non-monotonic lifetime evolution, with lifetimes initially increasing followed by decreasing as excitation fluence increased, which were indicators of the Shockley-Read-Hall (trap-filling) and radiative (bimolecular) recombination processes, respectively. In contrast, all MeBz/alkali-based samples showed monotonic decreases in PL lifetime with increasing fluence, consistent with the dominance of radiative pathways. Among them, MeBz/KOH-based PQDs consistently showed the longest PL lifetimes across all fluences, suggesting the strongest ability to suppress charge recombination. The detailed discussion is shown in the answer to Q3 of reviewer 2.

In addition to these dynamic measurements, our manuscript included PL lifetime mapping of PQD solids that underwent both ester antisolvent interlayer rinsing and 2-PeOH/PhAD⁺ post-treatment (Figs. 4j and 4k and Supplementary Fig. 31). These spatially resolved maps revealed that the MeBz/KOH-based PQD film exhibited a significantly longer average lifetime compared to the neat MeBz-based sample. Furthermore, the bi-exponential deconvolution map of the neat MeBz-based PQD solid showed scattered quenching spots in the fast component region, representing the nonradiative recombination sites, whereas the MeBz/KOH-based sample showed a more homogeneous carrier distribution.

In summary, results from both fluence-dependent TRPL and PL lifetime mapping strongly supported our claim that the AAAH strategy could suppress nonradiative recombination and improve charge transport on solid films by enabling more sufficient X-site ligand exchange of PQDs.

Modifications:

According to the reviewer's suggestion, we incorporated these experimental details, figures, and discussions in the revised manuscript, as follows,

"Fluence-dependent TRPL spectra were acquired by exciting the PQD solid films with a 405 nm laser diode (PDL 800-D, PicoQuant) operating at a 2.5 MHz repetition rate under varying fluences. The emitted signal was passed through a monochromator to select the desired wavelength and detected using a photomultiplier tube (PMA Hybrid 50, PicoQuant), with timing controlled by a time-correlated single photon counting module (Harp 300 Picosecond Event Timer, PicoQuant)." On page 30 of the manuscript.

Q7: The manuscript employed multiple antisolvent treatments (washing sequentially with MeBz, 2-PeOH) to purify the PQD film and remove the remaining ligands. While this method can enhance surface passivation, it introduces significant process complexity that undermines the usefulness of the method in scalable manufacturing. Is it possible to reduce the number of antisolvent uses by adjusting the polarity of anti-solvent uses?

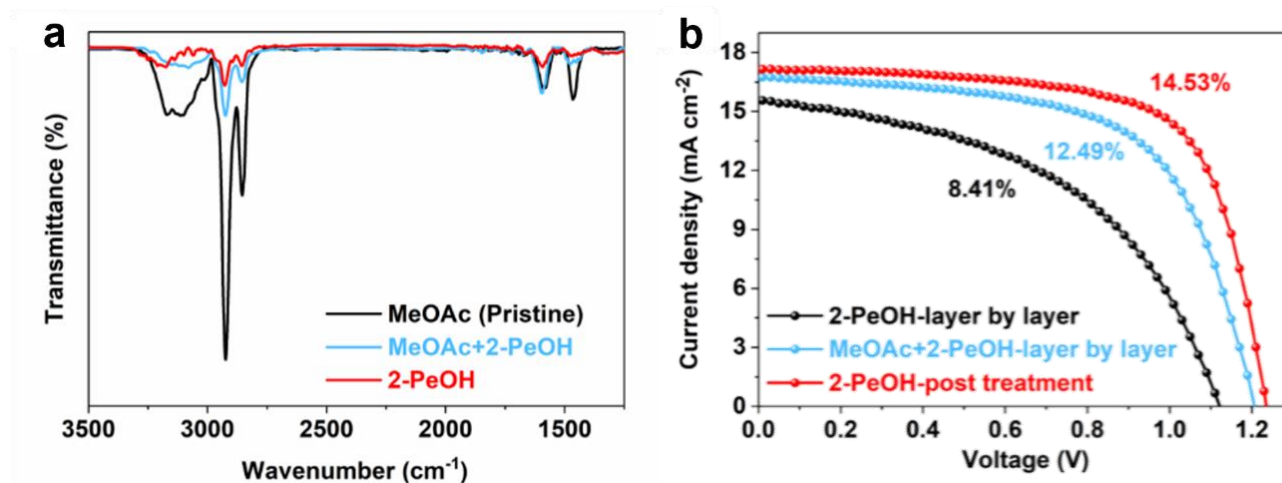
Response:

In response to the reviewer's suggestion to simplify the successive antisolvent treatment process in our manuscript by adjusting the polarity of the antisolvent, we discussed as follows,

***Firstly**, for PQDs with vulnerable ionic lattices, the polarity selection of their antisolvent is highly restricted. Polarity is a comprehensive concept, which in the following discussions are referred specifically to the $E_T(30)$ polarity. This can be determined primarily by the hydrogen-bond donor (HBD) ability and dipole moment of the solvent molecule (Chem. Soc. Rev., 1993, 22, 409-416).*

***Regarding the post-treatment of assembled PQD solids using 2-PeOH antisolvent in this work.** As reported in our previous article (Joule, 2022, 6, 1632-1653), this was selected from multiple protic antisolvents with different $E_T(30)$ polarities. Among these alternatives, 2-PeOH was identified as featuring the most appropriate combination of HBD acidity and dipole moment, which could selectively remove pristine OAm^+ ligands on the A-site of PQD surface through hydrogen-bonding interactions, without disrupting the short carboxylate ligands introduced on the X-site during the ester antisolvent interlayer rinsing process. This unique behavior led to a then-record efficiency for $CsPbI_3$ -PQDSCs, and this treatment strategy has since been widely adopted by other research groups (Nanoscale, 2023, 15, 3713-3729; Angew. Chem. Int. Ed., 2024, 64, 202416747).*

***In terms of antisolvents used for interlayer rinsing of PQD solids**, our previous work has shown that directly using protic antisolvents would lead to the uncontrolled removal of pristine ligands on both A- and X-sites simultaneously. As shown in the **following figures**, this would damage the underlying perovskite structure during the layer-by-layer assembly of subsequent PQDs, thus compromising the overall device performance. In contrast, aprotic ester antisolvents mainly reacted solely with the X-site pristine ligands, while preserving the pristine OAm^+ ligands on the A-site, thereby maintaining the basic structural integrity of PQDs during successive antisolvent treatments. However, as discussed in **Fig. 1a**, ester antisolvents with larger dipole moments, such as methyl formate (MeFo) and EtFo, could cause aggressive ligand stripping instead of the desired ligand exchange, leading to film cracking. Those with excessively high polarity could directly disrupt the perovskite lattice, resulting in material degradation.*



(a) Reported FT-IR spectra of CsPbI₃-PQD solids rinsed with aprotic MeOAc, protic 2-PeOH, and sequential aprotic MeOAc and protic 2-PeOH. (b) Reported J-V curves of CsPbI₃-PQDSCs fabricated using different interlayer antisolvent rinsing methods, including direct using protic 2-PeOH layer-by-layer, sequential aprotic MeOAc and protic 2-PeOH layer-by-layer, and aprotic MeOAc layer-by-layer with protic 2-PeOH post-treatment. (Joule, 2022, 6, 1632-1653)

Moreover, the light absorption layers of state-of-the-art PQDSCs are still fabricated through a layer-by-layer deposition process, involving interlayer X-site and post-treatment A-site ligand exchange via sequential antisolvent rinsing of PQD solids (Nat. Energy, 2024, 9, 324-332).

In summary, it is difficult to simplify the processing steps by merely adjusting the antisolvent polarity. To streamline this process, a potential approach is to perform liquid-state ligand exchange to prepare high-concentration PQD inks (≥ 200 mg/mL), enabling the single-step deposition of thick PQD solids with high conductivity (Adv. Mater., 2023, 35, 2209486; Nat. Energy, 2024, 9, 1378-1387). However, the best-performing device fabricated by this method has so far achieved a PCE of 16.2%, which still lags behind the advance. Further optimization of this method in the future is therefore necessary.

Q8: Capacitance-voltage (C-V) and transient photovoltage (TPV) analyses are suggested to perform for validating the proposed alkaline surface capping mechanism and its impact on charge storage, transport, and recombination dynamics.

Response and modifications: As recommended, we conducted C-V and TPV measurements on PQDSCs, the detailed discussion is shown in the answer to Q9 of reviewer 2. As shown in **Supplementary Figs. 33b and 33c**, the larger built-in potential (V_{bi}) and significantly reduced interfacial charge carrier density as determined by Mott-Schottky analysis, as well as prolonged carrier lifetimes evident from the TPV measurements for MeBz/KOH-based PQDSCs collectively confirmed that the device fabricated using the AAAH strategy exhibited suppressed charge recombination and enhanced charge extraction. According to

the reviewer's suggestion, we incorporated these findings and the corresponding testing method in the revised manuscript, as follows,

“Supplementary Note 4. Mott-Schottky analysis.

Capacitance-voltage (C-V) measurements were performed at 5 kHz over a voltage range of -0.1 to 1.5 V. The built-in potential (V_{bi}) and the carrier density (N_A) values were calculated by fitting the linear region of the $1/C^2$ -V curve using the following equation,

$$\frac{1}{C^2} = \frac{2(V_{bi}-V)}{A^2 q \epsilon_0 \epsilon_r N_A} \quad (5)$$

Where A and q are the device active area and elementary charge, respectively. V is the applied voltage, ϵ_0 and ϵ_r are vacuum permittivity and the relative dielectric constant of PQDs, respectively. V_{bi} is determined by the intersection of the tangent line of the linear region and the x-axis. N_A is calculated by the slope in the linear fitting region using the following equation,

$$Slope = \frac{2}{e \epsilon_0 \epsilon_r N_A A^2} \quad (6)$$

” On page 41 of the Supplementary Information.

Q9. The manuscript reports a certification efficiency of 18.3% for small-area perovskite quantum dot (PQD) solar cells (presumably $\leq 0.1 \text{ cm}^2$), but it ignores the key challenge of addressing scalability for commercial viability. To assess the actual potential of the proposed alkaline surface capping strategy, it is recommended that the authors provide data for large-area devices ($\geq 1 \text{ cm}^2$).

Response:

We agree with the reviewer's suggestion that scalability is a crucial aspect of the commercial viability of solar cells. Although our initial focus was to demonstrate that the AAAH strategy could enable higher efficiency in PQDSC devices, thereby addressing the pressing challenge in the field, we also recognize the importance of exploring its potential for large-area photovoltaic applications.

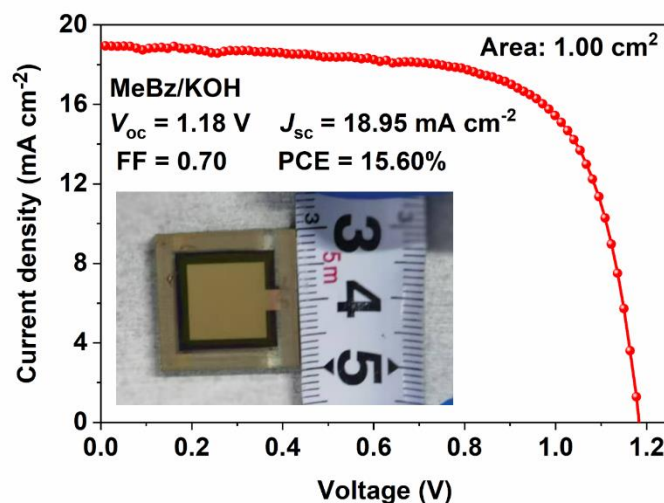
Therefore, we conducted explorations on large-area devices (1 cm^2) as recommended. As shown in **Supplementary Fig. 25**, the large-area PQDSCs fabricated using our AAAH strategy achieved an efficiency of 15.60%. Although this efficiency was inferior to the 18.37% of the corresponding small-area devices (0.036 cm^2), it still demonstrated a promising potential for PQDs employed in large-area photovoltaics.

The efficiency gap between small- and large-area devices could be attributed to several factors, such as non-uniform film morphology, increased charge transport losses over longer distances, and a higher trap density in large-area devices. However, we believe that with further optimization of the device fabrication process, this efficiency gap can be significantly narrowed.

Modifications:

According to the reviewer's suggestion, we included the relevant data and analysis on large-area photovoltaics in the revised manuscript, as follows,

“To further validate the potential of the AAAH-based ligand exchange for large-area photovoltaic applications, we fabricated 1 cm² solar cells (**Supplementary Fig. 25**), which achieved a champion PCE of 15.60%, highlighting the promising scalability of this strategy.” On page 17 of the manuscript.



Supplementary Fig. 25 J-V curve of the champion MeBz/KOH-based PQDSC with an area of 1.00 cm². The inset shows the photograph of a large-area device.

Q10: The manuscript would benefit from referencing recent advancements in high-efficiency PQD solar cells to provide context and highlight the novelty of this work.

Response and modifications: According to the reviewer's suggestion, to better contextualize our work and emphasize its novelty, we updated recent advancements in high-performing PQDSCs in the revised manuscript and Supplementary Information. Specifically, we referenced the most up-to-date reports on efficiencies, advanced surface ligand strategies, and novel device architectures, as follows,

“Continued advances in surface ligand chemistry, A-site composition regulation, and homo-/hetero-junction light-absorbing layer architecture design have significantly improved the power conversion efficiency (PCE) of PQD solar cells (PQDSC) from 10.7% to currently National Renewable Energy Laboratory (NREL) certified 19.1%.¹⁶⁻²⁰” On page 2 of the manuscript.

“Upon achieving the desired thickness, post-treatment with alternative short cationic ligands (such as FA⁺, phenethylammonium (PEA⁺) and the lately reported MA⁺) to substitute the pristine long-chain oleylammonium (OAm⁺) ligands on the A-site of PQD surface could further enhance electronic coupling

of inter-PQDs, thereby resulting in PQDSCs with advanced performance.^{16, 28-30}” On page 3 of the manuscript.

“Recent development of concentrated quantum dot inks (≥ 200 mg mL⁻¹) via liquid-state ligand exchange has demonstrated promising scalability, enabling the single-step deposition of light-absorbing layers with enough thickness and conductivity.^{7,8} However, the inherent fragility of the ionic perovskite lattice imposes limitations on selecting solvent for PQDs after ligand-exchange, which prevents the apply of sufficiently short ligands with high polarity, thus compromising the efficiency of resulting PQDSCs.” On page 3 of the manuscript.

Supplementary Table 9. Summary of device architectures and photovoltaic performance of published PQDSC reports, where devices with certified efficiencies are specifically labeled.

Type	Cell stack	PCE (%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	Ref.
CsPbI₃	FTO/TiO ₂ /PQDs/Spiro/MoO _x /Al	10.77	1.23	13.47	0.65	6
	FTO/TiO ₂ /PQDs/Spiro/MoO _x /Al	(Certified) 13.43	1.16	15.24	0.76	7
	ITO/SnO ₂ /PCBM/PQDs/PTB7/MoO _x /Ag	15.1	1.26	15.2	0.78	8
	ITO/SnO ₂ /PQDs/Spiro/Ag	16.21	1.27	17.71	0.72	9
	ITO/SnO ₂ /PQDs/Spiro/Ag	16.53	1.27	17.80	0.73	10
	ITO/SnO ₂ /PQDs/Spiro/Ag	16.64	1.26	17.65	0.75	11
	ITO/SnO ₂ /PQDs/Spiro/Ag	17.01	1.28	18.77	0.71	12
	FTO/TiO ₂ /PQDs/PTAA/MoO _x /Al	17.50	1.25	18.09	0.77	13
FAPbI₃	ITO/SnO ₂ /PQDs/Spiro/Au	8.38	1.10	11.83	0.64	14
	ITO/SnO ₂ /PQDs/Spiro/Ag	12.7	1.1	15.4	0.75	15
	FTO/TiO ₂ /PQDs/PTAA/MoO _x /Ag	13.2	1.12	16.7	0.71	16
	FTO/TiO ₂ /PQDs/PTAA/MoO _x /Ag	(Certified) 16.20	1.07	19.98	0.76	17
	FTO/TiO ₂ /PQDs/Spiro/MoO _x /Ag	16.23	1.17	19.3	0.72	18
	FTO/TiO ₂ /PQDs/Spiro/Ag	16.29	1.16	20.95	0.67	19
	ITO/ZnO/SnO ₂ /PQDs/Spiro/Au	(Certified) 18.06	1.14	20.89	0.76	20
	FTO/TiO ₂ /PQDs/PTAA/MoO _x /Ag	18.21	1.15	20.57	0.77	21
Hybrid	FTO/TiO ₂ /FA _{0.25} Cs _{0.75} PbI ₃ PQDs/Spiro/MoO _x /Al	11.14	1.15	14.36	0.68	22

FTO/TiO ₂ /FA _{0.75} Cs _{0.25} PbI ₃ PQDs/PTAA/MoO _x /Au	11.58	1.17	12.22	0.81	23
FTO/TiO ₂ /MA _{0.5} Cs _{0.5} PbI ₃ PQDs/Spiro/MoO _x /Ag	13.82	1.21	14.84	0.77	24
FTO/TiO ₂ /FA _{0.5} Cs _{0.5} PbI ₃ PQDs/Spiro/MoO _x /Ag	14.20	1.20	15.57	0.76	24
FTO/TiO ₂ /MA _{0.5} FA _{0.5} PbI ₃ PQDs/Spiro/MoO _x /Ag	15.01	1.19	16.33	0.75	24
FTO/TiO ₂ /CsPbI ₃ /FAPbI ₃ PQDs/PTAA/MoO _x /Ag	15.6	1.22	17.26	0.74	25
ITO/SnO ₂ /FA _{0.5} Cs _{0.5} PbI ₃ PQDs/Spiro/Au	(Certified) 16.6	1.17	18.3	0.78	26
ITO/SnO ₂ /FA _{0.25} Cs _{0.75} PbI ₃ /FA _{0.5} Cs _{0.5} PbI ₃ /FA _{0.75} Cs _{0.25} PbI ₃ PQDs/Spiro/Au	16.68	1.17	19.36	0.72	27
ITO/SnO ₂ /FA _{0.36} Cs _{0.64} PbI ₃ PQDs/Spiro/Ag	17.29	1.23	18.99	0.74	28
ITO/TiO ₂ /Cs _{0.25} FA _{0.75} PbI ₃ /CsPbI ₃ PQDs/Spiro /MoO _x /Al	17.39	1.2	18.91	0.76	29
ITO/SnO ₂ /FA _{0.5} Cs _{0.5} PbI ₃ PQDs/Spiro/Ag	17.49	1.22	19.35	0.74	30
ITO/SnO₂/FA_{0.47}Cs_{0.53}PbI₃ PQDs/Spiro/Au	(Self-tested) 18.37 (Certified) 18.30	1.19 1.18	19.87 19.89	0.78 0.78	This work

Best regards,

Meicheng Li

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July 2nd, 2025

We appreciate the Reviewers for their valuable time and suggestions. According to your professional comments, we have carefully revised the manuscript accordingly and answered the questions point-by-point, as follows. (The words in black are from Reviewers. Our responses are written in italics. The revised parts in the manuscript and Supplementary Information are marked in blue.)

Reviewer #1:

The revised manuscript provides clearer experimental details and improves the characterization of the MeBz/KOH treatment, bringing the work substantially closer to meeting publication standards. However, the following issues require attention:

1. O 1s Deconvolution and Pb–OH Assignment:

The claim that MeBz without alkaline treatment yields higher trap density and lower stability—due to increased Pb–OH formation—is supported solely by deconvoluted O 1s XPS peaks. These fitted peaks in Supplementary Fig. 8 and 14, however, bear little resemblance to the raw data, even accounting for O 1s contamination. The current COO[−]/OH[−] fitting appears arbitrary and undermines confidence.

Please replot the raw O 1s spectrum in a darker or thicker line to clearly show the original signal. Increase the number of XPS scans to improve the signal-to-noise ratio, then reattempt deconvolution on the higher-quality data.

If significant ambiguity remains, remove the COO[−]/OH[−] ratio analysis (Fig. 2d, Supplementary Fig. 8h) and the related discussion (p. 12, lines 253–255), or provide an alternative, more reliable indicator of hydroxyl content.

Response:

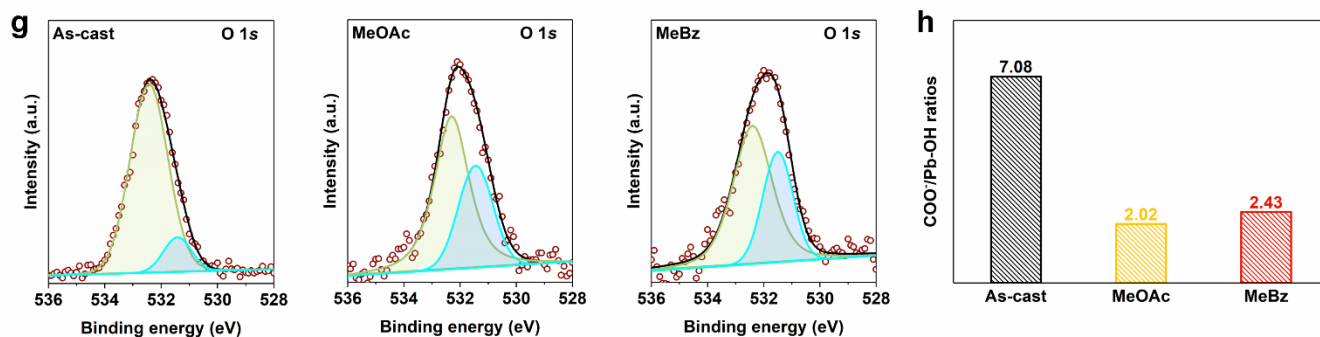
*We appreciate the reviewer's valuable comments. In response, we re-measured the O 1s core-level spectra of the samples and increased the number of XPS scans to 25 to improve the signal-to-noise ratio. Besides, we replotted the raw O 1s spectra using a thicker and darker line to clearly highlight the original signal, as shown in the **Supplementary Figs. 8f and 14f**.*

The deconvolution of O 1s spectra was performed using a sum of Lorentzian and Gaussian functions, and the integrated areas of the individual components were recalculated (Nano Energy, 2019, 66, 104130). The resulting ratio between carboxyl groups (~532.5 eV) and hydroxyl groups (~531.4 eV) was similar to the values reported in the original manuscript, which was increased with the pH value of the rinsed MeBz/alkali antisolvent.

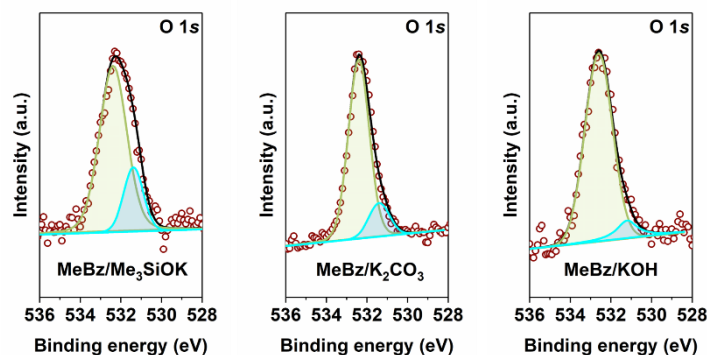
Modifications:

According to the reviewer's suggestions, we updated the relevant description, figures and data into the revised manuscript and Supplementary Information, as follows,

“Furthermore, the ratio between carboxyl groups (~ 532.5 eV) and hydroxyl groups (~ 531.4 eV) in samples increased with the pH value of the rinsed MeBz/alkali antisolvent, corresponding to a gradual reduction in anionic vacancies on the PQD surface.¹¹” On page 12 of the manuscript.



Supplementary Fig. 8 (g) O 1s core-level spectra, (h) statistical histogram of ratios between carboxyl and hydroxyl groups (COO^-/OH^-) of as-cast, MeOAc-, MeBz-based PQD solid films.



Supplementary Fig. 14 (f) O 1s core-level spectra of MeBz-, MeBz/K₂CO₃-, MeBz/Me₃SiOK-, and MeBz/KOH-based PQD solid films.

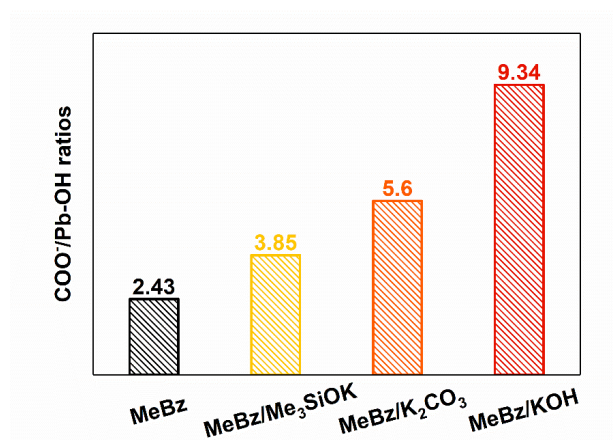


Fig. 2d Statistical histogram of ratios between carboxyl and hydroxyl groups (d) of MeBz-, MeBz/K₂CO₃-, MeBz/Me₃SiOK-, and MeBz/KOH-based PQD solid films.

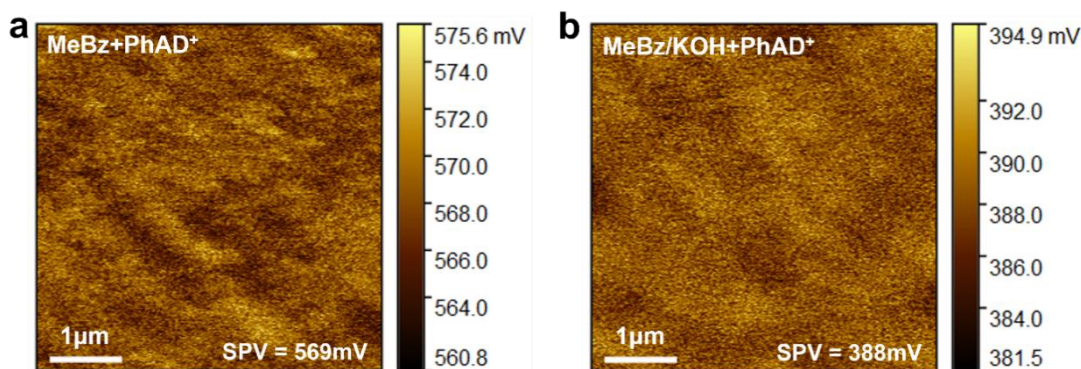
2. Work-Function Discrepancy:

KPFM and UPS should report comparable work-function shifts, yet the manuscript shows a 0.13 V shift by KPFM versus only ~0.02 eV by UPS when comparing MeBz and MeBz/KOH films. This discrepancy suggests either some reproducibility issue in fabrication or inconsistent measurement conditions.

Please provide the KPFM tip information (model, calibration results, illumination condition) and report the corresponding work function value of each sample. If necessary, repeat KPFM or UPS measurements under the same conditions to ensure consistency.

Response:

As the reviewer pointed out, the shift in contact potential difference (CPD) measured by KPFM for the two samples was noticeably larger than the shift in their Fermi level position obtained by UPS. To ensure the reliability of our results, we repeated the KPFM measurements on each sample under the same conditions as recommended. The **following figures** show the supplementary KPFM images of the samples, which display CPD values similar to those shown in the manuscript, confirming the validity of our data.



KPFM images of 2-PeOH/PhAD⁺ post-treated (a) MeBz- and (b) MeBz/KOH-based PQD solid films.

The information of the tip used in our KPFM test (Model: HA - FM/Pt/15) is shown in the **following figure**. The work function of Pt tip (4.6 eV) was calibrated by measuring the CPD relative to freshly cleaved highly oriented pyrolytic graphite (HOPG). The test was carried out in ambient conditions under indoor lighting. Therefore, according to KPFM results (**Figs. 4f and 4g**), surface work functions of 2-PeOH/PhAD⁺ post-treated MeBz- and MeBz/KOH-based PQD solids were calculated to be 5.192 eV and 4.966 eV, respectively.



Package of the tip used in our KPFM test.

*In response to the discrepancy between shift in CPD and in Fermi level position, we suggest that this was primarily due to the structural difference between the surface and the bulk of PQDs. KPFM measures the potential of the outermost position of the sample (< 1 nm), which corresponds to the ligand-capped PQD surface. In contrast, the detection depth of UPS for semiconductor samples can reach 8-10 nm, corresponding to the internal bulk position of PQDs (Adv. Funct. Mater., 2021, 31, 2101272; Adv. Mater., 2021, 34, 2105977). Therefore, we emphasized in the manuscript (**page 24, lines 517-519**) that the more pronounced difference in CPD of the two samples measured by KPFM reflected the influence of BZA⁻ electron-donor ligands on the surface potential of PQDs.*

Modifications:

According to the reviewer's suggestion, we added details regarding the KPFM measuring procedures in the Methods section of the manuscript, as follows,

“The Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) results were measured using an atomic force microscope (FMNanoview 1000), a Pt-coated Si tip (Model HA-FM/Pt/15) with a spring constant (k)= 3.5 Nm^{-1} was employed. Scans were performed over $5\text{ }\mu\text{m}$ at 256 pixels and 1 Hz frequency in a dual-pass setup, the first pass to record topography and the second to measure the contact-potential difference (CPD) in tapping mode. The work function of the Pt tip was calibrated by measuring the CPD relative to a freshly cleaved highly oriented pyrolytic graphite (HOPG) with a standard work function of 4.6 eV. All measurements were done in ambient conditions under indoor lighting.” On page 30 of the manuscript.

3. Minor text correction:

A duplicate sentence remains on page 20 (lines 430–434).

Response and modifications: *We appreciate the reviewer's careful review and valuable suggestion regarding the duplicate sentence. We thoroughly checked the relevant section and removed the redundant content on page 20.*

Reviewer #2:

This paper is now much improved, and I recommend publication after correcting for the following minor comments:

Q1: The English in this paper still needs to be improved. The title is cumbersome and not grammatically correct. Grammatical errors remain throughout the rest of the paper.

Response and modifications: *We thank the reviewer for pointing out the language issues in the manuscript. According to the reviewer's suggestion, we revised the title into "Enriching Conductive Surface Capping by Alkaline Environment for Perovskite Quantum Dot Solar Cells with 18.3% Certified Efficiency".*

We also revised the expression and grammar of the entire manuscript, as follows,

"However, neat ester antisolvents are difficult to hydrolyze directly into target ligands under ambient conditions, which impedes the integrity of conductive capping on PQD surface treated with these antisolvents." On page 1 of the manuscript (Abstract).

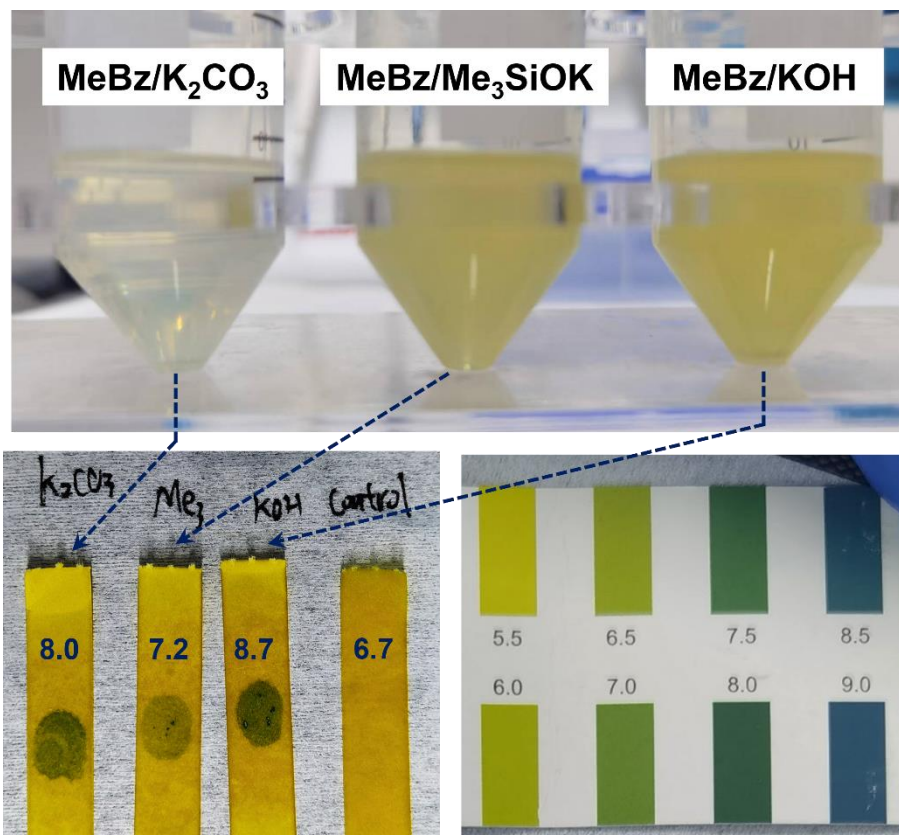
"Meanwhile, the colloidal synthesis of PQDs separates their crystal growth from film deposition, enabling device manufacturing processes to be more tolerant of environments.¹³⁻¹⁵" On page 2 of the manuscript (Introduction).

"To meet the above requirements, esters that possess short hydrocarbon chain lengths at both the acyl and alcohol ends were preferred," On page 5 of the manuscript (Results).

Q2: The authors refer to alkalinity in a qualitative way. Can they be more quantitative in their descriptions?

Response and modifications: *As shown in **Supplementary Fig. 9**, we used precision pH test strips to measure the alkalinity of the prepared antisolvents. In the previous version of the manuscript, we provided an approximate pH of 6.7 for the neat MeBz antisolvent based on the color comparison with the standard pH card. Herein, we further evaluated the pH values of MeBz with added alternative alkalis. Specifically, those for MeBz/Me₃SiOK, MeBz/K₂CO₃, MeBz/KOH, and MeBz/NaOH are approximately 7.2, 8.0, 8.7, and above 9, respectively. According to the reviewer's suggestion, we included these corresponding values to **Supplementary Fig. 9**, as follows,*

*"Firstly, pH values of the regulated antisolvents were first tested, showing about 6.7 for neat MeBz, and it elevates with increasing alkalinity of the added alkali, the corresponding quantitative results are shown in **Supplementary Fig. 9**." On page 10 of the manuscript.*



Supplementary Fig. 9 Photographs (top) and the corresponding PH values (bottom) of the as-prepared MeBz/K₂CO₃, MeBz/Me₃SiOK, and MeBz/KOH saturated solutions. The PH value of neat MeBz was included for comparison.

Q3: The authors need to provide more details on their XPS fitting. What were the profiles that they fit? Sum Lorentzian and **Gaussian**? Something else? What profile did they use to fit the background. The authors should justify all points.

Response: In this work, we employed a sum of Lorentzian and Gaussian functions to deconvolute the N 1s and O 1s core-level spectra of the samples. During fitting, the χ^2 values were maintained within the range of 0.95-1.1 to ensure the reliability. Additionally, we re-tested the O 1s core-level spectra of the samples by increasing the number of scans to 25 times, as detailed in our answer to Q1 of Reviewer 1.

Modifications:

According to the reviewer's suggestion, we added details regarding the XPS fitting procedures in the Methods section of the manuscript, as follows,

“X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were performed using a spectrometer (ESCALAB 250Xi, Thermo) with excitation using an X-ray and He I (21.22 eV) UV-light source, respectively. The N 1s and O 1s core-level XPS spectra of the samples were deconvoluted using a sum of Lorentzian and Gaussian functions. The fitting was performed with χ^2 values between 0.95 and 1.1 to ensure reliability.” On page 31 of the manuscript.

Reviewer #3:

In the revised manuscript, the author has made lots of changes and most of my previous concerns have been addressed, I would recommend the current version for publication in Nat. Commun. after updating some recent reports of high-efficiency PQD solar cells, e.g. 17.5% CsPbI₃ PQD (DOI: 10.1039/d4ee04628e); 18.21% FAPbI₃ PQD solar cells (DOI: 10.1002/adma.202417346) and latest review article on PQD solar cells towards 20% (DOI: 10.1039/d4cs01107d).

Response and modifications: *We thank the reviewer for the positive feedback and for acknowledging the improvements made in the revised manuscript. The valuable suggestions raised by the reviewer have greatly enhanced the quality of our work. We carefully reviewed the recommended articles and cited them in the revised manuscript, as follows,*

“Continued advances in surface ligand chemistry, A-site composition regulation, and homo-/hetero-junction light-absorbing layer architecture design have significantly improved the power conversion efficiency (PCE) of PQD solar cells (PQDSC) from 10.7% to currently National Renewable Energy Laboratory (NREL) certified 19.1%.¹⁶⁻²¹” On page 2 of the manuscript.

Appendix: Acknowledgments from the author

According to the previous and above responses, we have elaborated the scientific rationale, design novelty, and data interpretation from multiple perspectives. We believe this comprehensive and in-depth discussion helps to further highlight the scientific significance of our work. We also believe that the revised results and analysis clearly demonstrate the scientificity, novelty, consistency and reliability of the study, particularly in light of the improvements made in response to the reviewer’s valuable comments.

Best regards!



August 17th, 2025

We appreciate the Reviewers for their valuable time and suggestions. According to your professional comments, we have carefully revised the manuscript accordingly and answered the questions point-by-point, as follows. (The words in black are from Reviewers. Our responses are written in italics. The revisions are marked in blue.)

Reviewer #1:

The revised manuscript demonstrates that alkaline hydrolysis of methyl benzoate accelerates ligand exchange, increases COO⁻ formation, and enhances surface passivation. The arguments are now clearly presented and supported by solid evidence, and the reported high - PCE devices confirm that the work meets the high standard of Nature Communications. I recommend acceptance of this manuscript.

Response:

We thank the reviewer for the positive feedback and for recognizing the improvements in the revised manuscript. The reviewer's valuable suggestions have significantly contributed to enhancing the quality of our work.

Reviewer #2:

I am mostly satisfied with the changes made. The title still does not quite make sense. Here is a suggestion: "Alkaline treatment of perovskite nanocrystals to achieve certified 18.3%-efficient solar cells".

Response:

We thank the reviewer for your suggestion and example regarding the manuscript title.

Firstly, we fully agree with the reviewer's suggestion to simplify the title by changing "Alkaline Environment" to "Alkaline Treatment", which makes our core process more intuitively understandable to readers. Moreover, we incorporated the key outcome of the alkaline treatment of "Enriching Conductive Capping" into the title to clarify that our approach goes beyond simple ligand exchange and attract readership interest.

Regarding the use of "quantum dots" versus "nanocrystals" in the title, we believe that although the size of the synthesized materials does not differ from their exciton Bohr radius as significantly as in conventional quantum dots (e.g., PbS CQDs), they still exhibit clear quantum confinement effects (Sanehira et al. Sci.

Adv., 2017, 3, eaao4204), as evidenced by the pronounced blue shift in bandgap energy compared to their bulk counterparts, as well as their strong photoluminescence intensity, prolonged lifetime, and narrow emission linewidth. Furthermore, according to the titles established by previous authoritative reports, as shown in the following **Table**, we consequently defined the material as "quantum dots" in the title.

Table 1. Representative titles of recently published articles on photovoltaic applications of perovskite quantum dots/nanocrystals.

	Title	Citation
1	Alkyl Ammonium Iodide-Based Ligand Exchange Strategy for High-Efficiency Organic-Cation Perovskite Quantum Dot Solar Cells	<i>Nat. Energy</i> 9 , 324-332 (2024)
2	Conductive Colloidal Perovskite Quantum Dot Inks Towards Fast Printing of Solar Cells.	<i>Nat. Energy</i> 9 , 1378-1387 (2024)
3	Flexible and Efficient Perovskite Quantum Dot Solar Cells via Hybrid Interfacial Architecture	<i>Nat. Commun.</i> 12 , 466 (2021)
4	High Efficiency Perovskite Quantum Dot Solar Cells with Charge Separating Heterostructure	<i>Nat. Commun.</i> 10 , 2842 (2019)
5	Overcoming Charge Confinement in Perovskite Quantum Dot Solar Cells	<i>Adv. Mater.</i> 35 , 2304533 (2023)
6	Enhanced Mobility CsPbI ₃ Quantum Dot Arrays for Record-Efficiency, High-Voltage Photovoltaic Cells	<i>Sci. Adv.</i> 3 , eaao4204 (2017)

Modifications:

According to the reviewer's suggestion and the above discussion, we revised the title into "Enriching Conductive Capping by Alkaline Treatment of Perovskite Quantum Dots towards Certified 18.3%-Efficient Solar Cells".

Appendix: Acknowledgments from the authors

Building on the previous and above responses, we have elaborated on the scientific rationale, design novelty, and data interpretation from multiple perspectives. We believe that this comprehensive and in-depth discussion further underscores the scientific significance of our work, particularly in light of the improvements made in response to the reviewer's valuable comments.

Best regards!