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

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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 QDs1 and show remarkable stability without encapsulation.2,3 Both high efficiency and multidecade lifetime are critical for achieving a grid-competitive levelized cost of electricity.3 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.4−9 Thermal and structural disorder produce band tailing in the density of states and in the absorption spectra of conventional semiconductors,10 violating the SQ assumption of step-function absorptance (i.e., A = 1 for E > Eg and A = 0 for E < Eg).11 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.

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).

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—allogous to compositional fluctuations in polycrystalline Cu(In,Ga)(S,Se)$_2$ (CIGS) and Cu$_2$ZnSn(S,Se)$_4$ (CZTS) films and to vibrational broadening of charge-transfer-state absorption in organic blends—produces a Gaussian distribution of bandgaps. This distribution should lead to a Gaussian density of states (DOS) near the band edge, rather than the conventional Halperin-Lax form $(\exp(-\sqrt{E}))$.

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. Capping ligands may also induce disorder and rearrangement of the nanocrystal surface, leading to the formation of sub-bandgap states. 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, photoluminescence, and sub-bandgap DOS 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.

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 Kirchhoffs et al., 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 absorptance assuming ideal (Lambertian) light trapping with zero front-surface reflection and unity rear-surface reflection. We use a constant refractive index of $n = 3$ and an absorber layer thickness of $d = 1 \mu m$, 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 $\varepsilon(E)$ by Kirchhoff’s law, is used to calculate PV performance in the radiative limit:

$$J_{SC} = q \int \Phi_{sun}(E) A(E) \text{IQE}(E) dE$$

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

$$FF = \frac{J_{mpp}^2}{(1 + z_m - \exp(-z_m))(z_m + \ln(1 + z_m))}$$

where $J_{SC}$ is the short-circuit current density, $\Phi_{sun}(E)$ the AM1.5G photon flux $[\text{m}^{-2} \text{s}^{-1} \text{E}^{-1}]$, IQE($E$) the internal quantum efficiency (assumed to be unity), $V_{OC}$ the open-circuit voltage, $J_0 = q \int \Phi_{bb}(E) E \text{d}E$ the thermal generation current density $[\text{A} \text{m}^{-2}]$, $\Phi_{bb}(E) = \frac{2e}{h\nu} \frac{E^2}{\exp(E/E_0) - 1}$ the blackbody spectral photon flux $[\text{m}^{-2} \text{s}^{-1} \text{E}^{-1}]$, and FF the fill factor; $z_m$ is determined from $z_m = z_{bb} + \ln(1 + z_{bb})$ following Shockley and Queisser, $z_{bb} = \frac{\text{IQE}_{bb}(E)}{1 + \text{IQE}_{bb}(E)}$, and $V_{mpp}$ 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 Kirchhoff law. 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. 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 work, 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. 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., 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 QDs, Urbach energies ranging from 14 to 44 meV have been reported for different ligands, dot sizes, and measurement techniques, 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)—to a more complete ligand exchange and increased QD packing density. A thin ethanediethiol (EDT)-treated layer is also used, 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.

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Figure 2. Theoretical and reported PV performance limits with band tailing for commercial and emerging technologies. (a) $V_{OC}$ deficit ($E_U/\eta - V_{OC}$) and (b) power conversion efficiency (PCE) vs. Urbach energy. Open circles indicate ideal detailed-balance limits without band tailing ($E_U = 0$). Solid lines represent the $E_U$ range found in the literature and the corresponding range of detailed-balance limits. Filled circles indicate the performance of record-efficiency cells versus the lowest reported $E_U$ values, which are not necessarily the true $E_U$ for the record cells. Ideal light trapping is assumed for all calculations. All data used in calculations are available in the Supporting Information. The lowest $E_U$ values are observed for single-crystalline GaAs and c-Si, reflecting low structural disorder. Metal halide perovskites (MAPbI$_3$) exhibit unusually low $E_U$ for a solution-processed semiconductor, leading to a minimum $V_{OC}$ deficit of 0.35 V and a maximum efficiency of 31.1%. We note that $E_U$ is not commonly reported with devices; as a result, true $E_U$ values for leading devices may be lower than the lowest reported for a given absorber material. This is likely for a-Si:H, for which the minimum reported $V_{OC}$ deficit is below the minimum calculated deficit. For thin-film absorbers, bandgap variations due to processing differences may also contribute to discrepancies. A wide range of Urbach energies has been reported for colloidal PbS QD films, which may explain the large observed $V_{OC}$ deficit.
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 \(10^{-5}\) (see Experimental Methods and the Supporting Information), corresponding to a minimum absorption coefficient of \(\alpha = 10 \text{ cm}^{-1}\) 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{26}). 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{18,31} 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{2} 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), 30 ± 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. EDT-treated films exhibit a low Urbach energy of 24 ± 1 meV immediately after deposition. On the time scale of hours to days, however, air exposure in dark increases \(E_U\) substantially—to 30 meV after 1 day and 35 meV after 4 days—and also increases the bandgap (Figure 3g and Figure 4). The increase in bandgap is consistent with oxidation of the nanocrystal surface, leading to reduction of the core size and increased confinement.\textsuperscript{18,38} 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 thermomfluid (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 excessively strip native oleic acid ligands as well as halide passivants.\textsuperscript{39} One would thus expect an increase in the disorder and band tailing in PbS QD films treated with methanol for...
In contrast, EDT as well as TBAI upon air exposure for all EDT increase in band tailing. The bandgap increases logarithmically 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 organics (Figures 6 and 7). The extracted Urbach energies are well within the range of reported values for PbS QD films.
photocurrent spectroscopy (IMPS). In one previous study, dependent photoluminescence (PL) and intensity-modulated limits warrants further discussion.

Nevertheless, the wide variation among literature coefficients lower than the range plotted, the tail drops off sharply.

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 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 mercaptoethanol 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-exchanged 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 relatively 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 5b). 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\textsuperscript{28,42,43} or bands\textsuperscript{53} could constrain $E_{OC}$ 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 $E_{OC}$ limit. Even if they are not in equilibrium with the free-carrier population, however, midgap states can increase recombination and reduce $E_{OC}$ and efficiency. The PDS technique, coupled with transient spectroscopies\textsuperscript{58} and thermal admittance spectroscopy,\textsuperscript{55} 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 efficiency of 31%. On the basis of these measurements, we conclude that band tailing does not severely reduce the radiative efficiency limit of PbS QD solar cells from the ideal Shockley–Queisser limit.

\section*{Experimental Methods}

\textbf{PbS Quantum Dot Synthesis.} Colloidal PbS nanocrystals are synthesized by hot injection following literature methods.\textsuperscript{56,57} 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$^{-1}$.

\textbf{Ligand Solution Preparation.} Solutions for solid-state ligand exchange are prepared following well-characterized procedures from the literature. Unless otherwise specified, 27 mols (10 mg mL$^{-1}$) tetrabutylammonium iodide (TBAI) in methanol (MeOH) is used as the ligand solution.\textsuperscript{58} To compare halide ligands, we use 30 mols tetrabutylammonium fluoride, chloride, bromide, and iodide in MeOH. 1,2-ethanediethyl (EDT) is used at 2 mols in acetonitrile.\textsuperscript{59} All chemicals are purchased from Sigma-Aldrich at the highest purity available.

\textbf{PDS Substrate Preparation.} Custom 4 mm × 12 mm fused quartz slivers (500 μm thick) are cleaned by immersion in boiling isopropanol for 5 min. To improve QD film adhesion, clean substrates are immersed in 12 mls 3-mercaptopyrroltrimethoxysilane (MPTMS) in toluene for at least 8 h, sonicated for 1 min in isopropanol, and stored under nitrogen.

\textbf{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 μL 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 μm PTFE syringe filter immediately before spin-coating.

\textbf{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 × 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 μm 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.

\textbf{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,\textsuperscript{60} 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

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

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

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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Author Contributions
J.J. and V.B. designed the experiments. J.J., T.S.M., and D.B. developed the PDS system. J.J. and M.S. prepared the samples. J.J. performed the experiments and calculations. J.J., D.B., M.G.B., and V.B. analyzed the data. J.H. performed preliminary PDS measurements. All authors contributed to the writing of the manuscript.

Notes
The authors declare no competing financial interest.

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