nature portfolio

Peer Review File

Towards non-blinking and photostable perovskite quantum dots

Corresponding Author: Professor Yitong Dong

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

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)
The manuscript addresses the significant issue of surface defects in perovskite quantum dots (PQDs) arising from the detachment of weakly bound ligands, which hampers their application in light-emitting devices. The study focuses on monodentate phenylethylamine (PEA) ligands and their ability to stabilize PQDs through π-π interactions. The authors claim that the introduction of PEA ligands results in nearly blinking-free PQDs, optically stable for several hours under continuous illumination. Newly developed robust PQDs allow detailed spectroscopy investigations about size-dependent exciton radiative rates and emission linewidths of single PQDs ranging from strongly to weakly confined regimes.
The manuscript presents a novel approach by using PEA ligands to stabilize PQDs through π-π interactions, which shows promising results in terms of stability and blinking behaviour. The focus on creating non-blinking single photon emitters is highly relevant for advancements in quantum technologies. The detailed analysis of the ligand exchange process and its effects on PQD stability and emission properties is commendable. However, there are several open questions which prevent the current manuscript from being published in the current form.
1. The author's claim that π-π interactions are needed to achieve a dense ligand coverage and suppress PL blinking, is not fully supported by experimental evidence. In fact, IPA bromide-capped QDs exhibit suppressed blinking with ON-time fractions as good as PEA-capped QDs. π-π interactions seem to not be the sole important factor in suppressing blinking behaviour.
2. The manuscript does not adequately address the possibility of Zn incorporation given the use of $ZnBr2$ as a precursor in the hot injection synthesis of $CsPbBr3$ QDs. Recent studies have shown that Zn incorporation can significantly improve photoluminescence properties and stability, and this potential influence needs to be explicitly addressed (Nano Lett. 2023, 23, 22, 10228–10235).
3. Blinking studies are reported at very low excitation density, making the current results not very different from the ones already reported in the literature (Nano Lett. 2016, 16, 10, 6425–6430, ACS Photonics 2020, 7, 8, 2265–2272, ACS Nano 2021, 15, 2, 2831–2838)
4. Size-dependent radiative rates were found to increase by decreasing particle size, as reported in the literature for CdSe (cited references) and perovskite QDs (ACS Cent. Sci. 2021, 7, 1, 135–144). Radiative rates decrease, showing a non-monotonic trend, when the QD size is smaller than 4.5 nm. This novel behaviour was not elucidated and requires additional details.

Reviewer #2

(Remarks to the Author)
In this work, Mi et al. claimed an approach utilizing PEA ligands to suppress blinking in perovskite quantum dots by leveraging the intermolecular interaction between ligands to improve quantum dot passivation. The authors showed that this approach yields nearly non-blinking behavior, high purity (98%), reduced spectral shifting, and resistance to photodegradation. However, the manuscript is lacking in significance and novelty for Nature Communications. Firstly, the original concept of effective blinking suppression of perovskite quantum dots treated with low steric hindrance bromide ligands has already been reported (ACS Nano 2021, 15, 2, 2831–2838). Secondly, the method and its application for single-photon emission presented in this manuscript have already been published by the same research group in another journal

(J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474), which claimed an achievement of blinking free PQDs (ON period of >99%). The manuscript does not offer additional insights, such as comparisons of ligands with different π-π stacking degrees, comparisons of the effects of ligand chain length on this method, or whether it can be extended to blue and red emission systems (Cl, I-based perovskite quantum dots). Some discussions about long-term stability, the constant of size-dependent g(2)(0) and the radiative rate lack adequate supporting data or clear explanation. Overall, these findings proved that the PEA ligands can enhance the emission performance of strongly confined $CsPbBr_3$ PQDs, which is expected. Hence, the reviewer believes that the manuscript does not meet the standards of Nature Communications. Detailed comments are as follows:
1. In the abstract, the authors "posited that intermolecular interactions between will affect QD Surface Passivation" as a hypothesis and motivation for the work. This is merely stating the obvious.

2. On page 3, line 63 – "While tolerated by weakly confined perovskite QDs, under-passivated surfaces can be detrimental to strongly confined QDs." – please substantiate this statement. Under-passivated surfaces will affect the ON/OFF ratios (blinking) of both weakly and strongly confined perovskite quantum dots. A detailed comparison of a series of the dots from the weak to strong confinement using the authours approach is important to qualify this work.

3. Both J. Phys. Chem. Lett. 14, 23, 5466 (2023) and Nature 626, 542 (2024) have shown that the PEA ligands can suppress blinking behavior. How does the method described in this work differ from the previously published methods in terms of novelty and significance?

4. If PEACl and PEAI are used to replace PEABr as the pre-coating layer for the substrate, can single perovskite quantum dots with anion exchange be obtained? What would be their spectral tuning range, spectral stability, photodegradation resistance, and single-photon emission performance?

5. The authors claimed that the PEA ligands can full cover the surface of QDs in Figure 1. To verify the better combination of PEA ligands, could the author provide the QDs' PLQY with these three different ligands under different dilution times?

6. The authors did not clearly specify the method used to achieve the coating with different ligands. For example, were the DDA-covered and PEA-covered samples in Figure 2 obtained through the solid-state ligand exchange method described by the authors? According to the figure caption, the coating methods for these two ligands appear to be different, which affects any comparison of the performance. The reviewer suggests that a more reliable comparison could be made by using the solid-state ligand exchange method described by the authors for both DDABr and PEABr.

7. The comparison of blinking behavior in Figure 2 is also invalid: QDs covered with DDA were dispersed in polystyrene, whereas those covered with PEA were encapsulated in UV-curing optical adhesives. Include an examination of the blinking behavior of QDs covered with the PEA ligands without encapsulation, or QDs covered with DDA and encapsulated, would make the comparison fairer.

8. The use of the term "non-blinking" (in lines 273, 282, 281…) should be replaced by "nearly non-blinking". Please provide the bin time and size information for all the recorded intensity traces. The fluorescence lifetime intensity distribution (FLID) is an alternative efficient approach to evaluate the blinking behavior, could you please provide these data?

9. The probability statistical histograms for the different performances (the on-fraction/ Q parameter distribution, the duration of no spectral diffusion and the survive time under continuous excitation) should be provided rather than just a few examples, which will make the results more convinced.

10. The long-term stability evaluation is very confusing. How long these single QDs, collection of QDs or ensemble could survive for different performances under continuous excitation? The authors should make it clearer. Please also provide the whole intensity trace (12 h) of Figure 3e.

11. How does the PEA ligand affect the biexciton and exciton lifetimes? Did you observe longer exciton lifetime owing to the full covered surface treatment?

12. Please provide the histograms of size distribution for the $CsPbBr_3$ QDs of various sizes and the PEA-exchanged QDs in Supplementary Fig. 6.

13. Generally, as the size increases, the average of g(2)(0) tends to increase, as indicated by references 9-12 in Supplementary Fig. 15. Can you explain why the measured g(2)(0) are much smaller than the reported g(2)(0) with similar size? Please also provide the error bar of the measured g(2)(0).

Reviewer #3

(Remarks to the Author)
In this manuscript, Chenjia Mi, et al., report functional surface ligands for perovskite quantum dots (QDs) to improve their emission properties as single photon emitters, mainly focusing on non-blinking behavior in single QD level. Using phenethylammonium (PEA) ligands with attractive - stacking, they simulate and claim that these ligands can provide nearly complete passivation of the QD surface, which helps reduce or remove surface defects that are known to responsible for charge trapping, in sharp contrast to DDA ligands with two long chains that yields incomplete surface coverage. This is well analyzed by density functional theory (DFT) calculations, which supports the experimental results. In experiment, using PEA

ligands, they demonstrate non-blinking single-dot emission with ON time > 95 % from individual CsPbBr3 QDs. Side-by-side comparison to DDA ligand-covered QDs convinces the dramatic improvements in single-dot emission properties, such as blinking-free, reduced spectral diffusion, and long-time stability. The strategy to use PEA ligands was also applied to different sizes of CsPbBr3 QDs, especially in strongly confined regime, where photon-charging is known to be more stronger due to enhanced exciton-surface interaction, and they observed non-blinking emission from these size-varied QDs.
Severe blinking from perovskite QDs in single-dot level is a long-standing issue, especially to be used as single emitters. As pointed by the authors, unlike Cd-based QDs, effective shelling to suppress blinking behavior is not known yet for perovskite QDs, and the use of function ligands reported in this manuscript would be helpful and informational to the community.
However, I feel that this manuscript should be improved to be published in Nature Communications because of the following reasons.

Major concerns;
1.Author should be able to extend the use of PEA ligands to perovskite quantum dots with different chemical components, such as CsPbI3, CsPbCl3, and their mix, and demonstrate non-blinking behaviors.
2.Does all QDs show non-blinking emission with > 95% ON time? Please provide the statistics of ON time distribution (and any related emission properties) including QDs in different sizes.
3.I do not agree with the claim that there is “no” spectral diffusion. Can author quantify the error? If there is no change at all, it should be understood considering the spectral resolution of the system.
4.In Fig. 2g, probability distribution of ON/OFF durations are obtained from blinking traces of “60” CsPbBr3 QDs. I’m not sure it is correct since this distribution is normally analyzed from one single emitter, not from multiples. And, there should be dot-to-dot variation on ON/OFF durations.
5.In lines 274 – 277, a large variation on g(2)(0) is attributed to QD blinking. Do the authors observe any relationship between ON time and g(2)(0) values?
6.In lines 297 - 302 and Fig. 5b; I’m not quite sure that there is a trend in radiative rate vs PL peak energy. Do the authors also observe the same trend for ensemble samples?
7.What are the quantum yields of the samples used in this study?

Minors;
1.Please make the y-axis scale the same for Figs. 1b and 1d, then one can catch the difference easily, without misleading.
2.In Fig. 2f, it is not easy to see the dip at zero time. Please include a sub-figure (or something) that zooms in near zero-time delay.
3.Indicate the bin time in each (sub) figure that displays single-dot intensity trajectory.
4.In Fig. 2c, the start time should not be zero.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have revised the manuscript and adequately addressed three out of the four main points raised in the previous referee report. However, the explanation of the non-monotonic size-dependent radiative lifetime appears speculative and could be rephrased to avoid potential misunderstandings. A general statement suggesting that this aspect requires more detailed experiments may be a better approach. The manuscript can now be considered for publication.

Reviewer #2

(Remarks to the Author)
I greatly appreciate the authors’ efforts in their detailed reply that partially addressed my previous comments as well as for extending the method of ligand replacement by annealing organic halide molecules (e.g. PEABr) with perovskite nanocrystals in a small amount of solution to iodine-based perovskite systems. However, I am unable to recommend the current manuscript for publication in Nature Communications.

1. The authors’ supplement to the article basically shows that a suitable conjugated ligand system is conducive to adequate surface passivation to achieve further suppression of the blinking issue. However, by comparing this work with the authors’ previous work (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474), there is indeed a lack of novelty regarding of material preparation and application topics.

Preparation method in this manuscript: “In the glovebox, 200 mg PEABr was dissolved in 1 mL of anhydrous DMF and filtered through a PTFE syringe filter (VWR, 0.22 μm pore size). The stock QD colloid was diluted using anhydrous octane to ~ 200 pM. For the solid-state ligand exchange, 150 μL of the PEABr solution was spin-coated on a clean coverslip at 4000 rpm. After ~ 35 s (~ 15 s for larger QDs), 10 μL of the dilute CsPbBr3 QD colloid was swiftly dropped on the coverslip while spinning. The coverslip was then annealed on a hot plate at 50 – 70 °C for 30 – 120 s. Then, the sample coverslip was covered by a glass slide. The gaps between the coverslip and the glass slide were sealed using UV curing optical adhesives (Thorlabs NOA61).”

Preparation method in the previous work (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474): “To prepare SCPQD in PEABr matrix sample, 150 μL of PEABr DMF solution (250 mg/mL) was dropped onto a coverslip then spin-cast using a two-step procedure: first at 1000 rpm for 10s and then at 5000 rpm for 1 min. After 20s of spinning when the spin rate reaches 5000 rpm, 10 μL of the diluted SCPQD colloid was dropped onto the coverslip. The sample coverslip was annealed at 70 °C for 2 min and then encapsulated using optical adhesives."

Both of them all achieved ligand replacement by annealing the organic halide molecule PEABr with perovskite nanocrystals in a small amount of solvent. Furthermore, the reviewer feels that it is inappropriate for the authors to describe this preparation process as "solid-state ligand exchange".

And the application topics are all aimed at the suppression of blinking in single-photon emission.

Therefore, this manuscript is in fact a mechanistic or an incremental supplement to the previous discovery of the authors. However, looking through the entire manuscript, the authors do not mention this previous work at all (and even cite this previous finding in a way that misleads the readers, as shown below), but instead describe this as a completely new discovery, which the reviewer believe is inappropriate.

The content described for the previous finding (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474) in the main text: "Particularly, perovskite QDs show severe PL intermittency ("blinking") and photodegradation when their sizes are smaller than their exciton Bohr diameters.17-19", where the reference 17 is the previous finding of the authors (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474).

2. In the revised introduction, the authors state, "Particularly, perovskite QDs show …smaller than their exciton Bohr diameters. 17-19." However, they did not mention that a similar method was used previously in Ref.17. The authors should add a paragraph in the main text explicitly discussing how the current work differs from previously published ones in terms of novelty and significance. This will help clarify the unique contribution of this work.

3. The authors have demonstrated that the PLQY of diluted solutions of QDs passivated by different ligands did not change significantly. Could you also provide the PLQY of soild-state PEA-exchanged QDs? Additionally, what's the performance of PEA-capped QDs without encapsulation using optical adhesives?

4. In the revised SI Fig. 29c, the average g(2)(0) value is around 0.8 for sizes between 10 to 13 nm, whereas in SI Fig. 30, the value is below 0.5. Could the authors explain this discrepancy?

Reviewer #3

(Remarks to the Author)
I believe that Chenjia Mi, et al. have addressed the questions and concerns that were raised from the original manuscript; especially, extended studies on $CsPbI_3$ QDs to demonstrate PEA ligands capability for perovskite QDs with different chemical components, extensive single-dot statistics, and discussion of spectral diffusion at both room and cryogenic temperature. I appreciate the authors' hard work to improve the quality of this work. Now I recommend the revised manuscript for the publication in Nature Communications.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Reviewer #2

(Remarks to the Author)
After carefully reviewing the additional information provided by the authors, I remain unconvinced that the novelty of the work meets the high standards required for publication in Nature Communications. The central approach for achieving stable perovskite quantum dots still relies on the same conjugated ligand system for surface passivation. Although the current study explores adjustments to the spin-coating parameters and shifts from spherical to cubic perovskite quantum dots in an effort to improve the stacking of PEA ligand tails, as the authors themselves acknowledge—"This suggests that our previous method failed to yield well-stacked PEA ligand tails, whereas our current method promotes ligand tail stacking"—these changes appear to represent only incremental advances over their previous work published in JPCL. Given the lack of substantial novelty, I am unable to recommend this manuscript for publication in a high-impact journal such as Nature Communications.

Response Letter to Reviewers' Comments

For Reviewer #1:

The manuscript addresses the significant issue of surface defects in perovskite quantum dots (PQDs) arising from the detachment of weakly bound ligands, which hampers their application in light-emitting devices. The study focuses on monodentate phenylethylamine (PEA) ligands and their ability to stabilize PQDs through π-π interactions. The authors claim that the introduction of PEA ligands results in nearly blinking-free PQDs, optically stable for several hours under continuous illumination. Newly developed robust PQDs allow detailed spectroscopy investigations about size-dependent exciton radiative rates and emission linewidths of single PQDs ranging from strongly to weakly confined regimes.

The manuscript presents a novel approach by using PEA ligands to stabilize PQDs through π-π interactions, which shows promising results in terms of stability and blinking behaviour. The focus on creating non-blinking single photon emitters is highly relevant for advancements in quantum technologies. The detailed analysis of the ligand exchange process and its effects on PQD stability and emission properties is commendable. However, there are several open questions which prevent the current manuscript from being published in the current form.

We appreciate the reviewer's positive comments on our work. In the revised manuscript, we have demonstrated nearly non-blinking $CsPbBr_3$ and $CsPbI_3$ QDs at nearly saturating excitation densities. We have also characterized the impact of π-π stacking effects on the blinking behaviours of QDs. Finally, we have also revised the discussions on the size-dependent exciton dynamics.

Comments:

1. The author's claim that π-π interactions are needed to achieve a dense ligand coverage and suppress PL blinking, is not fully supported by experimental evidence. In fact, IPA bromide-capped QDs exhibit suppressed blinking with ON-time fractions as good as PEA-capped QDs. π-π interactions seem to not be the sole important factor in suppressing blinking behaviour.

Response 1:

We thank the reviewer for the careful review and insights. In the revised manuscript, we have measured 67 IPA-covered single QDs to statistically evaluate the passivation efficiency of IPA. The lower average ON-time fraction of IPA-QDs (83%) in comparison with that (95%) of PEA-QDs (**Figure R1.1**) and lower probability of achieving > 90% ON fraction in IPA-QDs suggest that the PEA with π-π stacking effect is necessary to achieve nearly non-blinking QDs (defined here as > 90% ON time fraction). IPA can partially suppress QD blinking because of its low steric ligand tail. However, IPA is unlikely to form epitaxial ligand coverage without attractive intermolecular interaction.

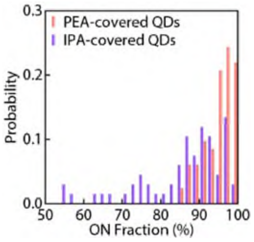


Figure R1.1. A summary of ON fractions of 81 PEA-covered QDs and 67 IPA-covered QDs extracted from single QD blinking measurements.

The π-π interaction is also important for suppressing QD photodarkening. As shown in **Figure R1.2**, IPA-covered QD exhibits severe photodarkening within only 20 min of laser Illumination, whereas PEA-covered QD stayed nearly non-blinking for >10 h. We have added the additional data and discussion to the revised manuscript on Page 11 – 12.

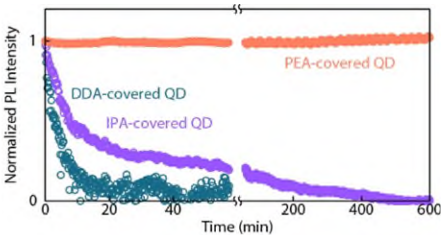


Figure R1.2. Normalized PL intensity of a collection of isolated PEA-covered $CsPbBr_3$ QDs (blue) and IPA-covered $CsPbBr_3$ QDs (purple) recorded during continuous laser excitation.

2. The manuscript does not adequately address the possibility of Zn incorporation given the use of $ZnBr_2$ as a precursor in the hot injection synthesis of $CsPbBr_3$ QDs. Recent studies have shown that Zn incorporation can significantly improve photoluminescence properties and stability, and this potential influence needs to be explicitly addressed (Nano Lett. 2023, 23, 22, 10228–10235).

Response 2:

We thank the reviewer's suggestion. Although $ZnBr_2$ is used in our strongly confined QD syntheses, Zn incorporation was not detected in the obtained QDs (*Nano Lett.* **2018**, 18, 3716–3722). We also performed an elemental analysis of the QD used in this study, and the amount of Zn in our QDs was below the detection limit of the inductively coupled plasma-mass spectrometer (< 1 Zn atom per QD). Additionally, no Zn source was involved in weakly confined perovskite QD syntheses.

3. Blinking studies are reported at very low excitation density, making the current results not very different from the ones already reported in the literature (Nano Lett. 2016, 16, 10, 6425–6430, ACS Photonics 2020, 7, 8, 2265–2272, ACS Nano 2021, 15, 2, 2831–2838)

Response 3:

We appreciate the reviewer's careful review and comments. In the revised manuscript, we have measured blinking traces of both single $CsPbBr_3$ QDs and $CsPbI_3$ QDs at high excitation densities.

Our PEA-covered QDs remained nearly non-blinking even under saturating excitations (**Figure R1.3)**. To better compare our results with reported works, we have listed several parameters related to QD blinking behaviour, the excitation densities used for blinking trace measurements, and the photostability of QDs in **Table R1.1** (for CsPbBr$_3$ QDs) and **Table R1.2** (for CsPbI$_3$ QDs). We have also noted the excitation laser repetition rates used during measurements to better compare the excitation densities.

Our work focuses on strongly size-confined QDs that are more susceptible to surface defects-induced blinking than weakly confined QDs or non-confined QDs. Our QDs are distinctively nearly nonblinking even at high single photon emission rates and have achieved unprecedented photostability.

Table R1.1. Emission performance of single CsPbBr$_3$ perovskite QDs

QD size	**Reported excitation density**	**ON state count rate (rep. rate)**	**PL ON fraction**	**Mandel Q parameter**	**Photostability (estimated)**	**Single photon purity**	**Reference**
8-10 nm	0.15 ~ 0.24	185 kcps (10 MHz)	80%	< 1	150 s	89%	Ref [1]
10 nm	-	-	-	-	-	73% (avg.)	Ref [2]
12 nm	0.09	30 kcps (5 MHz)	80%	24	300 s	-	Ref [3]
10 nm	0.2	25 kcps (10 MHz)	-	-	300 s	74%	Ref [4]
12 nm	3	60 kcps (2.5 MHz)	> 90%	3	600 s	0-92%	Ref [5]
5 nm	0.2	60 kcps (10 MHz)	78%	8	40 s	78%	Ref [6]
3.6 nm (thickness) 11.3 nm (lateral)	-	7.5 kcps (2.5 MHz)	68%	-	20 min	80% (median)	Ref [7]
3.6-14 nm	0.80 (strongly-confined)	89 kcps (2 MHz)	95% (avg.)	0.57 (avg.)	12 h	95% (avg.)	This work
		300 kcps (*cw*)					
	1.1 (weakly-confined)	160 kcps (2 MHz)					
		1300 kcps (*cw*)					

Table R1.2. Emission performance of single CsPbI$_3$ perovskite QDs

QD size	**Reported excitation density**	**ON state count rate (rep. rate)**	**PL ON fraction**	**Mandel *Q* parameter**	**Photostability (estimated)**	**Single photon purity**	**Reference**
9.8 nm	3.3	60 kcps (2.5 MHz)	86%	47	600 s	94% (avg.)	Ref [8]
9.3 nm	1.7	75 kcps (5 MHz)	> 80%	< 1	300 s	95%	Ref [9]
6.6 nm	~ 0.7	65 kcps (10 MHz)	92%	10	100 s	90% (avg.)	Ref [2]
5.0-8.0 nm	~ 1.6	60 kcps (2 MHz)	92% (avg.)	0.16 (avg.)	7 h	98% (avg.)	This work
		1100 kcps (*cw*)					

[1] *Nature* **2024**, *626*, 542–548

[2] *Nano Lett.* **2022**, 22, 3751–3760

[3] *J. Phys. Chem. Lett.* **2018**, 9, 7007–7014

[4] *J. Phys. Chem. Lett.* **2018**, 9, 6934–6940

[5] *Nano Lett.* **2023**, 23, 10228–10235

[6] *ACS Nano* **2023**, 17, 2089–2100

[7] *ACS Photonics* **2020**, 7, 2265–2272

[8] *ACS Nano* **2021**, 15, 11358–11368

[9] *Nano Lett.* **2016**, 16, 6425–6430

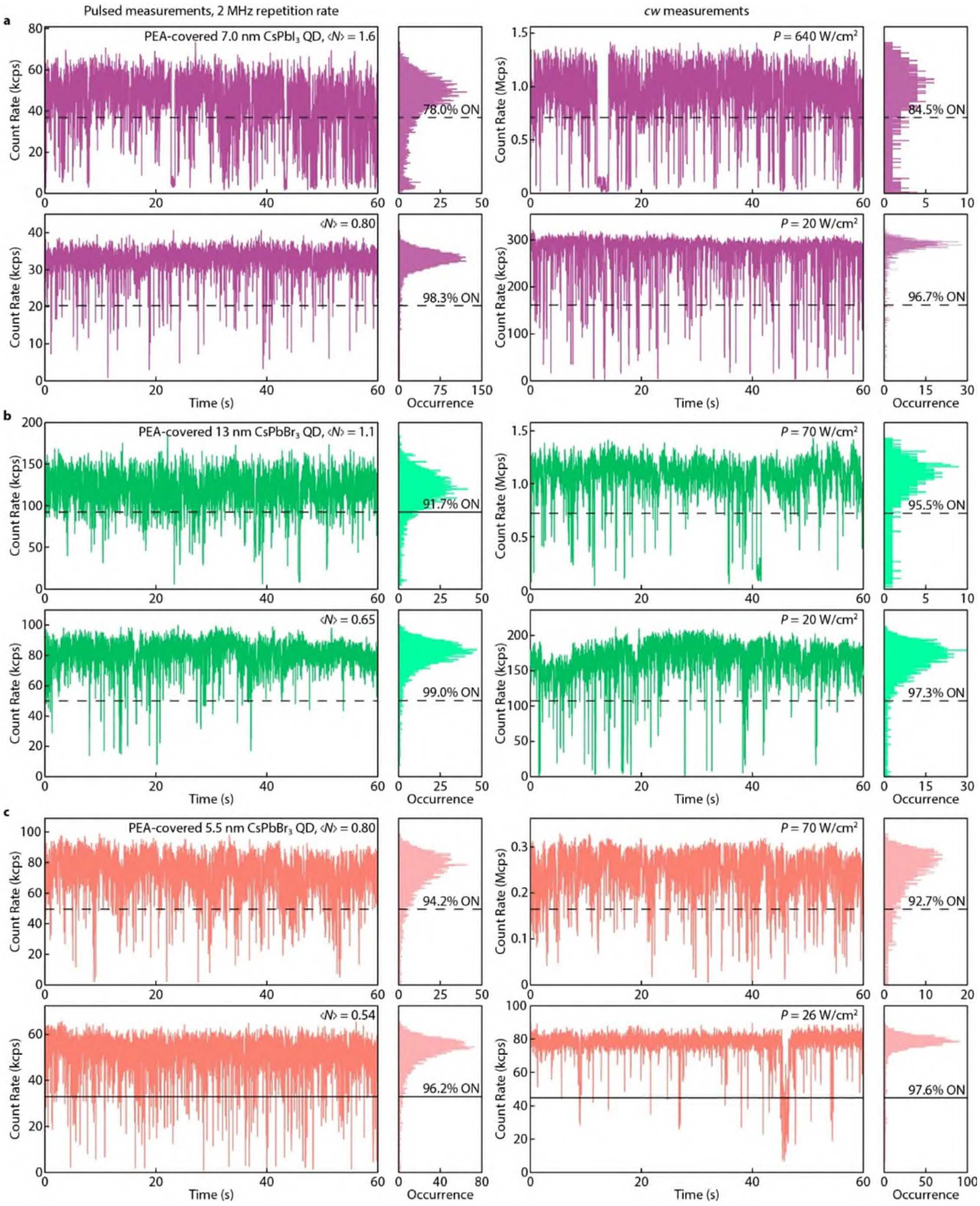


Figure R1.3. Blinking traces and PL intensity distribution histograms for (a) 7.0 nm $CsPbI_3$ QD, (b) 13 nm $CsPbBr_3$ QD and (c) 5.5 nm $CsPbBr_3$ QD, measured using pulsed (2 MHz, left column) and *cw* excitation conditions. The excitation densities/power densities were noted in the figure. When the excitation density approaches saturation, the *Q* parameter of the blinking traces increases. All blinking traces are built using a bin time of 10 ms.

4. Size-dependent radiative rates were found to increase by decreasing particle size, as reported in the literature for CdSe (cited references) and perovskite QDs (ACS Cent. Sci. 2021, 7, 1, 135–144). Radiative rates decrease, showing a non-monotonic trend, when the QD size is smaller than 4.5 nm. This novel behaviour was not elucidated and requires additional details.

Response 4:

We appreciate the comment and have added more discussions and references in the revised manuscript on Pages 15 – 16. In brief, the non-monotonic trend resulted from the combined effects of increasing bandgap and mixing dark exciton states on the apparent radiative recombination rate. *Firstly,* the rate of spontaneous emission transition rate between the excitonic state (ex) and the ground state can be derived from Fermi's golden rule:

$$\Gamma_{ex} \propto \omega_{ex} |\langle 0|\boldsymbol{p}|ex\rangle|^2$$

where Γ_{ex} is the transition rate, $|\langle 0|\boldsymbol{p}|ex\rangle|$ is the matrix element, and ω_{ex} is the frequency of light emitted by the exciton. Therefore, the transition rate is proportional to the emission frequency, which increases with decreasing size in the case of QDs. *Secondly,* the exciton recombination should be modelled as a three-level system, where the exciton state is further split into an optically active bright triplet state and an optically passive dark singlet state (*Nano Lett.* **2019,** 19, 4068–4077). Radiative recombination of the dark exciton is partially forbidden and slow (~µs scale, *Nat. Mater.* **2019,** 18, 717–724). When perovskite QDs are experiencing strong quantum confinement, the dark state becomes the ground state. Then, the apparent radiative recombination rate is determined by the relative thermal occupation of the bright and dark excitonic states. The energy spacing between bright and dark states increases with decreasing QD size. When the splitting becomes significant (i.e. > 10 meV for < 4.5 nm QDs) compared to *kT*, increasing contribution from the dark state will slow down the apparent radiative recombination rate. Similar size-dependent radiative rates were also observed in conventional II-VI QDs (*J. Semicond.* **2023,** 44, 032702). In addition, we have observed similar phenomena using ensemble samples with narrow size distributions (**Figure R1.4**). The radiative rates obtained in our study agree well with recently reported values (*J. Phys. Chem. Lett.* **2024,** 15, 6062–6068). These discussions have been added to the revised Supplementary Note 10.

[Figure redacted]

Figure R1.4. Radiative rates of QDs of various sizes obtained from PL lifetime measurements using ensemble QD colloids (blue solid triangles), and statistics of exciton radiative recombination rates of 81 non-blinking PEA-covered QDs with different sizes (red open triangles). The dashed curve is a visual guide. The overall lower radiative rate can be attributed to the smaller dielectric constant of hexane compared to PEABr solids (*ACS Photonics* **2018**, 5, 4139–4146, *ACS Nano* **2015**, 9, 1801–1808).

For Reviewer #2:

In this work, Mi et al. claimed an approach utilizing PEA ligands to suppress blinking in perovskite quantum dots by leveraging the intermolecular interaction between ligands to improve quantum dot passivation. The authors showed that this approach yields nearly non-blinking behavior, high purity (98%), reduced spectral shifting, and resistance to photodegradation. However, the manuscript is lacking in significance and novelty for Nature Communications. Firstly, the original concept of effective blinking suppression of perovskite quantum dots treated with low steric hindrance bromide ligands has already been reported (ACS Nano 2021, 15, 2, 2831–2838). Secondly, the method and its application for single-photon emission presented in this manuscript have already been published by the same research group in another journal (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474), which claimed an achievement of blinking free PQDs (ON period of >99%). The manuscript does not offer additional insights, such as comparisons of ligands with different π-π stacking degrees, comparisons of the effects of ligand chain length on this method, or whether it can be extended to blue and red emission systems (Cl, I-based perovskite quantum dots). Some discussions about long-term stability, the constant of size-dependent $g^{(2)}(0)$ and the radiative rate lack adequate supporting data or clear explanation. Overall, these findings proved that the PEA ligands can enhance the emission performance of strongly confined $CsPbBr_3$ PQDs, which is expected. Hence, the reviewer believes that the manuscript does not meet the standards of Nature Communications. Detailed comments are as follows:

We thank the reviewer for the constructive comments. The severe blinking and poor photostability of perovskite QDs, especially when there is strong size confinement, are a long-standing barrier to applying colloidal QDs on quantum light sources. In the revised manuscripts, we have provided additional insights on the effect of π-π stacking on QD blinking and extended our approach to $CsPbI_3$ QDs (**Figure R2.1**). The strongly confined $CsPbCl_3$ QDs cannot be properly measured in the fluorescence microscope since their UV emissions are incompatible with optics in the fluorescence microscope.

In brief, we have applied ultra-low frequency Raman spectroscopy (**Figure R2.2**) and linear absorption (**Figure R2.3**) measurements to evaluate the degrees of π-π stacking in PEA ligands. In this experiment, alkyl ligands, *n*-butylammonium bromide (NBABr) were introduced to interfere with the π-π stacking between phenyl rings in PEA ligands. The disrupted π-π stacking is demonstrated as reduced intermolecular Raman modes and blue-shifted absorption peaks. Correspondingly, QDs start to blink when π-π stacking is compromised. Additionally, we discovered that the attractive intermolecular interaction can potentially rigidify the perovskite lattices, leading to extraordinarily stable single photon emission from QDs at nearly saturating excitation densities. We have also revised and added more discussions about the optical properties of single perovskite QDs in the manuscript. Our report shows that the intermolecular interactions on the QD surface can foster near-epitaxial QD passivation, leading to nearly non-blinking QDs with a ~ 50-fold enhanced single photon emission stability compared with previous reports (**Table**

R2.1 and R2.2). The detailed discussions can be found in the point-to-point responses. We thank the reviewer for the positive comments and constructive suggestions that helped improve our work.

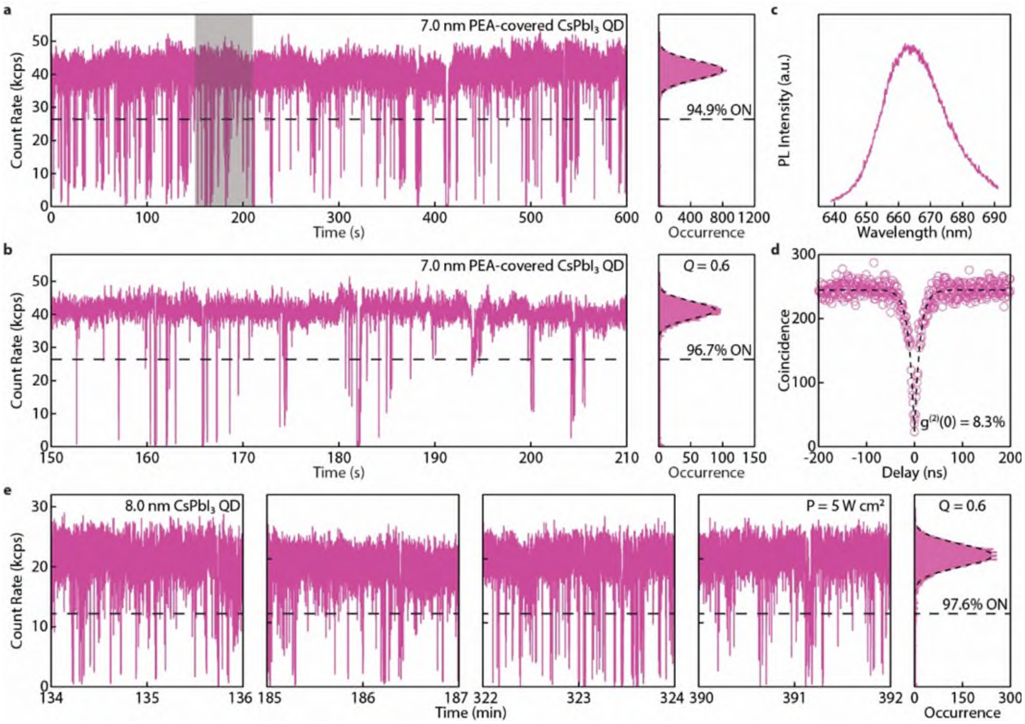


Figure R2.1. (a) PL blinking trace (10 ms bin time) and intensity distribution histograms of a ~ 7.0 nm PEA-covered $CsPbI_3$ QD. (b) A zoomed-in view of the blinking traces with a 1 min time window indicated by the shaded area in (a). The intensity distribution histograms are shot noise limited with a *Q* parameter of 0.6 in (b). The distribution is fitted by Poissonian functions (dashed curves). (c) PL spectra of the QD. (d) Second-order correlation ($g^{(2)}$) function of the QD, fitted (dashed curve) to yield a $g^{(2)}(0)$ value of 8.3%. The QDs were excited by a 405 nm laser at *cw* mode with an intensity of 20 W cm^{-2}. (e) Representative blinking traces (10 ms bin time) of a PEA-covered 8.0 nm $CsPbI_3$ QD measured continuously for 8.5 h. The PL intensity distribution histogram is built from the blinking trace of 390 to 392 min. The intensity fluctuations between blinking traces are due to the random sample stage drifting.

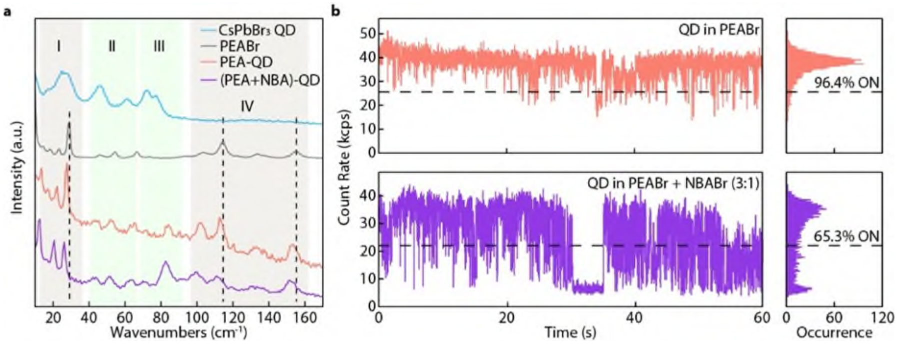


Figure R2.2. Effect of π-π stacking of PEA ligands on QD blinking. (a) Low-frequency Raman spectra of $CsPbBr_3$ QDs covered by the original ligands (oleates), Pristine PEABr polycrystalline thin film, PEA-covered CsPbBr3 QDs, and $CsPbBr_3$ QDs after solid-state exchange using a mixture of PEABr and NBABr (3:1 mass ratio), measured at 77 K. (b) Blinking traces (10 ms bin time) of single 4.3 nm $CsPbBr_3$ QDs covered by PEA (orange) and PEA + NBA (3:1) (purple).

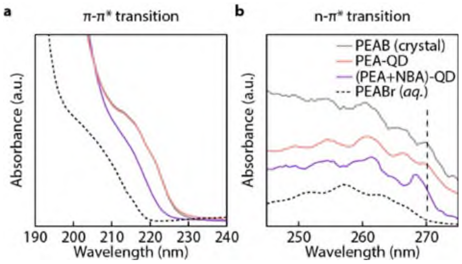


Figure R2.3. Linear absorption spectra of the thin film samples for pristine PEABr (grey), QDs in PEABr after solid-state exchange (orange), and QDs in a mixture of 3:1 ratio of PEABr and n-butylammonium bromide (NBABr) after solid-state ligand exchange (purple), showing (a) the π to **π*** transitions and (b) the n to **π*** transitions spectral windows. The spectrum of aqueous PEABr (black dotted curves) is plotted as a reference sample with no π-π stacking.

Table R2.1. Emission performance of single $CsPbBr_3$ perovskite QDs

QD size	Reported excitation density	ON state count rate (rep. rate)	PL ON fraction	Mandel *Q* parameter	Photostability (estimated)	Single photon purity	Reference
8-10 nm	0.15 ~ 0.24	185 kcps (10 MHz)	80%	< 1	150 s	89%	Ref [1]
10 nm	-	-	-	-	-	73% (avg.)	Ref [2]
12 nm	0.09	30 kcps (5 MHz)	80%	24	300 s	-	Ref [3]
10 nm	0.2	25 kcps (10 MHz)	-	-	300 s	74%	Ref [4]
12 nm	3	60 kcps (2.5 MHz)	> 90%	3	600 s	0-92%	Ref [5]
5 nm	0.2	60 kcps (10 MHz)	78%	8	40 s	78%	Ref [6]
3.6 nm (thickness) 11.3 nm (lateral)	-	7.5 kcps (2.5 MHz)	68%	-	20 min	80% (median)	Ref [7]
3.6-14 nm	0.80 (strongly-confined)	89 kcps (2 MHz)	95% (avg.)	0.57 (avg.)	12 h	95% (avg.)	This work
		300 kcps (*cw*)					
	1.1 (weakly-confined)	160 kcps (2 MHz)					
		1300 kcps (*cw*)					

Table R2.2. Emission performance of single $CsPbI_3$ perovskite QDs

QD size	Reported excitation density	ON state count rate (rep. rate)	PL ON fraction	Mandel *Q* parameter	Photostability (estimated)	Single photon purity	Reference
9.8 nm	3.3	60 kcps (2.5 MHz)	86%	47	600 s	94% (avg.)	Ref [8]
9.3 nm	1.7	75 kcps (5 MHz)	> 80%	< 1	300 s	95%	Ref [9]
6.6 nm	~ 0.7	65 kcps (10 MHz)	92%	10	100 s	90% (avg.)	Ref [2]
5.0-8.0 nm	~ 1.6	60 kcps (2 MHz)	92% (avg.)	0.16 (avg.)	7 h	98% (avg.)	This work
		1100 kcps (*cw*)					

[1] *Nature* **2024**, *626*, 542–548

[2] *Nano Lett.* **2022**, 22, 3751–3760

[3] *J. Phys. Chem. Lett.* **2018**, 9, 7007–7014

[4] *J. Phys. Chem. Lett.* **2018**, 9, 6934–6940

[5] *Nano Lett.* **2023**, 23, 10228–10235

[6] *ACS Nano* **2023**, 17, 2089–2100

[7] *ACS Photonics* **2020**, 7, 2265–2272

[8] *ACS Nano* **2021**, 15, 11358–11368

[9] *Nano Lett.* **2016**, 16, 6425–6430

Comments:

1. In the abstract, the authors "posited that intermolecular interactions between will affect QD Surface Passivation" as a hypothesis and motivation for the work. This is merely stating the obvious.

Response 1:

We agree with the comment. We have now specified our hypothesis in the revised abstract: "We posit that bulky ligands benefiting colloidal stability can prevent adequate quantum dot surface passivation in the solid state. Alternatively, attractive π-π stacking between low-steric phenethylammonium ligands is pivotal in forming a nearly epitaxial ligand layer that stabilizes the quantum dot surface."

2. On page 3, line 63 – "While tolerated by weakly confined perovskite QDs, under-passivated surfaces can be detrimental to strongly confined QDs." – please substantiate this statement. Under-passivated surfaces will affect the ON/OFF ratios (blinking) of both weakly and strongly confined perovskite quantum dots. A detailed comparison of a series of the dots from the weak to strong confinement using the authours approach is important to qualify this work.

Response 2:

Following the reviewer's suggestion, we have added blinking traces of a series of the $CsPbBr_3$ QDs ranging from weak to strong confinement regions to support our claim. The surface passivation of QDs was intentionally modified by using a mixture of NBABr and PEABr (1:3, mass ratio) for solid-state exchanges. Incorporating NBA will interfere with PEA stacking and lead to insufficient surface passivation (**Figure R2.2 and R2.3**). As shown in **Figure R2.4**, although passivated by identical ligand combinations, weakly confined QDs can better tolerate the under-passivated surface and exhibit fewer blinking events. The results and additional notes are added in the Supplementary Fig. 1 and Note 1.

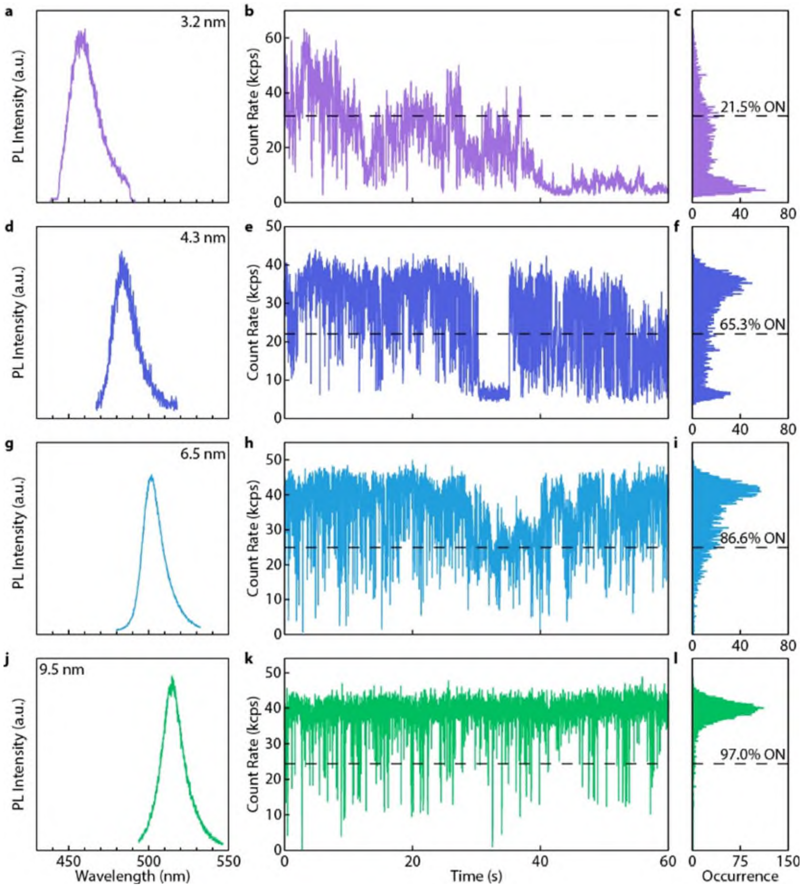


Figure R2.4. (a)(d)(g)(j) Single QD PL spectrum of four $CsPbBr_3$ QDs passivated by a mixture of PEABr and NBABr (3:1 mass ratio). (b)(e)(h)(k) blinking traces of the four QDs (10 ms bin time, $\langle N \rangle \sim 0.1$). (c)(f)(i)(l) The corresponding intensity distribution histograms.

3. Both J. Phys. Chem. Lett. 14, 23, 5466 (2023) and Nature 626, 542 (2024) have shown that the PEA ligands can suppress blinking behavior. How does the method described in this work differ from the previously published methods in terms of novelty and significance?

Response 3:

Firstly, the cited work (*Nature* **2024**, 626, 542) used a different PEA ligand (phosphoethanolamine) from that in our work (phenethylammonium). The phosphoethanolamine ligand still contains a bulky ligand tail.

In our previous work (*J. Phys. Chem. Lett.* **2023,** 14, 5466), the PEABr was only used to supply bromide anions to fix the bromide vacancies on the surface of $CsPbBr_3$ QDs. The PEA ligands may not form an ordered packing structure, manifested as PL intensity fluctuations in the previous report. In this work, we studied the effect of intermolecular interaction on QD blinking and the photostability of single perovskite QDs. By controlling the ligand stacking, we have achieved nearly non-blinking perovskite QDs and demonstrated their unprecedented photostability. We are also able to extend the mechanism and strategy to $CsPbI_3$ QDs. We appreciate the insights provided by the reviewer to improve our work.

4. If PEACl and PEAI are used to replace PEABr as the pre-coating layer for the substrate, can single perovskite quantum dots with anion exchange be obtained? What would be their spectral tuning range, spectral stability, photodegradation resistance, and single-photon emission performance?

Response 4:

Firstly, we would like to note that the PEABr is not a pre-coating layer. It crystallizes around the individual perovskite QDs. Unfortunately, using pure PEAI for the ligand exchange on CSPbBr3 QDs led to extremely low PL intensity. Following the suggestion, we have mixed PEAI in PEABr (1:1) to perform solid-state ligand exchange for $CsPbBr_3$ QDs (13 nm) **(Figure R2.5)**. Compared with QDs exchanged using 100% PEABr, we did not observe a noticeable PL redshift, suggesting the anion exchange is inefficient even if it may have happened. The anion exchange is potentially suppressed by the ion shells on QDs during ligand exchange, as reported in a previous study (*Nat. Nanotechnol.* **2020**, 15, 668–674). Instead of anion exchange, the emission wavelength can be tuned by sizes of $CsPbBr_3$ QDs and $CsPbI_3$ QDs, which can cover most of the visible spectral range (450 nm – 680 nm).

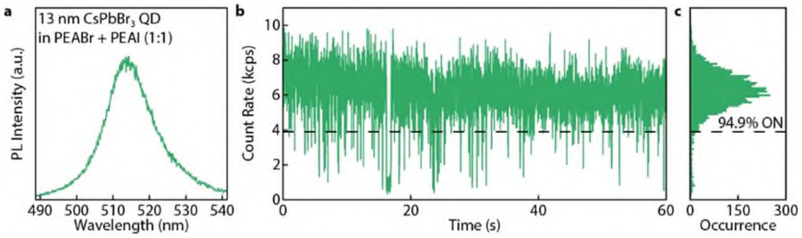


Figure R2.5. (a) PL spectrum, (b) blinking trace (with a bin time of 10 ms), and (c) PL intensity distribution histogram of a single 13 nm $CsPbBr_3$ QD exchanged using a 1:1 mixture of PEABr and PEAI following our solid-state exchange approach.

5. The authors claimed that the PEA ligands can full cover the surface of QDs in Figure 1. To verify the better combination of PEA ligands, could the author provide the QDs' PLQY with these three different ligands under different dilution times?

Response 5:

We would like to clarify that the mixed PEA and MPEA ligands were not used for the solid-state passivation of QDs. The 4-methyl group is to label the PEA molecules to resolve the nOe signals in the solution NOESY NMR experiments and confirm the stacking of the PEA moieties on the QD surface.

The PEA in this study is a solid-state ligand for $CsPbBr_3$ QDs. We have measured the PLQY of QDs passivated by oleates (native ligands), DDA, and PEA ligands (partially exchanged due to limited solubility) in solution with dilution factors ranging from 10^2 to 10^4 (**Figure R2.6a**). The PLQY of the diluted solutions did not change significantly. However, performing PEABr solid-state exchange on these QDs will still significantly improve the PLQY of QDs in the solid state, as shown in the longer and mono-exponential PL intensity decay in **Figure R2.6b**. This is because the surface passivation of QDs in solid-state is determined by the final status of the QD-PEA interface rather than their original PLQY in colloids. As a result, the QD's PLQY in solution does not necessarily affect the quality of QDs embedded in solid-state crystalline films.

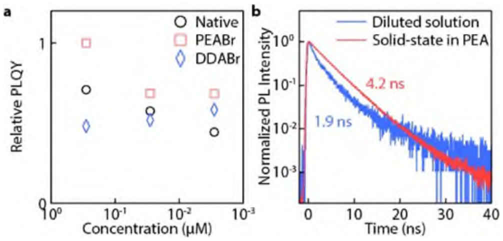


Figure R2.6. (a) Relative PLQYs of 5.1 nm $CsPbBr_3$ QDs in colloids exchanged with different ligands (noted in the figure) as a function of concentration. (b) Normalized PL decay traces of colloidal QDs (3 nM) in solution and crystalline films after solid-state ligand exchange with PEABr.

6. The authors did not clearly specify the method used to achieve the coating with different ligands. For example, were the DDA-covered and PEA-covered samples in Figure 2 obtained through the solid-state ligand exchange method described by the authors? According to the figure caption, the coating methods for these two ligands appear to be different, which affects any comparison of the performance. The reviewer suggests that a more reliable comparison could be made by using the solid-state ligand exchange method described by the authors for both DDABr and PEABr.

Response 6:

The DDA-covered QDs were prepared using a previously reported solution ligand-exchange method (*ACS Nano* **2023**, 17, 2089–2100). Alternatively, using DDABr instead of PEABr to perform the solid-state exchange will degrade QDs. As shown in **Figure R2.7**, single QDs from a 5 nm $CsPbBr_3$ QD sample showed a blue-shifted PL and short, multiexponential PL lifetime after DDAB solid-state exchange. The QD performance is much worse than the QDs prepared using the literature method, while still inferior to our PEA-covered QDs. This is expected in our study since the steric effect of DDA will not favour high ligand coverage in solid states. In the revised manuscript, we have added the DDAB solid-state exchange results in the revised Supplementary Fig. 14.

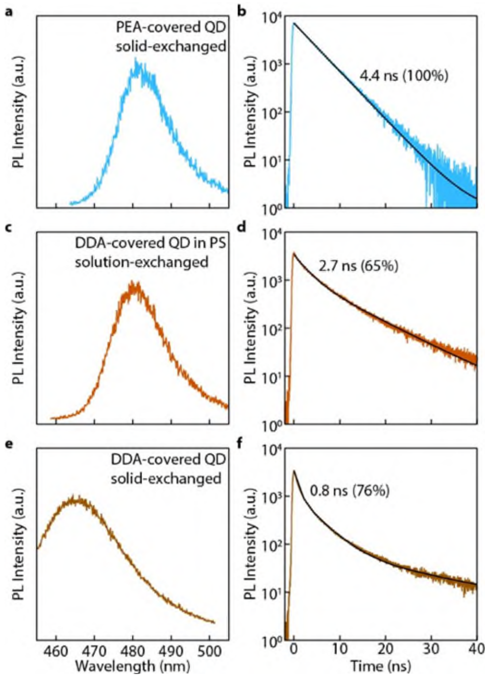


Figure R2.7. Comparison of the PL spectra and lifetime of single $CsPbBr_3$ QDs prepared via (a) solid-state ligand exchange using PEABr (our method), (c) solution-exchange using DDABr then dispersed in polystyrene (reported method), and (e) solid-state ligand exchange using DDABr. (b)(d)(f) Corresponding PL decay traces and the lifetimes of the fastest decay component.

7. The comparison of blinking behavior in Figure 2 is also invalid: QDs covered with DDA were dispersed in polystyrene, whereas those covered with PEA were encapsulated in UV-curing optical adhesives. Include an examination of the blinking behavior of QDs covered with the PEA ligands without encapsulation, or QDs covered with DDA and encapsulated, would make the comparison fairer.

Response 7:

All the samples, including single QDs dispersed in polystyrene, were encapsulated using optical adhesives. We have now added more detailed descriptions to the Methods section in the revised manuscript.

8. The use of the term "non-blinking" (in lines 273, 282, 281…) should be replaced by "nearly non-blinking". Please provide the bin time and size information for all the recorded intensity traces. The fluorescence lifetime intensity distribution (FLID) is an alternative efficient approach to evaluate the blinking behavior, could you please provide these data?

Response 8:

We replaced all the "non-blinking" terms with "nearly non-blinking".

Almost all of blinking traces (unless otherwise noted) were built using a 10 ms bin time. The bin time and sizes of the QDs are now provided in the revised figures and their captions.

We performed FLID analysis on representative blinking traces of PEA-covered QDs (**Figure R2.8**). We used a bin time of 50 ms in this analysis. All FLID plots show no clear blinking characterizations.

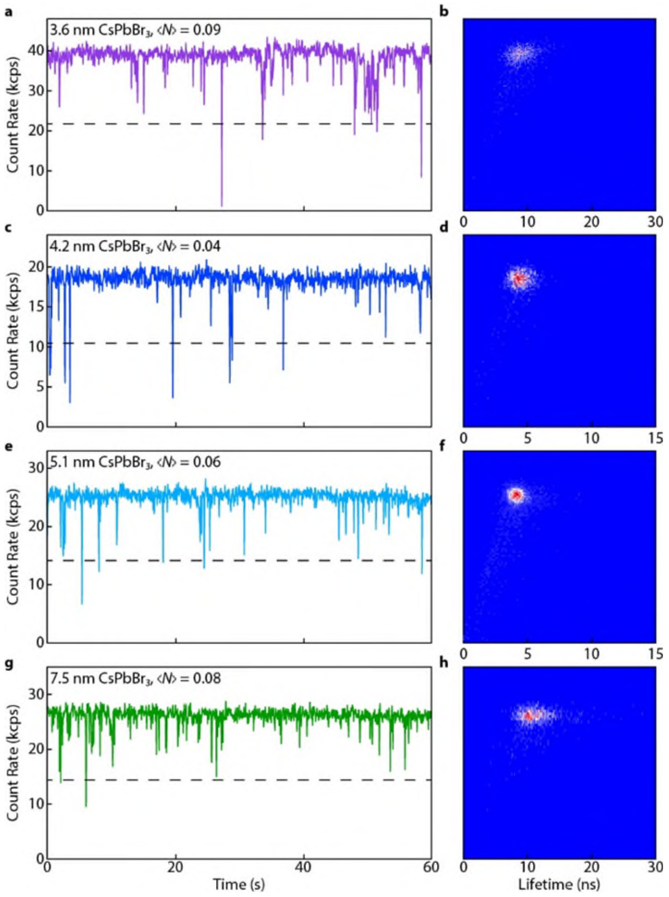


Figure R2.8. (a)(c)(e)(g) Blinking traces (50 ms bin time) and (b)(d)(f)(h) FLID heatmaps of the corresponding single PEA-covered $CsPbBr_3$ QDs.

9. The probability statistical histograms for the different performances (the on-fraction/ Q parameter distribution, the duration of no spectral diffusion and the survive time under continuous excitation) should be provided rather than just a few examples, which will make the results more convinced.

Response 9:

We appreciate the reviewer's careful review and suggestions. **Figure R2.9** shows the probability histograms of the ON fraction, *Q* parameters, and survival time under continuous excitation. It is worth noting that the photostability measurement time is limited to 10 h in this study due to sample stage drift. The actual survival time is expected to be longer than 10 h. These probability histograms are provided in the revised Supplementary Fig. 29.

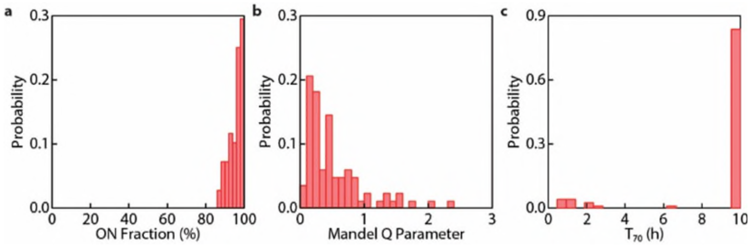


Figure R2.10. (a-b) Probability histograms of (a) ON fraction and (b) Mandel *Q* parameter distribution for blinking traces of 81 PEA-covered QDs. (c) The probability histogram of the duration distribution for QD survival times (defined as the time it takes to reach 70% of the initial PL intensity (T_{70}) when QDs show photodarkening. Most QDs did not show intensity decay over 10 h since the longest measurement time is limited by the sample stage drifting).

10. The long-term stability evaluation is very confusing. How long these single QDs, collection of QDs or ensemble could survive for different performances under continuous excitation? The authors should make it clearer. Please also provide the whole intensity trace (12 h) of Figure 3e.

Response 10:

Figure 3d shows the PL intensity traces of a collection of QDs, measured using a previously reported method (*Nat. Mater.* 2013, 12, 445). In **Figure R2.10**, we show a typical blinking trace of a QD in the laser-illuminated area before and after 12 h of excitations. There are no apparent changes in the blinking behaviours. The probability histograms of survival time extracted from this measurement are presented in **Figure R2.9c**.

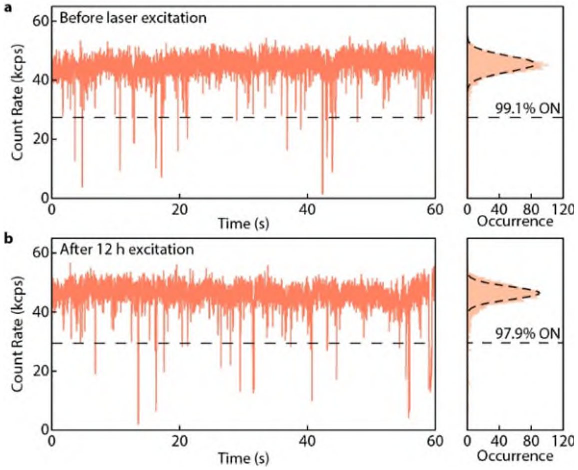


Figure R2.10. Blinking traces of a single 4.1 nm QD (a) before and (b) after 12 h of continuous operations, built with a bin time of 10 ms.

In addition, we now recorded the blinking trace of a single ~ 5.5 nm $CsPbBr_3$ QD over 10 h at a laser power of ~10 W cm^{-2}. Due to the unavoidable sample stage drifting, we needed to manually adjust the position and focus of the single QD every 3 ~ 5 minutes. This leads to the PL intensity fluctuations in the blinking trace, as noted in **Figure R2.11**. Due to the large data size, we show the overall blinking trace (1 minute bin time is used) and 12 separated blinking trace segments with a time window of 2 minutes and a bin time of 10 ms. To the best of our knowledge, this is among the most photostable QDs reported to date, even compared with II-VI QDs with inorganic shells. The new data is summarized in the revised manuscript Fig. 4d, and Supplementary Fig. 21

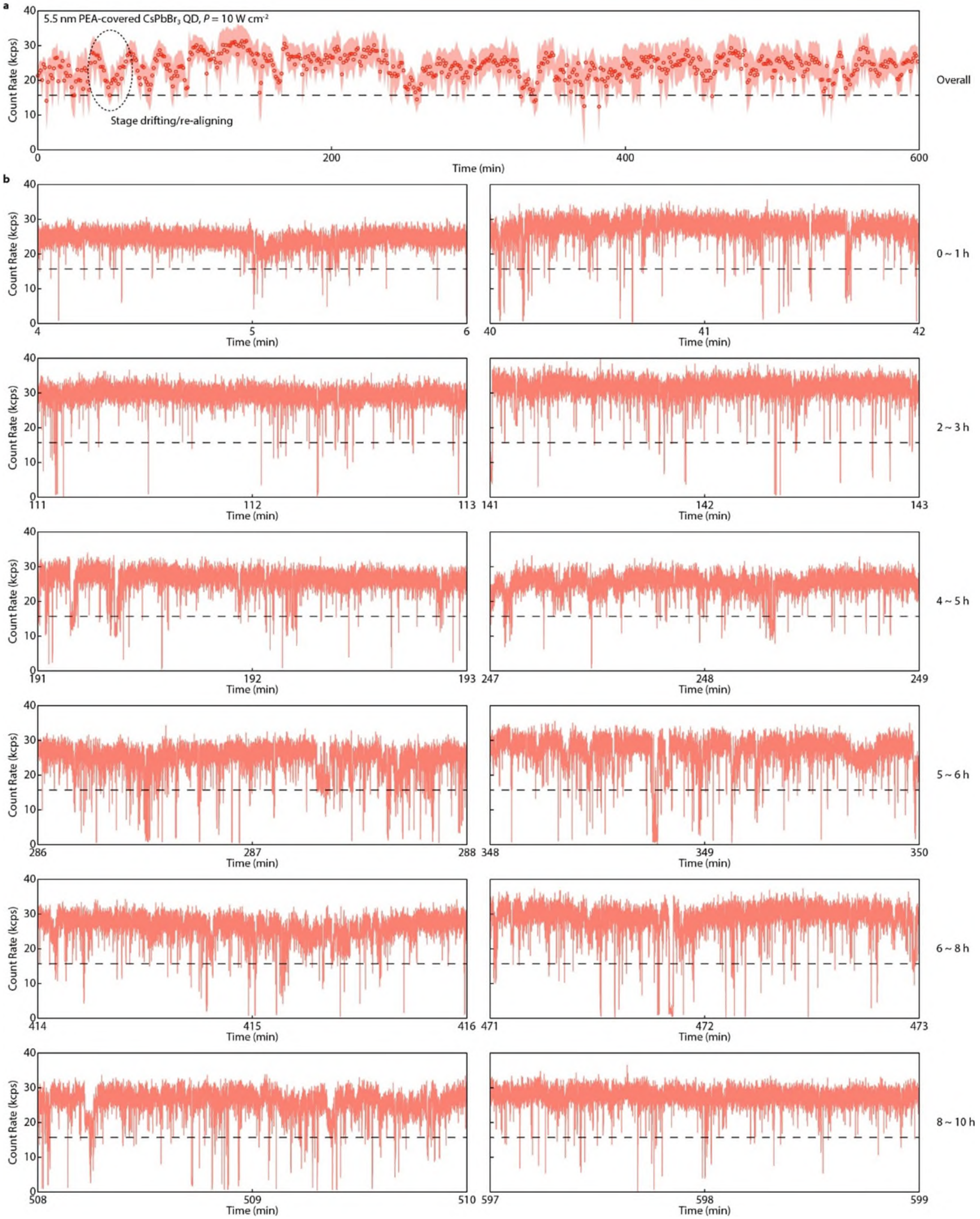


Figure R2.11. (a) The 10 h PL intensity of a single PEA-covered QD with a bin time of 10 ms and averaged over 1 minute. The shaded area indicates the standard deviation. (b) Representative 2-min blinking traces segments (with a bin time of 10 ms).

11. How does the PEA ligand affect the biexciton and exciton lifetimes? Did you observe longer exciton lifetime owing to the full covered surface treatment?

Response 11:

We observed the PEA-covered QDs exhibiting longer lifetimes compared to QDs with native ligands, and the PL decay trace of PEA-covered QDs is mono-exponential, as shown in **Figure R2.12**. This is due to the absence of non-radiative recombination channels. The lifetime of PEA-covered QDs represents the radiative lifetime of excitons in QDs and is consistent with reported values (*ACS Nano* **2023**, 17, 2089–2100)

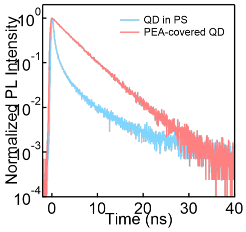


Figure R2.12. Normalized time-resolved PL decay traces for a single QD (5 nm) with native ligand (dispersed in poly-styrene, blue), compared to the PL lifetime of a PEA-covered QD (5 nm, red).

We found no clear trend on how biexciton lifetime changes under the influence of PEA. In general, the PEA-covered QDs exhibit a $g^{(2)}(0)$ value of ~ 0.1. Since $g^{(2)}(0)$ value represents the biexciton quantum yield (*Nano Lett.* **2011,** 11, 1136–1140) and assuming that biexciton radiative lifetime is ¼ of the single exciton radiative lifetime (~ 12 ns), we estimated the biexciton recombination lifetime to be ~ 300 ps, which agrees well with the reported value of 230 ~ 770 ps (*J. Phys. Chem. Lett.* **2018,** 9, 6934–6940). This suggests that the biexciton lifetime is mainly determined by its Auger recombination rate and is not significantly impacted by the QD's surface ligand coverage.

12. Please provide the histograms of size distribution for the $CsPbBr_3$ QDs of various sizes and the PEA-exchanged QDs in Supplementary Fig. 6.

Response 12:

The size histograms are provided in **Figure R2.13** and Supplementary Fig. 8.

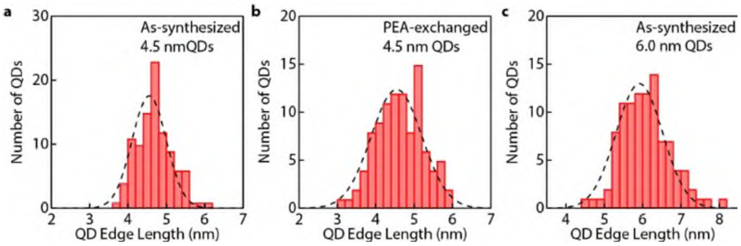


Figure R2.13. Histograms of size distribution for (a) as-synthesized $CsPbBr_3$ QDs and (b) PEA-exchanged QDs, corresponding to the *previous Supplementary Fig. 6* (revised Supplementary Fig. 8). (c) Histogram of size distribution for another batch of QDs.

13. Generally, as the size increases, the average of $g^{(2)}(0)$ tends to increase, as indicated by references 9-12 in Supplementary Fig. 15. Can you explain why the measured $g^{(2)}(0)$ are much smaller than the reported $g^{(2)}(0)$ with similar size? Please also provide the error bar of the measured $g^{(2)}(0)$.

Response 13:

We have provided error bars on the $g^{(2)}(0)$ plot in **Figure R2.14** (also in the revised Supplementary Fig. 29).

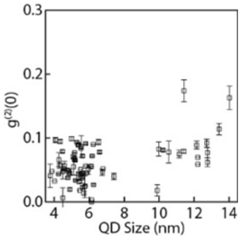


Figure R2.14. $g^{(2)}(0)$ values plotted as a function of QD sizes. The error bars represent standard deviations.

Figure R2.14 shows a clear trend that the $g^2(0)$ values increase when the QD sizes increase to above 10 nm. However, we did not observe a clear trend in $g^2(0)$ values when the QD sizes reached the strong quantum confinement region. Considering the fast biexciton Auger recombination rates in strongly confined $CsPbBr_3$ QDs (~ 20 ps), the theoretical $g^2(0)$ value can reach ~ 0.02, which is close to our average $g^2(0)$ values (0.05).

According to reported discussions (*Nano Lett.* 2012, 12, 9, 4477–4483), the $g^{(2)}(0)$ values will increase when there are intermediate emissive states such as grey states and emissive trion states. Almost all defects are passivated in our nearly non-blinking QDs, and the intermediate emissive states are largely removed (manifested as low Q parameters). Therefore, our study's smaller $g^{(2)}(0)$ values are attributed to the suppressed blinking. The detailed discussion has been added to Supplementary Note 9.

For Reviewer #3:

In this manuscript, Chenjia Mi, et al., report functional surface ligands for perovskite quantum dots (QDs) to improve their emission properties as single photon emitters, mainly focusing on non-blinking behavior in single QD level. Using phenethylammonium (PEA) ligands with attractive p-p stacking, they simulate and claim that these ligands can provide nearly complete passivation of the QD surface, which helps reduce or remove surface defects that are known to responsible for charge trapping, in sharp contrast to DDA ligands with two long chains that yields incomplete surface coverage. This is well analyzed by density functional theory (DFT) calculations, which supports the experimental results. In experiment, using PEA ligands, they demonstrate non-blinking single-dot emission with ON time > 95 % from individual $CsPbBr_3$ QDs. Side-by-side comparison to DDA ligand-covered QDs convinces the dramatic improvements in single-dot emission properties, such as blinking-free, reduced spectral diffusion, and long-time stability. The strategy to use PEA ligands was also applied to different sizes of $CsPbBr_3$ QDs, especially in strongly confined regime, where photon-charging is known to be more stronger due to enhanced exciton-surface interaction, and they observed non-blinking emission from these size-varied QDs.

Severe blinking from perovskite QDs in single-dot level is a long-standing issue, especially to be used as single emitters. As pointed by the authors, unlike Cd-based QDs, effective shelling to suppress blinking behavior is not known yet for perovskite QDs, and the use of function ligands reported in this manuscript would be helpful and informational to the community. However, I feel that this manuscript should be improved to be published in Nature Communications because of the following reasons.

We thank the reviewer for the positive comments and constructive suggestions that helped improve our work. In the revised manuscript, we have extended the passivation strategy to $CsPbI_3$ QDs, provided the statistics for the single QD emission properties, and added discussions about the observed non-monotonic trend of the size-dependent exciton radiative rates.

Major concerns;

1. Author should be able to extend the use of PEA ligands to perovskite quantum dots with different chemical components, such as $CsPbI_3$, $CsPbCl_3$, and their mix, and demonstrate non-blinking behaviors.

Response 1:

We appreciate the reviewer's insightful suggestions.

We have prepared PEA-covered $CsPbI_3$ QDs of various sizes following our solid-state exchange approach using PEAI instead of PEABr. The resulting QDs exhibit nearly non-blinking behaviour (**Figure R3.1**). In addition, the PEA-covered $CsPbI_3$ QDs also exhibit significantly improved photostability, allowing for a continuous excitation for over 7 h while remaining nearly non-blinking (**Figure R3.2**). These data have been added to the revised manuscript Fig. 2, Supplementary Fig. 16 and 22.

$CsPbCl_3$ QDs emit in the UV spectral region. Unfortunately, our instruments (most of the optics and the single-photon detectors) are not compatible with UV radiations.

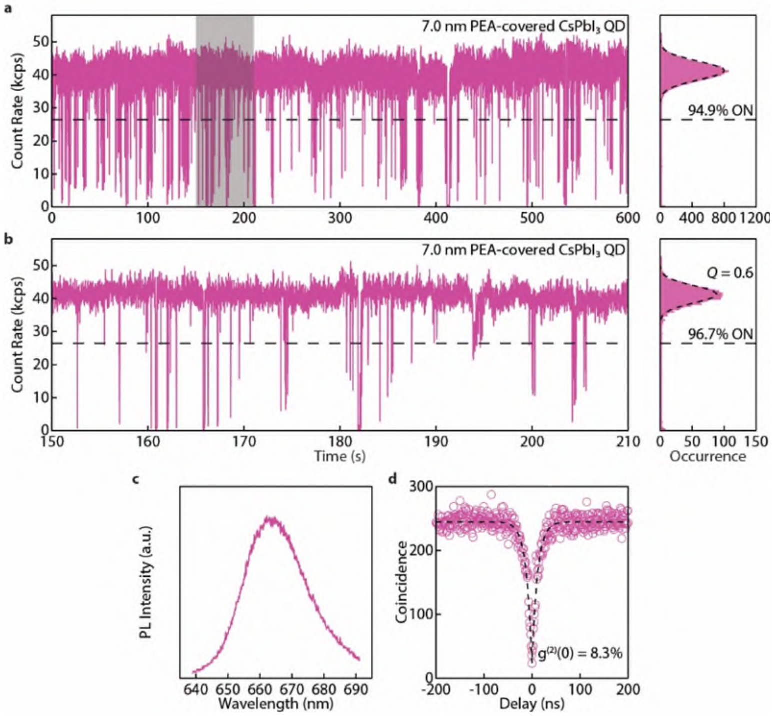


Figure R3.1. (a – b) PL blinking traces (with a bin time of 10 ms) and intensity distribution histograms of a ~ 7.0 nm PEA-covered $CsPbI_3$ QD. (b) shows zoomed-in view of the blinking traces with a 1 min time window indicated by the shaded area in (a). The intensity distribution histograms are shot noise limited with a *Q* parameter of 0.6 in (b). The distributions are fit by Poissonian functions (dashed curves). (c) PL spectra of the QD. (d) Second-order correlation ($g^{(2)}$) function of the QD, fitted (dashed curve) to yield a $g^{(2)}(0)$ value of 8.3%. The QDs were excited by a 405 nm laser at *cw* mode with an intensity of 20 W cm^{-2} for these measurements.

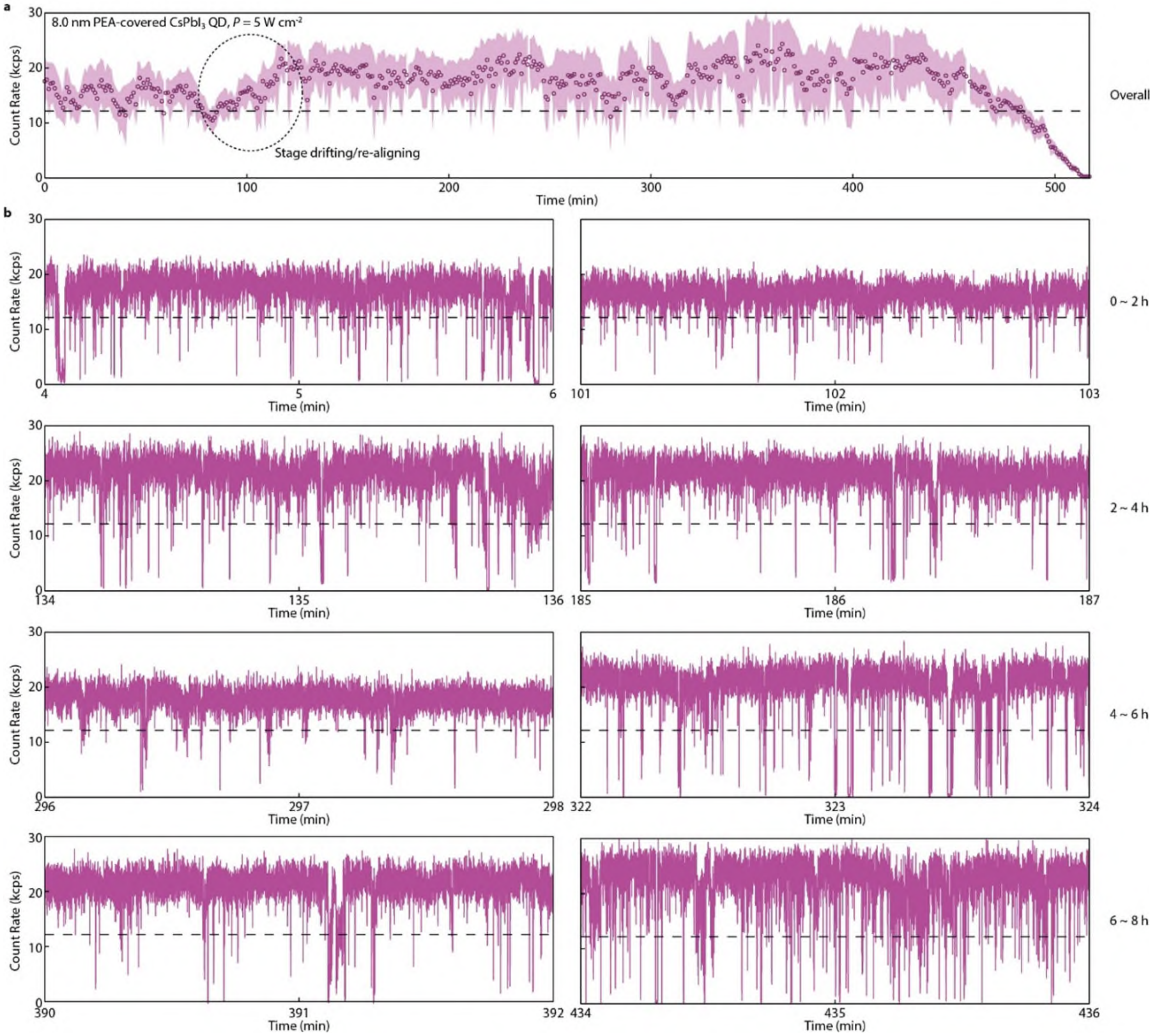


Figure R3.2 (a) PL intensity trace of a single 8.0 nm PEA-covered $CsPbI_3$ QD measured continuously over 8.5 h, binned every 10 ms and averaged for every 1 min. The shaded area marks the standard deviation. The QD was excited with 405 nm laser at an intensity of 5 W cm^{-2}. (b) Representative 2-min segment blinking traces (10 ms bin time).

2. Does all QDs show non-blinking emission with > 95% ON time? Please provide the statistics of ON time distribution (and any related emission properties) including QDs in different sizes.

Response 2:

We now provide statistics on PL ON fractions, *Q* parameters, and $g^{(2)}(0)$ values for 81 QDs, varying sizes from 3.6 nm to 14 nm in **Figure R3.3**. The ON fraction is generally greater than 85%, with an average of 94.7% and a standard deviation of 3.8%. These statistics are provided in the revised Supplementary Fig. 29. The statistics of PL radiative rates and the PL spectral position/FWHM have been shown in the manuscript Page 15, Fig. 6.

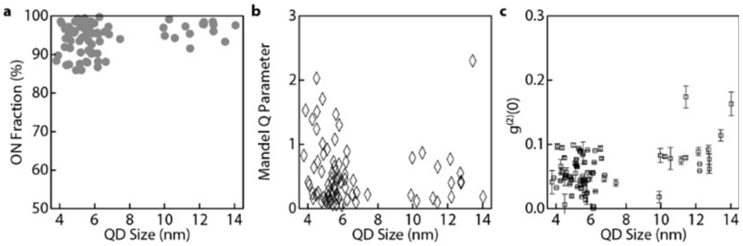


Figure R3.3. Statistics of emission properties: (a) ON fraction, (b) Mandel *Q* parameter and (c) $g^{(2)}(0)$ value of 81 QDs with size varying from 3.6 nm to 14 nm. Error bars on the $g^{(2)}(0)$ data points indicate the standard deviation.

3. I do not agree with the claim that there is "no" spectral diffusion. Can author quantify the error? If there is no change at all, it should be understood considering the spectral resolution of the system.

Response 3:

We appreciate the reviewer's careful review. We agree that spectral diffusion and jumping can happen through multiple mechanisms, and some of them may not be able to be resolved in our study. Here, we focus on those induced by QD charging. For room-temperature measurements, the instrument can detect a spectral diffusion of ~2.5 meV, which is limited mainly by random noise. We then revised our description of the room-temperature spectra as: "no observable spectral diffusion/jumping over 2.5 meV."

In addition, we measured our PEA-covered QDs at ~ 3 K using a higher-resolution grating, as shown in **Figure R3.4**. We found that the ~ 13 nm $CsPbBr_3$ QDs show no observable spectral diffusion larger than 0.1 meV, and the strongly-confined QDs (~ 5 nm) exhibit no observable spectral diffusion over 0.5 meV (both measurements were limited by the spectrograph camera resolution). The potential spectral diffusions are considerably smaller than the spectral jumping (~ 17 meV) and spectral fluctuation (~ 1 meV) (*Science* **2019,** 363, 1068–1072).

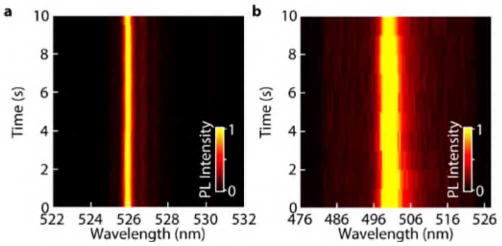


Figure R3.4. Time-resolved steady-state PL spectra of PEA-covered (a) weakly confined and (b) strongly confined QD at 3.2 K. The spectra were collected at a rate of 0.5 s per frame (a) and 1 s per frame (b), with an energy resolution of 0.1 meV per pixel for (a) and 0.5 meV per pixel for (b).

4. In Fig. 2g, probability distribution of ON/OFF durations are obtained from blinking traces of "60" $CsPbBr_3$ QDs. I'm not sure it is correct since this distribution is normally analyzed from one single emitter, not from multiples. And, there should be dot-to-dot variation on ON/OFF durations.

Response 4:

We appreciate the comments and suggestions. The probability distribution analysis on a collection of QDs is to understand the effectiveness of our ligand passivation approach. This method was previously used to study CdSe single QDs (*Nat. Mater.* **2013,** 12, 445–451). In the revised manuscript, we have also continuously measured a single QD blinking trace over 10 h, and a probability distribution of ON/OFF durations for this single QD is obtained (**Figure R3.5**). The K_{ON} and K_{OFF} values from a single QD and the 60 isolated QDs are similar, suggesting relatively small dot-to-dot variations. We have added this analysis to the revised manuscript Fig. 2i.

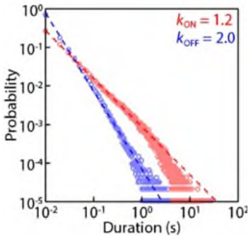


Figure R3.5. Probability distributions of ON/OFF durations obtained from a single PEA-covered QD (~ 5.5 nm) blinking trace measured for 10 h.

5. In lines 274 – 277, a large variation on $g^{(2)}(0)$ is attributed to QD blinking. Do the authors observe any relationship between ON time and $g^{(2)}(0)$ values?

Response 5:

We have summarized the $g^{(2)}(0)$ values of QDs with carious ON time fractions (**Figure R3.6**). We do not observe a clear relationship between the ON time and $g^{(2)}(0)$ values.

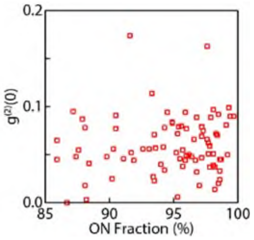


Figure R3.6. $g^{(2)}(0)$ values plotted as a function of ON time fractions of 81 PEA-covered QDs (3.6 – 14 nm).

Considering the fast biexciton Auger recombination rates in strongly confined $CsPbBr_3$ QDs (~ 20 ps), the theoretical $g^{(2)}(0)$ value of strongly confined QDs can reach ~ 0.02, which is close to our average $g^{(2)}(0)$ values (0.05). According to reported discussions (*Nano Lett.* **2012**, 12, 4477–4483), the $g^{(2)}(0)$ values will increase when there are intermediate emissive states such as grey states and emissive trion states. Almost all defects are passivated in our nearly non-blinking QDs, and the intermediate emissive states are largely removed (manifested as low *Q* parameters). Therefore, our study's smaller $g^{(2)}(0)$ values are attributed to the suppressed blinking. These discussions have been added to the Supplementary Note 9.

6. In lines 297 - 302 and Fig. 5b; I'm not quite sure that there is a trend in radiative rate vs PL peak energy. Do the authors also observe the same trend for ensemble samples?

Response 6:

We measured PL lifetimes for five QD colloidal samples (**Figure R3.7**). The average sizes of QDs are estimated using their PL peak positions. The size-dependent radiative rate (corrected by the PLQY following the method reported in *Nano Lett.* **2016**, 16, 4, 2349–2362) exhibits a similar trend as the single QD measurements. It is worth noting that rates are systematically slower for QD colloids. This is presumably due to the smaller refractive index of the hexanes compared to that of the PEABr crystalline films (*ACS Photonics* **2018**, 5, 4139–4146, *ACS Nano* **2015**, 9, 1801–1808).

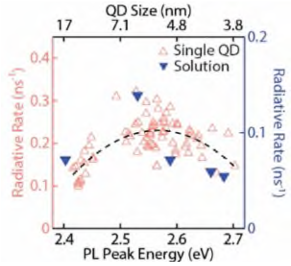


Figure R3.7. Radiative rates of QDs of various sizes obtained from PL lifetime measurements using ensemble QD colloids (blue solid triangles), and statistics of exciton radiative recombination rates of 81 non-blinking PEA-covered QDs with different sizes (red open triangles). The dashed curve is a visual guide. The overall lower radiative rate can be attributed to the smaller dielectric constant of hexane compared to PEABr solids.

7. What are the quantum yields of the samples used in this study?

Response 7:

The PLQY of the as-synthesized QDs are listed in **Table R3.1**, estimated using Rhodamine 6G as the standard. This is also reported in the Supplementary Table 1.

Table R3.1. PLQY of as-synthesized QDs.

QD Size	PL peak wavelength	PLQY
> 10 nm	515 nm	64% ~ 95%
5.1 nm	491 nm	58% ~ 92%
4.2 nm	478 nm	39% ~ 86%
3.6 nm	467 nm	38% ~ 67%
3.0 nm	462 nm	34%

Minors;

1. Please make the y-axis scale the same for Figs. 1b and 1d, then one can catch the difference easily, without misleading.

Response 1:

We have made the corresponding changes to Fig. 1.

2. In Fig. 2f, it is not easy to see the dip at zero time. Please include a sub-figure (or something) that zooms in near zero-time delay.

Response 2:

We have added an inset presenting a close view of the $g^{(2)}$ function near zero-time delay in Fig. 2.

3. Indicate the bin time in each (sub) figure that displays single-dot intensity trajectory.

Response 3:

For all blinking traces in Fig. 2 – 5 in the revised manuscript, a 10 ms bin time was used. We have noted the bin time in each figure's caption. We have also noted all bin time used (mostly 10 ms) in all the blinking traces presented in Supplementary Information.

4. In Fig. 2c, the start time should not be zero.

Response 4:

We have made the corresponding changes to Fig. 2.

We really appreciate the careful and constructive review.

Response Letter to Reviewers' Comments

For Reviewer #1:

The authors have revised the manuscript and adequately addressed three out of the four main points raised in the previous referee report. However, the explanation of the non-monotonic size-dependent radiative lifetime appears speculative and could be rephrased to avoid potential misunderstandings. A general statement suggesting that this aspect requires more detailed experiments may be a better approach. The manuscript can now be considered for publication.

We appreciate the suggestions and comments. We have rephrased the discussions on the size-dependent radiative lifetime in the revised manuscript (page 17 – 18). We now clearly state that more experiments and studies are needed to understand this observation. We again appreciate the constructive review provided by the reviewer.

For Reviewer #2:

I greatly appreciate the authors' efforts in their detailed reply that partially addressed my previous comments as well as for extending the method of ligand replacement by annealing organic halide molecules (e.g. PEABr) with perovskite nanocrystals in a small amount of solution to iodine-based perovskite systems. However, I am unable to recommend the current manuscript for publication in Nature Communications.

We appreciate the careful review, which helped us to improve our work and manuscript. In this revision, we edited the manuscript to explain this work's significance and unique contributions more clearly. We provide additional discussions and data to demonstrate that our current work fundamentally differs from our previous work. In summary, our current study reveals that the attractive intermolecular interaction of ligand tails can lead to significantly improved resistance to photodarkening of single perovskite QDs in the solid state. The ligand tail engineering enabled stable single QDs under long-time (~ 12 h) or high-intensity photoexcitation (saturated) have not been demonstrated before, including our previous work.

Comments:

1. The authors' supplement to the article basically shows that a suitable conjugated ligand system is conducive to adequate surface passivation to achieve further suppression of the blinking issue. However, by comparing this work with the authors' previous work (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474), there is indeed a lack of novelty regarding of material preparation and application topics.

Preparation method in this manuscript: "In the glovebox, 200 mg PEABr was dissolved in 1 mL of anhydrous DMF and filtered through a PTFE syringe filter (VWR, 0.22 μm pore size). The stock QD colloid was diluted using anhydrous octane to ~ 200 pM. For the solid-state ligand exchange, 150 µL of the PEABr solution was spin-coated on a clean coverslip at 4000 rpm. After ~ 35 s (~ 15 s for larger QDs), 10 µL of the dilute $CsPbBr_3$ QD colloid was swiftly dropped on the coverslip while spinning. The coverslip was then annealed on a hot plate at 50 – 70 °C for 30 – 120 s. Then, the sample coverslip was covered by a glass slide. The gaps between the coverslip and the glass slide were sealed using UV curing optical adhesives (Thorlabs NOA61).”

Preparation method in the previous work (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474): “To prepare SCPQD in PEABr matrix sample, 150 µL of PEABr DMF solution (250 mg/mL) was dropped onto a coverslip then spin-cast using a two-step procedure: first at 1000 rpm for 10s and then at 5000 rpm for 1 min. After 20s of spinning when the spin rate reaches 5000 rpm, 10 µL of the diluted SCPQD colloid was dropped onto the coverslip. The sample coverslip was annealed at 70 °C for 2 min and then encapsulated using optical adhesives.”

Both of them all achieved ligand replacement by annealing the organic halide molecule PEABr with perovskite nanocrystals in a small amount of solvent. Furthermore, the reviewer feels that it is inappropriate for the authors to describe this preparation process as "solid-state ligand exchange".

And the application topics are all aimed at the suppression of blinking in single-photon emission.

Therefore, this manuscript is in fact a mechanistic or an incremental supplement to the previous discovery of the authors. However, looking through the entire manuscript, the authors do not mention this previous work at all (and even cite this previous finding in a way that misleads the readers, as shown below), but instead describe this as a completely new discovery, which the reviewer believe is inappropriate.

The content described for the previous finding (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474) in the main text: “Particularly, perovskite QDs show severe PL intermittency (“blinking”) and photodegradation when their sizes are smaller than their exciton Bohr diameters.17-19”, where the reference 17 is the previous finding of the authors (J. Phys. Chem. Lett. 2023, 14, 23, 5466–5474).

Response 1:

The preparation methods in this work were inspired by the solvent-engineering method to prepare crystalline thin films and the solid-state ligand exchange methods. Following the reviewer's suggestion, we have changed the term “solid-state ligand exchange” to “solution-engineering ligand exchange.”

Herein, we discuss the novelties in our current work regarding the material preparation and application topics.

i) Material preparation:

In our previous work (*J. Phys. Chem. Lett.* **2023**, 14, 23, 5466–5474), we heated the QDs in saturated PEABr solution to utilize the high chemical potential of bromide anions to fill the bromide vacancies on QDs; similar results can also be achieved using other organic ammonium bromide salts. The effect of ligand tails was not discovered in our previous method. In the current work, learning from solvent-engineering methods to prepare crystallized thin film, we tuned spin-coating parameters to focus on achieving ligand exchange and tail stacking using solution engineering to facilitate PEA crystallization on QDs.

The solution-engineering process is very sensitive to the spin rate and the anti-solvent dripping time. It has been widely reported that thin-film materials produced by solvent-engineering protocols are very sensitive to spin-coating parameters (*Nat. Commun.* **2021,** *12*, 1878, *Phys. Chem. Chem. Phys.* **2020,** *22*, 26592-26604, *Adv. Mater.* **2021,** *33*, 2005410, *Adv. Sci.* **2022,** *9*, 2201807). In our current work, spin rate and acceleration, solution-dripping time, and drying/annealing conditions were carefully developed to facilitate ordered ligand tail stacking. To support this, we have compared the absorption spectra of the as-prepared thin films using the current and the previous procedures. As shown in **Figure R1**, in the film prepared using the previous method, the absorption features corresponding to both π-π* and n-π* transitions blue-shifted compared to the film prepared using our current method, of which the PEA stacking extent is comparable to that of pristine PEABr crystals. Additionally, the n-π* absorption peaks are less distinct in films prepared using our previous method. This suggests that our previous method failed to yield well-stacked PEA ligand tails, whereas our current method promotes ligand tail stacking, which is necessary for achieving the nearly blinking behaviour and, more importantly, extraordinary photostability for our single perovskite QDs.

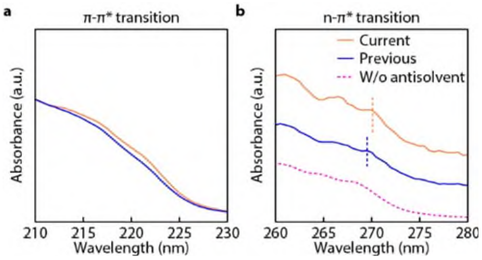


Figure R1. Absorption spectra of PEABr thin films prepared using the current method (orange) and the previous method (blue). Both **(a)** the π-π* transition and **(b)** the n-π* transition features of the sample prepared using the previous method exhibit a blueshift. The absorption spectrum of a thin-film PEABr sample prepared without dripping anti-solvent (pink, dotted) is plotted for comparison, showing indistinct n-π* transition features. The vertical dashed lines mark the lowest energy peak positions.

It is also worth noting that the QDs used in our two works are also different: spherical QDs were used in the previous work, while cubical QDs were used in the current work (**Figure R2**). The (100) facets favoured in cubical QDs can facilitate the strong π-π interaction of PEA ligands due to smaller inter-ligand distance.

[Figure redacted]

Figure R2. STEM images of QDs used **(a)** in our previous work (*J. Phys. Chem. Lett.* **2023**, 14, 23, 5466–5474, reproduced) and **(b)** in the current work (reproduced).

To better elaborate on our current method, we added more detailed solution-engineering parameters, including the acceleration rate during spin coating and the detailed dripping time of each QD size, in the revised Supplementary Fig. 36 (also attached as **Figure R3**). In summary, our current preparation method, despite sharing certain procedures with our previous one, are distinct and novel since it is carefully developed and targeting specifically on promoting ligand tail stacking, which subsequently leads to unprecedently photostable single perovskite QDs.

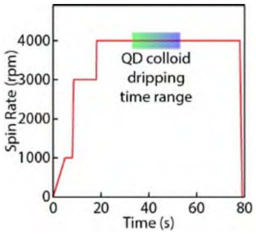


Figure R3. Spin coating program and parameters. The red curve shows the programmed spin rate and stepped acceleration. The coloured window indicates the optimized time range for dripping the QD colloids to achieve solution-engineering ligand exchange. The exact dripping time depends on the QD size (earlier dripping for increasing QD sizes, detailed added in the Methods section).

ii) Application topics:

Our previous work proposed a new blinking mechanism (biexciton-like Auger blinking) in strongly confined perovskite QDs. Although we must suppress other blinking behaviours (i.e. trion Auger blinking) in the otherwise very dim QDs, it was not the main topic discussed in the paper. In fact, the QDs in our previous work were still considered blinking, especially when moderate excitation intensity was used (**Figure R4**). In contrast, our current work aims to significantly improve the photostability of the QDs under long-time and intense light excitations while the QDs' blinking is almost eliminated (**Figure R4**).

[Figure redacted]

Figure R4. Comparison of the blinking traces and intensity distribution histograms of two similar single $CsPbBr_3$ QDs **(a)** in the previous (*J. Phys. Chem. Lett.* **2023**, 14, 23, 5466–5474, reproduced) and **(b)** in the current work, under similar excitation intensities. When applying the ON/OFF threshold in this work, the ON time fraction of the previous QD becomes 77.8%, much lower than that of the current QD (98.0%). The previous QD exhibits a much larger Mandel Q parameter, owing to the biexciton-like Auger blinking mechanism we discussed in our previous work.

The photo instability of perovskite QDs, especially single QDs with strong size confinement, has been a long-standing problem for their practical applications. The labile perovskite QD surface makes it vulnerable to photodarkening and blinking intensified by photo-illumination. Our current work reveals that the attractive ligand-tail interactions can significantly stabilize perovskite QDs. To better demonstrate that our current study aims at solving perovskite QD photostability issue, which is not the topic in our previous work, we have compared photostability of both single QDs and a collection of multiple single QDs fabricated using our previously reported method with that of our current QDs. QDs from our previous work still experience severe photodarkening and irreversible photodegradation under continuous photoexcitation. These QDs show photostability comparable to the IPA-covered QDs without ligand tails stacking effects, and both are much inferior to the stacked PEA-covered QDs in our current work (**Figure R5**). This suggests that ligand tail engineering is crucial to achieving photostable single perovskite QDs. Our current QDs exhibit nearly non-blinking over 10 h continuous operation, showing ~ 100-fold improvement than the QDs we reported previously, making them one of the most photostable (in the aspect of both blinking suppression under intense photoexcitation and long-term durability) single colloidal QDs. We believe our current work makes a progress towards practical single-photon source applications using perovskite QDs.

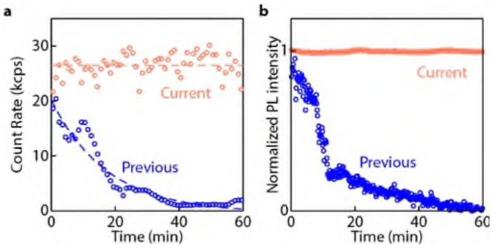


Figure R5. (a) PL intensities of a single $CsPbBr_3$ QD prepared using the previous method (blue), measured over 1 h of continuous laser excitation, binned every 10 ms, and averaged over every 1 min (dashed curves are visual guides). **(b)** Normalized PL intensity of a collection of QDs prepared using the previous method (blue) under 1 h of continuous laser excitation. The PL intensity traces of QDs prepared using the current method (orange) are plotted for comparisons: **(a)** a single QD (extracted from Supplementary Fig. 22a, measurements in the 4th hour are shown since the interference of sample stage drifting was insignificant) and **(b)** a collection of single QDs (extracted from Fig. 4f).

To summarize, only the method developed in the current work can promote ligand tail stacking, producing single QDs with unprecedent long-term photostability and robust blinking resistance to high excitation intensities compared to QDs in our previous work. We believe this work is significant since it resolved the long-standing roadblock of fast photodarkening and photodegradation in single perovskite QDs. We also think this work is novel since insights into ligand tail interaction in the solid states are newly proposed for perovskite QDs, to the best of our knowledge, and are absent from our previous work. Therefore, we believe this work is not supplementing our previous discoveries. To more clearly express the target of resolving photostability (including photo-charging (blinking) and photodegradation) in our current work, we have changed the title of the revised manuscript to "Towards non-blinking and photostable perovskite quantum dots" and made corresponding edits to better reflect the novel application topics of this work.

2. In the revised introduction, the authors state, "Particularly, perovskite QDs show …smaller than their exciton Bohr diameters. 17-19." However, they did not mention that a similar method was used previously in Ref.17. The authors should add a paragraph in the main text explicitly discussing how the current work differs from previously published ones in terms of novelty and significance. This will help clarify the unique contribution of this work.

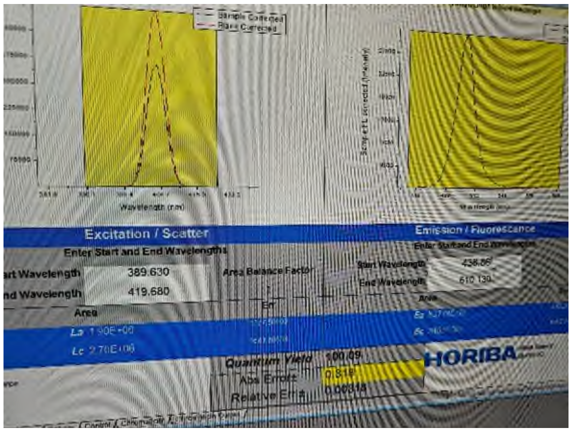
Response 2:

We have added a paragraph to the Introduction (page 3 – 4) and additional discussions to the Results section (pages 10 – 11, 11 – 12, and 14) in the revised manuscript that explicitly compared the current study with our previous work and discussed their differences. Shown in **Response 1**, we have provided detailed solution-engineering parameters in the revised Methods and Supplementary Fig. 36. In the revised Results section, we have also compared the blinking behaviours (page 11) and long-term photostability (revised Supplementary Fig. 20) of single QDs produced using current and previous methods. We hope that the new discussions and data clarify that our current work has achieved uniquely high photostable QDs through ligand tail stacking. We are very grateful for the comments and suggestions that helped us improve the clarity of our manuscript.

3. The authors have demonstrated that the PLQY of diluted solutions of QDs passivated by different ligands did not change significantly. Could you also provide the PLQY of soild-state PEA-exchanged QDs? Additionally, what's the performance of PEA-capped QDs without encapsulation using optical adhesives?

Response 3:

The PLQY of solution-engineering ligand exchanged QDs on the thin-film is near unity (**Figure R6**).



Excitation / Scatter
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Start Wavelength 438.86
End Wavelength 610.130
Area
Quantum Yield 100.09
Abs Error 0.818
Relative Error 0.00818

Figure R6. A screenshot of the result of the absolute PLQY measurement on the solution-engineering ligand exchanged QDs on the thin-film, showing unity quantum yield (with ~5% uncertainty). The experiment was performed on Horiba Fluorolog fluorometer quipped with a Quanta-Φ integration sphere.

The optical adhesive encapsulation isolates the slightly hygroscopic PEABr crystalline thin film from the ambient moisture since water can solvate PEABr and negatively affect ligand stacking. We have measured the blinking trace of a QD covered by stacked PEA without optical adhesive encapsulation (**Figure R7**). The as-prepared QD exhibited nearly non-blinking behaviour under the ambient condition (21 °C, 30 ~ 50 % relative humidity). The QD stays stable for continuous operation over 1 h and starts blinking after 24 h without significant photodarkening or photodegradation. Additionally, QD size degradation due to photo-accelerated chemical reactions with water or other chemicals in ambient did not happen since no spectral shift is observed before or after measurements (Figure R7d, also added to the revised Supplementary Fig. 27).

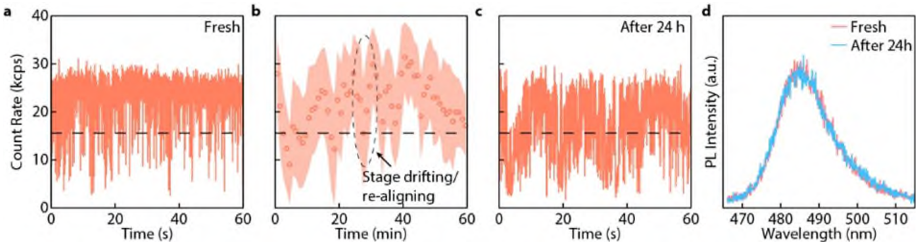

Figure R7. (a) PL blinking trace of a single 4.5 nm PEA-covered QD freshly prepared and unencapsulated, using a bin time of 10 ms. **(b)** PL intensities of the same QD over 1 h continuous operation, binned every 10 ms and averaged over 1 min (shaded areas mark the standard deviation). **(c)** PL blinking trace of the same QD measured after storing the sample in dark for 24 h. **(d)** PL spectra measured for the QD before and after the 24 h storage.

4. In the revised SI Fig. 29c, the average $g^{(2)}(0)$ value is around 0.8 for sizes between 10 to 13 nm, whereas in SI Fig. 30, the value is below 0.5. Could the authors explain this discrepancy?

Response 4:

We appreciate the careful review. We have mistakenly included $g^{(2)}(0)$ values in the averaged values in Supplementary Fig. 30. We have now replaced the average values in Supplementary Fig. 30 (revised Supplementary Fig. 32, also attached here as **Figure R8**) with all the actual $g^{(2)}(0)$ values for improved accuracy.

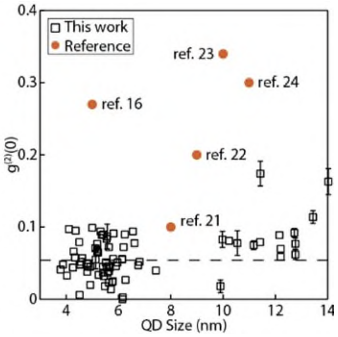

Figure R8. Reported $g^{(2)}(0)$ values of single $CsPbBr_3$ QDs. The $g^{(2)}(0)$ values obtained in this work are shown for comparison. The dashed line is a visual guide that marks the average $g^{(2)}(0)$ value of 0.054 for our strongly confined QDs (< 7 nm)

For Reviewer #3:

I believe that Chenjia Mi, et al. have addressed the questions and concerns that were raised from the original manuscript; especially, extended studies on CsPbI3 QDs to demonstrate PEA ligands capability for perovskite QDs with different chemical components, extensive single-dot statistics, and discussion of spectral diffusion at both room and cryogenic temperature. I appreciate the authors' hard work to improve the quality of this work. Now I recommend the revised manuscript for the publication in Nature Communications.

We really appreciate the constructive comments and suggestions provided by the reviewer.

Response Letter to Reviewers' Comments

For Reviewer #2:

Comments:

After carefully reviewing the additional information provided by the authors, I remain unconvinced that the novelty of the work meets the high standards required for publication in Nature Communications. The central approach for achieving stable perovskite quantum dots still relies on the same conjugated ligand system for surface passivation. Although the current study explores adjustments to the spin-coating parameters and shifts from spherical to cubic perovskite quantum dots in an effort to improve the stacking of PEA ligand tails, as the authors themselves acknowledge—"This suggests that our previous method failed to yield well-stacked PEA ligand tails, whereas our current method promotes ligand tail stacking"—these changes appear to represent only incremental advances over their previous work published in JPCL. Given the lack of substantial novelty, I am unable to recommend this manuscript for publication in a high-impact journal such as Nature Communications.

Response:

Passivating ligands of quantum dots (QDs) have two functional parts: the ligand heads binding to the QD surfaces and the ligand tails imparting the colloidal stability of QDs. While most studies focused on improving the affinity between the ligand heads and the QD surfaces, the effect of ligand tails on QD photostability, particularly when QDs are isolated and immobilized in the solid state, received less attention. Our previous work (*J. Phys. Chem. Lett.* **2023**, 14, 5466–5474) only targeted taking advantage of *the halide-containing ligand head group* and low steric hindrance of PEABr accompanied by n-butylammonium bromide to fill the bromide vacancies to enhance the photoluminescence quantum yield of perovskite QDs. However, the effect of *the ligand tail* stacking was absent and not targeted. Our current work has revealed that *ligand tail packing through attractive intermolecular interaction is critical to achieving superior single QD photostability.* The resultant single $CsPbBr_3/I_3$ QD single-photon emitters that can remain nearly non-blinking after > 12 h continuous operation and can sustain saturated laser excitations are firstly reported and represent a *significant advance (~ 100-fold enhanced photostability)* over QDs prepared in our previous work (data included in the last letter under Response #1). To our knowledge, this is the first time that the critical role and degree of ligand-tail intermolecular interaction in the solid state has been discovered. Moreover, our current work provides new insights into tuning intrinsic excitonic dynamics and exciton-surface lattice couplings that are otherwise difficult to modify by changing ligand tails and their intermolecular interactions. We thus believe our findings are novel and can impact the future design of colloidal perovskite QD-based single photon emitters.

We now provide a side-by-side comparison between this work and our previous work to better address their differences in **Table R1** below. We have also revised the introduction paragraphs that were added during the last revision suggested by the reviewer, in which the different aims between our previous and current works are clearly discussed. The different single QD photostability between the two works is also discussed in detail in the Results Section (highlighted in the revised manuscript). The revised paragraphs are attached here:

Reducing the steric hindrance of ligands can promote ligand access to QD surfaces. Since halide vacancies on the QD surface are proven optical traps,[36] excess small ligand molecules containing halides can repair the QD surface and improve the PLQY. Previously, we aimed to supply excess ammonium bromides using small-sized ligands to enhance the PLQY of single $CsPbBr_3$ QDs.[42] By immersing the n-butylammonium bromide (NBABr) treated QDs in a small amount of saturated phenethylammonium bromide (PEABr) solution followed by heating, surface halide vacancies on the $CsPbBr_3$ QDs were efficiently filled, resulting in QDs with suppressed trion-induced blinking. This allowed us to discover a biexciton-like Auger blinking mechanism in strongly confined QDs at increased excitation intensity. However, the QD PL intensity still fluctuates, and the resistance to photodarkening was not demonstrated. This suggests that simply reducing the ligand steric effect is inadequate. Instead, we posit that the attractive inter-ligand-tail interaction is a critical yet missing factor toward non-blinking and photostable perovskite QDs.

In this work, we focused on studying the impact of ligand tail stacking on the photostability of $CsPbBr_3/I_3$ QDs in the solid state. Using density function theory (DFT) calculations and a combination of low-frequency Raman and single QD PL spectroscopies, we demonstrate that attractive π-π interaction between PEA ligand tails can significantly reduce the QD surface energy in the solid state and the degree of ligand tail stacking is critical to achieving nearly non-blinking and photostable QDs. Ligands on strongly confined $CsPbBr_3/I_3$ QD surfaces with long-chain tails are thoroughly exchanged with PEA using a solution-engineering method that promotes ligand tail stacking. Our single QDs exhibit nearly non-blinking PL emissions with high single photon purities (~ 98%). Furthermore, the stabilized surface lattices endow QDs with unprecedented photostability: they remain nearly blinking-free and photodarkening-free during 12 h of continuous laser irradiation and can sustain excitations at saturation intensities. These advantages enable the determination of size-dependent exciton radiative rates and emission line widths of $CsPbBr_3$ QDs at the single particle level.

Table R1. Comparison between our previous and current works

		Previous work	**This work**
Experimental methodology	**Material**	Colloidal $CsPbBr_3$ QDs, spherical, strongly-confined	Colloidal $CsPbBr_3$ and $CsPbI_3$ QDs, cubical, from weakly- to strongly-confined
	Ligands	PEABr, with the presence of n-butylammonium bromide (NBABr)	PEABr
	Sample preparation	Spin-coating and heating	solution engineering ligand exchange
QD performance	**Blinking behaviour**	PL intensity fluctuation (high Mandel *Q* parameter)	Nearly non-blinking (near-zero Mandel *Q* parameter)
	Operation durability	Photodarkening starts after ~ 3 min.*	Photostable over 12 h
	Excitation intensity	Unstable at high excitation rates	Stable at saturated excitations
Research topic	**Aim**	QD blinking mechanisms and bromide vacancies filling	Impact of the ligand tail intermolecular interaction on single QD photostability in the solid state

*Operation durability was not demonstrated in the previously published work and was later measured on a reproduced sample.