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Radiative Efficiency Limit with Band Tailing Exceeds 30% for Quantum Dot Solar Cells

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Supporting Information

ABSTRACT: Thin films of colloidal quantum dots (QDs) are promising solar photovoltaic (PV) absorbers in spite of their disordered nature. Disordered PV materials face a power conversion efficiency limit lower than the ideal Shockley–Queisser bound because of increased radiative recombination through band-tail states. However, investigations of band tailing in QD solar cells have been largely restricted to indirect measurements, leaving their ultimate efficiency in question. Here we use photothermal deflection spectroscopy (PDS) to robustly characterize the absorption edge of lead sulfide (PbS) QD films for different bandgaps, ligands, and processing conditions used in leading devices. We also present a comprehensive overview of band tailing in many commercial and emerging PV technologies—including c-Si, GaAs, a-Si:H, CdTe, CIGS, and perovskites—then calculate detailed-balance efficiency limits incorporating Urbach band tailing for each technology. Our PDS measurements on PbS QDs show sharp exponential band tails, with Urbach energies of 22 ± 1 meV for iodide-treated films and 24 ± 1 meV for ethanedithiol-treated films, comparable to those of polycrystalline CdTe and CIGS films. From these results, we calculate a maximum efficiency of 31%, close to the ideal limit without band tailing. This finding suggests that disorder does not constrain the long-term potential of QD solar cells.

Emerging thin-film photovoltaic (PV) technologies may reduce module manufacturing costs with low-cost precursors and high-throughput processing, enable new applications with lightweight and flexible form factors, and scale up quickly with low capex and small factory footprints. While these advantages have yet to be realized commercially, perovskite, organic, and colloidal quantum dot (QD) solar cells are improving rapidly in power conversion efficiency and operational stability. For example, PbS QD solar cells fabricated using all-room-temperature processes have reached efficiencies around 12% with 1.28 eV bandgap QDs and show remarkable stability without encapsulation. Both high efficiency and multidecade lifetime are critical for achieving a grid-competitive levelized cost of electricity. For QD photovoltaics, however, comparatively low efficiencies inhibit commercial development today. It is thus important to understand whether QD solar cells can reach high efficiencies with further engineering or if they are intrinsically limited by disorder.

Photovoltaic technologies based on disordered materials face a radiative efficiency limit lower than the ideal Shockley–Queisser (SQ) bound. Thermal and structural disorder produce band tailing in the density of states and in the absorption spectra of conventional semiconductors, violating the SQ assumption of step-function absorptance (i.e., $A = 1$ for $E > E_g$ and $A = 0$ for $E < E_g$). Band tailing increases the thermal generation and emission rate and thus reduces the radiative limit of PV performance, as we show below and in the Supporting Information.

In this work, we report a systematic study of band tailing in PbS QD films, varying the QD bandgap, ligands, and processing conditions across those used in the highest-performing devices to date. Using photothermal deflection spectroscopy, we measure sub-bandgap absorption and extract Urbach energies for these films. We then use our experimental data to calculate modified detailed-balance efficiency limits for QD solar cells.

Linear exponential band tails have been observed in many conventional semiconductors, including crystalline silicon (c-
Si), hydrogenated amorphous silicon (a-Si:H), and gallium arsenide (GaAs). This phenomenon, specifically the temperature dependence of the exponential absorption edge, was first reported by Urbach in 1953 for AgBr and other ionic crystals.12

An absorption tail with the form \( \alpha = \alpha_0 \exp \left( \frac{E - E_U}{E_U} \right) \) is known as an Urbach tail, with a slope described by the Urbach energy \( E_U \). The theory of John et al. satisfactorily explains Urbach band tailing in terms of the density of states for an electron in a disorder-induced static random potential (see the Supporting Information).13 Although the physical origin of absorption band tailing may differ between materials, any linear exponential band tail can be characterized by an Urbach energy.

In nanostructured materials such as organic and QD films, however, there may exist additional sources of disorder that produce band tailing with a different functional form. For example, size polydispersity in QD solids—alogous to compositional fluctuations in polycrystalline \( \text{Cu(In,Ga)}(\text{S,Se})_2 \) (CIGS) and \( \text{Cu}_{x}\text{ZnSn(S,Se)}_4 \) (CZTS) films14 and to vibrational broadening of charge-transfer-state absorption in organic blends—produces a Gaussian distribution of bandgaps.15 This distribution should lead to a Gaussian density of states (DOS) near the band edge, rather than the conventional Halperin–Lax form \( \exp \left( -\sqrt{E} \right) \).13,15 Furthermore, significant thermal disorder may arise from the abundance of surfaces in QD films. The mechanically soft surfaces of PbS nanocrystals enable large atomic displacements and strong electron–phonon coupling.16 Capping ligands may also induce disorder and rearrangement of the nanocrystal surface, leading to the formation of sub-bandgap states.17 In general, surface and excitonic phenomena in nanocrystal solids may affect electronic energy levels differently from conventional disorder. By these arguments, it is not clear whether exponential tails should be expected in QD and organic films.

Despite the lack of theoretical basis, measurements of absorption,1,16 photoluminescence,19 and sub-bandgap DOS20 in PbS QD films suggest a linear exponential Urbach-type regime in the band-tail DOS. An exponential band tail may be justified for lead chalcogenide QDs in spite of their excitonic nature in the limit of device-type films with inter-QD coupling, high dielectric constants, and low effective masses.19 Although we cannot definitively conclude that Urbach tailing occurs in PbS QD films, we treat the absorption band tail as a linear exponential to obtain a conservative estimate of PV performance limits (see the Supporting Information for further discussion).

A modified Shockley–Queisser efficiency limit with Urbach band tailing can be calculated by introducing a finite absorption coefficient \( \alpha \) below the bandgap, as shown in Figure 1. Here we adapt the approach of Kirchhart et al.,6 originally applied to Gaussian band tails, to linear exponential Urbach tails. We model the absorption spectrum with band tailing as \( \alpha = \alpha_0 \exp \left( \frac{E - E_U}{E_U} \right) \) below the bandgap. We then calculate the most optimistic absorbance assuming ideal (Lambertian) light trapping with zero front-surface reflection and unity rear-surface reflection.6,21,22 We use a constant refractive index of \( n = 3 \) and an absorber layer thickness of \( d = 1 \mu\text{m} \), although we note that the results are not sensitive to these parameters (Figures S9 and S10).

The modified absorptivity \( A(E) \), equal to the emissivity \( \epsilon(E) \) by Kirchhoff’s law, is used to calculate PV performance in the radiative limit:6

\[
J_{SC} = q \int \Phi_{\text{sun}}(E) A(E) \epsilon(E) dE
\]

\[
V_{OC} = \frac{kT}{q} \ln \left( 1 + \frac{J_{SC}}{J_0} \right)
\]

\[
FF = \frac{z_m^2}{1 + z_m - \exp \left( -z_m \right)(z_m + \ln(1 + z_m))}
\]

where \( J_{SC} \) is the short-circuit current density, \( \Phi_{\text{sun}}(E) \) the AM1.5G photon flux [m\(^{-2}\) s\(^{-1}\) Ev\(^{-1}\)], \( \epsilon(E) \) the internal quantum efficiency (assumed to be unity), \( V_{OC} \) the open-circuit voltage, \( J_0 = q \int \Phi_{\text{bb}}(E) \epsilon(E) dE \) the thermal generation current density [A m\(^{-2}\)], \( \Phi_{\text{bb}}(E) = \frac{2\pi}{k_B^2 \hbar} E^2 \exp \left( \frac{\pi E}{k_B T} \right) \) the blackbody spectral photon flux [m\(^{-2}\) s\(^{-1}\) Ev\(^{-1}\)], and FF the fill factor; \( z_m \) is determined from \( z_m = z_m + \ln(1 + z_m) \) following Shockley and Queisser;4 \( z_{\text{OC}} = \frac{q V_{\text{OC}}}{kT} \); \( z_m = \frac{q V_{\text{mpp}}}{kT} \); and \( V_{\text{mpp}} \) is the maximum power point voltage. Given the light-trapping assumptions above, these performance limits depend only on the absorber bandgap and Urbach energy. The dependence of \( J_{SC} \), \( V_{OC} \), and FF on \( E_g \) and \( E_U \) is shown in the Supporting Information (Figure S7).
The introduction of band tailing reduces the effective bandgap, increasing $J_{SC}$ slightly and decreasing $V_{OC}$ substantially. Absorption of below-bandgap photons in the band tail contributes to the photocurrent under the assumption of unity IQE (Figure S6). Emission of below-bandgap photons similarly contributes to the saturation current: Assuming all carriers are thermalized and thus can be described by a single Fermi level, the solar cell must emit radiation equal to the Planck blackbody spectrum $\Phi_{BB}(E)$ modified by the emissivity $\epsilon(E)$ according to the generalized Kirchoff law.23 For a solar cell at room temperature, the Planck spectrum decays exponentially with increasing energy, with an exponential slope approaching $kT$ at typical bandgap values (see the Supporting Information). With a sharp band tail ($E_U < kT$), the radiative efficiency limit matches or exceeds the ideal value with no band tailing, particularly for larger bandgaps, because of the increase in $J_{SC}$ without a substantial loss in $V_{OC}$ and FF (Figure 1). With a broad band tail ($E_U > kT$), however, the efficiency limit decreases dramatically because of the exponential increase in $J_0$ and corresponding reduction in $V_{OC}$. The energetic threshold at $E_U = kT$ naturally increases with temperature but can be considered fixed at terrestrial PV operating temperatures (Figure S8).

It is important to note that the calculated performance limits for large Urbach energies ($E_U > kT$) contain substantial uncertainty due to material-dependent assumptions about the nature of tail states and recombination. In thermal equilibrium, when $E_U$ exceeds $kT$, the emission peak shifts abruptly from near the bandgap to low energies near the peak of the Planck distribution (Figure S1). This peak shift reflects a change in the dominant radiative recombination mechanism from band-to-band to tail-to-tail, band-to-tail, or tail-to-band.24 With radiative transitions occurring between localized states, the actual emission rate becomes dependent on the overlap matrix elements for these transitions. Depending on the nature of the tail states in a particular PV material, one would expect that the true radiative efficiency limit could be either higher than calculated (e.g., if tail states are spatially separated) or lower than calculated (e.g., if tail states are colocalized). Furthermore, under illumination, filling of localized tail states by photo-generated carriers impedes radiative transitions at energies less than the quasi-Fermi-level splitting. This effect makes the emission peak position dependent on the applied voltage and the total emission rate dependent on the occupation of tail states near the quasi Fermi levels, potentially leading to a higher limiting efficiency than calculated here.

A full theoretical treatment of the above effects is beyond the scope of this work23,24,25 but can be effectively circumvented by measuring the voltage-dependent electroluminescence (EL) spectrum from a PV device. For example, Rau et al. use EL and external quantum efficiency measurements to generalize the SQ model to real devices with a distribution of bandgaps.11 This approach enables a detailed loss analysis on a variety of PV technologies, breaking down the $V_{OC}$ loss contributions from $J_{SC}$ loss, red-shifted emission, and nonradiative recombination.

As observed by De Wolf et al.,26 PV technologies with larger Urbach energies typically have larger $V_{OC}$ deficits and lower efficiencies (Figure 2). For several technologies—CIGS, CZTS, QDs, and organics—reported Urbach energies span a wide range around the $KT$ threshold, leading to uncertainty about their efficiency limits. For PbS QD films, Urbach energies ranging from 14 to 44 meV have been reported for different ligands, dot sizes, and measurement techniques,1,6,17,20 corresponding to a wide range of limiting efficiencies: 32% to 18% for $E_U = 1.4$ eV. A recent report of record-efficiency PbS QD solar cells attributes improved device performance to reduced band tailing—$E_U$ decreases from 33 meV with tetrabutylammonium iodide (TBAI) ligands to 29 meV with PbX$_2$/ammonium acetate (AA)—due to a more complete ligand exchange and increased QD packing density.1 A thin ethanedithiol (EDT)-treated layer is also used,2 although the authors do not report $E_U$ for EDT films. These results motivate further investigation of the extent of band tailing in PbS QD absorbers.
A sensitive near-infrared absorption measurement is needed to characterize band tailing in thin PbS QD films. Photothermal deflection spectroscopy offers high dynamic range and sensitivity,\textsuperscript{29,30} isolates absorption from the device structure and transport properties, and has been used previously to obtain Urbach energies of colloidal QD films.\textsuperscript{1,8,16,31} The photothermal deflection spectroscopy (PDS) technique relies on absorption of a monochromatic pump beam in the sample, creating a temperature and refractive index gradient in the adjacent deflection medium. A probe beam passes through this index gradient, parallel to the sample surface, and is deflected in direct proportion to the absorbed power. The probe deflection is then measured using a position-sensitive detector.

We implemented a transverse PDS system optimized for near-infrared wavelengths to obtain sub-bandgap absorptances down to 10\textsuperscript{−4} (see Experimental Methods and the Supporting Information), corresponding to a minimum absorption coefficient of $\alpha = 10$ cm\textsuperscript{−1} for a 100 nm thick film. Typical PDS spectra span 4 orders of magnitude in absorptance and extend more than 200 meV below the bandgap for $E_U = 25$ meV, giving a direct measure of absorption band tailing. To fully confirm the assumption of exponential band tailing, the absorption must be measured at low energies beyond the range accessible with PDS (e.g., using photocurrent spectroscopy).\textsuperscript{35} For sharp band tails ($E_U < kT$), however, the majority, over 70\%, for $E_U = 1.4$ eV, of the calculated efficiency loss from the ideal SQ limit can be attributed to the portion of the band tail within 200 meV of the bandgap (see Figure S1). PDS measurements can thus provide a fair estimate of radiative efficiency limits with band tailing.

Absorption coefficients calculated from PDS spectra for PbS QD films across all experimental conditions are shown in Figure 3. Urbach energies are obtained by fitting the linear exponential part of the absorption band tail (see Experimental Methods). We note that the Urbach energy is independent of the film thickness (Figure 3d) and the approach used to convert the measured absorbance to absorption coefficients.

The choice of ligand is a critical parameter for tuning QD film properties, from optical properties\textsuperscript{19} to charge separation and transport\textsuperscript{32–36} to energy levels.\textsuperscript{37} Disorder and band tailing are also affected by ligands.\textsuperscript{19,31} The most efficient QD solar cells today use two different ligands, combining a thick iodide-treated layer with a thin EDT-treated layer.\textsuperscript{12} These devices improve substantially after minutes to days of air exposure,\textsuperscript{22} however, the mechanism of improvement remains unexplained.

Our PDS measurements confirm that ligands strongly influence band tailing in PbS QD films. PbS QDs with $E_U = 1.37$ eV (905 nm) treated with different halide ligands exhibit Urbach energies of 33 ± 4 meV (TBAB), 26 ± 2 meV (TBAC), 26 ± 2 meV (TBAB), and 23 ± 1 meV (TBAI) (Figure 3b). For fluoride-treated films, broadening and red-shifting of the band edge indicates a partial loss of confinement.\textsuperscript{38,39} But the Urbach energy trend, more band tailing with air exposure, is unexpected, given that device performance improves with air exposure, which suggests that band tailing is not a primary limitation for devices based on this chemistry. EDT films stored in an inert thermofluid (Fluorinert FC-72) in air show a similar increase in bandgap but no increase in Urbach energy over 20 days (Figure 3h). Over a similar time scale, TBAI-treated films show no change in Urbach energy and a small increase in bandgap (Figure 3c). Subsequent experiments are carried out on TBAI-treated films because of their air stability and prevalence in leading devices.

QD solar cells are traditionally fabricated using layer-by-layer deposition methods, requiring immersion of a freshly deposited QD film in ligand solution for up to 30 s. The completeness of the ligand exchange depends on the treatment time and solvent. Long treatments employing methanol as the solvent can substantially strip native oleic acid ligands as well as halide passivants.\textsuperscript{40} One would thus expect an increase in the disorder and band tailing in PbS QD films treated with methanol for...
long periods. However, our PDS measurements show a relatively weak dependence of the Urbach energy on ligand treatment time for 1.37 eV PbS QDs treated with TBAI in methanol. With treatment times increasing from 5 to 60 s, $E_U$ increases moderately from 22 ± 2 to 27 ± 0.5 meV (Figure 3f). A 30 s TBAI/methanol treatment followed by an additional 30 s soak in neat methanol yields the same Urbach energy as a 60 s TBAI/methanol treatment, consistent with the stripping of ligands by methanol.

QD size can also affect band tailing by modifying disorder-related parameters in QD films. For example, smaller dots exhibit higher surface-to-volume ratios, increased surface curvature, and more dangling bonds. A weak size dependence of band tailing in EDT-treated PbS QD devices has been observed using modulated photocurrent spectroscopy, with $E_U$ ranging from 13.5 to 15 meV for bandgaps of 0.76 to 1.96 eV.

Our PDS measurements show a stronger size dependence for TBAI-treated films (Figure 3a and Figure 5). The Urbach energy increases from 16 ± 0.5 meV for a bandgap of 0.71 eV (1757 nm) to 39 ± 2 meV for a bandgap of 1.62 eV (765 nm). Increased band tailing for larger bandgaps and smaller QD sizes may be due to changing surface chemistry or a size-independent trap level that enters the bandgap for small QDs. Depending on its DOS distribution, a sub-bandgap trap could broaden the Urbach tail or appear as a distinct absorption peak. We observe a shoulder in the sub-bandgap absorption spectra of the smallest QDs, approximately 0.6 eV below the 1.62 eV bandgap, which may signify a size-independent trap level. The observed $E_U$ trend with dot size is consistent with temperature-dependent PL and modulated photocurrent measurements. We note that for the bandgap range of interest for PbS QD solar cells, below 1.4 eV, the Urbach energy of TBAI-treated films remains below the $kT$ threshold. Interestingly, solutions of the same QDs in octane with native oleic acid ligands yield slightly higher Urbach energies, based on transmittance measurements, than thin-film samples. This observation may point to the contribution of QD-solvent interactions to band tailing, although further characterization of films with oleic acid ligands is needed to confirm such effects.

One key advantage of colloidal QD solar cells is the potential for all-room-temperature device processing. To maximize manufacturing throughput, however, heating may be needed to remove excess solvent after film deposition. Here we vary the annealing temperature to investigate the effect of heating on disorder in PbS QD films (Figure 3e). A loss of quantum confinement and substantial increase in band tailing is observed when PbS QD films are annealed above 150 °C for 30 min in air, consistent with the fusing of nanocrystals at high temperatures.

Our PDS measurements show that device-quality colloidal PbS QD films exhibit band tailing more severe than c-Si, GaAs, and perovskites; comparable to polycrystalline thin films of CdTe, CIGS, and CZTS; and less severe than a-Si:H and organic films (Figures 6 and 7). The extracted Urbach energies are well within the range of reported values for PbS QD films with.

Figure 4. Effect of air exposure on band tailing and bandgap of PbS QD films. (a) Urbach energy as a function of time for PbS QD films with TBAI and EDT ligands and stored in air vs inert thermoluid (FC-72). (b) Energy of the first excitonic peak as a function of time for the same samples as in panel a. Within a few days of air exposure, the Urbach energy of EDT films increases by nearly 50%. In contrast, EDT films deposited in air and stored in inert FC-72, as well as TBAI films deposited and stored in air, show very little increase in band tailing. The bandgap increases logarithmically upon air exposure for all EDT films, consistent with QD surface oxidation.

Figure 5. Effect of nanocrystal size on band tailing and PbS QD PV efficiency limits. (a) Measured Urbach energies for different QD sizes, with the bandgap defined by the energy of the first excitonic peak in thin films. Smaller QDs (larger $E_g$) show increased band tailing. Oleic acid capped QDs in octane are measured with transmission spectrophotometry and exhibit Urbach energies that are higher than those of TBAI-treated films. (b) Radiative efficiency limits based on measured film Urbach energies for different sizes of QDs. Absorptance spectra used in detailed-balance calculations are derived from idealized absorption coefficient spectra, i.e., $\alpha = \alpha_0 = 10^4 \text{cm}^{-1}$ above the bandgap and $\alpha = \alpha_0 \exp \left( \frac{E-E_g}{E_U} \right)$ below the bandgap for measured $E_U$ assuming perfect light trapping with a film thickness of 1 µm and refractive index of $n = 3$. Contours represent theoretical limiting efficiencies for $E_U = 0, 25, \text{and } 50 \text{ meV}$. All samples with bandgaps below 1.4 eV exhibit Urbach energies below the $kT$ threshold, leading to high limiting efficiencies.
Figure 6. Absorption spectra of commercial and emerging PV technologies. High-efficiency PV technologies including c-Si, GaAs, CdTe, CIGS, and MAPbI$_3$ have sharp band edges, while lower-efficiency technologies such as a-Si:H and CZTS have broader band edges. Because of its indirect bandgap, c-Si appears to suffer from severe band tailing; however, at absorption coefficients lower than the range plotted, the tail drops off sharply.

Figure 7. Comparison of reported Urbach energies for commercial and emerging PV technologies. Most commercial wafer-based (c-Si and GaAs) and thin-film (CdTe and CIGS) PV absorbers have low Urbach energies and radiative efficiency limits above 30%. In contrast, amorphous silicon and organic materials have higher Urbach energies and lower efficiency limits. Despite their disordered nature, colloidal PbS QD films have consistently sharp band tails and theoretical efficiency limits above 30%. Data for PbS QDs correspond to commonly used ligands (iodide, EDT, mercapto- or propionic acid) and different measurement techniques as discussed in the text. Reported $E_U$ values are obtained at room temperature or below. All data are available in the Supporting Information.

different bandgaps, ligands, and measurement techniques (Figure S12). Nevertheless, the wide variation among literature values warrants further discussion.

Higher Urbach energies are generally obtained for PbS QD films with PDS than with other techniques such as temperature-dependent photoluminescence (PL) and intensity-modulated photocurrent spectroscopy (IMPS). In one previous study, temperature-dependent PL produced Urbach energies ranging from 15 to 29 meV for mercaptoacrylic acid (MPA) and EDT ligands. To obtain $E_U$, using temperature-dependent PL, one must assume an exponential band tail, fitting the data with a Boltzmann model to obtain the thermal energy required to quench emission, i.e., to activate carriers to the transport edge, facilitating charge separation and multiple trapping. This approach is internally consistent and allows comparative analysis; however, the authors report that some covariance between model parameters cannot be resolved, leading to uncertainty in the absolute Urbach energy. This method also cannot determine Urbach energies of samples that do not exhibit temperature-dependent PL quenching (e.g., large QDs of >5 nm diameter). In another study, sharp exponential band tails were obtained with IMPS ($E_U = 13.5–19$ meV) for various alkanedithiol ligands. IMPS relies on the delayed contribution of trapped carriers to the AC photocurrent; deeper traps give a slower response. Based on the phase shift and magnitude of the photocurrent, the band-edge DOS can thus be derived and fitted for the Urbach energy. One limitation of IMPS is that it primarily probes one type of trapped carrier and one band tail—the one with a larger mobility and lower sub-bandgap trap density. Thus, the primary contributor to the IMPS signal is likely the band with less severe tailing, leading to an underestimation of $E_U$. Furthermore, previous IMPS measurements were performed at low temperatures, potentially underestimating the effect of thermal disorder at typical PV operating temperatures. Our PDS-derived Urbach energies for EDT (without air exposure) are larger than those measured with IMPS, as expected from the arguments above. However, our values remain below the $kT$ threshold, yielding a similar conclusion about efficiency limits.

A previous report of PDS measurements on PbS QDs with iodide ligands showed Urbach energies ranging from 29 to 44 meV. For solid-state-replaced TBAI films, our values are lower by roughly 10 meV. This difference may be attributed to synthetic differences, although we note that our results are generally stable across different dot sizes and batches of 900–950 nm (1.31–1.38 eV) bandgap dots used in high-efficiency devices.

We can place a conservative bound on the efficiency limit of single-junction PbS QD solar cells following the modified Shockley–Queisser approach outlined above (Figure Sb). For bandgaps between 1.2 and 1.4 eV, the measured Urbach energies of 22–38 meV across all experimental conditions yield radiative efficiency limits of 20–31%. TBAI- and EDT-treated films used in leading devices exhibit Urbach energies of 22 and 24 meV before air exposure, respectively, corresponding to a radiative limit of 31%. These results imply that solar cells made of PbS QD films, unlike amorphous materials, are not severely limited by disorder.

Given the high radiative efficiency limits identified above, it is clear that PbS QD solar cells are not practically constrained by band tailing today. Other deviations from the assumptions of the Shockley–Queisser theory suggest areas for improvement for QD photovoltaics. In particular, approaching 100% IQE in thick absorber layers will be difficult for QD films dominated by hopping transport, while complete elimination of nonradiative recombination will require major advances in nanocrystal synthesis and material engineering.

Although band tailing may not be thermodynamically limiting for device performance, tail states below the mobility edge can impede charge transport and extraction. It may be possible to further mitigate band tailing with more sophisticated chemical treatments or synthesis techniques. Changing the QD size polydispersity changes the ensemble absorption peak width, but should not significantly affect either the Urbach energy extracted from PDS data or the radiative efficiency limit for typical QD samples (see the Supporting Information and Moore et al.). Furthermore, experimental evidence suggests that reducing polydispersity beyond current levels is unlikely to improve QDPV performance in the near term, although...
future devices with few midgap states may benefit from improved synthetic routes.

Sub-bandgap recombination centers must be eliminated before QD solar cells can approach fundamental radiative limits. The presence of discrete midgap states\(^1\,^2\,^3\) or bands\(^4\) could constrain \(V_{OC}\) much more severely than band tailing. If they are well-coupled to the above-gap carrier populations, and thus can trap carriers before charge extraction, even a small density of midgap states can prevent separation of the quasi Fermi levels and reduce the radiative \(V_{OC}\) limit. Even if they are not in equilibrium with the free-carrier population, however, midgap states can increase recombination and reduce \(V_{OC}\) and efficiency. The PDS technique, coupled with transient spectroscopies\(^5\) and thermal admittance spectroscopy,\(^6\) may be useful for characterizing deep trap states in PbS QD films.

In summary, we report absorption band tailing in colloidal PbS QD films characterized by photothermal deflection spectroscopy under different processing conditions. Disorder-induced band tailing is sensitive to the QD size and ligand treatment, as well as to air exposure when organic ligands are used. Despite the presence of a high density of interfaces, colloidal PbS QD films deposited at room temperature exhibit relatively low structural disorder and sharp band tails, comparable to high-quality polycrystalline semiconductors grown at high temperatures. Measured Urbach energies are 16–39 meV across all bandgaps and experimental conditions and 22–38 meV for films with bandgaps between 1.2 and 1.4 eV, corresponding to limiting efficiencies of 20–31%. TBAI and EDT ligand treatments used in leading devices produce Urbach energies of 22 and 24 meV, respectively, yielding a limiting \(E_U\) ligand treatments used in leading devices produce Urbach energies of 22 and 24 meV, respectively, yielding a limiting \(E_U\) ligand solutions are filtered with a 0.1 \(\mu m\) PTFE syringe filter immediately before spin-coating.

**PDS Measurements.** PDS measurements are performed using a custom system optimized for the near-infrared (Figure S11). The pump beam consists of a 300 W Xe arc lamp chopped at 10 Hz, a dual-grating monochromator (300 lines per mm) with 1 mm slits (15 nm output FWHM), a periscope, and achromatic lenses to collimate and focus the beam. The illuminated spot size at the sample is approximately 3.5 mm wide \(\times\) 0.4 mm tall, corresponding to a monochromatic intensity of 50–750 mW cm\(^{-2}\).

The sample is secured using a custom holder in a standard 10 mm quartz cuvette. Perfluorohexane (Fluorinert FC-72) filtered with 0.02 \(\mu m\) PTFE is used as a deflection medium. PbS QD films immersed in FC-72 show no change in optical properties over many days. A commercial physical-vapor-deposited black film on fused quartz (>96% flat absorbance from 400–2500 nm) is used as a reference sample to correct for spectral variation and residual nonlinearity in the system.

The probe beam consists of a 658 nm, 40 mW temperature-controlled laser diode, an anamorphic prism pair, spatial filter, and iris to circularize the beam and isolate the fundamental mode; a bandpass filter to eliminate scattered light; and a quadrant detector with built-in transimpedance amplifier. A DAQ is used to drive the chopper and acquire the quad detector signal. AC lock-in detection is performed using custom LabView software with a low-pass filter cutoff frequency of 0.5 Hz. The entire PDS system is assembled on an optical table to minimize vibrations and enclosed in a box to mitigate stray light and air flow.

Measurements are typically performed over a wavelength range of 400–2500 nm (0.5–3.1 eV). Each sample is measured twice to ensure repeatability, and reported results are averaged over 2–4 samples.

**PDS Data Analysis.** The sample PDS spectrum is divided by the black reference spectrum to obtain an absorbance spectrum with arbitrary scaling. The absorbance is then normalized and scaled by \(1 - R\) or \(1 - R - T\), measured with spectrophotometry at a highly absorbing wavelength, to obtain the absolute absorbance. The absolute absorbance spectrum is converted into absorption coefficients following Ritter and Weiser,\(^7\) using transmission data from spectrophotometry and thicknesses and optical constants from ellipsometry. Absorption coefficient spectra are plotted against photon energy and fitted at the band edge using the Urbach expression

\[
\alpha = \alpha_0 \exp \left( \frac{E-U}{E_U} \right).
\]

The Urbach energy is the inverse slope of the natural log of the absorption coefficient: \(E_U = \frac{1}{\alpha} \ln(\alpha)\).

To reduce the subjectivity of the fitting procedure, we systematically vary the start energy and range of the fit for each PDS spectrum. All fits that appear accurate by eye are recorded, yielding a range for \(E_U\). Reported values and error bars

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**EXPERIMENTAL METHODS**

**PbS Quantum Dot Synthesis.** Colloidal PbS nanocrystals are synthesized by hot injection following literature methods.\(^8\,^9\) Lead acetate (11.38 g) is dissolved in 21 mL of oleic acid and 300 mL of 1-octadecene at 100 °C. After degassing overnight, this solution is heated to 150 °C under nitrogen, and a sulfur precursor solution, 3.15 mL of bis(trimethylsilyl)sulfide (TMS-S) and 150 mL of 1-octadecene, is rapidly injected. The QD solution is transferred into a nitrogen glovebox; purified by precipitating with methanol, acetone, and/or butanol; redispersed in hexane; and stored under nitrogen. Prior to film deposition, QDs are precipitated twice with a mixture of acetone and butanol and redispersed in octane at 50 mg mL\(^{-1}\).

**Ligand Solution Preparation.** Solutions for solid-state ligand exchange are prepared following well-characterized procedures from the literature. Unless otherwise specified, 27 mM (10 mg mL\(^{-1}\)) tetrabutylammonium iodide (TBAI) in methanol (MeOH) is used as the ligand solution.\(^10\) To compare halide ligands, we use 30 mM tetrabutylammonium fluoride, chloride, bromide, and iodide in MeOH. 1,2-ethanediol (EDT) is used at 2 mM in acetonitrile.\(^11\) All chemicals are purchased from Sigma-Aldrich at the highest purity available.

**PDS Substrate Preparation.** Custom 4 mm \(\times\) 12 mm fused quartz slides (500 \(\mu m\) thick) are cleaned by immersion in boiling isopropanol for 5 min. To improve QD film adhesion, clean substrates are immersed in 12 mL 3-mercaptopropyl-trimethoxysilane (MPTMS) in toluene for at least 8 h, sonicated for 1 min in isopropanol, and stored under nitrogen.

**QD Film Deposition.** PbS QD films are deposited by layer-by-layer spin-coating in air at room temperature and under ambient conditions (relative humidity under 30%). A 10 \(\mu\)L sample of 50 mg mL\(^{-1}\) PbS QD solution is dispensed onto the substrate and spun dry at 2500 rpm with an acceleration of 2500 rpm s\(^{-1}\). The ligand solution is dispensed and soaked for 30 s, then spun dry and rinsed three times with MeOH. Each layer is approximately 20 nm thick. This cycle is typically repeated 5, 10, or 20 times, yielding a final film thickness of 100, 200, or 400 nm. All QD and ligand solutions are filtered with a 0.1 \(\mu m\) PTFE syringe filter immediately before spin-coating.

**GENERAL NOTES**

1. The ligand solution is dispensed and soaked for 30 s, then spun dry and rinsed three times with MeOH. Each layer is approximately 20 nm thick. This cycle is typically repeated 5, 10, or 20 times, yielding a final film thickness of 100, 200, or 400 nm. All QD and ligand solutions are filtered with a 0.1 \(\mu m\) PTFE syringe filter immediately before spin-coating.
Ellipsometry data are measured using an Agilent Cary 5000 dual-beam UV–vis–NIR spectrophotometer. Specular reflectance is collected at an incident angle of 8°. A 3 mm round aperture is used for all measurements. Spectroscopic ellipsometry is performed using a variable angle spectroscopic ellipsoid at 40°, 70°, and 115° angles of incidence. Focusing probes are used to reduce the spot size. Backside reflections are eliminated by roughening the substrate. Ellipsometry data are fitted to obtain film optical constants and thicknesses used in PDS data analysis.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00923.

Discussion of device physics of solar cells with band tailing and importance of band tail shape, calculated detailed-balance limits with band tailing, discussion of sensitivity of calculated limits to light trapping, and compilation of reported Urbach energies for all PV technologies (PDF)

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Notes
The authors declare no competing financial interest.

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