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Enhanced Open-Circuit Voltage of Wide-Bandgap Perovskite Photovoltaics by Using Alloyed $(FA_{1-x}Cs_x)Pb(I_{1-x}Br_x)_3$ Quantum Dots

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ABSTRACT

We report a detailed study on $APbX_3$ (A=Formamidinium (FA^+), Cs^+; X=I^-, Br^-) perovskite quantum dots (PQDs) with combined A- and X-site alloying that exhibits, both, a wide bandgap and high open circuit voltage (*Voc*) for the application of a potential top cell in tandem junction photovoltaic (PV) devices. The nanocrystal alloying affords control over the optical bandgap and is readily achieved by solution-phase cation and anion exchange between previously synthesized $FAPbI_3$ and $CsPbBr_3$ PQDs. Increasing only the Br^- content of the PQDs widens the bandgap but results in shorter carrier lifetimes and associated *Voc* losses in devices. These deleterious effects can be mitigated by replacing Cs^+ with FA^+, resulting in wide bandgap PQD absorbers with improved charge-carrier mobility and PVs with higher *Voc*. Although further device optimization is required, these results demonstrate the potential of $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs for wide bandgap perovskite PVs with high *Voc*.

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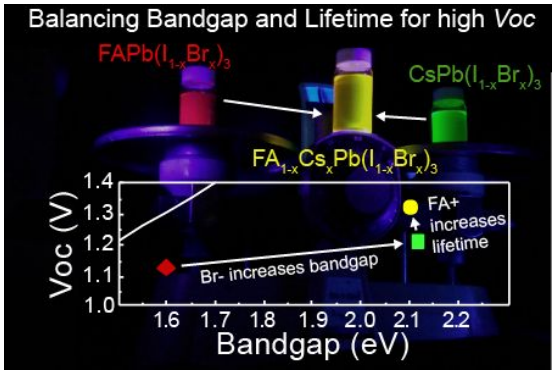

The search for high-efficiency, wide bandgap absorber materials that can be implemented as a top cell in a tandem architecture to boost the overall efficiency of existing commercial photovoltaic (PV) devices (e.g., Si, CIGS, CdTe) remains a challenge.[1–10] The tunable nature of perovskite (ABX_3) absorbers, coupled with their impressive optoelectronic performance and amenability to low-cost deposition techniques, identifies them as a promising candidate for such applications.[11–19]

Although triple-cation bulk perovskite absorbers – $Cs_x(FA_yMA_{(1-y)})_{(1-x)}Pb(I_zBr_{(1-z)})_3$ – exhibit impressive solar light to electricity power conversion efficiencies (PCEs), with the current PCE record at 24.2%, their bandgap (1.55-1.60 eV) is too narrow for use as the top cell in multijunction PVs.[20,21] Tuning halide composition on the X site enables wider optical bandgaps, but has not led to the expected subsequent increase in *Voc*, and mixed-halide bulk perovskites often suffer from photoinduced halide segregation and crystal phase instability that leads to device degradation.[12,13,22–26] Perovskite quantum dots (PQDs) provide a route to circumvent these structural instabilities, with the added benefit that they afford additional tunability of the optical and electronic properties (by tuning the QD size and composition).[12,13,15,22–24,27,28] For instance, mixed cation PQDs with the composition $FA_{1-x}Cs_xPbI_3$ exhibit broader compositional tunability (wider *x* range) than thin film $FA_{1-x}Cs_xPbI_3$. $FA_{1-x}Cs_xPbI_3$ PQD PVs achieve *Voc's* that approach 90% of the radiative limit (similar to single crystal III-V PVs, *i.e.* $GaInP_2$), surpassing the *Voc* of bulk perovskite PVs with similar composition in the bandgap range of 1.55-1.77 eV as shown in Fig S1.[29–31] Taken together, these observations suggest that PQDs may provide an ideal solution for inexpensive, high-performance, wide bandgap top cell absorber layers in multijunction PVs.

Wider bandgap PQDs (beyond 1.77 eV), thus far, do not show the same low *Voc* losses, as those with bandgap between 1.55 eV to 1.77 eV. Compositionally increasing the bandgap of PQDs with Br^- incorporation results in a decreasing voltage fraction in PVs from 0.9 to 0.63 (in this work we define voltage fraction as: device-*Voc* / maximum *Voc* based on device bandgap).[22,31,32] Thus, finding solutions to this unexpected voltage loss would be beneficial for the wide bandgap top cell in multijunction PVs.

Here, we show that combined A- and X-site alloying of wide bandgap $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs can provide increased device *Voc* as compared to $CsPb(I_{1-x}Br_x)_3$ and $FAPb(I_{1-x}Br_x)_3$ PQDs

at bandgaps wider than 1.8 eV. The addition of Br in $CsPb(I_{1-x}Br_x)_3$ PQDs—typically used to increase the bandgap—leads to a significantly decreased photoluminescence (PL) lifetime and correlates with lost *Voc* in PVs made from these PQDs.[22,32,33] To counter this, FA^+ was added in addition to Br^- to develop long PL lifetime, wide bandgap materials. This co-alloying strategy was found to improve charge transport in PQD films and reduce the voltage loss in PVs with Eg>1.8 eV.

To synthesize the PQDs of such complicated composition, two simple compositions were first synthesized and alloyed using an ion exchange reaction. Fig. 1A illustrates the ion exchange between $CsPbBr_3$ and $FAPbI_3$ PQDs used to generate $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs. $CsPbBr_3$ and $FAPbI_3$ PQDs were prepared using previously reported recipes.[12,29] By mixing dispersions of $FAPbI_3$ and $CsPbBr_3$ PQDs at 70 °C, rapid and efficient compositional alloying occurs. This enables PQDs with a wide tunability of the bandgap from 1.55 eV to 2.40 eV to be obtained from similar starting materials simply by controlling the relative amount of $CsPbBr_3$ to $FAPbI_3$ in the ion-exchange reaction. Figs. 1B and 1C show absorbance and PL spectra of PQDs generated from the same $CsPbBr_3$ and $FAPbI_3$ PQDs starting materials. The nanocrystals retain a relatively narrow size distribution comparable to the starting materials.

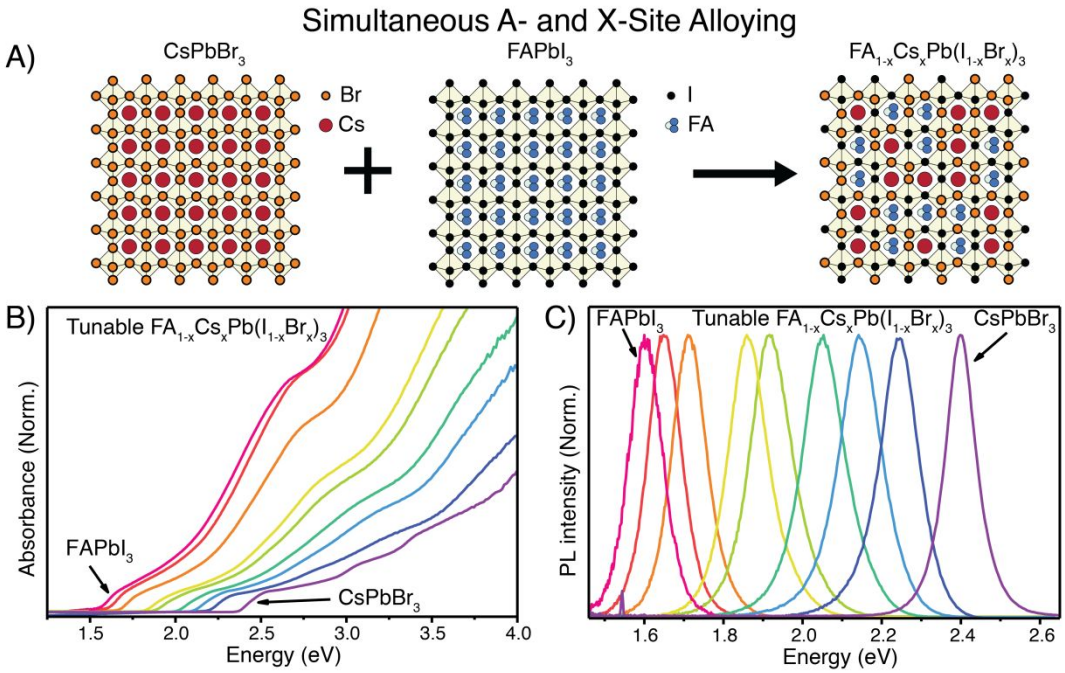

Figure 1. A) Crystal models showing the ion exchange process used to generate alloyed PQDs. $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs are generated when dispersions of $CsPbBr_3$ and $FAPbI_3$ PQDs are mixed at 70°C. Room temperature **(B)** absorbance and **(C)** PL emission spectra of PQDs with varying $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ composition dispersed in octane (excitation wavelength of 400 nm).

We first highlight the deleterious effects of Br^- incorporation in single A-site PQD PVs by using colloidal PQDs with bandgaps ranging between 1.8 eV and 1.94 eV containing only Cs^+ on the A-site. Unlike PQDs of $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ composition, $CsPb(I_{1-x}Br_x)_3$ and $FAPb(I_{1-x}Br_x)_3$ PQDs were synthesized using previously reported methods of single-pot direct synthesis using controlled ratios of Pb-halide salts.[12] Fig. 2A shows a scanning electron microscopy (SEM) image of a cross-sectioned $CsPbI_3$ PQD PV. The PQD solar cells were fabricated using previously reported methods.[34–37] For ideal removal of the oleate ligands, it is especially important to maintain an ambient environment that exhibits 15-25% relative humidity (RH) during the ligand exchange procedure performed after deposition of the nanocrystals.[35] Fig. 2B shows the device responses of $CsPbI_3$ PQDs and $CsPb(I_{1-x}Br_x)_3$ PQD PVs with Br^- alloying to widen the bandgap. The $CsPbI_3$ PQD PV exhibits a PCE of ~14% (reverse scan). The $CsPb(I_{1-x}Br_x)_3$ PQD PVs have lower device efficiency, which can be expected based on the widened bandgap and corresponding reduced light absorption; however, they also show a decrease in the *Voc* contrary to the expectations for the widened bandgap with increased Br^- content. A noticeable drop in fill factor is also observed with increasing Br^- incorporation, which suggests increased series resistance in the device possibly originating from non-ideal contact layers in the device structure. Full device metrics for the devices shown in Figure 2B are provided in Table S1 as Supporting Information.

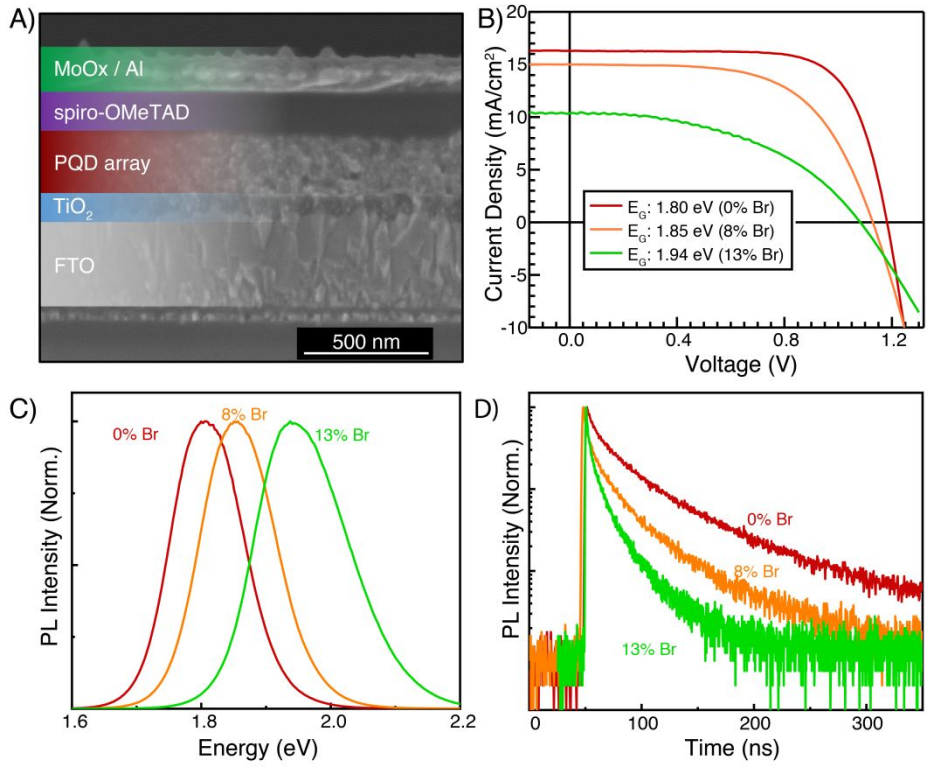

Figure 2. A) SEM image of a cross-sectioned $CsPbI_3$ PQD PV device. **B)** *J/V* curves of $CsPb(I_xBr_{1-x})_3$ PQD PVs with varying Br^- composition and bandgap. Note that the reported bandgaps correspond to the PL peak energies. The device absorption onset is redshifted by 0.05-0.1 eV due to electronic coupling.[17,33] **C)** Room temperature normalized PL emission spectra of the colloidal PQDs used to fabricate devices tested in (B). Excitation wavelength was 400 nm. **D)** Time-resolved PL transients of the $CsPb(I_xBr_{1-x})_3$ PQDs used to make the devices from panel B. The excitation wavelength is 442 nm and the emission are collected at the PL peak position.

Figs. 2C and 2D show solution-phase photoluminescence (PL) emission spectra and solution-phase time-resolved photoluminescence (TRPL) measurements on $CsPbI_3$ PQDs compared to $CsPb(I_{1-x}Br_x)_3$ PQDs with 8% and 13% Br^- compositions. The composition of all PQD samples in this work are estimated using Vegard's Law.[38] As expected, the increase in the Br^-/I^- ratio results in a hypsochromic shift of the PL spectrum, but the mixed anion systems also exhibit broadening of the emission spectrum, which may be related to an increase in the polydispersity of the PQDs or a non-uniform anion composition within the ensemble. We find that $CsPb(I_{1-x}Br_x)_3$ PQDs show significantly reduced PL lifetime compared to the $CsPbI_3$ PQDs. Based on previous reports, we believe that increased Br^- composition leads to higher PL quantum yield and decreased PL lifetime, which suggests that shorter radiative lifetimes are intrinsic to Br-rich

PQDs.[11,13,15,17] See Supporting Information Figure S2 for a plot summarizing the radiative lifetimes versus bandgap and Br^- content of PQDs samples. From the results in Fig. 2, we hypothesize that increased bromine content in PQDs leads to a decreased PL lifetime, and that the PL lifetime of colloidal PQDs is related to PQD device performance, especially the deteriorating *Voc* performance at wide bandgaps as discussed above.

To test this hypothesis, TRPL measurements of several colloidal PQD compositions ($CsPb(I_{1-x}Br_x)_3$, $FAPb(I_{1-x}Br_x)_3$, and $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$) were conducted using a streak-camera system that records spectral- and time-dependent emission data. Fig. 3A shows two-dimensional solution-phase TRPL data for $CsPbI_3$ colloidal PQDs, and the red-dashed box in Fig. 3A shows the region of the response that is integrated to produce a TRPL transient decay curve. The inset in Fig. 3A shows the actual transient that is extracted from the streak camera response. While the TRPL measurements were performed in the solution phase, we believe that the reduced PL lifetime of colloidal $CsPb(I_{1-x}Br_x)_3$ PQDs is at least partly related to the observed loss in device *Voc*. To overcome this, we aimed to lengthen the PL lifetime of these PQDs through compositional alloying. While that challenge at face value is not so straightforward, it has been reported that $FAPbI_3$ QDs have substantially longer PL lifetime than $CsPbI_3$, but unfortunately replacing Cs^+ with FA^+ also lowers the bandgap.[39] We, therefore, hypothesized that by balancing the FA^+ to Cs^+, along with the Br^- to I^-, we could engineer the PQDs to have an appropriate bandgap (from Br^+ incorporation) with lengthened PL lifetimes (from FA^+ incorporation). To test this specific hypothesis, we show in Fig. 3B, $CsPb(I_{1-x}Br_x)_3$, $FAPb(I_{1-x}Br_x)_3$, and $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ colloidal PQDs each with composition tuned to achieve a bandgap of approximately 1.9 eV. The TRPL transients show that FA^+ incorporation nearly doubles the lifetime from 29 ns to 55 ns for the FA^+/Cs^+ alloy-sample or 64 ns for the sample with pure FA^+ on the A-site. Thus, in this case, the A-site mediated lengthening of the PL lifetime overrules X-site mediated PL lifetime shortening. Next, we aim to understand the general trends of how the lifetimes vary as a function of bandgap for each of these A-site conditions.

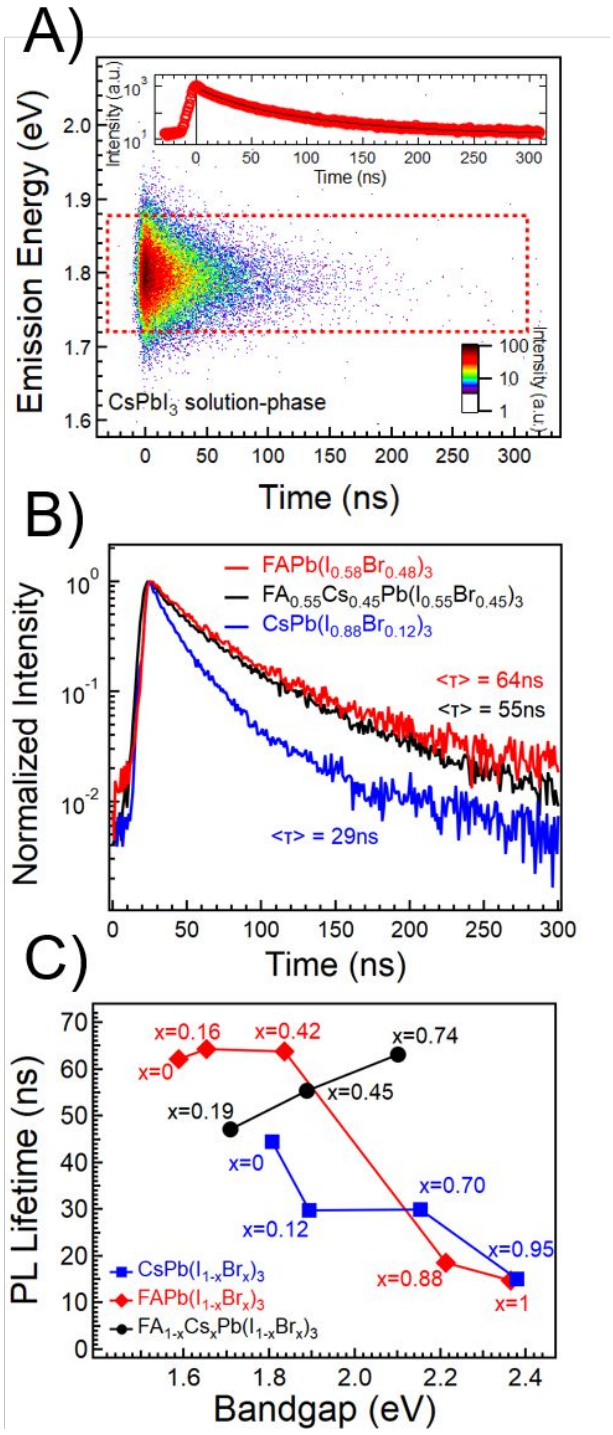

Figure 3. A) Two-dimensional spectrotemporal solution-phase TRPL data of $CsPbI_3$ PQDs, measured using a streak-camera. The red rectangle represents the portion of the trace that was integrated to construct an intensity versus decay-time transient. **B)** Solution-phase TRPL transients of $CsPb(I_{1-x}Br_x)_3$, $FAPb(I_{1-x}Br_x)_3$ and $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ solution-phase PQDs with bandgap energies of ca. 1.9 eV. (These PQD

compositions are estimated using Vegard's Law based on the PL peak energy.[38]) **C)** Intensity-averaged PL lifetime versus bandgap of all solution-phase PQD samples including $CsPb(I_{1-x}Br_x)_3$, $FAPb(I_{1-x}Br_x)_3$, and $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs. See Fig. S2 for the estimated radiative lifetime-component versus bandgap of each sample.

As shown in Figs. 2D and 3B, the solution-phase intensity-averaged TRPL decays cannot be described by a single-exponential function. While the origin of this deviation from simple first-order decay kinetics is beyond the scope of this work, we analyze our data with a bi-exponential decay and compare the intensity-weighted average PL lifetimes (Fig. 3C) of the $CsPb(I_{1-x}Br_x)_3$, $FAPb(I_{1-x}Br_x)_3$, and $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs as a function of bandgap. The intensity-weighted average PL lifetime of the $CsPb(I_{1-x}Br_x)_3$ PQDs decreases significantly from about 45 ns to 15 ns across the compositional range, with a sharp decrease observed even for small bromide contents (c.f. Fig. 2D). In contrast, the $FAPb(I_{1-x}Br_x)_3$ and $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs appear to be less sensitive to the substitution of I^- with Br^-. Single-cation $FAPb(I_{1-x}Br_x)_3$ PQDs exhibit similar lifetimes of >60 ns until the bandgap exceeds 1.8 eV (Br^- content of 42%) where the lifetime drops precipitously to 15 ns, similar to the average lifetimes observed for the single-cation Cs-containing PQDs. The mixed-cation $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs, on the other hand, exhibit PL lifetimes that actually increase with bandgap energy, and reach 65 ns for a bandgap of 2.1 eV. To our knowledge, this increase in PL lifetime with increasing bandgap for the $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ composition is unique among PQDs. The full set of TRPL decay transient data and fitting parameters are provided as Supporting Information in Fig. S3 and Table S2.

To explore the impact of the observed colloidal-optoelectronic properties of the PQDs on their PV performance, solar cells were fabricated with $CsPb(I_{1-x}Br_x)_3$, $FAPb(I_{1-x}Br_x)_3$, and $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs with bandgaps ranging from 1.55 eV to 2.15 eV. Fig. 4A plots the *Voc* of over 140 PQD PVs with 10 different compositions across a wide alloy-space and bandgap regime. By displaying results from a large sample set, we are able to determine which composition of PQDs provides the most promise for use as wide-bandgap top cells in tandem devices. Of the PQD devices, those with A-site alloying of FA^+ and Cs^+ exhibit the highest *Voc* at bandgaps wider than 1.8 eV. This trend is especially noticeable at bandgap of ~1.85 eV where the *Voc* increases by over 100 mV as the PQD composition is changed from $CsPb(I_{0.88}Br_{0.12})_3$ to $FAPb(I_{0.58}Br_{0.42})_3$ to

$FA_{0.45}Cs_{0.55}Pb(I_{0.55}Br_{0.45})_3$. At a bandgap of ~2.1 eV, the maximum *Voc* of the $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQD devices was about 100 mV higher than that of $CsPb(I_{1-x}Br_x)_3$ PQD PVs. Fig. 4B shows a plot of the voltage fraction against the bandgap of the PQD PVs. Voltage fraction decreases with increasing Br^- incorporation and widening bandgap. The PVs of $FAPbI_3$ PQDs with a bandgap of 1.55 eV exhibit the highest voltage fraction of ~0.9 and the PL lifetime of these PQDs is 62 ns. (Note: in Fig. S1 we plot the voltage fraction of our PQD PVs against perovskite-literature values to compare our results to the immense field of perovskite PV and show the future promise of PQD PVs).

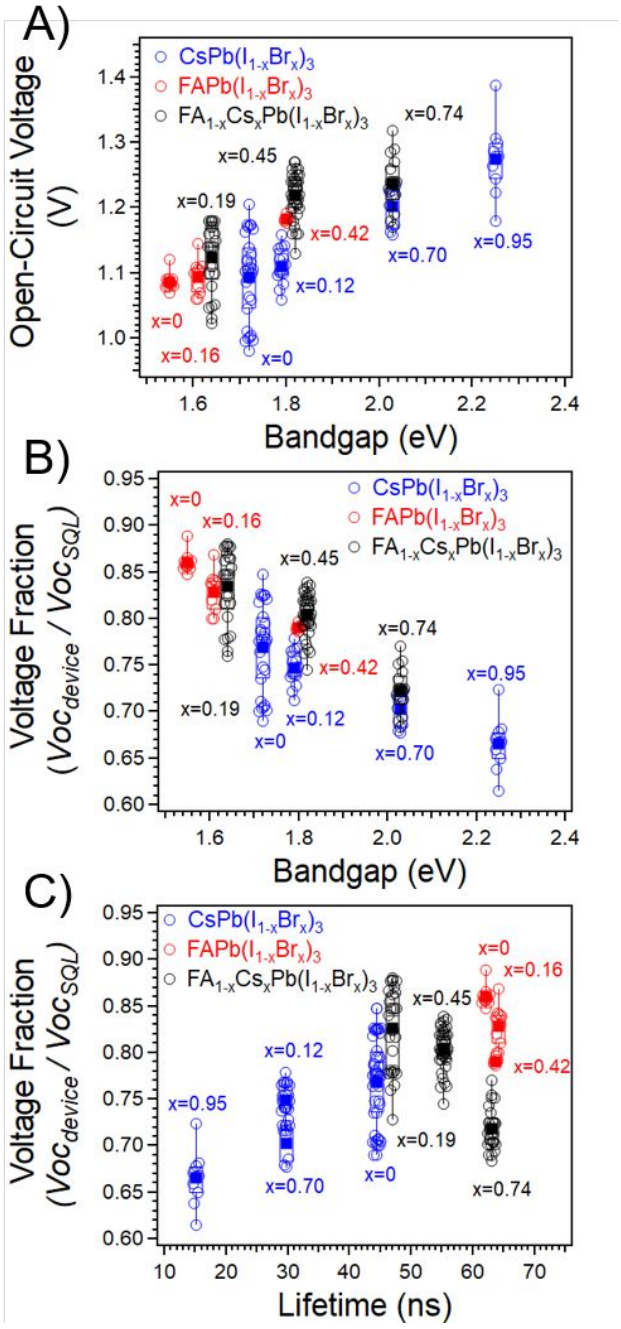

Figure 4 A) *Voc* versus bandgap of the full set of PQD samples **B)** Voltage fraction versus bandgap of the full data set of PQD samples**. C)** Voltage fraction versus PL lifetime of the full data set of PQD samples. Full device metrics are provided as Supporting Information (Table S3).

To test our hypothesis that PQD PV voltage performance is correlated to PL lifetime of colloidal PQDs, we plot voltage fraction of PQD PVs versus PL lifetime of solution-phase PQDs in Fig. 4C. We observe that $CsPb(I_{1-x}Br_x)_3$ PQDs show a fairly direct relationship between solution-phase PL lifetime and device voltage fraction. However, the voltage fraction of $FAPb(I_{1-x}Br_x)_3$ PQDs demonstrates a more compositional dependence - the voltage fraction of $FAPb(I_{1-x}Br_x)_3$ PQDs increases as the Br composition decreases. The fully alloyed PQDs ($FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$) generally exhibit voltage fraction between 0.70 and 0.85, which is comparable to current, state-of-the-art bulk-phase $CsPbI_3$ devices (See Fig S1).[40] Although the A- and X-site alloying of $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs succeeded in producing devices with higher *Voc* at wide bandgaps, the PCE was still low—only 6% for a bandgap of 1.9 eV. We attribute these observations of lower PCE and the slight drop in voltage fraction of $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs, as "x" increases from 0.45-0.74, to poor charge transport in the PQD films and/or carrier extraction at the contact layers, which limits the *Jsc* and *FF* of the devices (see Supporting Information Table S3). We employed time-resolved microwave conductivity (TRMC) to determine how the A-site and X-site alloying influences the charge transport in the PQD films. The photoconductance, ΔG, extracted from the TRMC data can be related to a free-carrier yield-mobility product, $\phi\Sigma\mu$, which can be difficult to decompose into the individual contributions.[41,42] However, the large dielectric constant of PQDs and large photoluminescence lifetimes (>20 ns) allows us to make the assumption that each photon generates an unbound electron-hole pair on the 4 ns timescale of the laser pulse in the TRMC measurement (i.e., $\phi = 1$), which simplifies the figure of merit to sum of carrier mobilities.[42] Although we are able to make assumptions about the free-carrier yield, we cannot decouple the individual contributions of the electrons and holes to the photoconductance. Under such circumstances, the TRMC technique can be considered similar to other optical pump-probe techniques, except that the sum of the free-carrier mobilities, $\Sigma\mu$, now represents the absorption coefficient of the microwave probe. The transient photoconductance, $\Delta G(t)$, is therefore related to the number density, and associated kinetics, of the free electrons and holes in the PQD layer. Since we expect both carriers to contribute to the measured photoconductance, and the carrier lifetime to be related to the likelihood of the carriers to be extracted in a functioning device, we suggest that the yield-mobility-tau product represents a reasonable metric to describe the free-carrier transport and dynamics (in fact, this quantity can be related to the carrier diffusion length).

Fig. 5 shows the yield-mobility-tau products determined by TRMC of the ligand-exchanged PQD films on quartz substrates (the TRMC yield-mobilities and free carrier lifetimes are also provided as Supporting Information Fig.S4-S5). In all cases, the yield is assumed to be 1, meaning that we expect all charge carriers to diffuse, the mobility describes the sum of hole and electron mobility, and carrier lifetime takes into consideration all holes and electrons. $CsPbI_3$ PQDs show the largest yield-mobility-tau product at ~500 * 10^{-9} cm^2/V. The yield-mobility-tau product decreases logarithmically with increasing bandgap for single A-site PQDs, indicating that charge transport becomes less efficient with increasing Br composition. For $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs, the yield-mobility-tau product remains fairly stable across all three samples (~30-50 * 10^{-9} cm^2/V), and the 2.1 eV bandgap $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs leads to an enhanced yield-mobility-tau product over the single A-site PQDs with similar bandgap. Thus, at wide bandgaps, simultaneous alloying at the A- and X-sites leads to increased charge transport, but there is still room for improvement because the yield-mobility-tau products of $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs are an order of magnitude less than that of $CsPbI_3$. Improvements in PQD synthesis, purification, and device fabrication are potential methods to improve charge transport in these films and improve PCE.

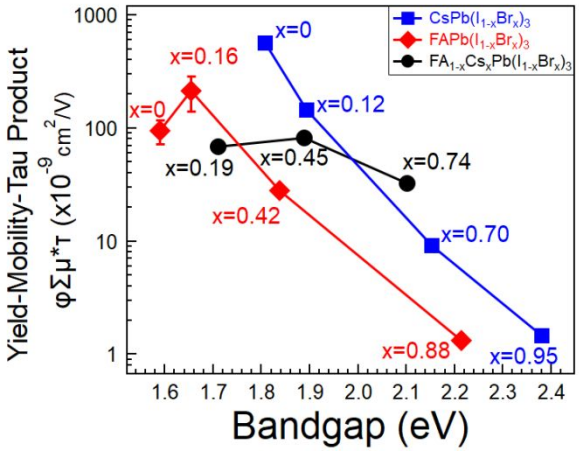

Figure 5. Yield-mobility-tau product determined by TRMC of $CsPb(I_{1-x}Br_x)_3$, $FAPb(I_{1-x}Br_x)_3$, and $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQD films on quartz substrates.

In conclusion, we show that the substitution of I^- for Br^- in metal halide PQDs results in faster electron-hole recombination, less efficient charge transport, and significant loss in device

Voc, that hinders their performance in PQD PV devices. Simultaneous alloying on the A-site with Cs^+ and FA^+ to generate $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs counteracts these adverse effects of increased Br^- content. To our knowledge, $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs are the only PQDs to exhibit longer PL lifetimes with increased bandgap. The *Voc* of $FA_{1-x}Cs_xPb(I_{1-x}Br_x)_3$ PQDs with bandgaps larger than 1.8 eV exhibit *Voc* nearly 100 mV higher than $CsPb(I_{1-x}Br_x)_3$ PQDs of similar bandgap. While further optimization of wide bandgap PQD PVs is needed, these results suggest considerable promise for the continued improvement of wide bandgap perovskite PV device layers needed for high-efficiency, low-cost multijunction solar cells.

Supporting Information. Experimental methods, characterizations, absorbance and photoluminescence of colloidal PQDs, TRPL transients including fitting parameters of colloidal PQDs, estimated radiative lifetimes for all colloidal PQD compositions, device metrics for PQD PVs in Fig. 2, device metrics for all other PQD PVs for this study, TRMC lifetime of PQD thin films, and TRMC yield-mobility product of PQD thin films.

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Notes

The authors declare no competing financial interest.

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