Strong bidentate coordination for surface passivation and ligand-shell engineering of lead halide perovskite nanocrystals in the strongly quantum confined regime

Aaron Malinoski, Guoxiang Hu, Chen Wang*

Department of Chemistry and Biochemistry, Queens College, City University of New York, 65-30 Kissena Blvd., Flushing, NY 11432

*corresponding author. Email: chen.wang@qc.cuny.edu

ABSTRACT
The surface of lead halide perovskite nanocrystals (PNCs) is unique compared to conventional metal chalcogenide or pnictogenide semiconductor nanoparticles for its ionic character and the dynamic ligand layer, which makes them unstable in stock solutions and hinders the development of surface engineering strategies. This work employs a chelating strategy to form stable coordination on the PNC surface. Through screening a series of heterocyclic aromatic carboxylates, we found the best ligand, picolinate (PIC), with exceptional passivation effect to the surface traps of CsPbBr$_3$ PNCs in the strongly quantum confined regime, resulting in > 0.8 photoluminescence quantum yields. The exciton lifetime in the passivated PNC approaches the radiative decay limit in various solvents. From an NMR titration experiment, the binding affinity of PIC is estimated to be at least 15 to 30 folds stronger than the original ligand from synthesis. The NMR and FTIR spectroscopic data and first-principles calculations elucidate the bidentate nature of the PIC coordination at the surface Pb site and the coadsorption of the ammonium-PIC ion pair. In apolar solvents, such as cyclohexane, the binding of PIC is stoichiometric to the available surface sites, suggesting the structure as a potent candidate for anchoring functional molecular structures to the PNC surface. In polar solvents, the strong affinity of PIC on the PNC surface provides protection for carrying out the precipitation-redissolution purification procedure that removes synthetic residual from the as-synthetic PNC samples. By modifying the purification procedure, we also develop a cation exchange procedure to replace the original oleylammonium cation with desired structures that consist of an ammonium anchoring group. Our results provide a direction for constructing strong interactions to protect the vulnerable surface of PNCs and pave the road for developing surface engineering strategies to functionalize these nanoparticles.

KEYWORDS: perovskite nanocrystal, chelating, picolinate, surface engineering, passivation
INTRODUCTION

Inorganic cesium lead halide perovskites have attracted intense research interest for their promising potentials in applications such as optoelectronics\(^1\)\(^-\)\(^3\) and photocatalysis.\(^4\) The advances in nanotechnology enable precise control of the size\(^5\), shape\(^6\)\(^-\)\(^9\), and chemical doping\(^10\)\(^-\)\(^15\) of inorganic perovskite nanocrystals (PNCs), providing abundant approaches to tune the optical and electronic properties of this material.

Surface chemistry is one of the most intriguing fields in the research of nanomaterials. For conventional semiconductor nanocrystals, such as metal chalcogenides, their large surface-to-volume ratio and rich ligand chemistry offer opportunities to mediate the electronic properties and control the exciton behaviors via tailoring the ligand layer.\(^16\)\(^-\)\(^22\) It had been demonstrated that the compact ligand layer could play roles beyond a passive protective shell and act as an active handle to control the accessibility of the semiconductor core to molecules in the environment.\(^23\)\(^-\)\(^26\) Conjugating the nanoparticle and substrates through a designed ligand linker can selectively promote carrier migration.\(^27\) By introducing proper physical and chemical interactions, it is possible to fabricate hybrid superstructures with nanoparticles and molecules that direct the flow of excitonic energy.\(^28\)\(^-\)\(^33\) Through functionalizing the particle surface, researchers have developed various biosensors based on colloidal quantum dots.\(^34\)\(^-\)\(^36\)

PNCs differ from the abovementioned conventional semiconductor nanocrystals because the highly ionic perovskite core is capped with weakly bound, dynamic surface ligands.\(^37\)\(^-\)\(^39\) The vibrant surface delivers opportunities to mediate the shape and dimension of PNCs through modifying the surface ions\(^40\)\(^-\)\(^41\), but more often, the unstable ligand layer leaves a large number of defects and affects the stability of these materials in the solution phase. Although perovskite semiconductors, such as CsPbBr\(_3\), are well-known for defect-tolerance\(^42\)\(^-\)\(^43\), when the dimension approaches the strongly quantum confined regime, i.e., small nanocrystals and thin nanoplatelets,
the loss of excitonic energy becomes severe due to the trapping.\textsuperscript{44} The vulnerable surface also makes it difficult to purify PNCs from the synthetic mixture without losing control of their dimension and surface integrity.\textsuperscript{45-46} Moreover, the lack of stable interaction between the ligand and the perovskite crystal restricts the development of surface engineering strategies for functionalizing PNCs. Although intense research efforts for PNCs have been focused on eliminating surface defects and stabilizing the nanocrystals,\textsuperscript{47-56} until recently, there are only a few reports discussing how surface ligands influence the charge carrier migration from PNCs.\textsuperscript{57-59}

This paper describes the use of cooperative bidentate coordination to realize a strong affinity to the cesium lead halide PNC surface, which do not only reliably protect the vulnerable surface but also provide opportunities to develop the engineering strategy for modifying the ligand shell. Ligands with multiple binding centers have been reported for improving the surface passivation, and stability of PNCs.\textsuperscript{50, 54} We focus on a group of heterocyclic aromatic carboxylates because they integrate two coordination sites that can effectively bind to the Pb-based perovskite surface: the carboxylic group that is connected with aromatic rings as the relatively soft Lewis base\textsuperscript{47}, and the heteroatoms that can donate the lone-pair electrons.\textsuperscript{49, 60} We identify a strong ligand, picolinate (PIC), which has a bound affinity to the PNC surface that is 15 to 30 folds stronger than the original ligands and can quantitatively binding to the PNC surface in apolar solvents. The cooperative chelating coordination of PIC at the surface Pb site is illustrated by NMR and FT-IR spectroscopy and interpreted with first-principle computation. As shown in Figure 1, the strong coordination of the PIC ligand provides effective passivation for surface traps and has the potentials to serve as anchoring motifs for functionalizing the PNC
surface. We also design a cation exchange procedure based on the strong PIC ligand to introduce new cation ligands to the shell.

**Figure 1.** The strongly bound ligand picolinate (PIC) for passivation and modifications of the PNC surface.

**RESULTS AND DISCUSSION**

Heterocyclic carboxylate ligands, in particular, picolinate, can effectively protect the surface of PNCs in various solvents. The PNCs used in the present study are in the strongly quantum confined regime with bandgap energies spanning from 2.51 eV to 2.76 eV, as shown in **Figure 2A**, corresponding to edge dimensions (d) between 3.7 nm and 6.6 nm.\(^{61}\) The photoluminescence quantum yield (PLQY) monotonically decreases with the decrease of the particle sizes (**Figure 2C**) due to the enhanced exciton trapping at surface defects for PNCs in the strongly quantum confined regime (See the **Supporting Information**). The PLQY of PNCs is also sensitive to solvent polarity, as shown in **Figure 2D** and reported in earlier work.\(^{45-46}\) Polar solvents tend to facilitate the detachment of original ligands from the ionic PNC surface and generate more defect sites that lower the PLQY.\(^{51}\) In solvents with high polarities, such as ethyl acetate, the detachment of original ligands is so severe that the exposed defects can induce the fusion of small nanocrystals to large structures with loosened quantum confinement (**Figure**
S2 and S3). The vulnerable PNC surface prevents employing the commonly-used precipitation-redissolution procedure to purify the as-synthesized PNCs. Therefore, it is an urgent need to find ligands that are firmly bound to the PNC surface for protecting the nanoparticles in various environments.

We studied the passivation effect of various aromatic carboxylates and found that all of them can improve the PLQY of PNCs in toluene, as shown in Figure 2B. Two of them, picolinate (PIC) and 2-thiophene carboxylate (TC), can increase the PLQY of the small PNC (d = 4.3 nm) to > 0.8. The UV-vis absorption and PL spectra remain unchanged after passivation (Figure S4). The presence of the carboxylic group and the heteroatom site in the adjacent position is critical to achieve the best passivation. When using the single-role carboxylic ligand, benzoate, to passivate the same PNC, 3000 equivalents of ligands are needed to achieve a PLQY of 0.67. Single-role ligands with lone-pair electrons, such as pyridine and thiophene, show little influence on the PLQY of PNCs in the solution phase (See the Supporting Information, Figure S5), though they were reported as effective passivation reagents for improving the performance of photovoltaic devices made of organic-inorganic hybrid perovskites.60 Titrating PNCs with a mixture of benzoate and pyridine show a similar passivation effect as OlAm⁺BA⁻, which is less effective compared to the heterocyclic carboxylate ligands (Figure S5). Finally, isonicotinate, the para-pattern isomer of picolinate, shows poor passivation among all ligands.

The passivation of PIC is exceptionally effective: with 400 equivalents of addition to the PNC with d = 4.3 nm (corresponding to 3.6 PIC per nm² of the PNC surface), the sample reaches the maximum PLQY of 0.81. The amount of PIC to achieve the optimal passivation is only 25% surpass the total number of Pb atoms on the surface layer of perovskite crystal, suggesting its strong surface affinity. The decline of PL intensity after 400 equivalents is caused by the
degradation of PNCs in the presence of extra PIC. (See the Supporting Information, Figure S6, and S7.) We speculate that at high concentration, the extra amount of PIC anion can etch the PNC by stripping off the surface Pb to form neutral Pb(PIC)$_2$ complexes that are easier to dissolve in the solution phase. The PIC passivation increases the PLQYs of PNCs with all sizes and in various solvents, as shown in Figure 2C and D. The improvement of PLQY is more prominent for samples that originally have a low PL such as small-size PNCs and PNCs in relatively polar solvents. Strikingly, the PIC can prevent the fusion of small-size PNCs in polar solvents, such as ethyl acetate and dimethoxyethane, in which PNCs with the native ligands have poor solubility. (See the Supporting Information, Figure S2, and S3)
Figure 2. (A) Normalized UV-vis absorption and photoluminescence spectra in toluene. The sizes of PNCs are listed in the graph. (B) The change of PLQYS of the PNC with d = 4.3 nm in toluene with the addition of six different passivation ligands: benzoate (BC), thiophene-2-carboxylate (TC), Furan-2-carboxylate (FC), pyrrole-2-carboxylate (PC), picolinate (PIC), and isonicotinate (INC). The amounts of titration ligands are converted to equivalents per PNC. The lines are employed to follow the trend of changes. Molecular structures of the ligands are shown above the graph and coded with the same colors as the PLQY traces. The concentration of the PNC solution is 0.05 µM. Ligands were titrated as their oleylammonium (OlAm⁺) salts to the PNC sample dissolved in toluene. PLQYS were determined with 405 nm excitation. (C) PLQYS of PNCs with different sizes in toluene before and after PIC passivation. All samples have an optical density of 0.22 at 405 nm. Note that the PLQY here for the unpassivated, d = 4.3 nm PNC is higher than the value shown in (B) because we had to use a lower concentration in the titration experiment. For PNCs that are capped with weakly bound original ligands, their PLQY depends on the concentration.¹⁷ (D) PLQYS of PNCs with d = 4.3 nm in various solvents before and after PIC passivation. Abbreviations of the solvents: Pen: pentane, CyH: cyclohexane, Tol: toluene, DCB: 1,2-dichlorobenzene, and CHCl₃: chloroform.
Time-resolved photoluminescence (TR-PL) kinetics (Figure 3A and Figure S8) illustrate that PNC samples consist of two subensembles with distinct exciton decay lifetimes: a fast-decay ensemble that relaxes rapidly at a rate faster than the instrument response (< 0.57 ns) representing the “dark” population of PNCs, and a slowly-decay ensemble featuring observable time constants of 3.2 - 6.2 ns representing the “bright” population. The inhomogeneous emission is common for semiconductor nanocrystal samples, including PNCs.62-63 The PIC passivation has two effects: increasing the population of the “bright” and elongating the observable exciton lifetimes, in which the former is the major contribution to the enhancement of PL in solvents such as toluene, DCB, and CHCl₃. For instance, in toluene, the integrated intensity of the long-lifetime component increases by 2.2 folds upon passivation, while the observed lifetime before and after passivation only elongates from 3.5 to 4.7 ns. In comparison, the steady-state experiment measures a 2.5-fold increase for the PLQY. The initial fast-decay component remains in the kinetics for all passivated samples, suggesting that a subgroup of the “dark” PNCs possess defects that cannot be fully removed with PIC passivation, leading to the less-than-unity PLQY after PIC passivation.
Figure 3. (A) Time-resolved PL kinetics of PNCs with \( d = 4.3 \) nm before (black) and after (red) passivation with PIC recorded in toluene. The kinetics traces of the passivated sample are recorded when the highest PL intensity is achieved by titrating OAm-PIC ligands. The PL intensity is normalized to the maximum of the passivated sample. The kinetic traces are fit to a convoluted function of the IRS function (FWHM = 0.57 ns) and a double-exponential decay. We determine that an exponential component with a time constant that is significantly shorter than the IRS is necessary to yield the best fit of the initial fast decay, but it has no physical meaning because it is beyond the limit of our instrument. The observable lifetimes from the fit of the long-lived decay are listed in the figure. PL kinetics of PNCs in other solvents are shown in the Supporting Information. Lifetimes of the passivated sample in different solvents are plotted as the function of the dielectric factor, \( \frac{(\varepsilon + 2\varepsilon_s)^2}{\varepsilon_s^{5/2}} \), in (B). The red line shows the linear fit for the lifetimes of the passivated samples in different solvents.

For the passivated PNC sample, the measurable exciton lifetimes monotonically decrease with the increase of the solvent optical dielectric constants. In contrast, before passivation, the lifetimes have no apparent correlations with the solvent properties. The radiative lifetime of a
transition dipole within the nanoparticle is proportional to the factor of \( \frac{(2\varepsilon_s + \varepsilon)^2}{\varepsilon_s^{5/2}} \), when considering the dielectric screening effect of the radiating field inside the nanoparticles,\(^{64-65}\) where \( \varepsilon_s \) is the optical dielectric constants of solvents and \( \varepsilon \approx 4 \) for CsPbBr\(_3\) in the pertained spectral window.\(^{66}\) Our measurements of the passivated sample show a good linear relationship when plotted against the dielectric factors (Figure 3B), suggesting that exciton lifetimes in the passivated PNC proximate the radiative limit of PNCs. These lifetimes are indeed very close to the reported lifetimes of PNCs with near-unity PLQY\(^{47-48}\), implying that after PIC passivation, PNCs in the “bright” subensemble are nearly trap-free. Our observation also provides evidence for the close contact between perovskite cores and solvent molecules, as it has been suggested for the PNCs with original weakly bound bound ligands.\(^{61}\)

We summarize the passivation of the PNCs in Scheme 1, with the consideration of exciton traps with different energy levels: the shallow trap that causes the slow non-radiative decay in the nanosecond regime, and the deep trap that is responsible for the ultrafast PL decay beyond the instrument response. These traps are likely induced by different defects, and their distributions in PNCs are affected by solvent properties, as suggested by the PL kinetics (See the Supporting Information). Without passivation, the “bright” subensemble of PNCs must be free of deep traps, which otherwise overrun the radiative process. For these “bright” PNCs, the PIC passivation removes shallow traps and enhances their emission. The more prominent effect of the PIC passivation lies in the elimination of a large portion of defects that induce deep traps, which transforms the original “dark” PNCs to bright. The remaining of a small subensemble of “dark” PNC with an ultrafast PL decay after passivation is similar to persistent traps observed for perovskite nanoplatelets.\(^{62}\) We speculate that these PNCs may have defects inside the crystal that are not accessible by the surface ligands. Another possibility is that due to the relatively large
steric hindrance of the PIC ligands, they cannot fill in all surface sites and leave some particles with partially passivated surfaces. A more detailed investigation on the properties of different types of defects and their interactions with the passivating ligands and the surrounding is currently being carried out in our group.

**Scheme 1.** The PIC passivation effect on PNC subensembles with different defects

The excellent passivation/protection effect results from the strong bidentate coordination of PIC to the PNC surface. To evaluate the bound affinity of PIC, we designed an NMR titration experiment. We added a series of known amounts of OlAm PIC− ligands to the solution of as-synthesized PNCs, as shown in **Figure 4A**. The concentration of OlAm PIC− was kept in the range that the decomposition of PNCs due to the possible formation of Pb(PIC)2 complex was neglectable, as demonstrated in the UV-vis absorption spectra (**Figure S6**). Severe broadening of 1H resonance signals is observed for PIC at 8.4-8.7 and 8.1-8.3 ppm. The broadened NMR signals imply the association of PIC to the nanoparticle surface, which restricts the tumbling and leads to more efficient transversal relaxation, caused by dipolar couplings.67-68 The broadening effect is more prominent for the signal of 1H(I, 8.4~8.7 ppm) than that of 1H(II, 8.1~8.3 ppm), suggesting the former is closer to the PNC surface when bound.68 Since 1H(I) and 1H(II) are located at the opposite positions relative to the pyridine N atom, the distinct
broadening effects illustrate the proximity of the nitrogen to the PNC surface, which implies the participation of the pyridine in coordination with the surface site.

Moreover, the integrated intensities of PIC NMR signals are significantly lower than the expected values based on the addition, as listed in Table 1. It is known for small and rigid ligands that the broadening can be so severe that their NMR signals are obscured when they are tightly bound to the nanoparticle surface. We, therefore, assign the disappeared PIC signals to the tightly bound ligands, while the observed signals to PIC that is dispersed in the solution and undergoes fast exchange.

With this assumption, we model the competitive adsorption between OlAm+PIC− and the coexisted original ligands OlAm+Br− (notated as L) with Langmuir isotherms:

\[
\theta_L = \frac{N_L}{N_{\text{total}}} = \frac{K_{eq}^L[L]}{1 + K_{eq}^L[L] + K_{eq}^{PIC}[PIC]} \quad \text{Eq. 1}
\]
\[
\theta_{PIC} = \frac{N_{PIC}}{N_{\text{total}}} = \frac{K_{eq}^{PIC}[PIC]}{1 + K_{eq}^L[L] + K_{eq}^{PIC}[PIC]} \quad \text{Eq. 2}
\]

in which \(K_{eq}^L = 10.5 \text{ mM}^{-1}\), is the bound equilibrium constant for the original ligand. [L] is the concentration of original ligands in the solution phase, and [L] = \(C_L - \theta_L C_{PNC} N_{\text{total}}\). \(C_{PNC} = 2 \mu\text{M}\) is the concentration of the PNC, and \(C_L = 2.12 \text{ mM}\) is total concentrations of the original ligand determined by NMR for the sample. \(N_{\text{total}}\) is the maximum number of potential Pb sites on one nanocrystal, given by \(N_{\text{total}} = 6 \left(\frac{d}{a}\right)^2\), in which \(a = 0.587 \text{ nm}\) is the dimension of the unit cell and \(d = 4.3 \text{ nm}\). [PIC] is the concentration of PIC dispersed in the solution, obtained by comparing the integrated NMR intensity with the internal standard, and \(N_{PIC}\) is the equivalent number of the disappeared PIC. In this model, the competitive adsorption from oleate (OA−) is not included because OA− is known as a weaker ligand compared to OlAm+Br−, and we estimate the bound affinity of OA− is only 1/250 compared to that of PIC (See the Supporting
Information). It also needs to point out that the model does not consider the inhomogeneity of surface sites.

Figure 4. The evolution of $^1$HNMR signals of PIC when titrating different amounts of OlAm$^+$PIC ligands to the PNC solutions of (A) toluene-D8 (B) cyclohexane-D12. The number of observed PIC ligands per PNC is determined by comparing integrated peak intensities in (A) with that of the internal standard, and the results are listed in Table 1. The molecular structure of PIC is shown to illustrate the $^1$H positions. A spectrum with 350 equivalents addition of PIC in the toluene-D8 solution of PNCs is shown in (B) on the same scale for comparison.

With Eq. 1 and 2, we solve for the bound equilibrium constant, $K_{eq}^{PIC}$, for each PIC titration point, and the results are listed in Table 1. From the different intensities of the $^1$H(I) and $^1$H(II) signals, we obtained average values of $K_{eq}^{PIC} = 310 \pm 60$ mM$^{-1}$ and $150 \pm 20$ mM$^{-1}$, respectively. The affinity of PIC is thus 15~30 folds greater than that of the original ligand, OlAm$^+$Br$^-$.

Table 1 Bound and unbound PIC at different titration points and $K_{eq}^{PIC}$ calculated from the NMR data using Eq. 1 and 2

| Titration (per PNC) | [PIC] H(I)$^1$ (per PNC) | $K_{eq}^{PIC}$ (mM$^{-1}$) based on H(I) | [PIC] H(II)$^2$ (per PNC) | $K_{eq}^{PIC}$ (mM$^{-1}$) based on H(II) |
|---------------------|--------------------------|---------------------------------------|--------------------------|---------------------------------------|
| 100                 | 12                       | 329                                   | 22                       | 136                                   |
| 150                 | 24                       | 262                                   | 38                       | 136                                   |
| 200                 | 40                       | 250                                   | 60                       | 127                                   |
| 250                 | 57                       | 273                                   | 74                       | 167                                   |
| 300                 | 77                       | 313                                   | 100                      | 172                                   |
| 350                 | 96                       | 427                                   | 135                      | 158                                   |
| Average             | --                       | 310 ± 60                              | --                       | 150 ± 20                              |

$^1$ determined based on the integrated NMR intensity of $^1$H(I): 8.4~8.7 ppm.

$^2$ determined based on the integrated NMR intensity of $^1$H(II): 8.1~8.3 ppm.
In the less polar solvent, cyclohexane, the broadened PIC signals only become prominent when >350 equivalents of ligands are added (Figure 4B). Though it is unlikely that the bulky PIC ligands can form a dense coverage of 3.2 nm$^2$ (given all 350 PIC are tightly bound to the surface), the absence of the NMR signal suggests the strong association of OlAm$^+$PIC$^-$ ion pairs to the PNC surface in the apolar environment. At relatively low ligand loadings (< 200 equivalents), we believe that PIC can achieve a close-to-stoichiometric bound to the available surface site, and therefore can be employed as the anchoring group to graft functional structures to the PNC surface, provided its aromatic ring can be decorated.

To further understand the binding of the ligands on PNC, we performed ab initio density functional theory (DFT) simulations. We find that the stabilization energy of PIC as a bidentate ligand is prominently lower than the monodentate counterparts. (Figure 5, and Figure S13) The theoretical prediction agrees with the results of the passivation experiments, in which single-role ligands such as isonicotinate, benzoate, and pyridine all show poorer passivation for the PNC surface. When PIC binds to the PNC surface, the O atom of the carboxylic group and the N atom of the pyridinic ring coordinate to the undercoordinated Pb site cooperatively, as shown in Figure 5B, which gains extra stabilization energy of 0.31 eV compared to the single-role binding mode through the carboxylic group. This binding configuration predicted by DFT calculations agrees with the $^1$HNMR observation that suggests proximation of the N atom of PIC to the surface. The chelating coordination with two distinct atoms covalently interacted with the same surface Pb site differs from previously reported bidentate ligands and zwitterion ligands for PNCs.$^{50,53-54}$
Figure 5. (A) Calculated binding energies (eV) of the ligands on PNC and (B) the optimized binding configuration of PIC on the PNC surface. H, white; C, grey; O, red; N, blue; Cs, purple; Br, brown; Pb, dark grey.

The strong interaction of PIC on the PNC surface enables thorough purification of as-synthesized PNCs and modification of the ligand shell. We developed a precipitation-redissolution purification strategy for PNCs based on the effective protection of PIC in ethyl acetate. Typically, 10 nanomoles of as-synthesized PNCs were dispersed in a 10 ml solution of ethyl acetate containing a mixture of 0.7 mM picolinic acid and 1.4 mM OlAm. The turbid suspension was sonicated for 30 min and centrifuged at 3500 rpm for 5 min at 4 °C to recover the PNCs. The recovered PNC was redissolved in toluene or cyclohexane, and insoluble solids are removed by centrifugation. The UV-vis absorption and the PL spectra (Figure 6A) of the purified PNC are narrower, with reduced intensity on the blue side of the first exciton band, likely because smaller-size PNCs are harder to precipitate from ethyl acetate. The recovery of PNCs after one round of purification is typical > 0.85. The purification step can be repeated to further eliminate the synthetic residue, but the recovery decreases to ~0.20 due to the poor solubility of PNCs after the second ethyl acetate wash. The PLQY of PNCs after the first and second purification is 0.32 and 0.54, respectively. For the one-round purified sample, the PLQY can be increased to 0.75 by adding another 200 equivalents of OlAm’PIC’ during the
redissolving step. The insoluble PNCs after the second purification remain quantum-confined. Using a procedure developed by Sargent and coauthors\textsuperscript{46}, we fabricated a solid-state film with PNCs after two rounds of purification. As shown in Figure 6A, the PNC film demonstrates a similar PL spectrum as in the solution phase, suggesting PIC can protect the nanocrystals from fusion in the solid.

>97\% of the residual synthetic solvent, ODE (from 4000 ± 400 to < 100 per PNC), can be removed with one round of purification, and ODE can be fully removed after repeating the procedure. The residual OA\textsuperscript{-} and OIAM\textsuperscript{+} from synthesis decrease from 5000 ± 600 to 350 ± 60 per PNC, corresponding to a surface coverage of 3.2 ± 0.6 nm\textsuperscript{-2}, and 200 ± 40 per PNC (1.8 ± 0.4 nm\textsuperscript{-2}) after the first and second round of purification, respectively. For the insoluble PNCs, the coverage of the long-chain ligands is only ~0.7 nm\textsuperscript{-2}. We, therefore, attribute the poor solubility of samples after two rounds of purification to the loss of long-chain surface ligands during the ethyl acetate wash.
**Figure 6.** Comparison of PNC samples (d=4.3 nm) before and after the first and second purification with OlAm⁺PIC⁻ and the cation exchange treatment with OctAm⁺PIC⁻. (A) UV-vis absorption and the PL spectra. The PL spectrum of the film made of PNCs after the two rounds of purification is shown. Inset: images of the film with and without the 365 nm UV illumination. (B) NMR in toluene-D₈. Right: the high chemical shift region and Left: the alkene resonance region. The spectral intensity is normalized according to the intensity of the internal standard and adjusted to the same PNC concentration. The spectrum of the as-synthesized PNC in the right panel is scaled down to its 1/30 so that the intensities are comparable to the purified samples.

We employ ¹H-NMR spectroscopy to characterize the surface ligands of the as-synthesized and the purified PNC (Figure 6B). The remained original ligands (OA⁻ and OlAm⁺) show two distinct NMR features in the alkene resonance region. We assigned the broad resonance band above 5.5 ppm to OlAm⁺ and the relatively sharp multiplet at 5.46 ppm to oleate, according to the result of a titration experiment (See the Supporting Information). The former accounts for >80% of the long-chain ligands after purification. Surprisingly, NMR observes
nearly no $^1$H resonance from PIC for the purified samples. After completely decomposing the purified PNC in deuterated DMSO, we quantify that there are $30 \pm 5$ equivalents of PIC per PNC for samples after the first purification, and $90 \pm 30$ equivalents for samples after the second purification, corresponding to PIC coverage of $0.27 \pm 0.05$ and $0.8 \pm 0.3$ nm$^{-2}$, respectively. The absence of PIC signals in the NMR spectrum in toluene suggests that all PIC ligands are tightly bound to the PNC surface when there is a lack of competitive adsorption from the remained extra synthetic ligand. We, therefore, believe if one decorates the aromatic ring of PIC with desired chemical structure, the PIC motif can serve the role of anchoring groups for grafting functional chemicals to the PNC ligand shell.

FTIR spectroscopy confirms the result of purification (Figure S14). The IR signal of the as-synthesized PNC is a combination of absorption from ODE and the OlAm$^{+}$OA$^{-}$ ligand. After purification, the sharp ODE signals at 991 and 908 cm$^{-1}$ disappear from the spectrum. FTIR also captures notable PIC signals despite the absence of the PIC NMR signals. These unique vibrational features provide important information for illustrating the detailed binding configuration of PIC and will be discussed in a later section.

By comparing the surface components of PNC samples after the first and second purification, we notice that the loss of OlAm$^{+}$ cations (-120 equivalents per PNC) is greater than the increase of PIC$^{-}$ anion (60 e.q. per PNC) after the second purification step. The unbalanced component change implies that when the ethyl acetate treatment rips off OlAm$^{+}$Br$^{-}$ from the PNC surface, the bulkier PIC$^{-}$ anion cannot fill all Br vacancies. The downshift of OlAm$^{+}$ alkene resonance from 5.54 to 5.51 ppm after the second purification also indicates the relative weaker association of OlAm$^{+}$ to the PNC surface, likely due to the decrease of the negatively charged hydrogen bond acceptors.
The purification procedure can be adapted to a cation exchange process for replacing the original OIAm+ with other cationic ligands. As a demonstration, we substituted oleylamine in the ethyl acetate washing solution with short-chain octyamine (OctAm), while the rest of the procedure remains the same. The UV-vis absorption and the PL spectra of the resulted sample are identical to the purified PNCs (Figure 6A). With one round of cation exchange, the total number of OIAm+ reduces to 170 per PNC, 40% smaller than the OIAm-treated sample, according to the alkene 1H resonance in the NMR spectrum (Figure 6B). Although 1HNMR cannot distinguish OctAm+, the replacement of OIAm+ with OctAm+ is supported by the downshift of the OIAm+ from 5.54 to 5.51 ppm, compared to the OIAm-treated sample. We attribute the downshift to a more dynamic exchange of OIAm+ on and off the PNC surface due to the competition from OctAm+. The shorter surface ligand can reduce the insulation of the nanocrystal surface and hence facilitate carrier transportation.70-72 It is also possible to employ the cation exchange procedure to introduce functional organic molecules to the surface of PNCs. For example, organic semiconductors have been anchored to the surface of hybrid perovskite materials as ammonium-associated ligands.73-74 Our method can be employed to realize similar functionalization for all-inorganic colloidal PNCs.

NMR and IR characterization of the purified sample reveals the chelating configuration and the coadsorption of PIC-ammonium ion pairs. With 200 equivalents of OIAm+PIC− added to the purified PNC sample, 1D-1HNMR captures two broadened 1H resonance signals of PIC in toluene-D8 at 8.95 (1H(I)) and 8.18 ppm (1H(II)), and the alkene resonance of OIAm+ downshifted to 5.50 ppm, indicating faster exchange on and off the surface for OIAm+ when the total amount of amine increases. (Figure 7A). The 2D NOESY experiment identifies negative NOE at the off-diagonal cross-peaks for bound OIAm+ and PIC, as shown in
**Figure 7B** (and magnified in **Figure S12**). The negative NOE confirms the binding of these ligands. In the alkene proton resonance region, we found that the broad resonance at 5.50 ppm shows clear off-diagonal cross-peaks with negative NOE. In contrast, the NOE effect associated with the 5.46 ppm shoulder is nearly null. The distinction in NOESY confirms the assignments of the former signal to the surface-associated OlAm\(^+\) and the latter to the weakly bound OA\(^-\). For PIC, the negative NOE uncovered the resonance signals of \(^1\)H(III) and \(^1\)H(IV) at 7.17 and 6.86 ppm, respectively, which are buried underneath the strong solvent (toluene) residual signals in the 1D spectrum. Moreover, we identify NOE signals belonging to the intermolecular coupling between PIC and OlAm. The NOE associated with the \(^1\)H(II) signal of PIC at 8.18 ppm and the \(^1\)H(2) of OlAm at 1.86 ppm provides evidence OlAm\(^+\) and PIC\(^-\) are adsorbed on the PNC surface as cation-anion pairs. The coadsorption of OlAm\(^+\)PIC\(^-\) pair is also supported by our observation while optimizing the purification procedure: when reducing the PIC from 700 to 350 equivalents and using the same 1400 equivalents of OlAm, after crushing the PNC with ethyl acetate, the precipitated PNC is hardly soluble in toluene, likely due to inadequate coverage of the long-chain ammonium ligand. This phenomenon suggests that it is the PIC anion that assists the adsorption of the ammonium species.
Figure 7. (A) 1D-^{1}H NMR spectra of the purified PNC with 200 equivalents addition of OlAm^+PIC^- ligands (Black) and the free OlAm^+PIC^- ligand (Blue) in toluene-D8. “*” marked signals belong to solvents. (B) 2D-NOESY of the PNC sample in (A). Critical off-diagonal cross-peaks featuring negative NOE are highlighted as red for oleylammonium protons, green for PIC protons, and yellow for OlAm/PIC intermolecular coupling. The magnified cross-peak regions can be found in the Supporting Information.

At last, we employed vibrational spectroscopy to characterize PIC bound on the PNC surface. In general, we notice a trend of hypsochromic shifts for vibrational patterns upon the bound to the PNC surface, as illustrated in Figure 8. Because of the coexistence of oleylammonium and residual oleate, we turn to DFT calculations to assist the assignment of
vibrational bands of PIC, and the results are listed in Table S3. In line with the experimental spectra, when PIC is adsorbed to the PNC surface, most calculated vibrational modes show upshifted frequencies. It is known that the coordination of pyridine at the N atom as a Lewis base causes an increase in the overall bond strength of the aromatic ring, resulting in hypochromic shifts for the vibrational signals. The systematic vibrational frequency shift supports the participation of the pyridinic N atom in the coordination. In addition, vibrational frequencies observed for PIC on the PNC surface are similar to those of the Ba(PIC)₂ complex, in which PIC behaves as a bidentate chelating ligand.

**Figure 8.** The comparison of the fingerprint region of FTIR spectra of purified PNCs (blue) and the pure OiAm⁺PIC⁻ ligand (red). The notable frequency shifts upon binding are labeled above the spectrum of the purified PNC. Full spectra in between 400-3400 cm⁻¹ are shown in Figure S14.

**CONCLUSIONS**

We demonstrate stable covalent interaction on the surface of PNC can be achieved through chelating coordination of a heterocyclic carboxylate, picolinate. With a bound affinity that is 15-30 folds stronger than the original ligand, the PIC can effectively passivate the surface defect of PNCs in the strongly quantum confined regime in various solvents and bring the PLQY up to > 0.8. The PL kinetics prove that the PIC passivation eliminates most of the surface traps and prolongs the exciton lifetimes in a subensemble of PNCs approaching the radiative
relaxation limit. Combined NMR, IR, and DFT studies reveal the bidentate nature of PIC and the coadsorption of OlAm⁺PIC⁻ ion pair on the PNC surface. In apolar solvents, the binding of PIC can approach stoichiometry, making PIC a good candidate of anchoring motifs to graft functional structures. The binding of PIC is strong enough to protect the small-size PNCs in polar solvents, including ethyl acetate. Based on the protective effect, we design a precipitation-redissolution purification procedure that can thoroughly remove the undesired synthetic residuals while maintaining strong quantum confinement in PNCs. We also demonstrate the potential of adapting this purification procedure to introduce new ammonium species to the PNC surface. The strong chelating coordination promises surface engineering that can modify the ligand shell of PNCs.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the website.

AUTHOR INFORMATION
Corresponding Author
*

ACKNOWLEDGEMENTS
The authors would like to thank Queens College and the City University of New York for financial and facility support. The work is partly supported by the PSC-CUNY award. This research used resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility located at Lawrence Berkeley National Laboratory, operated under Contract No. DE-AC02-05CH11231.

REFERENCES
1. Weidman, M. C.; Goodman, A. J.; Tisdale, W. A., Colloidal Halide Perovskite Nanoplatelets: An Exciting New Class of Semiconductor Nanomaterials. Chem. Mater. 2017, 29 (12), 5019-5030.
2. Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L., Genesis, challenges and opportunities for colloidal lead halide perovskite nanocrystals. *Nat. Mater.* **2018**, *17* (5), 394-405.
3. Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I., Properties and potential optoelectronic applications of lead halide perovskite nanocrystals. *Science* **2017**, *358* (6364), 745-750.
4. Schanze, K. S.; Kamat, P. V.; Yang, P.; Bisquert, J., Progress in Perovskite Photocatalysis. *ACS Energy Lett.* **2020**, *5* (8), 2602-2604.
5. Dong, Y.; Qiao, T.; Kim, D.; Parobek, D.; Rossi, D.; Son, D. H., Precise Control of Quantum Confinement in Cesium Lead Halide Perovskite Quantum Dots via Thermodynamic Equilibrium. *Nano Lett.* **2018**, *18* (6), 3716-3722.
6. Yang, D.; Zou, Y.; Li, P.; Liu, Q.; Wu, L.; Hu, H.; Xu, Y.; Sun, B.; Zhang, Q.; Lee, S.-T., Large-scale synthesis of ultrathin cesium lead bromide perovskite nanoplates with precisely tunable dimensions and their application in blue light-emitting diodes. *Nano Energy* **2018**, *47*, 235-242.
7. Akkerman, Q. A.; Motti, S. G.; Srimath Kandada, A. R.; Mosconi, E.; D’Innocenzo, V.; Bertoni, G.; Marras, S.; Kamino, B. A.; Miranda, L.; De Angelis, F., Solution Synthesis Approach to Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control. *J. Am. Chem. Soc.* **2016**, *138*, 1010.
8. Bekenstein, Y.; Koscher, B. A.; Eaton, S. W.; Yang, P. D.; Alivisatos, A. P., Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies. *J. Am. Chem. Soc.* **2015**, *137*, 16008.
9. Liu, M.; Zhong, G.; Yin, Y.; Miao, J.; Li, K.; Wang, C.; Xu, X.; Shen, C.; Meng, H., Aluminum-Doped Cesium Lead Bromide Perovskite Nanocrystals with Stable Blue Photoluminescence Used for Display Backlight. *Adv. Sci.* **2017**, *4* (11), 1700335.
10. Pan, G.; Bai, X.; Yang, D.; Chen, X.; Jing, P.; Qu, S.; Zhang, L.; Zhou, D.; Zhu, J.; Xu, W.; Dong, B.; Song, H., Doping Lanthanide into Perovskite Nanocrystals: Highly Improved and Expanded Optical Properties. *Nano Lett.* **2017**, *17* (12), 8005-8011.
11. Hines, D. A.; Kamat, P. V., Recent Advances in Quantum Dot Surface Chemistry. *ACS Appl. Mater. Interf.* **2014**, *6* (5), 3041-3057.
17. Weiss, E. A., Organic Molecules as Tools To Control the Growth, Surface Structure, and Redox Activity of Colloidal Quantum Dots. Acc. Chem. Res. 2013, 46 (11), 2607-2615.
18. Brown, P. R.; Kim, D.; Lunt, R. R.; Zhao, N.; Bawendi, M. G.; Grossman, J. C.; Bulovic, V., Energy Level Modification in Lead Sulfide Quantum Dot Thin Films through Ligand Exchange. ACS Nano 2014, 8 (6), 5863-5872.
19. Scheele, M.; Hanifi, D.; Zherebetskyy, D.; Chourou, S. T.; Axnanda, S.; Rancatore, B. J.; Thorkelsson, K.; Xu, T.; Liu, Z.; Wang, L.-W.; Liu, Y.; Alivisatos, A. P., PbS Nanoparticles Capped with Tetrathiafulvalenetetracarboxylate: Utilizing Energy Level Alignment for Efficient Carrier Transport. ACS Nano 2014, 8 (3), 2532-2540.
20. Kroupa, D. M.; Vörös, M.; Brawand, N. P.; McNichols, B. W.; Miller, E. M.; Gu, J.; Nozik, A. J.; Sellinger, A.; Galli, G.; Beard, M. C., Tuning colloidal quantum dot band edge positions through solution-phase surface chemistry modification. Nat. Comm. 2017, 8 (1), 15257.
21. Kroupa, D. M.; Vörös, M.; Brawand, N. P.; Bronstein, N.; McNichols, B. W.; Castaneda, C. V.; Nozik, A. J.; Sellinger, A.; Galli, G.; Beard, M. C., Optical Absorbance Enhancement in PbS QD/Cinnamate Ligand Complexes. J. Phys. Chem. Lett. 2018, 3425-3433.
22. Buckley, J. J.; Couderc, E.; Greaney, M. J.; Munteanu, J.; Riche, C. T.; Bradford, S. E.; Brutchez, R. L., Chalcogenol Ligand Toolbox for CdSe Nanocrystals and Their Influence on Exciton Relaxation Pathways. ACS Nano 2014, 8 (3), 2512-2521.
23. He, C.; Weinberg, D. J.; Nepomnyashchii, A. B.; Lian, S.; Weiss, E. A., Control of the Redox Activity of PbS Quantum Dots by Tuning Electrostatic Interactions at the Quantum Dot/Solvent Interface. J. Am. Chem. Soc. 2016, 138 (28), 8847-8854.
24. Weinberg, D. J.; He, C.; Weiss, E. A., Control of the Redox Activity of Quantum Dots through Introduction of Fluoroalkanethiolates into Their Ligand Shells. J. Am. Chem. Soc. 2016, 138 (7), 2319-2326.
25. Kroupa, D. M.; Arias, D. H.; Blackburn, J. L.; Carroll, G. M.; Granger, D. B.; Anthony, J. E.; Beard, M. C.; Johnson, J. C., Control of Energy Flow Dynamics between Tetracene Ligands and PbS Quantum Dots by Size Tuning and Ligand Coverage. Nano Lett. 2018, 18 (2), 865-873.
26. Frederick, M. T.; Weiss, E. A., Relaxation of Exciton Confinement in CdSe Quantum Dots by Modification with a Conjugated Dithiocarbamate Ligand. ACS Nano 2010, 4 (6), 3195-3200.
27. Lian, S.; Weinberg, D. J.; Harris, R. D.; Kodaimati, M. S.; Weiss, E. A., Subpicosecond Photoinduced Hole Transfer from a CdS Quantum Dot to a Molecular Acceptor Bound Through an Exciton-Delocalizing Ligand. ACS Nano 2016, 10 (6), 6372-6382.
28. Wang, C.; Kodaimati, M. S.; Schatz, G. C.; Weiss, E. A., The photoluminescence spectral profiles of water-soluble aggregates of PbS quantum dots assembled through reversible metal coordination. Chem. Commun. 2017.
29. Wang, C.; Weiss, E. A., Accelerating FRET between Near-Infrared Emitting Quantum Dots Using a Molecular J-Aggregate as an Exciton Bridge. Nano Lett. 2017, 17 (9), 5666-5671.
30. Mayilo, S.; Hilhorst, J.; Susha, A. S.; Hohl, C.; Franzl, T.; Klar, T. A.; Rogach, A. L.; Feldmann, J., Energy transfer in solution-based clusters of CdTe nanocrystals electrostatically bound by calcium ions. J. Phys. Chem. C 2008, 112 (37), 14589-14594.
31. Halpert, J. E.; Tischler, J. R.; Nair, G.; Walker, B. J.; Liu, W.; Bulovic, V.; Bawendi, M. G., Electrostatic Formation of Quantum Dot/J-aggregate FRET Pairs in Solution. J. Phys. Chem. C 2009, 113 (23), 9986-9992.
32. Zhang, Q.; Atay, T.; Tischler, J. R.; Bradley, M. S.; Bulovic, V.; Nurmikko, A. V., Highly efficient resonant coupling of optical excitations in hybrid organic/inorganic semiconductor nanostructures. *Nat Nano* 2007, 2 (9), 555-559.
33. Qiao, Y.; Polzer, F.; Kirmse, H.; Steeg, E.; Kühn, S.; Friede, S.; Kirstein, S.; Rabe, J. P., Nanotubular J-Aggregates and Quantum Dots Coupled for Efficient Resonance Excitation Energy Transfer. *ACS Nano* 2015, 9 (2), 1552-1560.
34. Howes, P. D.; Chandrawati, R.; Stevens, M. M., Colloidal nanoparticles as advanced biological sensors. *Science* 2014, 346 (6205).
35. Zhang, Y.; Wang, T.-H., Quantum Dot Enabled Molecular Sensing and Diagnostics. *Theranostics* 2012, 2 (7), 631-654.
36. Wu, Y.; Eisele, K.; Doroshenko, M.; Algarra-Siller, G.; Kaiser, U.; Koynov, K.; Weil, T., Quantum Dots: A Quantum Dot Photoswitch for DNA Detection, Gene Transfection, and Live-Cell Imaging (Small 22/2012). *Small* 2012, 8 (22), 3381-3381.
37. De Roo, J.; Ibáñez, M.; Geiregat, P.; Nedelcu, G.; Walravens, W.; Maes, J.; Martins, J. C.; Van Driessche, I.; Kovalenko, M. V.; Hens, Z., Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* 2016, 10 (2), 2071-2081.
38. Smock, S. R.; Williams, T. J.; Brutchey, R. L., Quantifying the Thermodynamics of Ligand Binding to CsPbBr$_3$ Quantum Dots. *Angew. Chem., Int. Ed.* 2018, 57 (36), 11711-11715.
39. Smock, S. R.; Chen, Y.; Rossini, A. J.; Brutchey, R. L., The Surface Chemistry and Structure of Colloidal Lead Halide Perovskite Nanocrystals. *Acc. Chem. Res.* 2021, 54 (3), 707-718.
40. Pradhan, N., Alkylammonium Halides for Facet Reconstruction and Shape Modulation in Lead Halide Perovskite Nanocrystals. *Acc. Chem. Res.* 2021, 54 (5), 1200-1208.
41. Tosó, S.; Baranov, D.; Manna, L., Metamorphoses of Cesium Lead Halide Nanocrystals. *Acc. Chem. Res.* 2021, 54 (3), 498-508.
42. Kang, J.; Wang, L.-W., High Defect Tolerance in Lead Halide Perovskite CsPbBr$_3$. *J. Phys. Chem. Lett.* 2017, 8 (2), 489-493.
43. Shi, H.; Du, M.-H., Shallow halogen vacancies in halide optoelectronic materials. *Phys. Rev. B* 2014, 90 (17), 174103.
44. Ravi, V. K.; Swarnkar, A.; Chakraborty, R.; Nag, A., Excellent green but less impressive blue luminescence from CsPbBr$_3$ Perovskite Nanocubes and Nanoplatelets. *Nanotechnology* 2016, 27, 325708.
45. Hoshi, K.; Chiba, T.; Sato, J.; Hayashi, Y.; Takahashi, Y.; Ebe, H.; Ohisa, S.; Kido, J., Purification of Perovskite Quantum Dots Using Low-Dielectric-Constant Washing Solvent “Diglyme” for Highly Efficient Light-Emitting Devices. *ACS Appl. Mater. Interf.* 2018, 10 (29), 24607-24612.
46. Kim, Y.; Yassitepe, E.; Voznyy, O.; Comin, R.; Walters, G.; Gong, X.; Kanjanaboos, P.; Nogueira, A. F.; Sargent, E. H., Efficient Luminescence from Perovskite Quantum Dot Solids. *ACS Appl. Mater. Interf.* 2015, 7 (45), 25007-25013.
47. Nenon, D. P.; Pressler, K.; Kang, J.; Koscher, B. A.; Olshansky, J. H.; Osowiecki, W. T.; Koc, M. A.; Wang, L.-W.; Alivisatos, A. P., Design Principles for Trap-Free CsPbX$_3$ Nanocrystals: Enumerating and Eliminating Surface Halide Vacancies with Softer Lewis Bases. *J. Am. Chem. Soc.* 2018, 140 (50), 17760-17772.
48. Koscher, B. A.; Swabeck, J. K.; Bronstein, N. D.; Alivisatos, A. P., Essentially Trap-Free CsPbBr$_3$ Colloidal Nanocrystals by Postsynthetic Thiocyanate Surface Treatment. *J. Am. Chem. Soc.* **2017**, *139*(19), 6566-6569.

49. Zhong, Q.; Cao, M.; Xu, Y.; Li, P.; Zhang, Y.; Hu, H.; Yang, D.; Xu, Y.; Wang, L.; Li, Y.; Zhang, X.; Zhang, Q., L-Type Ligand-Assisted Acid-Free Synthesis of CsPbBr$_3$ Nanocrystals with Near-Unity Photoluminescence Quantum Yield and High Stability. *Nano Lett.* **2019**, *19*(6), 4151-4157.

50. Krieg, F.; Ochsenbein, S. T.; Yakunin, S.; ten Brinck, S.; Aellen, P.; Süess, A.; Clerc, B.; Guggisberg, D.; Nazarenko, O.; Shynkarenko, Y.; Kumar, S.; Shih, C.-J.; Infante, I.; Kovalenko, M. V., Colloidal CsPbX$_3$ (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability. *ACS Energy Lett.* **2018**, *3*(3), 641-646.

51. Yang, D.; Li, X.; Zhou, W.; Zhang, S.; Meng, C.; Wu, Y.; Wang, Y.; Zeng, H., CsPbBr$_3$ Quantum Dots 2.0: Benzenesulfonic Acid Equivalent Ligand Awakens Complete Purification. *Adv. Mater.* **2019**, *31*(30), 1900767.

52. Pan, J.; Quan, L. N.; Zhao, Y.; Peng, W.; Murali, B.; Sarma, S. P.; Yuan, M.; Sinatra, L.; Alyami, N. M.; Liu, J.; Yassitepe, E.; Yang, Z.; Voznyy, O.; Comin, R.; Hedhili, M. N.; Mohammed, O. F.; Lu, Z. H.; Kim, D. H.; Sargent, E. H.; Bakr, O. M., Highly Efficient Perovskite-Quantum-Dot Light-Emitting Diodes by Surface Engineering. *Adv. Mater.* **2016**, *28*(39), 8718-8725.

53. Khan, J.; Zhang, X.; Yuan, J.; Wang, Y.; Shi, G.; Patterson, R.; Shi, J.; Ling, X.; Hu, L.; Wu, T.; Dai, S.; Ma, W., Tuning the Surface-Passivating Ligand Anchoring Position Enables Phase Robustness in CsPbI$_3$ Perovskite Quantum Dot Solar Cells. *ACS Energy Lett.* **2020**, *5*(10), 3322-3329.

54. Pan, J.; Shang, Y.; Yin, J.; De Bastiani, M.; Peng, W.; Dursun, I.; Sinatra, L.; El-Zohry, A. M.; Hedhili, M. N.; Emwas, A.-H.; Mohammed, O. F.; Ning, Z.; Bakr, O. M., Bidentate Ligand-Passivated CsPbI$_3$ Perovskite Nanocrystals for Stable Near-Unity Photoluminescence Quantum Yield and Efficient Red Light-Emitting Diodes. *J. Am. Chem. Soc.* **2018**, *140*(2), 562-565.

55. Bodnarchuk, M. I.; Boehme, S. C.; ten Brinck, S.; Bernasconi, C.; Shynkarenko, Y.; Krieg, F.; Widmer, R.; Aeschlimann, B.; Günther, D.; Kovalenko, M. V.; Infante, I., Rationalizing and Controlling the Surface Structure and Electronic Passivation of Cesium Lead Halide Nanocrystals. *ACS Energy Lett.* **2019**, *4*(1), 63-74.

56. Imran, M.; Ijaz, P.; Goldoni, L.; Maggioni, D.; Petralanda, U.; Prato, M.; Almeida, G.; Infante, I.; Manna, L., Simultaneous Cationic and Anionic Ligand Exchange For Colloidaly Stable CsPbBr$_3$ Nanocrystals. *ACS Energy Lett.* **2019**, *4*(4), 819-824.

57. DuBose, J. T.; Kamat, P. V., Surface Chemistry Matters. How Ligands Influence Excited State Interactions between CsPbBr$_3$ and Methyl Viologen. *J. Phys. Chem. C* **2020**, *124*(24), 12990-12998.

58. Vickers, E. T.; Enlow, E. E.; Delmas, W. G.; DiBenedetto, A. C.; Chowdhury, A. H.; Bahrami, B.; Dreskin, B. W.; Graham, T. A.; Hernandez, I. N.; Carter, S. A.; Ghosh, S.; Qiao, Q.; Zhang, J. Z., Enhancing Charge Carrier Delocalization in Perovskite Quantum Dot Solids with Energetically Aligned Conjugated Capping Ligands. *ACS Energy Lett.* **2020**, *5*(3), 817-825.

59. Li, Y.; Shu, Q.; Du, Q.; Dai, Y.; Zhao, S.; Zhang, J.; Li, L.; Chen, K., Surface Modification for Improving the Photocatalytic Polymerization of 3,4-Ethylenedioxythiophene over Inorganic Lead Halide Perovskite Quantum Dots. *ACS Appl. Mater. Interf.* **2020**, *12*(1), 451-460.
60. Noel, N. K.; Abate, A.; Stranks, S. D.; Parrott, E. S.; Burlakov, V. M.; Goriely, A.; Snaith, H. J., Enhanced Photoluminescence and Solar Cell Performance via Lewis Base Passivation of Organic–Inorganic Lead Halide Perovskites. *ACS Nano* 2014, 8 (10), 9815-9821.

61. Maes, J.; Balcaen, L.; Drijvers, E.; Zhao, Q.; De Roo, J.; Vantomme, A.; Vanhaecke, F.; Geiregat, P.; Hens, Z., Light Absorption Coefficient of CsPbBr$_3$ Perovskite Nanocrystals. *J. Phys. Chem. Lett.* 2018, 9 (11), 3093-3097.

62. Bohn, B. J.; Tong, Y.; Gramlich, M.; Lai, M. L.; Döblinger, M.; Wang, K.; Hoye, R. L. Z.; Müller-Buschbaum, P.; Stranks, S. D.; Urban, A. S.; Polavarapu, L.; Feldmann, J., Boosting Tunable Blue Luminescence of Halide Perovskite Nanoplatelets through Postsynthetic Surface Trap Repair. *Nano Lett.* 2018, 18 (8), 5231-5238.

63. Ebenstein, Y.; Mokari, T.; Banin, U., Fluorescence quantum yield of CdSe/ZnS nanocrystals investigated by correlated atomic-force and single-particle fluorescence microscopy. *Appl. Phys. Lett.* 2002, 80 (21), 4033-4035.

64. Wehrenberg, B. L.; Wang, C.; Guyot-Sionnest, P., Interband and Intraband Optical Studies of PbSe Colloidal Quantum Dots. *J. Phys. Chem. B* 2002, 106 (41), 10634-10640.

65. Hens, Z.; Moreels, I., Light absorption by colloidal semiconductor quantum dots. *J. Mater. Chem.* 2012, 22 (21), 10406-10415.

66. Yan, W.; Mao, L.; Zhao, P.; Mertens, A.; Dottermusch, S.; Hu, H.; Jin, Z.; Richards, B. S., Determination of complex optical constants and photovoltaic device design of all-inorganic CsPbBr$_3$ perovskite thin films. *Opt. Express* 2020, 28 (10), 15706-15717.

67. Marbella, L. E.; Millstone, J. E., NMR Techniques for Noble Metal Nanoparticles. *Chem. Mater.* 2015, 27 (8), 2721-2739.

68. Hens, Z.; Martins, J. C., A Solution NMR Toolbox for Characterizing the Surface Chemistry of Colloidal Nanocrystals. *Chem. Mater.* 2013, 25 (8), 1211-1221.

69. Harris, R. D.; Amin, V. A.; Lau, B.; Weiss, E. A., Role of Interligand Coupling in Determining the Interfacial Electronic Structure of Colloidal CdS Quantum Dots. *ACS Nano* 2016, 10 (1), 1395-1403.

70. Chen, K.; Zhong, Q.; Chen, W.; Sang, B.; Wang, Y.; Yang, T.; Liu, Y.; Zhang, Y.; Zhang, H., Short-Chain Ligand-Passivated Stable α-CsPbI$_3$ Quantum Dot for All-Inorganic Perovskite Solar Cells. *Adv. Func. Mater.* 2019, 29 (24), 1900991.

71. Thompson, N. J.; Wilson, M. W. B.; Congreve, D. N.; Brown, P. R.; Scherer, J. M.; Bischof, T. S.; Wu, M.; Geva, N.; Welborn, M.; Voorhis, T. V.; Bulović, V.; Bawendi, M. G.; Baldo, M. A., Energy harvesting of non-emissive triplet excitons in tetracene by emissive PbS nanocrystals. *Nat Mater* 2014, 13 (11), 1039-1043.

72. Zhang, Z.; Edme, K.; Lian, S.; Weiss, E. A., Enhancing the Rate of Quantum-Dot-Photocatalyzed Carbon–Carbon Coupling by Tuning the Composition of the Dot’s Ligand Shell. *J. Am. Chem. Soc.* 2017, 139 (12), 4246-4249.

73. Gao, Y.; Shi, E.; Deng, S.; Shiring, S. B.; Snaider, J. M.; Liang, C.; Yuan, B.; Song, R.; Janke, S. M.; Liebman-Peláez, A.; Yoo, P.; Zeller, M.; Boudouris, B. W.; Liao, P.; Zhu, C.; Blum, V.; Yu, Y.; Savoie, B. M.; Huang, L.; Dou, L., Molecular engineering of organic–inorganic hybrid perovskites quantum wells. *Nat. Chem.* 2019, 11 (12), 1151-1157.

74. Xue, J.; Wang, R.; Chen, X.; Yao, C.; Jin, X.; Wang, K.-L.; Huang, W.; Huang, T.; Zhao, Y.; Zhai, Y.; Meng, D.; Tan, S.; Liu, R.; Wang, Z.-K.; Zhu, C.; Zhu, K.; Beard, M. C.; Yan, Y.; Yang, Y., Reconfiguring the band-edge states of photovoltaic perovskites by conjugated organic cations. *Science* 2021, 371 (6529), 636-640.
75. Ferwerda, R.; van der Maas, J. H.; van Duijneveldt, F. B., Pyridine adsorption onto metal oxides: an ab initio study of model systems. *J. Mol. Catal. A Chem.* **1996**, *104* (3), 319-328.
76. Świderski, G.; Kalinowska, M.; Wojtulewski, S.; Lewandowski, W., Experimental (FT-IR, FT-Raman, $^1$H NMR) and theoretical study of magnesium, calcium, strontium, and barium picolinates. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2006**, *64* (1), 24-33.
Supporting Information

Strong bidentate coordination for surface passivation and ligand-shell engineering of lead halide perovskite nanocrystals in the strongly quantum confined regime

Aaron Malinoski, Guoxiang Hu, Chen Wang*

Department of Chemistry and Biochemistry, Queens College, City University of New York, 65-30 Kissena Blvd., Flushing, NY 11432

*corresponding author. Email: chen.wang@qc.cuny.edu

Table of Contents

1. Materials and Experimental ........................................ 2
2. Estimation of $k_f/k_{nr,trap}$ for PNCs with $d = 4.3$ nm. ........ 8
3. The protection effect of PIC for small-size PNCs in polar solvents 11
4. The PIC passivation does not affect the quantum confinement of PNC. 13
5. Simple L-type ligands show little passivation effect. ............. 13
6. The degradation of PNCs with overly added PIC .................. 14
7. PL kinetics of PNCs in various solvents. ......................... 15
8. Decomposition of $^1$HNMR signals in the alkene region .......... 16
9. Quantifying the strongly adsorbed PIC ligands ................. 16
10. Titrating the purified PNC sample with the OctAm$^+$OA$^-$ ligand 17
11. 2D-NOESY NMR spectrum ..................................... 20
12. DFT results of different binding configurations .................. 21
13. FTIR spectra of PNC and the vibrational modes of PIC ........ 21

References ........................................................................ 25
1. Materials and Experimental

1.1 Materials.

Unless specified, the following chemicals were used as received without any further treatment. Hexanes (Certified ACS, Fisher). Toluene (Certified ACS, Fisher). Cyclohexane (HPLC, Fisher). Chloroform (HPLC, VWR). 1,2-dichlorobenzene (99%, Sigma-Aldrich). Pentane (HPLC, Baker).

The abovementioned solvents were dried with the molecular sieve 4Å overnight before being used. Acetone (Certified ACS, Fisher). Methanol (HPLC, Fisher). Ethyl acetate (Certified ACS, Fisher). 1,2-Dimethoxyethane (99%, stabilized with BHT, Alfa Aesar). 1-octadecene (ODE, 90%, Acros). Oleic acid (OA, 90%, Sigma-Aldrich). Oleylamine (OlAm, 70%, Sigma-Aldrich). Lead (II) bromide (PbBr₂, 99.998, Alfa Aesar). Anhydrous zinc bromide (ZnBr₂, 99.9%, Alfa Aesar). Cesium carbonate (Cs₂CO₃, 99.9%, Acros). Benzyllic acid (99.5%, Alfa Aesar). Picolinic acid (99%, Acros). 2-thiophenecarboxylic acid (99%, Acros). 2-pyrrolocarboxylic acid (99%, Alfa Aesar). 2-furancarboxylic acid (98%, Acros). Isonicotinic acid (99%, Acros). 9,10-diphenyl anthracene (99%, Alfa Aesar).

1.2 Preparation of CsPbBr₃ nanocrystals.

CPB QDs were synthesized via a procedure developed by Son and coauthors with some modifications. Briefly, 150 mg PbBr₂, 368 mg anhydrous ZnBr₂, and 10 ml 1-octadecene were added to a 50 ml three-neck round bottom flask. The mixture was heated to 125 ºC under vacuum for 1 hour to remove the water. In another flask, a 1/1 (v/v) mixture of OA and OlAm ligands was preheated to 125 ºC under vacuum for 1 hour. From the OlAm/OA ligand mixture, 0.9 mL was injected into the PbBr₂/ZnBr₂ precursor. The reaction was carried out at 120 ºC until solids were fully dissolved. The resulting solution was then set to the desired temperature before injecting the CsOA precursor. The CsOA precursor was prepared by dissolving 250 mg Cs₂CO₃ in a solution
consisting of 0.9 ml OA and 9 ml ODE at 120 °C under vacuum. The reaction mixture was then placed in the N₂ atmosphere, and the temperature of the solution was raised to 150 °C to complete the reaction. The CsOA precursor was then preserved at 100 °C under N₂. From the Cs precursor, 0.8 mL was injected into the Pb precursor at different temperatures, varying from 85 to 140 °C, to obtain PNCs of different sizes. The reaction took 10 s for 140 °C and 90 s for 85 °C. After the reaction, the raw solution was cooled to room temperature with an ice bath and centrifuged at 3500 rpm for 30 min. For samples prepared with injection temperatures between 85 °C and 130 °C, the upper solutions were collected. Samples prepared with low injecting temperature (85 -110 °C) needed to be aged for a few hours for the undesired species to precipitate. For samples with 140 °C injection temperature, both the upper solution and the precipitated pellet were collected. The precipitated pellet was redissolved to a solution consisting of 5 ml of hexanes, 1 ml of OA, and 1 ml of OiAm. Various sizes of PNCs were obtained by stepwise precipitation with acetone. Detailed precipitation conditions are listed in Table S1. The PNCs were collected by centrifuging at 3500 rpm for 5 min, dried under vacuum overnight, and redissolved in hexanes.
Table S1 Preparation conditions for different sizes of PNCs

| Injecting T (°C) | Size (nm) | First excitonic absorption peak (nm) | Aged or not | The batch of precipitation | Volume of acetone |
|------------------|-----------|-------------------------------------|-------------|----------------------------|-------------------|
| 85               | 4.0       | 457 – 459                           | Y           | 1st                        | 1.3               |
|                  | 3.7       | 450 – 453                           | Y           | 2nd                        | 0.5               |
| 110              | 4.6       | 469 – 471                           | Y           | 1st                        | 1.2               |
|                  | 4.3       | 462 – 465                           | Y           | 2nd                        | 0.6               |
| 130              | 4.9       | 476 – 478                           | N           | 1st                        | 1.1               |
|                  | 4.6       | 470 – 473                           | N           | 2nd                        | 0.3               |
| 140              | 5.5       | 484                                 | N           | Upper                      | 1.1               |
|                  | 6.6       | 495                                 | N           | Precipitate                | 0.6               |

1 For different batches, the sizes of the products slightly differ from each other that causes fluctuating absorption peaks.
2 Stepwise size-selective precipitation was carried out to obtain the narrow distribution of absorption bands. Particles with larger sizes were precipitated first. The second round of precipitation was carried out after obtaining the larger-size particles from the first precipitation.
3 Volume ratios between the used acetone and raw PNC solutions.
4 PNCs prepared from different batches were used in the study, as long as the position of the 1st excitonic band matches the requirement.

1.3 Passivation of PNCs

The passivation solutions were prepared by dissolving the ligands, i.e., benzylic acid, picolinic acid, 2-thiophenecarboxylic acid, 2-pyrrolecarboxylic acid, 2-furancarboxylic acid, and isonicotinic acid, to the solution of OlAm. The yielded solutions had a 1-to-1 mole ratio between the ligand and OlAm. The concentrations of the ligand used in the experiment are 3, 6, or 30mM.

For passivating the PNCs, the ligand solutions are titrated to 3 ml of PNC solutions. The PL intensities of the sample were monitored. The concentrated ligand solution was used when high equivalents of ligands were needed to achieve the passivation. The maximum volume of the added ligand solution was kept under 3% (< 90 ul) of the original PNC solution. For this reason, we did not compensate for the change of the PNC concentration during titration.

1.4 Fabrication of the film with PNCs after the second-round purification.

We fabricated a solid-state film with PNCs with a procedure developed by Sargent and coauthors.²

The substrate glass slide was cleaned by alternately sonicating it in 0.15 M KOH and acetonitrile.
three times each and thoroughly rinsing with DI water. The PNC after the first purification step was directly dispersed in a 10 ml solution of ethyl acetate containing a mixture of 0.7 mM picolinic acid and 1.4 mM OlAm. The mixture was sonicated for 30 min. The glass substrate was placed at the bottom of the centrifugation tube, and the mixture was centrifuged at 3500 rpm for 5 min at 4 °C, so that the PNC equally distribute on the glass substrate to form a film, as it is shown in Figure 3.

1.5 Steady-State Absorption and Photoluminescence

UV-vis absorption spectroscopy was carried out with an Agilent Cary 5000 spectrometer using a quartz cuvette with a pathlength of 1 cm. The photoluminescence spectra were measured with a Horiba FluoroMax 3 fluorometer with an excitation wavelength of 405 nm.

1.6 Photoluminescence quantum yield (PLQY) measurement

PLQYs of PNCs were measured by comparing the PL intensity of the PNC sample ($I_s$) to that of a fluorescence reference standard ($I_r$), 9,10-diphenyl anthracene (DPA), which has a known quantum yield of 0.97 in cyclohexane. Samples and the standard were excited at 405 nm, and the photoluminescence spectra were recorded from 415 to 550 nm. The optical density of the standard at 405 nm was adjusted to be identical to that of the sample at the same wavelength, allowing a derivation of ±2% to ensure that they have the same transmittance during the measurement. The slight differences between the absorbed light between the sample and the standard were compensated by counting their ratio. The self-absorption of the PL from samples was corrected by dividing the sample's absorbance. The PLQYs is calculated using the following equation:

$$\Phi_s = \frac{I_s}{I_r/f} \cdot \frac{Abs_r n_s^2}{Abs_s n_r^2} \cdot \Phi_r$$
in which $f = 0.81$ is a factor to compensate the fluorescence intensity of DPA between 405 and 415 nm that were not captured when measuring the PL of the standard with 405 nm excitation. $n_s$ and $n_r$ are refractive indexes of the sample and the reference solution, respectively.

### 1.7 Attenuated total reflectance FTIR spectroscopy

The FTIR spectra were collected with a Bruker ALPHA spectrometer using an ATR module. PNCs samples and the unbound OlAm-PIC ligand were first dissolved in cyclohexane, dried on the ATR crystal (diamond) surface to form thin films of the sample. The spectra of ODE and the OlAm-OA ligand were measured by directly applying a small amount of these samples to the ATR crystal. The FTIR measurements were carried out by averaging 64 scans with a spectral resolution of 2 cm$^{-1}$.

### 1.8 Nuclear magnetic resonance spectroscopy

NMR measurements were carried out with a Bruker 500 MHz spectrometer equipped with a reversed probe for enhancing the $^1$H sensitivity. 1D $^1$H NMR was acquired with standard pulse sequence, and the relaxation delay was as 7 s. For quantitative NMR measurement, 1 mM mesitylene was added to the solution as the internal standard. The integrated intensities of the sample were compared to the aromatic $^1$H resonance at 6.65 ppm. 2D Nuclear Overhauser Effect Spectroscopy (NOESY) was conducted with a mixing time of 300 ms and a relaxation delay of 7 s. 4096 and 512 data points were collected for the direct and indirect dimensions, respectively, and both dimensions span from -0.5 to 9.5 ppm.

### 1.9 Time-resolved photoluminescence measurement

The time-resolved photoluminescence (TRPL) kinetics were measured with a home-built system, powered by 800 nm, 4 mJ, 150 fs pulses with a repetition rate of 1 kHz, generated from a pulse regenerated amplifier (Regen, Phidia-C, Uptek). Half of the pulse energy was sent to an optical
Amplifier (TOPAS, Light-Conversion) to obtain the idler pulses at 1680 nm. The frequency of the 1680 nm pulse was doubled by a BBO crystal to yield the 840 nm pulse, picked up with two 1000 nm long-pass dielectric beamsplitters. The 840 nm pulse was doubled again with a second BBO to generate the 420 nm pulse that pumped the experiment. The residual of the 840 nm pulse was filtered by two 450 nm long-pass dielectric beamsplitters. The 420 nm pulse was attenuated to 0.3 µJ, focused by a convex lens with a focal length of 500 mm to the sample. The photoluminescence signal was collected with a planoconvex lens (f.l. = 60 mm) and focused by an Aspheric condenser lens (f.l. = 32 mm) to a photodiode (DET025AL, Thorlabs). The pump scattering was removed by a 430 nm long-pass filter. The photocurrent generated by the photodiode was enhanced by a 25 dB preamplifier (8447F, Hewlett-Packaged) and recorded with an oscilloscope (TDS 680C, Tektronix) that was synchronized with the Regen output. Each kinetic trace was averaged for 10 s and saved to the computer via a LabView program. The system had an instrumental response of 0.57 ns based on measuring the full-wave half-maximum width of the 420 nm pump pulse signal collected with the same system.

1.9 Computation

Density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP). Electron exchange-correlation was represented by the functional of Perdew, Burke, and Ernzerhof (PBE) of generalized gradient approximation (GGA). The ion-electron interaction was described with the projector augmented wave (PAW) method. A cutoff energy of 400 eV was used for the plane-wave basis set. The energies were converged with a 1×10⁻⁴ eV tolerance, and the forces were optimized to within 0.025 eV/Å. The Brillouin zone was sampled by a 3 × 3 × 1 Monkhorst-Pack k-point mesh. The CsPbBr₃(001) surface (CsBr termination) with Br and Cs defects was examined in this work, as suggested by previous
experimental characterization of the PNC surface.\cite{8} It was modeled with seven atomic layers with 2 × 2 supercells. A vacuum of 15 Å along the z-direction was employed to avoid artificial interactions between images. The topmost three atomic layers of the slabs, together with the adsorbates, were allowed to relax, while the bottom four atomic layers were kept frozen during the structure optimizations. The binding energy of the ligands on the surface was defined as \( \Delta E = E_{\text{total}} - (E_{\text{slab}} + E_{\text{ligand}}) \), where \( E_{\text{total}} \), \( E_{\text{slab}} \), and \( E_{\text{ligand}} \) correspond to the energies of the slab with adsorbed ligand, the slab without ligand, and the isolated ligand, respectively. A negative value of \( \Delta E \) suggests favorable absorption. Vibrational frequencies of PIC on PNC were calculated using the method of finite-difference.

2. Estimation of \( k_r / k_{nr,trap} \) for PNCs with \( d = 4.3 \text{ nm} \).

In toluene, the photoluminescence quantum yield (PLQY) of the as-synthesized PNCs drop from 0.76 to 0.19 with the decrease of the particle sizes. The monotonic decrease of PLQYs with the increase of quantum confinement is in contrast to conventional metal chalcogenide nanocrystals, for which the PL can benefit from strong quantum confinement to a certain degree.\cite{9-11} We estimated the ratio between the radiative decay rate constant, \( k_r \), and the rate constant of exciton trapping at each of the surface traps, \( k_{nr,trap} \), using the model developed by Alivisatos and coauthors.\cite{12} In this model, only surface traps are considered, and all traps are treated equally. The PLQY of PNC is related to the number of surface traps, \( N_{\text{trap}} \) by:

\[
PLQY = \frac{k_r}{k_r + N_{\text{trap}} k_{nr,trap}} = \frac{k_r / k_{nr,trap}}{k_r / k_{nr,trap} + N_{\text{trap}}} \quad \text{Eq. S1}
\]

\( N_{\text{trap}} \) can be obtained from the Langmuir isotherm:

\[
N_{\text{trap}} = \frac{N_{\text{max}}}{1 + KL_{eq}[L]} \quad \text{Eq. S2}
\]
where $N_{\text{max}} = 322$ is the maximum number of surface defects that one PNC crystal can have, $K_{eq}^L = 10.5 \text{ mM}^{-1}$, is the bound equilibrium constant of the surface ligands, $[L] = C_L - C_{\text{PNC}}(N_{\text{max}} - N_{\text{trap}})$ is the concentration of unbound ligands in the solution, in which $C_L = N_L C_{\text{PNC}}$ is the total concentration of the surface ligand. Therefore, $N_{\text{trap}}$ can be rewritten as

$$N_{\text{trap}} = \frac{N_{\text{max}}}{1 + K_{eq}^L C_{\text{PNC}}(N_L - N_{\text{max}} + N_{\text{trap}})} \quad \text{Eq. S3}$$

For the PNC sample used in this experiment, we measured 4600 intrinsic ligands (OA and OlAm) in total per PNC by NMR, and therefore, $N_L = 2300$ per PNC given half of the NMR signal is from OlAm. We prepared a series of PNC solutions with different concentrations, as listed in Table S2. For every concentration of PNC ($C_{\text{PNC}}$), we can calculate the number of surface traps, $N_{\text{trap}}$, based on Eq. S3, which are related to the measured PLQYs by Eq. S1. The results are listed in Table S2.

We plot the PLQY as the function of $N_{\text{trap}}$ at different concentrations of PNC as shown in Figure S1, and the value of $k_r/k_{nr,\text{trap}} = 40 \pm 2$ is obtained by fitting the data with Eq. S1.

| $C_{\text{PNC}}$ (µM) | $N_{\text{trap}}$ | PLQY |
|-----------------------|-------------------|------|
| 0.283                 | 46                | 0.46 |
| 0.243                 | 52                | 0.41 |
| 0.232                 | 54                | 0.40 |
| 0.217                 | 57                | 0.38 |
| 0.18                  | 66                | 0.36 |
| 0.152                 | 76                | 0.35 |
| 0.111                 | 95                | 0.33 |
| 0.095                 | 105               | 0.32 |
| 0.068                 | 129               | 0.25 |
| 0.033                 | 185               | 0.20 |
Figure S1. PLQYs of the PNC with $d = 4.3$ nm in toluene as a function of the number of surface traps at different PNC concentrations. The red curve shows the fitted line using the function of Eq. S1.

It is worth pointing out that the model considers that all traps induced by surface defects are identical. Moreover, the model ignored the influence of defect sites that are not associated with the surface. Nevertheless, the comparison of the ratio, $k_r/k_{nr,\text{trap}}$, of the small PNC in relatively strongly quantum confinement regime ($d = 4.3$ nm, $k_r/k_{nr,\text{trap}} = 40$) with that of the literature data for the weakly confined, large PNC ($d = 9.4$ nm, and $k_r/k_{nr,\text{trap}} = 390$) demonstrates that the exciton trapping rate at the surface defect site is much faster in the case of strong quantum confinement.

The increasing exciton trapping rate in the small-size PNC can be understood by considering the evolution of the exciton state and the trap state under the influence of quantum confinement. First, the energy level of the delocalized band-edge exciton rises in the small PNC due to enhanced quantum confinement, whereas the energy of trap states induced by local defects is less sensitive to the change of particle sizes. Previous DFT results suggested that the energy level of the shallow trap is 0.16-0.23 eV above the conduction band energy of bulk CsPbBr$_3$.$^{13-14}$ In our cases of small nanoparticles, the increasing energy gap due to the quantum confinement effect is enough to bring the conduction band above the trap state, and result in deep traps. Second,
with the increase of quantum confinement, the probability density of charge carriers on the PNC surface increases,$^{15-16}$ raising the probability of carrier trapping at the surface defect. Finally, the number of surface defects also increases due to the increasing surface-to-volume ratio when the dimension of nanoparticles decreases.

For semiconductor nanomaterials, adjusting quantum confinement by controlling their dimensions is an appealing strategy for tailoring the energy landscape without varying the chemical composition. The strong quantum confinement effect can also enhance the electronic coupling between excitons and the surrounding molecules for facilitating charge carrier transportation.$^{16}$ Therefore, effective passivation of surface defects on small PNCs is in urgent need.

3. The protection effect of PIC for small-size PNCs in polar solvents

In polar solvents such as dimethoxyethane and ethyl acetate, small-size PNCs agglomerate and fuse to larger particles, which results in a bathochromic shift in their UV-vis absorption and PL spectra (Figure S2 and S3). This is likely because the detachment of intrinsic ligands is more severe in these polar solvents, which causes the exposure of a large area of the uncovered surface that serves as the site for small nanocrystals to fuse to larger structures. This effect has been employed to fabricate PNC with various shapes,$^{17-18}$ but is detrimental for maintaining the strong quantum confinement effect in small PNCs, because it diminishes quantum confinement.$^2$ For PNCs with $d = 4.3$ nm, we found that 350 equivalents addition of PIC ligands is enough for preserving the spectral feature of PNC in dimethoxyethane. In ethyl acetate, 700 equivalents of PIC are needed to preserve the narrow emission band centered at 478 nm. The PLQY of PNCs with $d = 4.3$ nm also reaches its maximum, 0.48, in ethyl acetate when adding 700 equivalents of PIC ligands. Extra PIC ligands can cause degradation that diminishes the PL intensity of PNCs.
Therefore, we choose to use 700 equivalents of PIC ligands to protect PNCs in ethyl acetate during the purification/cation-exchange process.

**Figure S2.** (A) UV-vis absorption and (B) PL spectra of PNCs with d = 4.3 nm in dimethoxyethane when adding different equivalents of PIC ligands.

**Figure S3.** (A) UV-vis absorption and (B) PL spectra of PNCs with d = 4.3 nm in ethyl acetate when adding different equivalents PIC ligands. PNCs are not fully soluble in ethyl acetate, and therefore there is a strong scattering background in the UV-vis spectra.
4. The PIC passivation does not affect the quantum confinement of PNC.

![Image](image1)

**Figure S4.** UV-vis absorption and PL spectra of PNCs (d = 4.3 nm) in toluene before and after adding 400 equivalents of PIC. The inset shows normalized PL spectra of the PNC before and after the passivation.

5. Simple L-type ligands show little passivation effect.

![Image](image2)

**Figure S5.** The change of PLQYs of the PNC with d = 4.3 nm in toluene with the addition of passivation ligands: thiophene, TC, pyridine (Py), pyridine/benzoate (BA), and PIC. Compared to TC and PIC, the single-role counterparts, thiophene, and pyridine, only enhanced the PL by 15% and 20%, respectively. Titrating Py/BA shows a similar passivation result as directly adding oleylammonium benzoate.
6. The degradation of PNCs with overly added PIC

Figure S6. (A) UV-vis absorption and (B) PL spectra of PNC with \(d=4.3\) nm in toluene when adding different equivalents of OlAm-PIC ligands. At 400 equivalents addition, the PL reaches the maximum, while the UV-vis spectrum shows little change compared to the original sample. With 1800 equivalents of addition, the absorbance at 405 nm (excitation wavelength of the PL spectrum) decreases by 36\%, and we observe a 39\% decrease from the maximum PL intensity. The comparison suggests that in toluene, the decrease of PL intensity with an extra addition of PIC is primarily due to the degradation of PNC.

Figure S7. (A) UV-vis absorption and (B) PL spectra of PNC with \(d=4.3\) nm in cyclohexane when adding different equivalents of OlAm-PIC ligands. The absorbance at the excitation wavelength, 405 nm, decreases by 16\% after increasing the equivalent of PIC ligands from 400 to 1100, while the PL intensity decrease by 28\%. A more significant decrease of the PL intensity implies that extra PIC does not only cause the decomposition of PNC and has a detrimental effect on the surface passivation of the survived PNC in cyclohexanes.
7. PL kinetics of PNCs in various solvents.

Figure S8. Time-resolved PL kinetics of PNCs with d = 4.3 nm before (black) and after (red) passivation with PIC recorded in (A) Tol (B) DCB (C) CHCl₃ (D) CyH and (E) Pen. The kinetics traces of the passivated sample are recorded when the highest PL intensity is achieved by titrating OlAm⁺PIC⁻ ligands. In each graph, the PL intensity is normalized to the maximum of the passivated sample. The kinetic traces are fit to a convoluted function of the IRS function (FWHM = 0.57 ns) and a double-exponential decay. It can be noticed that in relatively polar solvents, the passivation results in an increase of the "bright" population, while in apolar solvents, where PIC passivation shows less improvement on the PLQY, only minor changes for the TR-PL kinetics are observed.
8. Decomposition of $^1$HNMR signals in the alkene region

The $^1$H-NMR signals of purified PNC in the alkene region are deconvolved to two Lorentzian functions. Since we are interested in the ratio of the integrated intensity of the >5.5 ppm band in the alkene region, we do not distinguish every peak in the 5.46 ppm multiplets but simulating the multiplets with a single Lorentzian band that generally follows the lineshape. The deconvolution determines that the 5.54 ppm band in the OlAm-PIC spectrum accounts for 80% of the integrated intensity. In the OctAm-PIC spectrum, the 5.51 ppm band accounts for 70% of the total intensity in the entire region.

![Figure S9](image)

**Figure S9.** Decomposition of the NMR signals in the alkene region for PNCs purified with OlAm-PIC and PNCs after cation exchange with OctAm-PIC.

9. Quantifying the strongly adsorbed PIC ligands.

The strongly bound PIC on the purified PNC samples is invisible in the NMR spectra collected in toluene-D8. To quantify the bound PIC, after NMR experiments, we recovered the samples from toluene-D8 by drying them in a vacuum chamber. 0.7 ml of DMSO-D6 with pre-added mesitylene as the internal standard was added directly to the sample to destroy the PNC and release the surface ligands. The clear solution of DMSO-D6 was transferred into the NMR tube for taking the measurement. A comparison of NMR spectra of the purified PNC in toluene-D8 and the decomposed sample in DMSO-D6 is illustrated in **Figure S10**. In DMSO, the nanoparticle
decomposes and releases the ligands from the surface, and therefore PIC signals, absent from the original spectrum collected in toluene, appear. We determined the amount of PIC by comparing the integrated area of the PIC peak with that of the internal standard.

**Figure S10.** Comparison of the NMR spectra of the purified PNC sample in toluene-D8 and the decomposed sample in DMSO-D6. Signals are normalized to the intensity of mesitylene standard internal peaks at 6.63 ppm in toluene-D8 and 6.77 ppm in DMSO-D6.

10. **Titrating the purified PNC sample with the OctAm+OA− ligand.**

This titration experiment helps assign the NMR signals in the alkene region around 5.5 ppm. The starting sample consists of 4 µM of PNCs (d = 4.3 nm) after one round of purification. As determined by NMR before titration, the sample has 230 OlAm+, 50 OA− and 31 equivalents PIC per PNC. As shown in **Figure S11**, with the addition of OctAm+OA−, in the alkene resonance region, the broad NMR band originally peaked at 5.54 ppm becomes narrower and downshifted to 5.49 ppm, while the overall integration area of this band slightly decreases by 10%, as the addition of OctAm+OA− increases to 300 equivalents. In contrast, the overall integration area of the narrow band at 5.46 ppm increases proportionally with the addition of OA−, showing a slope (k = 0.94)
close to 1 (Figure S11B). The results reveal that the 5.46 ppm band corresponds to the alkene proton of OAc\(^-\), and the broad band with the higher chemical shift corresponds to the OIAm\(^+\).
**Figure S11.** Titration of the PNC sample after one round of purification with OctAm\(^{+}\)OA\(^{-}\). (A) NMR spectra change in the alkene region with the addition of OctAm\(^{+}\)-OA\(^{-}\) ligands. The numbers indicate equivalents of OctAm\(^{+}\)OA\(^{-}\) ligands added to the system. Band decomposition was carried out with the abovementioned method. (B) The plot of the measured numbers of ligands (OlAm\(^{+}\) and OA\(^{-}\)) against the number of added OctAm\(^{+}\)OA\(^{-}\). The numbers of ligands were measured by comparing the integrated area of the 5.54-5.49 ppm band and the 5.46 ppm band with the signal of the internal standard. (C) The appearance of the PIC signal with titration.

With the addition of the OA\(^{-}\) ligand, we also observed the appearance of signals in the aromatic region (**Figure S10C**) as a sign of desorption of the tightly bound PIC from the PNC surface due to the competitive adsorption of OA\(^{-}\). The reaction can be written as follows:

\[
(PNC) - PIC + OA^- \rightleftharpoons (PNC) - OA + PIC^- \quad \text{Eq. S4}
\]

The exchange equilibrium constant of the reaction, \(K_{eq}^{ex} = \frac{[PIC^-][(PNC) - OA]}{[OA^-][(PNC) - PIC]}\), reflects the relative affinity between PIC\(^{-}\) and OA\(^{-}\). When OA\(^{-}\) in the system increased to 330 equivalents, we observed about 6 equivalents PIC desorbed out of the total 31 equivalents PIC, which gives \(K_{eq}^{ex} = \frac{6 \times 6}{(330 - 6)(31 - 6)} \approx 4 \times 10^{-3}\). Therefore, the affinity of PIC is about 250 folds greater than OA\(^{-}\).
11. 2D-NOESY NMR spectrum

Figure S12. (A) 2D-NOESY of the PNC sample in Figure 5. The black rectangles in (A) circle the spectral areas magnified in (B) for the alkene signal of OlAm, (C) for PIC cross-peaks. Molecular structures of the ligands and (D) for the PIC-OlAm intermolecular coupling region.
12. DFT results of different binding configurations

![Diagram](image)

**Figure S13.** Binding configurations of isonicotinate (A), benzoate (B), and pyridine (C) on PNC. H, white; C, grey; O, red; N, blue; Cs, purple; Br, brown; Pb, dark grey.

13. FTIR spectra of PNC and the vibrational modes of PIC

As shown in **Figure S14**, the IR feature of as-synthesized PNC is, in general, a combination of signals from the ODE solvent and the intrinsic ligands. The only exception is the 1712 cm\(^{-1}\) band that does not show in the OlAm-OA spectrum. The frequency of this band is close to the vibrational features of the asymmetric stretch of the COO in the oleic acid, which suggests that a part of oleates becomes protonated after the PNC has been synthesized. After purification, ODE features at 3078, 991, and 908 cm\(^{-1}\) disappear entirely from the spectrum. Most IR bands appearing in the finger-print region are from the bound PIC and remained OlAm\(^+\). Tentative assignments of these vibrational modes are made according to Ref. 19, and listed in **Table S3**.
Figure S14. (A) FTIR spectra of as-synthesized PNCs, the OlAm-OA (1:1, v/v) ligand that was injected during the synthesis, and ODE. Blue and red dotted lines indicate the IR features of ODE and the intrinsic ligand, respectively. (B) FTIR spectra of as-synthesized and purified PNCs (d=4.3 nm) and the unbound OlAm-PIC ligand. Featured ODE peaks are labeled for the spectrum of the original PNC.
| Free ligands       | PIC on PNC | Calculated vibrational modes of PIC<sup>2</sup> | Assignments                                      |
|-------------------|------------|-----------------------------------------------|--------------------------------------------------|
|                   |            |                                               | (N-H) of OlAm<sup>3</sup>                          |
| 3000-3200 b<sup>1</sup> | 3005 w     |                                               |                                                  |
| 3005 w            | 3005 w     |                                               |                                                  |
| 2956 s            | 2956 s     | OlAm v(C-H)                                   |                                                  |
| 2920 s            | 2920 s     | OlAm v(C-H)                                   |                                                  |
| 2852 s            | 2852 s     | OlAm v(C-H)                                   |                                                  |
| <3000 m b         |            | OlAm v(C-H)                                   | v(N-H) of OlAm and v(O-H)                         |
| 1637 m            | 1636 m     | OlAm                                          | v(CC)ar<sup>4</sup>                              |
| 1608 m            |            |                                               | v(CC)ar<sup>4</sup>                              |
| 1581 s            | 1586s      | OlAm                                          | v(CC)ar + v(COO<sup>-</sup>)                      |
| 1556 s            | 1568s      | OlAm                                          | v(CC)ar + v(COO<sup>-</sup>)                      |
| 1532s             |            | OlAm                                          | v(CC)ar + v(CN)ar + v(COO<sup>-</sup>)            |
| 1480 (shoulder)   | 1483-1563  | OlAm                                          | v(CC)ar                                          |
| 1464 m & 1432 m   | 1464 s     | OlAm                                          | v(CC)ar + OlAm                                   |
| 1432 s            | 1418-1426  | OlAm                                          | v(CC)ar + OlAm                                   |
| 1404 s            | 1316-1361  | OlAm                                          | v(CC)ar + v(COO<sup>-</sup>)                      |
| 1380 s            | 1377 w     | OlAm                                          | v(CC)ar + OlAm                                   |
| 1380 s            |            |                                               |                                                  |
| 1288 w            | 1290 w     | OlAm                                          | β(CH)+v(C-N)ar                                   |
| 1253 w            | 1254 w     | OlAm                                          |                                                  |
1228 w 1232 w 1248-1274

1165 w 1164 w β(CH) 1151-1161

1140 w 1140 w β(CH) 1149-1153

1084 w 1086 w β(CH) 1085-1088

1042 w 1045 w β(CH) 1045-1049

998 w 1010 Ring breathe + γ (CH) 989-1000

966 w 965 w γ (CH) + OlAm 957-960

837 m 847 w β₆(COO⁻) + γ (CH) 815-828

981-996

793-816
25 m 25 m
746 m 754 m γ(CH)
746-738 m

710 s 721 m φ(CCC) + OlAm
694 s 705 m φ(CCC)
678-686 m

621 m 634 m α(CCC)
609-627 m

1 s – strong, m – medium, w – week, b – broad.
2 Mode diagrams and calculated vibrational frequency shifts: "Free ligand"-"Bound ligand". Vibrational modes of the bound PIC are visualized by an open-source Java viewer Jmol.20
3 The CH stretching region is dominated by the OlAm modes. Vibrational modes of OlAm are not specified because they are irrelevant to the PIC binding.
4 ν - stretching, β – in-plane deformation, γ – out-of-plane deformation, φ(CCC) – aromatic ring out-of-plane deformation, α(CCC) – aromatic ring in-plane deformations.

References
1. Dong, Y.; Qiao, T.; Kim, D.; Parobek, D.; Rossi, D.; Son, D. H., Precise Control of Quantum Confinement in Cesium Lead Halide Perovskite Quantum Dots via Thermodynamic Equilibrium. *Nano Lett.* 2018, 18 (6), 3716-3722.
2. Kim, Y.; Yassitepe, E.; Voznyy, O.; Comin, R.; Walters, G.; Gong, X.; Kanjanaboos, P.; Nogueira, A. F.; Sargent, E. H., Efficient Luminescence from Perovskite Quantum Dot Solids. *ACS Appl. Mater. Interf.* 2015, 7 (45), 25007-25013.
3. Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S., Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector. *Phys. Chem. Chem. Phys.* 2009, 11 (42), 9850-9860.
4. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, 54 (16), 11169-11186.
5. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 1996, 6 (1), 15-50.
6. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77 (18), 3865.
7. Blöchl, P. E., Projector augmented-wave method. *Phys. Rev. B* 1994, 50 (24), 17953-17979.
8. Chen, Y.; Smock, S. R.; Flintgruber, A. H.; Perras, F. A.; Bruchey, R. L.; Rossini, A. J., Surface Termination of CsPbBr₃ Perovskite Quantum Dots Determined by Solid-State NMR Spectroscopy. *J. Am. Chem. Soc.* 2020, 142 (13), 6117-6127.
9. Semonin, O. E.; Johnson, J. C.; Luther, J. M.; Midgett, A. G.; Nozik, A. J.; Beard, M. C., Absolute Photoluminescence Quantum Yields of IR-26 Dye, PbS, and PbSe Quantum Dots. *J. Phys. Chem. Lett.* 2010, 1 (16), 2445-2450.
10. Zhang, J.; Zhang, X.; Zhang, J. Y., Size-Dependent Time-Resolved Photoluminescence of Colloidal CdSe Nanocrystals. *J. Phys. Chem. C* 2009, 113 (22), 9512-9515.

11. Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G., (CdSe)ZnS Core–Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites. *J. Phys. Chem. B* 1997, 101 (46), 9463-9475.

12. Nenon, D. P.; Pressler, K.; Kang, J.; Koscher, B. A.; Olshansky, J. H.; Osowiecki, W. T.; Koc, M. A.; Wang, L.-W.; Alivisatos, A. P., Design Principles for Trap-Free CsPbX3 Nanocrystals: Enumerating and Eliminating Surface Halide Vacancies with Softer Lewis Bases. *J. Am. Chem. Soc.* 2018, 140 (50), 174103.

13. Sebastian, M.; Peters, J. A.; Stoumpos, C. C.; Im, J.; Kostina, S. S.; Liu, Z.; Kanatzidis, M. G.; Freeman, A. J.; Wessels, B. W., Excitonic emissions and above-band-gap luminescence in the single-crystal perovskite semiconductors CsPbBr3 and CsPbI3. *Phys. Rev. B* 2015, 92 (23), 235210.

14. Shi, H.; Du, M.-H., Shallow halogen vacancies in halide optoelectronic materials. *Phys. Rev. B* 2014, 90 (17), 174103.

15. Xiong, W.; Hickstein, D. D.; Schnitzenbaumer, K. J.; Ellis, J. L.; Palm, B. B.; Keister, K. E.; Ding, C.; Miaja-Avila, L.; Dukovic, G.; Jimenez, J. L.; Murnane, M. M.; Kapteyn, H. C., Photoelectron Spectroscopy of CdSe Nanocrystals in the Gas Phase: A Direct Measure of the Evanescent Electron Wave Function of Quantum Dots. *Nano Lett.* 2013, 13 (6), 2924-2930.

16. Luo, X.; Lai, R.; Li, Y.; Han, Y.; Liang, G.; Liu, X.; Ding, T.; Wang, J.; Wu, K., Triplet Energy Transfer from CsPbBr3 Nanocrystals Enabled by Quantum Confinement. *J. Am. Chem. Soc.* 2019, 141 (10), 4186-4190.

17. Pan, J.; Li, X.; Gong, X.; Yin, J.; Zhou, D.; Sinatra, L.; Huang, R.; Liu, J.; Chen, J.; Dursun, I.; El-Zohry, A. M.; Saidaminov, M. I.; Sun, H.-T.; Mohammed, O. F.; Ye, C.; Sargent, E. H.; Bakr, O. M., Halogen Vacancies Enable Ligand-Assisted Self-Assembly of Perovskite Quantum Dots into Nanowires. *Angew. Chem., Int. Ed.* 2019, 58 (45), 16077-16081.

18. Zhang, X.; Bai, X.; Wu, H.; Zhang, X.; Sun, C.; Zhang, Y.; Zhang, W.; Zheng, W.; Yu, W. W.; Rogach, A. L., Water-Assisted Size and Shape Control of CsPbBr3 Perovskite Nanocrystals. *Angew. Chem., Int. Ed.* 2018, 57 (13), 3337-3342.

19. Marsh, J. L.; Wayman, A. E.; Smiddy, N. M.; Campbell, D. J.; Parker, J. C.; Bosma, W. B.; Remsen, E. E., Infrared Spectroscopic Analysis of the Adsorption of Pyridine Carboxylic Acids on Colloidal Ceria. *Langmuir* 2017, 33 (46), 13224-13233.

20. Jmol: an open-source Java viewer for chemical structures in 3D. [http://www.jmol.org/](http://www.jmol.org/)