

Colloidal-quantum-dot photovoltaics using atomic-ligand passivation

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Colloidal-quantum-dot (CQD) optoelectronics offer a compelling combination of solution processing and spectral tunability through quantum size effects. So far, CQD solar cells have relied on the use of organic ligands to passivate the surface of the semiconductor nanoparticles. Although inorganic metal chalcogenide ligands have led to record electronic transport parameters in CQD films, no photovoltaic device has been reported based on such compounds. Here we establish an atomic ligand strategy that makes use of monovalent halide anions to enhance electronic transport and successfully passivate surface defects in PbS CQD films. Both time-resolved infrared spectroscopy and transient device characterization indicate that the scheme leads to a shallower trap state distribution than the best organic ligands. Solar cells fabricated following this strategy show up to 6% solar AM1.5G power-conversion efficiency. The CQD films are deposited at room temperature and under ambient atmosphere, rendering the process amenable to low-cost, roll-by-roll fabrication.

Solution-synthesized quantum dots unite the attractive customization of the semiconductor energy bandgap with low-cost solution-processed fabrication. The power of these concepts has been proven in optoelectronic device applications: including high-detectivity radiation sensing in the infrared¹, visible², and ultraviolet³; in highly emissive electroluminescent devices for lighting and displays⁴; and in solution-processed lasers⁵ and photovoltaics⁶.

The tunability of CQDs enables optimal matching of the absorbance of single-junction solar cells to the solar spectrum⁷ and permits multiple-junction devices for further efficiency improvements⁸. However, the benefits of the tunability and processability of CQDs are counterbalanced by the challenge of achieving superior device performance. CQDs, following their synthesis in solution, are generally capped by organic ligands that employ long chains (8–18 carbons) to ensure their solution processability⁹. These produce insulating barriers between CQDs that militate against efficient carrier transport when processed into films. Much attention has therefore been devoted to the development of new ligand strategies that minimize the interparticle spacing to promote carrier transport and lower the defect density to reduce recombination loss. CQD photovoltaics have been realized using a variety of short mono- and bidentate organic ligand strategies (Fig. 1a). Short alkylthiols^{10,11}, aromatic thiols¹², alkylamines¹³, and mercaptocarboxylic acids (MPA; ref. 14) have all shown promise in achieving effective passivation while reducing interparticle spacing, achieving a best reported efficiency of 5.1% (ref. 14).

The bulkiness of these organic ligands, as well as their vulnerability to oxidation and thermal degradation, has motivated

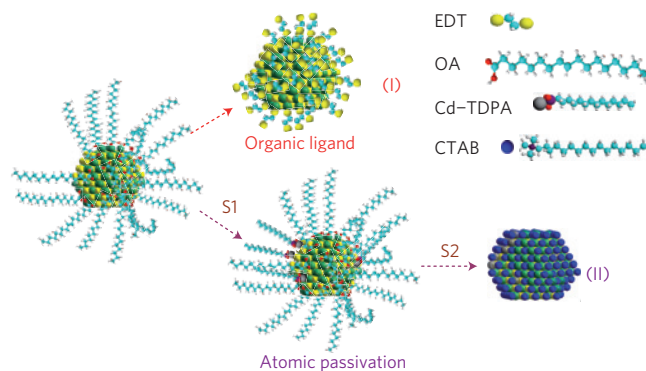


Figure 1 | Organic and atomic passivation strategies. PbS CQDs having a Pb^{2+} -rich surface are initially capped with deprotonated oleic acid (OA). In the organic route, EDT substitutes the long OA ligands and binds to Pb^{2+} on the surface. In the atomic ligand route described herein, a cadmium-tetradecylphosphonic acid (Cd-TDPA) complex was first introduced to the PbS CQD surface to passivate the exposed S^{2-} anions (S1). A solid-state halide anion treatment, such as that employing cetyltrimethylammonium bromide (CTAB), introduced Br^- to cap the surface cations (S2), forming all-inorganic, halide anion-passivated PbS CQDs. The molecular structures of EDT, OA, Cd-TDPA and CTAB are shown as insets. Colours are green (lead), yellow (sulphur), cyan (carbon), white (hydrogen), red (oxygen), grey (cadmium), blue (bromine) and purple (nitrogen).

an inorganic ligand strategy. These new and highly promising inorganic ligands, especially the metal chalcogenide complexes

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(MCCs; refs 15,16), have—once annealed at 200 °C—led to impressive field effect transistor (FET) electron mobilities, as high as $16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in $\text{In}_2\text{Se}_4^{2-}$ -capped CdSe CQDs (ref. 17). Once bonded to the nanoparticle surface, the multivalent ligands render the CQDs negatively charged, providing the strong electrostatic repulsion needed to achieve a stable colloidal dispersion¹⁵. Processing these MCC-CQDs into films requires thermal annealing to cure dangling bonds, with the goal of achieving a film that is free from deep traps—defects that would otherwise lead to unacceptable recombination.

No photovoltaic device has yet been reported based on inorganic ligands. We took the view that a new inorganic ligand concept—one specifically targeted at achieving inherently well-passivated films—was warranted. We believed that monovalent inorganic ligands bonded to cations on nanoparticle surfaces would offer a direct path to highly effective passivation. Rather than requiring annealing to remove dangling bonds, a monovalent ligand would tend to form charge-neutral nanoparticle films, even with only room-temperature processing. We focused on atomic halide anions^{18,19}—analogous to hydrogen successfully employed in amorphous silicon passivation—with the goal of using the shortest imaginable ligands. Whereas short organics such as ethanedithiol have $\sim 0.5 \text{ nm}$ size, and MCCs such as $\text{Sn}_2\text{S}_6^{4-}$ are approximately 0.7 nm , halide anions such as Cl^- , Br^- and I^- offer size scales down to 0.1 nm . Halide anions also have a strong affinity to cations on the CQD surface and offer the possibility of a strong X-type (as distinct from L-type, or dative²⁰) bond. Furthermore, this strategy would enable an entire process flow achievable at room temperature, under ambient atmosphere, making it amenable to low-cost, roll-by-roll production of CQD photovoltaics on flexible polymer substrates.

In Fig. 1 we depict our route to atomic-ligand passivation. As synthesized PbS CQDs are capped with oleic acid ligands. Conventional thiol treatments remove oleic acid, passivating the PbS CQDs through the formation of a Pb–S bond²¹. We sought first to improve the passivation of any surface defects associated with dangling bonds due to unpassivated sulphur surface anions²². We treated the PbS CQDs using a mixture of CdCl_2 , tetradecylphosphonic acid (TDPA), and oleylamine (OLA). A CdCl_2 –TDPA–OLA mixture was used instead of cadmium oleate to reduce its reactivity. The less-reactive precursors, deployed in a gentle treatment (60 °C, 5 min), led to small redshift (3–18 nm) in the absorption excitonic peak following treatment. In contrast, the widely explored Cd cation exchange strategy produces a significant blueshift in the absorption peak²³. Our Cd–TDPA–OLA-treated PbS CQDs exhibited an improved size distribution, better stability, and fewer surface defects, as evidenced by photoluminescence enhancement (see Supplementary Fig. S1 and Table S1).

We then applied a solid-state treatment, variously using either cetyltrimethylammonium bromide (CTAB), hexadecyltrimethylammonium chloride (HTAC), or tetrabutylammonium iodide (TBAI) salt dissolved in anhydrous methanol, to treat the oleic-acid capped PbS CQD film. This step produced halide-passivated PbS CQD films. We delivered the halide anions with the aid of bulky ammonium cations to avoid the complication of possible cation exchange with PbS CQDs (ref. 24). Recent studies have shown that the CQD–ligand bond strength can be explained by means of simple electrostatic interactions²⁵: the negatively charged halide anions (Cl^- , Br^- and I^-) bind to Pb^{2+} or Cd^{2+} on the PbS CQD surface during the solid-state treatment and are immobilized inside the film. The ammonium cations combine with the deprotonated oleic acid and are washed away in the methanol rinse²⁶. Fourier transform infrared spectroscopy (FTIR) spectra (Fig. 2a) show the complete removal of the oleate ligands (C–H vibrations at $2,922 \text{ cm}^{-1}$ and $2,852 \text{ cm}^{-1}$, and COO^- vibrations at $1,545 \text{ cm}^{-1}$ and $1,403 \text{ cm}^{-1}$, are all eliminated following treatment). The completeness of our ligand-exchange procedure was facilitated by the nucleophilic

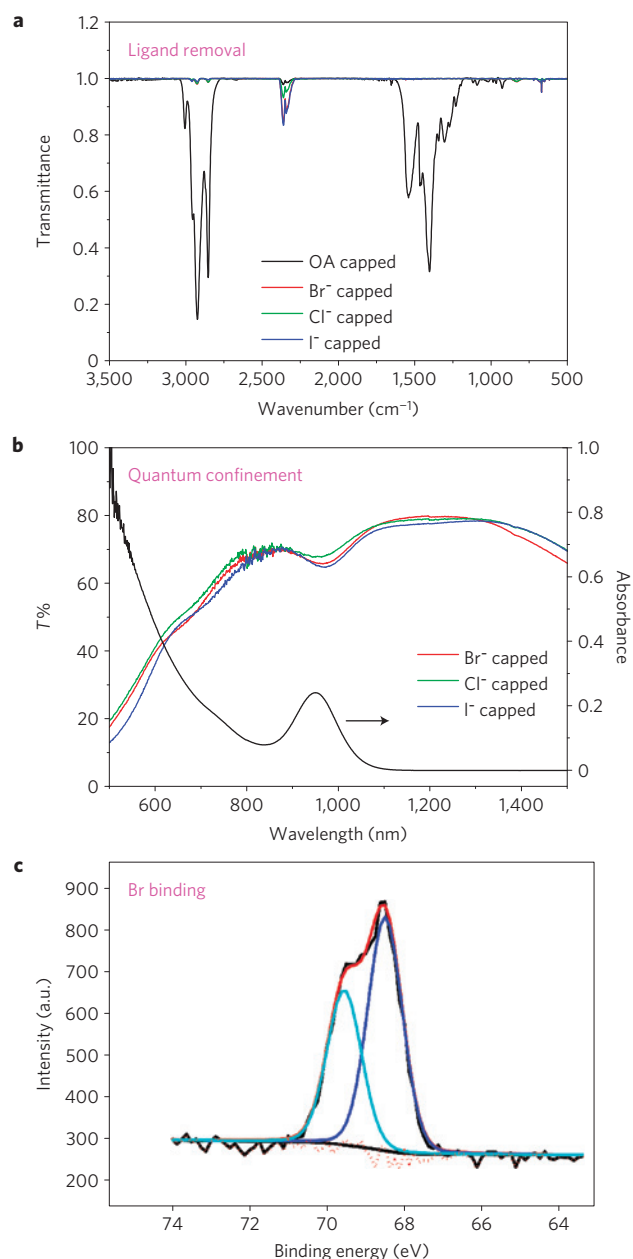


Figure 2 | Materials characterization following halide anion treatment.

a, FTIR spectra of PbS CQD films treated by HTAC, CTAB and TBAI. The vibrations at $2,922 \text{ cm}^{-1}$ and $2,852 \text{ cm}^{-1}$ are ν_{asym} (C–H) and ν_{sym} (C–H), and at $1,545 \text{ cm}^{-1}$ and $1,403 \text{ cm}^{-1}$ are ν_{asym} (COO^-) and ν_{sym} (COO^-), respectively, which are associated with the original oleate ligands. The flat absorption spectra for Cl^- , Br^- and I^- -capped CQD film indicate that the final PbS CQD films were free of organic ligands. **b**, The transmittance of Cl^- , Br^- and I^- -capped PbS CQD films measured inside an integrating sphere. The arrow indicates the absorption of oleate-capped PbS CQDs dispersed in toluene. **c**, Binding energy of Br 3d in Br^- -capped PbS CQD films. The dark curve is the original data and the red curve is the superposition of the Gauss-Lorentz fitting (blue and cyan) of the doublet of the Br 3d peak.

nature of the halide anion, the electrophilicity of undercoordinated Pb^{2+} and Cd^{2+} at the CQD surface, and the partial removal of oleic acid by methanol (see Supplementary Fig. S2).

After the halide treatment, the quantum-confined bandgap was fully retained, as indicated by the well-defined excitonic peak in the absorption spectra of Cl^- , Br^- , and I^- -capped PbS CQD

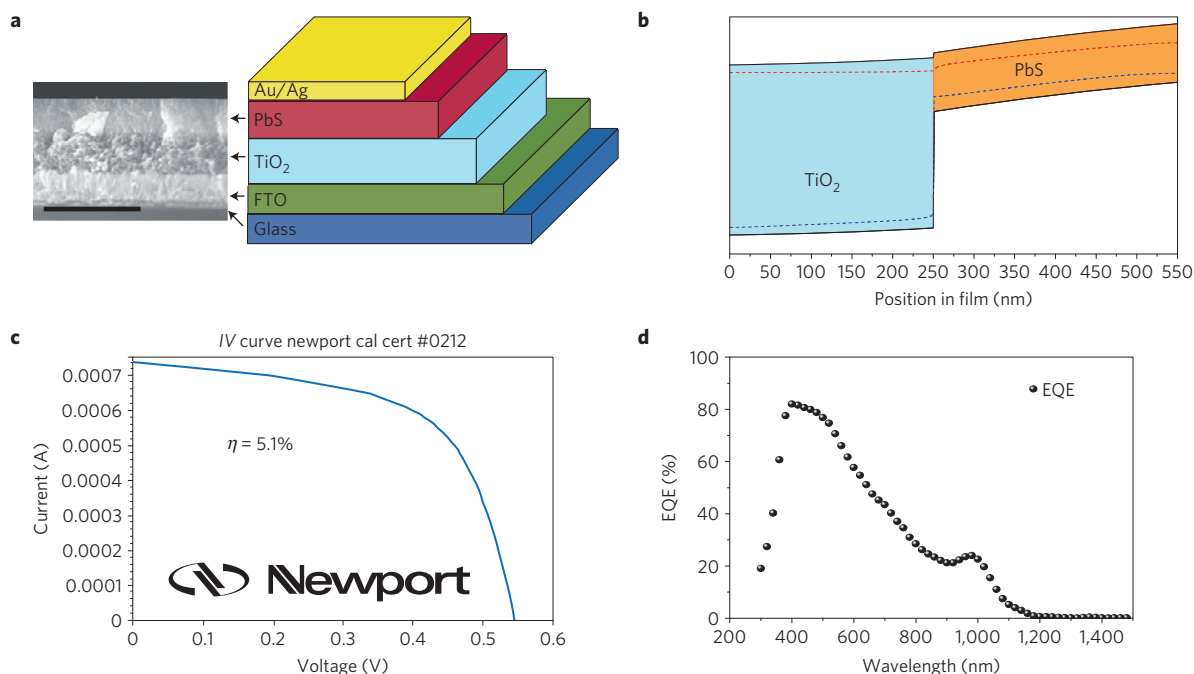


Figure 3 | Photovoltaic device physics and performance. **a**, Schematic of FTO/TiO₂/PbS/Au/Ag device architecture. The inset is the cross-sectional SEM images of a representative device. The scale bar is 1 μm. **b**, Band bending of an illuminated TiO₂/PbS device under open-circuit conditions. The dashed red and blue lines represent the quasi-Fermi energy of the electrons and holes, respectively. **c**, Device performance measured by a NREL-accredited laboratory (Newport) at 25 °C under 0.93 sun illumination: $V_{oc} = 0.544 \pm 0.006$ V, $I_{sc} = 0.00071 \pm 0.0001$ A, FF = $62 \pm 2\%$ and efficiency = $5.1 \pm 0.2\%$. **d**, The white light-biased EQE spectrum of a champion device. The sharp drop in EQE below 400 nm is due to the TiO₂ absorption.

films (Fig. 2b). The ~ 30 meV redshift in optical transitions of the PbS film suggests delocalization of electron and hole wavefunctions due to electronic coupling arising from the reduced interparticle distance (see Supplementary Fig. S3), combined with the effect of the increased dielectric constant²⁷. Scanning transmission electron microscopy (STEM) showed that the halide anion treatment resulted—within each sub-layer making up the total multilayer film—in small cracks arising from significant volume contraction when the bulky oleic acid was removed. The analogous effect has been widely observed in CQD films treated with short organic ligands^{21,28}. These small cracks were filled by the top layers during the layer-by-layer coating process, leading to the compact and pinhole-free films necessary for photovoltaic device realization (see Supplementary Fig. S4). Grazing-incidence small-angle X-ray scattering (GISAXS) showed no scattering peak in CTAB-treated PbS CQD films, suggesting the absence of in-plane and out-of-plane ordering (see Supplementary Fig. S5), similar to the reduced ordering seen in PbSe CQD film after liquid²⁷ or vapour²⁹ phase ethanedithiol (EDT) treatment.

Energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) analysis (see Supplementary Fig. S6 and Table S2) showed quantitatively significant bromide anion levels in the CTAB-treated PbS CQD film, the quantity consistent with a 1:1 ratio of Br⁻ to surface Pb²⁺ cations. This 1:1 ratio is reminiscent of the oleate ligand to surface Pb²⁺ concentration in PbSe CQDs seen using NMR (ref. 30). Energy filtered-TEM imaging and elemental mapping were conducted on CTAB-treated samples (see Supplementary Fig. S7). A strong spatial correlation was found between Br, Pb, and S, consistent with bromine present on the quantum dot surface. XPS further indicated a binding energy of Br 3d^{5/2} of 68.6 eV (Fig. 2c), in agreement with the binding energy of Br 3d^{5/2} in bulk PbBr₂ (ref. 31). No other Br chemical state was found in the XPS spectrum. The EDX, energy filtered-TEM, and XPS results confirmed the binding of Br⁻ to Pb²⁺ on the PbS CQD surface²⁰.

Minority carrier electron mobility inside our p-type CQD films is a key determinant of overall solar power-conversion efficiency. We employed FET mobility measurements³² and showed that our halide-terminated films achieved electron mobilities of 4×10^{-2} cm² V⁻¹ s⁻¹ (see Supplementary Fig. S8). These results, achieved using a room-temperature process, are comparable to those achieved using the hydrazine-based metal-chalcogenide complex route followed by 200 °C annealing¹⁵. As detailed below, our process provided—compared with organics—an order-of-magnitude enhancement in minority carrier mobility compared with MPA-treated films, and two orders-of-magnitude relative to EDT.

In summary, our atomic-ligand passivation strategy—implemented at room temperature, in air, with no hydrazine, and requiring no annealing—produced an all-inorganic film in which cation-enriched quantum dots were capped with a complete monolayer of halide anions and the mobilities of our films were among the best reported in PbS CQD films^{15,32,33}.

To build photovoltaic devices, we formed a 270–300 nm thick layer of this inorganic CQD film on a Zr-doped TiO₂ electrode residing on fluorine-doped tin oxide (FTO) on glass. The CQD film was ohmically contacted using a sputtered Au top electrode, or equivalently a MoO₃/Ag contact. Band bending occurs at the junction between the p-type PbS and n-type TiO₂, causing photoelectrons generated in the CQDs to be injected into the TiO₂ and collected by the FTO (Fig. 3b). Photogenerated holes travel to the top Au electrode. The cross-sectional SEM micrograph of the TiO₂–PbS heterojunction device is included in Fig. 3a.

Device performance was measured by an internationally accredited PV calibration laboratory (Newport Technology and Application Center PV Lab) at 25 °C under 0.93 sun. A certified solar power conversion efficiency of $5.1 \pm 0.2\%$ was obtained. An open circuit voltage $V_{oc} = 0.544$ V, short circuit current density $J_{sc} = 14.6$ mA cm⁻² and fill factor FF = 62% were obtained. This is the first certified CQD solar cell with efficiency >5% (ref. 34) that

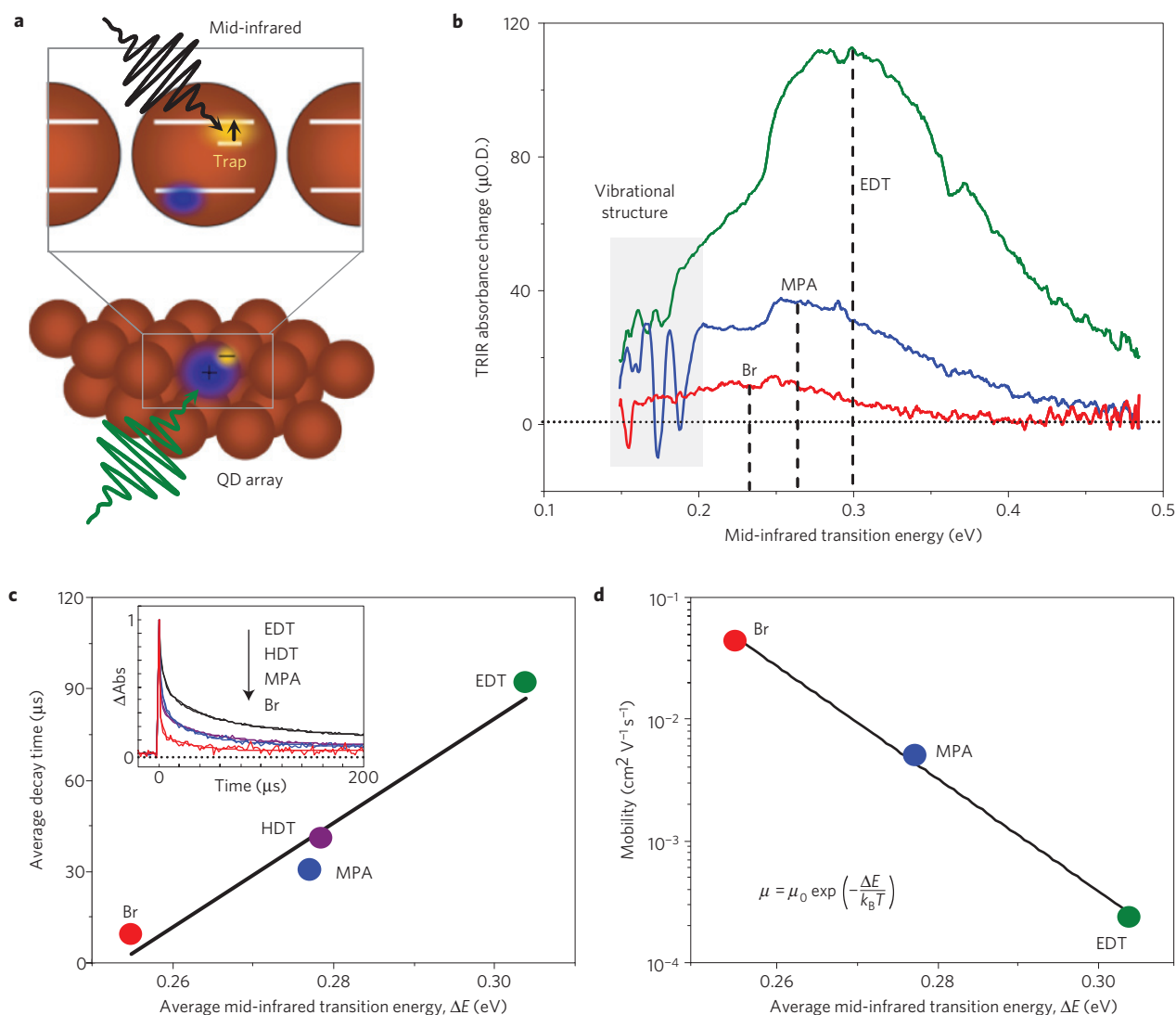


Figure 4 | TRIR characterization of Br^- -capped PbS CQD film. **a**, Cartoon illustrating the trap-to-band transitions observed in TRIR transient absorption spectra. Bandgap excitation of CQDs results in the formation of excitons from which electrons (holes) can become trapped. Trapped carriers are promoted back into conduction (valence) states through trap-to-band transitions. **b**, The broad features in the TRIR spectra result from trap-to-band transitions observed in PbS CQDs treated with various ligands. The amplitude and shape of the spectra reflect the number and depth of trapped carriers. The narrow features appearing between 0.15 and 0.2 eV correspond to vibrational spectra of ligands that are perturbed by localization of charges at surface trap sites. **c**, The average decay times of the trap-to-band transitions in PbS CQD films are strongly correlated with the average mid-infrared transition energies. **d**, The mobilities of electrons in PbS CQD films are also strongly correlated with the average mid-infrared transition energies for a variety of passivation methods. The Br^- -capped PbS CQD film has the highest mobility within the set, consistent with the lower average trap energy as determined by TRIR spectroscopy.

agreed within 0.2 power points with the numbers measured in our own laboratories. Depending on the details of treatment conditions, solar cells showed a V_{oc} ranging between 0.42 and 0.55 V, J_{sc} ranging between 14–24 mA cm^{-2} , and FF of 50%–63%. Our measured solar power-conversion efficiencies ranged from 4.8–6.0% (see Supplementary Fig. S9) and a champion device showing static efficiency of 6.0% ($V_{\text{oc}} = 0.48 \text{ V}$, $J_{\text{sc}} = 20.2 \text{ mA cm}^{-2}$, FF = 62%) is presented in Supplementary Fig. S10. The corresponding external quantum efficiency (EQE) spectrum is shown in Fig. 3d. The EQE reached 80% in the blue spectral region, consistent with an internal quantum efficiency (IQE) exceeding 90%. Integrating the white light-biased EQE spectrum with the AM1.5G solar spectrum yielded a short circuit current density J_{sc} of 20.4 mA cm^{-2} , in good agreement with the measured J_{sc} .

TiO_2 was measured to have an n-type doping density N_{D} of $\sim 4 \times 10^{15} \text{ cm}^{-3}$, in good agreement with literature values for TiO_2 processed in air and post-treated with TiCl_4 ; (ref. 35) PbS CQD

films were determined from capacitance–voltage measurement to have a p-type doping density $N_{\text{A}} \sim 10^{15}$ – 10^{16} cm^{-3} (see Supplementary Figs S11–S13). Using the band edge energy measured by cyclic voltammetry³⁶, we predicted a built-in potential (V_{bi}) in our p–n heterojunction device in the range 0.47–0.53 V, in good agreement with the V_{bi} measured using capacitance–voltage characterization and the device V_{oc} (see Supplementary Figs S14, S15). The measured doping density of the Br^- -capped PbS CQD film was one order of magnitude lower than the previously reported MPA- and EDT-treated PbS films. This is consistent with the strong suppression of defect states by our monovalent inorganic passivation strategy.

We therefore sought to investigate the density and energy depth of trap states in the film. Time-resolved infrared (TRIR) spectroscopy^{37,38} permits the direct examination of charge traps in quantum dots through excitation of carriers from surface trap states into band states of the quantum dots (see Fig. 4a and Supplementary Fig. S16). Figure 4b presents TRIR spectra measured 500 ns after

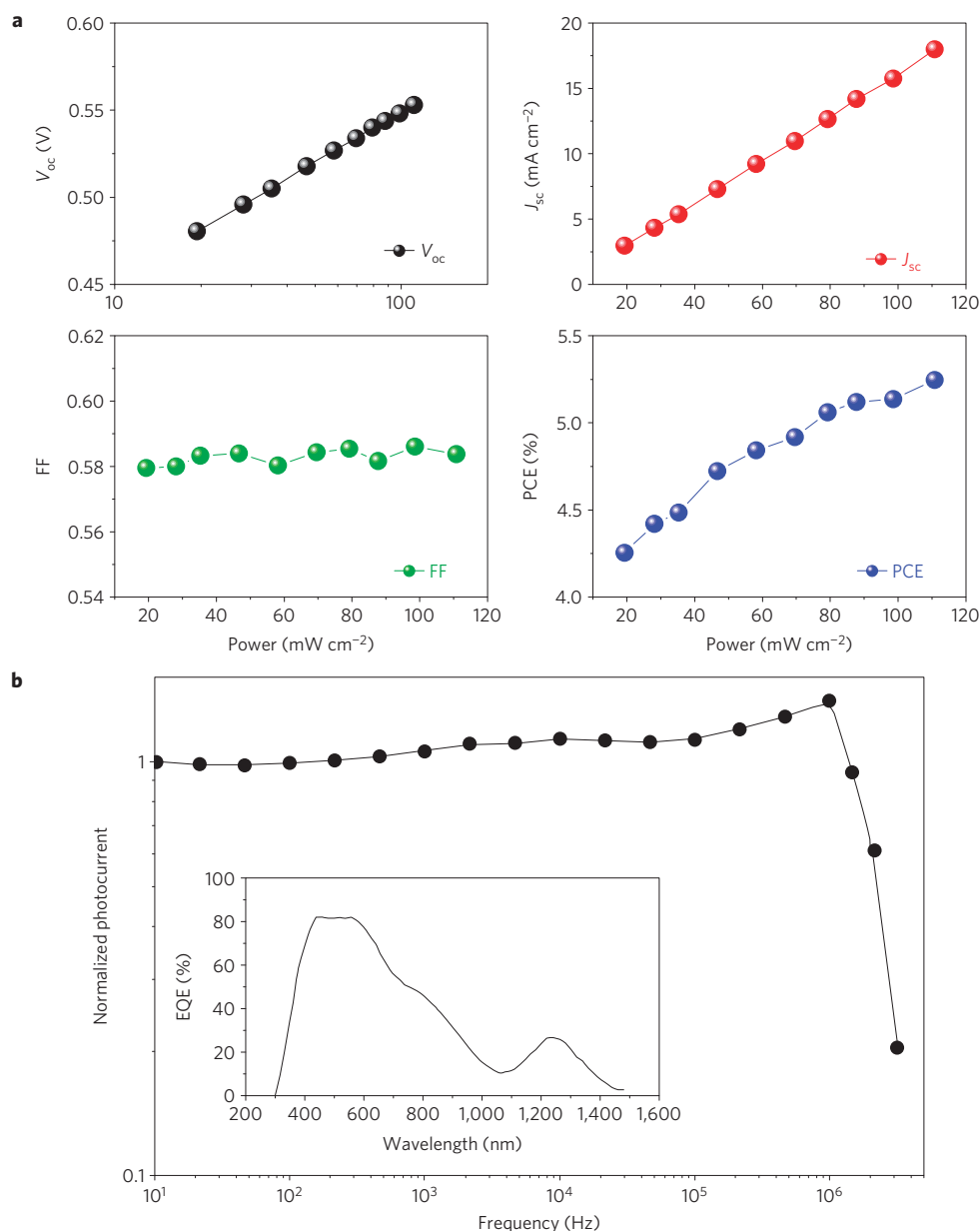


Figure 5 | Light-intensity-dependent photovoltaic performance and frequency dependent photodiode performance. **a**, Br⁻-passivated CQD photovoltaic devices show a logarithmic increase of V_{oc} , a linear increase of J_{sc} , a constant FF, and a consequent increase in efficiency as the incident light intensity increases from 0.2 sun to 1.1 sun. The results indicate that passivation is sufficient to maintain acceptably low recombination even at high electron-hole pair generation rates. **b**, Normalized photodiode EQE versus illumination frequency at zero bias. Data were obtained at room temperature using a 640 nm laser diode modulated with a square wave pulse produced by a 20 MHz frequency generator. The inset is the measured wavelength-dependent EQE.

bandgap excitation of PbS CQD solids treated using various organic and inorganic ligands. The spectra are scaled according to the optical absorption of the corresponding CQD films at the excitation wavelength (532 nm) such that the relative signal amplitudes can be compared quantitatively. The spectra contain broad electronic absorption bands arising from excitation of trapped electrons into the band states of the CQD films (see Supplementary Information for detailed assignments). Superimposed on the broad trap-to-band absorption are the narrow vibration features of the ligands that are perturbed by localization of electrons in the surface trap states.

Comparison of the TRIR spectroscopy results with electrical mobility measurements reveals that electrons are trapped in energetically shallower trap states in PbS CQD films capped with Br⁻ compared with the case of the best organic ligand treatments. The amplitudes of the trap-to-band transitions measured in the

TRIR spectra are proportional to the density of trapped carriers at the time of the measurement. Therefore, the lower signal amplitude of the Br⁻-capped CQD film indicates a lower density of trapped carriers, due in part to the lower trap density and in part to electron and hole recombination. Figure 4c illustrates the average decay time calculated from a multi-exponential fit to normalized TRIR decay curves (inset) measured at the maximum of the corresponding TRIR spectra. The average decay time of the mid-infrared absorption of various CQD solids is strongly correlated with the average trap-to-band transition energy, indicating that Br⁻-capped PbS CQD solids have on average a smaller trap state energy measured relative to the conduction band. The lower average trap energy from the Br⁻ treatment also results in higher average mobility, as observed in field-effect mobility measurements (Fig. 4d). The variation of the mobility with the mid-infrared

Table 1 | Summary of photovoltaic performance of champion devices treated with other inorganic anions.

Treated chemicals	Ligands	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF%	PCE%	R_s (Ω cm ²)
HTAC	Cl ⁻	15.8	0.52	55	4.50	5.4
TBAI	I ⁻	18.0	0.53	59	5.54	4.9
TBAT	SCN ⁻	13.6	0.52	44	2.95	15.9

Cl⁻, I⁻ and SCN⁻-passivated PbS CQD photovoltaic devices showed power-conversion efficiencies of 4.50%, 5.54% and 2.95%, respectively. R_s is the series resistance.

transition energy indicates that the transition energy is related to the activation energy, ΔE , for charge transport in the CQD solids³³, further supporting the interpretation of the mid-infrared transition in terms of a trap-to-band transition.

The data reveal a 200-fold increase in electron mobility but only a 10-fold decrease in charge recombination lifetime. Our atomic passivation strategy results in a factor of 20 enhancement of the mobility–lifetime product in comparison to EDT passivation, indicating superior charge carrier diffusion in the atomic-ligand-passivated films. The combination of lower trap density, lower trap depth, and higher mobility–lifetime product enables CTAB-treated PbS CQD photovoltaics to achieve unprecedented power-conversion efficiencies.

The good carrier transport in Br⁻-capped PbS CQD film was also evidenced by the strong suppression of bimolecular recombination. Light-intensity-dependent photovoltaic performance measurement showed a linear correlation between J_{sc} and light intensity, suggesting that no space charge was accumulated because of slow exciton dissociation and carrier transport, even under 1.1 sun illumination³⁹. Through the logarithmic increase of V_{oc} and constant FF with increasing light intensity, the devices showed an increased efficiency at higher light intensity (Fig. 5a).

We have made more than 30 nominally identical devices with efficiency above 5.5%. Devices stored in dry ambient for up to 6 days resulted in 1% absolute efficiency loss, associated primarily with loss of J_{sc} and FF (see Supplementary Fig. S17). Ambient oxidation or reaction with moisture may create detrimental defects on PbS CQDs and the TiO₂/PbS interface, giving rise to more recombination loss and mobility reduction. Devices stored in a glovebox for three weeks resulted in a 4% relative efficiency loss.

Our atomic-ligand passivation is not limited to Br⁻-passivated PbS CQD photovoltaics. Photovoltaic devices with the same architecture of FTO/TiO₂/PbS/Au, but treated instead with solutions containing salts of Cl⁻, I⁻ and SCN⁻, showed similar performance (Table 1). FET measurement indicated both Cl⁻ and I⁻ treatment yield CQD films with electron mobilities exceeding 0.01 cm² V⁻¹ s⁻¹, and devices using I⁻ consistently produce a performance comparable to, and in some cases better than CTAB treatment.

To illustrate the versatility of our atomic ligand strategy, we characterized devices from the perspective of fast photodetection. We adopted a similar device architecture, but used larger PbS CQDs having their absorption peaks at ~1,250 nm. As shown in Fig. 5b, the device showed an EQE reaching 80% in the visible up to 600 nm, proving that Br⁻ was an effective passivant for much larger CQDs as well. The photodiode showed a 3 dB frequency of 2.4 MHz at room temperature, faster than the previous speed record for PbS CQD photodetectors⁴⁰. We attribute the fast transit time to the high mobility in CTAB-treated PbS CQDs film, leading to a very short drift time in the depletion region. The resultant device provides a record gain–bandwidth product (see Supplementary Fig. S18) for solution-processed photodetectors^{1,2,40}.

To conclude, we report the first inorganic ligand-passivated CQD photovoltaics. The devices exhibited 6% solar power-conversion efficiency. Our monovalent inorganic ligand passivation

strategy enables good passivation of surface defects, high carrier mobility and good device stability, whilst using inexpensive chemicals readily processed in ambient at room temperature. The combined features hold the promise their broad application for other optoelectronic devices based on nanoparticles.

Methods

Materials preparation: 950 nm and 1,250 nm PbS CQDs are synthesized using a modified recipe described before¹⁷. CdCl₂–TDPA–OLA solution was produced by mixing 2 mM CdCl₂ (0.256 g), 0.1 g TDPA and 10 ml OLA in a flask and heating at 100 °C under vacuum for 30 min. CdCl₂–TDPA–OLA treatment was carried out using a Schlenk line. For the treatment, 12 ml PbS CQDs solution (50 mg ml⁻¹ in octane) and 24 ml toluene were mixed and heated to 60 °C, then 4 ml CdCl₂–TDPA–OLA stock solution was injected and kept at 60 °C for 5 min under magnetic stirring. The reaction was terminated by injection of 40 ml acetone and isolated by centrifugation. A further methanol wash was applied to these dots, which were finally dispersed in octane to produce a 50 mg ml⁻¹ solution. Such a CdCl₂–TDPA–OLA treatment consistently produced 6–18 nm redshift in the excitonic peak of the PbS CQDs.

Photovoltaic Device and Photodiode Fabrication: PbS CQD film was fabricated in ambient atmosphere with low relative moisture (<30%) using a layer-by-layer spin-coating method. 50 mg ml⁻¹ Cd-treated PbS CQDs octane solution and 10 mg ml⁻¹ CTAB, methanol solution were prepared in advance. All spin-coating steps were at 2,500 r.p.m. Each iteration in the layer-by-layer deposition consisted of three steps: (1) three drops of PbS solution was dropped onto a static TiO₂ substrate and spun for 15 s; (2) the film was flushed with 0.25 ml, 0.5 ml or 0.75 ml CTAB methanol solution, left for 1 min and spun (~3 s) to dry the film; the CTAB treatment was repeated another two times; (3) the film was washed by methanol flush and then spun dry three times. We repeated each iteration 6–9 times to obtain a smooth, shiny PbS CQD film. For other halide anion treatments, all fabrication procedures were identical to the CTAB treatment except that 8.8 mg ml⁻¹ HTAC, 10.1 mg ml⁻¹ TBAI or 8.2 mg ml⁻¹ tetrabutylammonium thiocyanate (TBAT) methanol solution were used instead. Electrodes were deposited with an Edward 306 evaporator located in ambient environment. 20 nm Au was first deposited by d.c. sputtering (50 W, 0.1 nm s⁻¹ under a N₂ pressure of 5 × 10⁻³ torr), followed by thermal evaporation of a 100 nm Ag layer (0.5 nm s⁻¹ at a pressure of <1.5 × 10⁻⁵ torr). A shadow mask was used to define a 4 × 4 array of 2.78 mm diameter circular contacts. The active device area is 6.07 mm². The photodiode was constructed in a similar way to the photovoltaics described above. 1,250 nm PbS quantum dots and 20 mg ml⁻¹ CTAB in methanol solution were used to fabricate the 6 LBL film. Molybdenum oxide/silver (15 nm/90 nm) contacts were deposited in an Angstrom Engineering thermal evaporation system. A total active area of 0.049 cm² was achieved.

Current–voltage (I – V) data were measured using a Keithley 2400 sourcemeter. The solar spectrum at AM1.5 was simulated to within class A specifications (less than 25% spectral mismatch) with a Xe lamp and filters (Solar Light) and the intensity was adjusted to 100 mW cm⁻². The source intensity was measured with a Melles–Griot broadband powermeter and a Thorlabs broadband powermeter (responsive from 300 nm to 2,000 nm) through a circular 4.91 mm² aperture at the position of the sample and confirmed with a calibrated reference solar cell (Newport). The accuracy of the power measurements was estimated to be ±7%. Three strategies were employed in combination to avoid overestimating the power-conversion efficiency: (1) we divided the entire power through the 4.91 mm² aperture to calculate the efficiency; (2) the spectral mismatch between our simulator spectrum and the reference spectrum ASTM G173-03 was carefully and periodically re-measured; (3) the efficiency variation between different scan rates and between different sweep directions, as well as the maximum power point, was measured to avoid any potential overestimation of efficiency due to hysteresis.

Time-resolved infrared (TRIR) spectroscopy experiments were performed on a home-built instrument consisting of a nanosecond Nd:YAG laser with second harmonic generation (532 nm) as a pulsed laser source to excite the bandgap of the CQD solids. The pulse energy used for the experiments was 150 ± 20 μJ with a corresponding beam diameter of 8 mm, which corresponds to an excitation density of approximately one photon per CQD in the solid film. A compact ceramic Global Light Source (HORIBA Jobin Yvon) was used to generate the infrared probe. The

continuous wave infrared probe radiation was focused on the sample, overlapped with the laser pulse, and subsequently dispersed in a monochromator (HORIBA Jobin Yvon). Transient absorption measurements were performed by dispersing the probe radiation onto a $1 \times 1 \text{ mm}^2$ MCT (mercury cadmium telluride) single element detector (Infrared Associates) positioned at the focal plane of the monochromator. A preamplifier with band pass frequencies of 1.5 Hz to 1.0 MHz (Infrared Systems Development) was used to amplify the detector signal before digitization with a computer-mounted 1 MHz analog–digital converter card (National Instruments). Throughout the experiment, the monochromator was purged with dry air and the sample stage was raster-scanned using computer-controlled translation stages to prevent photodegradation of the CQD film.

Photodiode characterization was carried out by illuminating the device with a Melles–Griot (56RCS009/HS) 640 nm laser diode, which was modulated using a square wave pulse from a 20 MHz frequency generator (Agilent 33220A). The photocurrent of the device was measured across a resistor placed in series with the device using an Agilent Infiniium Oscilloscope (DSO8104A). A 5 Ω resistor was selected to minimize the effective RC constant. The laser response was also measured as a function of frequency, with the amplitude being found to be constant over the range of the experimental measurements.

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Author contributions

J.T. and E.H.S. designed and directed this study and analysed the experimental results. J.T. contributed to all the experimental work. K.W.K. and S.H. carried out the photodiode work and K.W.K. assisted in all the experimental work. K.S.J. and J.B.A. carried out the TRIR experiments and analysed the data. H.L. fabricated the TiO₂ electrodes. L.L. synthesized the PbS CQDs. K.W.K., L.L. and R.D. contributed to the solution Cd treatment experiment. D.C., K.W.C. and A.A. carried out the GISAXS and TEM measurements and analysed the data. S.H., M.F., X.W., H.L., A.F. and R.D. assisted in device fabrication and characterization. J.T., J.B.A. and E.H.S. wrote the manuscript. All authors commented on the paper.

Additional information

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