

Supplementary information for Micron Thick Colloidal Quantum Dot Solids

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Experimental Methods

Synthesis of oleate capped PbS quantum dots (OA-PbS)

The exact synthetic procedure was reproduced from *Killilea et al.*¹ For a typical synthesis with an exciton peak targeted around 1650 nm, 2.25 g of PbO (99.999% Alfa-Aesar) and 5.9 g of distilled oleic acid (tech. 90% Sigma-Aldrich) were dissolved in 75 mL of 1-octadecene ($\geq 95\%$, Sigma-Aldrich) in a 250 mL Schlenk flask. This solution was heated to 120°C for two hours

under vacuum to degas the solution and form lead oleate in-situ. In a separate flask, the thiourea precursor was prepared by stirring 2.28 g of distilled phenylisothiocyanate (reagent grade, 98%, Sigma-Aldrich) and 4.51 g of distilled oleylamine (tech. 90%, Sigma-Aldrich) for two hours at 60°C in a N₂-filled glovebox. To synthesize the CQDs, the lead oleate solution was heated to 135°C under nitrogen, and 4 mL of the thiourea precursor solution was injected swiftly into the lead oleate flask. The solution turned black after ~ 60 seconds, and the solution stirred for exactly 20 minutes to form CQDs. After 20 minutes the heating mantle was removed to allow the solution to cool to room temperature before isolation with acetone (distilled in glass, Caledon). The CQDs were then washed two times by dissolution in toluene (distilled in glass, Caledon) and precipitation in acetone, after which they were dissolved in octane (98%, Alfa Aesar) at a concentration of 60 mg.mL⁻¹.

Ligand Exchange and CQD redispersion

A solution of 100 mM PbI₂ (99.999%, Alfa Aesar), 20 mM PbBr₂ (98%, Sigma Aldrich), and 44 mM NaAc (99.999%, Sigma Aldrich) was prepared in 10 mL of N,N-dimethylformamide (DMF) (Anhydrous, 98% Sigma-Aldrich) in a 50 mL centrifuge tube. 30mL of octane was added to the tube, and 1 mL of the 1650 nm OA-PbS CQD solution was added to the octane phase. The mixture was vigorously shaken for 30 s to facilitate ligand exchange. After the transfer of CQDs to the DMF phase, the tube was centrifuged at 7860 revolutions per minute (RPM) for 30 seconds, and the octane phase was discarded. After the initial phase transfer, the solution was washed three times with octane, with a centrifuge step in between each washing phase. After the 3rd wash, the supernatant was discarded (both octane and DMF phases) from the precipitated CQDs. 250 µL of DMF was added to the tubes to partially re-disperse the CQDs. After vortexing, a 10 µL volume of 50% v/v DMF: butylamine (99%, Sigma Aldrich) was added to the

tubes to promote redispersion. The CQD mixture was vortexed to ensure uniform dispersion. Then, the antisolvent, 600 μL of toluene (distilled in glass, Caledon), was added to precipitate the CQDs, and the tubes were centrifuged again for 120 seconds. The supernatant was removed, and the tubes were dried under vacuum for 6 minutes. The CQDs were dispersed in a solution of 50% DMF, 30% dimethylsulfoxide (DMSO) (Anhydrous, 99.9% Sigma-Aldrich), 17% butylamine, and 3% phenethylamine (PEA) ($\geq 99\%$, Sigma-Aldrich) at a concentration of 300 $\text{mg}\cdot\text{mL}^{-1}$. This solution was vortexed and transferred to a microcentrifuge tube and centrifuged at 13000 RPM for 60 seconds. The supernatant was extracted for subsequent solar cell fabrication.

Blade coating Solar Cell fabrication

The devices were prepared on an indium-doped tin oxide (ITO) substrate (Delta Technologies, 80- 90 $\Omega/1''\times 1''$ square). First, a ~ 30 nm layer of sol-gel ZnO was first deposited on the ITO by spin coating at 4000 RPM and annealing at 210°C for 35 minutes. The preparation of sol-gel ZnO was described in detail in another publication.² Then a ~ 135 nm layer of nanoparticle- ZnO was deposited by spin coating at 3000 RPM for 30 s. The preparation of nanoparticle ZnO was described in detail in another publication.³ The CQDs were deposited on the substrate via blade-coating. The ITO/ZnO substrate was placed on a 70°C heated plate, and allowed to warm for approximately one minute before blade coating. The CQD ink was blade coated at a speed between 70 – 90 mm/s and a height of 50 μm above the substrate (a total height of 750 μm). 30 μL of CQD ink was used to fabricate one 1 inch x 1 inch film. The film was allowed to dry for several minutes and was subsequently annealed in a glovebox at 80°C. A 40 nm film of 1,2-ethanedithiol treated PbS was deposited on top of the IR-CQD film through layer-by-layer deposition to act as hole transporting layer. The exact method for 1,2- ethanedithiol solid state

ligand exchange is described here.⁴ Finally, a 120 nm layer of Au was deposited by electron beam evaporation to complete the device. Each pixel has an area of 4.9 mm².

JV and EQE characterization

Full spectrum current density-voltage measurements were taken using a sourcemeter (Keithley 2400) under simulated AM1.5G illumination (Sciencetech class A). The simulator was set to 1 Sun power density using a NIST-traceable calibrated reference cell (Newport 91150 V). Devices were measured under continuous nitrogen gas flow. To simulate additionally-added Si power points, an 1100 nm long-pass dielectric filter (Thorlabs FEL 1100) was placed between the sample and illumination source during J-V scanning.

EQE spectra were measured using a Newport Quant-X 300 system. A mechanical chopper operating at a frequency of 25 Hz was used to chop the monochromatic excitation light source. The solar cell was operated under continuous white light bias. IR-short circuit current density was obtained by integrating the EQE spectra for each sample between 1100 nm – 1800 nm.

Steady state Absorbance and photoluminescence Measurements

Absorption measurements were carried out in a Lambda 950 500 UV-Vis-IR spectrophotometer. Photoluminescence measurements were performed with a Horiba Fluorolog Time Correlated Single Photon Counting System equipped with UV/Vis/NIR photomultiplier detectors, dual grating spectrometers, and a monochromatized xenon lamp excitation source. The excitation measurement was performed at $\lambda=500\text{nm}$.

X-Ray Photoelectron Measurements

Blade-coated CQD films were prepared on a glass substrate. The film was then mounted onto a stainless steel mounting plate. XPS measurements were performed using a Thermo Scientific K-Alpha system. An Al K α source was used. The takeoff angle was 90°. In order to account for charging, XPS spectra were calibrated to the samples' respective C 1s peak at 284.8 eV.

Thermogravimetric (TGA) Analysis

TGA experiments were conducted using a PerkinElmer Pyris 1 TGA. Sample preparation: about a 6-8 mg of CQD solids were taken on a platinum sample pan. TGA was performed by an equilibration or isothermal step at 50°C for 15 minutes and later heated to 800°C with a heating rate of 10 °C/min under nitrogen.

Optical microscope surface imaging

Optical microscope images were collected using Nikon LV150A with a mercury lamp fiber illuminator as a light source. Short working-distance objective lenses were used to achieve a magnification of 5x and 50x.

Transmission Electron Microscope Imaging

TEM measurements were performed on a Hitachi HF3300 instrument with an accelerating voltage of 300 kV. Samples were prepared by diluting a 100 mgmL⁻¹ PbX₂ capped SWIR-CQDs dispersed in 50% DMF, 30% DMSO, 17% BA, and 3% PEA were diluted about 3000 x in the same solvent mixture. Then, 20 μ L of CQDs was blade coated onto a 400 mesh copper grid.

Atomic Force Microscope Imaging

An Asylum Research Cypher AFM equipped with AC240TM-R3 probes was used to obtain AFM images.

Supplementary Figures

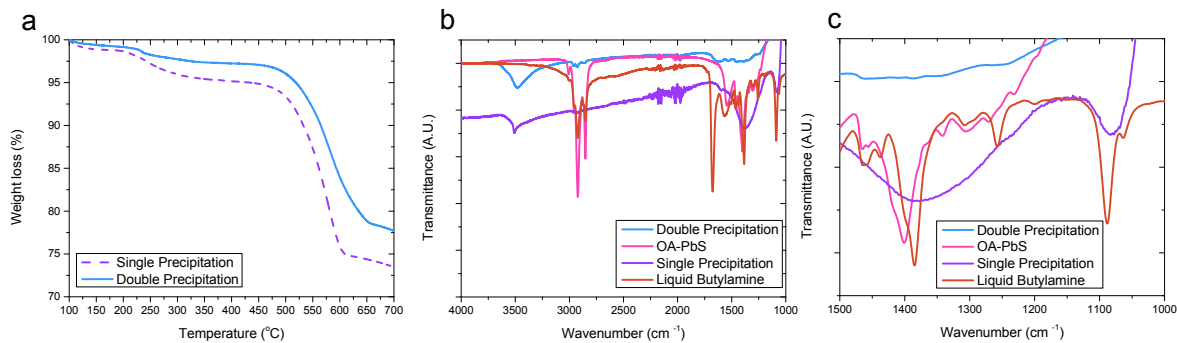


Figure S1: Single vs. double precipitation. Thermogravimetric plot of SWIR CQDs undergoing the single precipitation and double precipitation treatment (a). FTIR comparing SWIR-CQDs undergoing the single precipitation and double precipitation treatment (b). Zoom-in of the FTIR signal between 1000 – 1500 cm⁻¹ shows the presence of excess organic residues for the single precipitated CQDs.

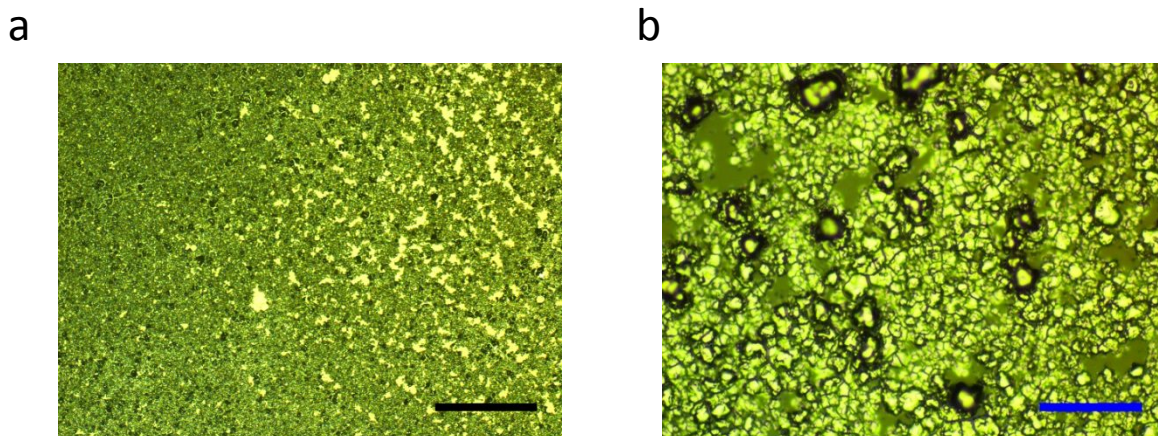


Figure S2: Microscope image of SWIR QDs films made with the butylamine solvent. Black scale bars represent 500 μm. Blue scale bars represent 50 μm.

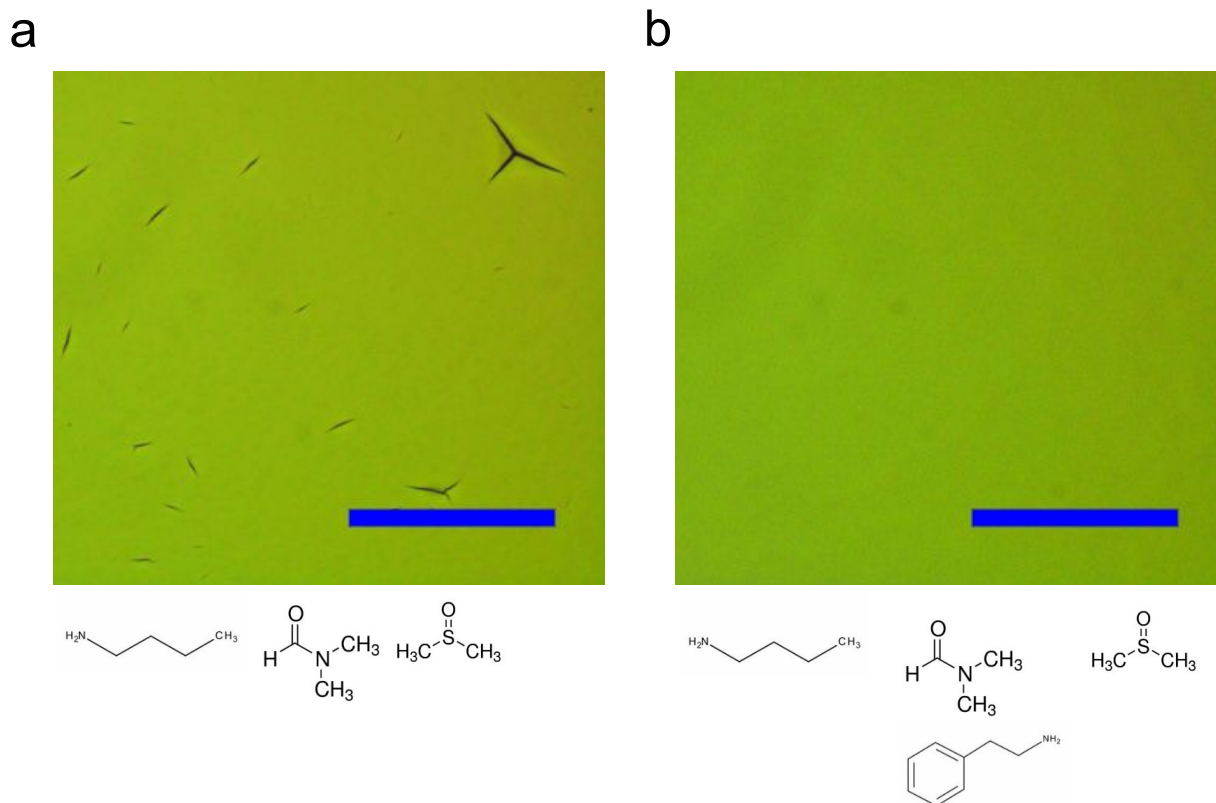


Figure S3: Optical microscope images comparing the triple solvent blade coated film (a) and the quaternary solvent blade coated film (b) Blue scale bars represent 50 μm.

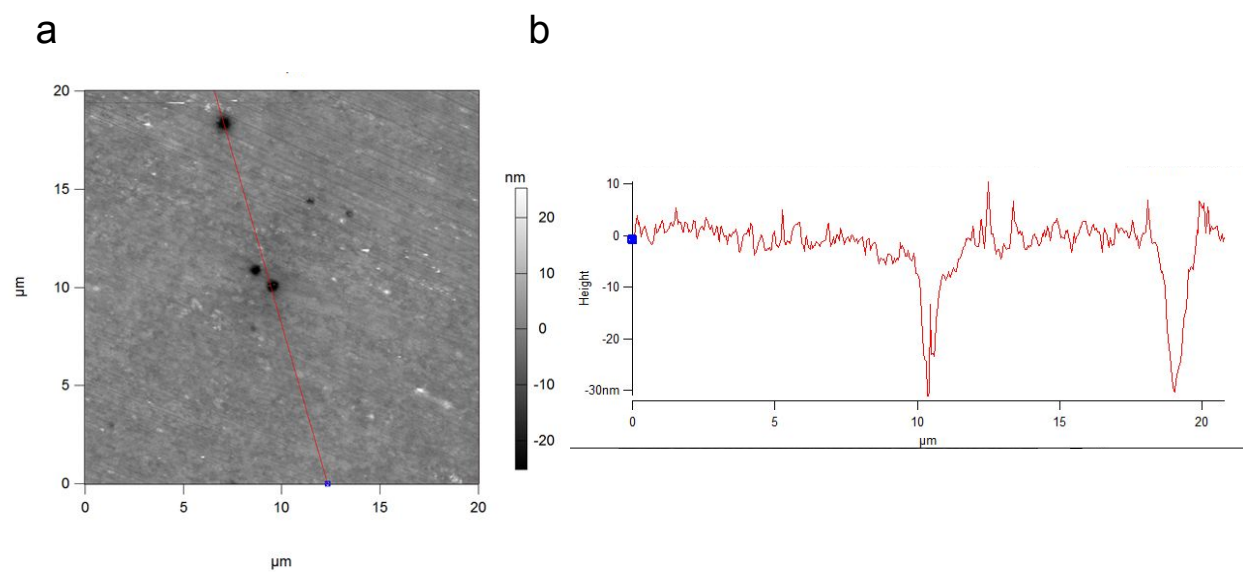
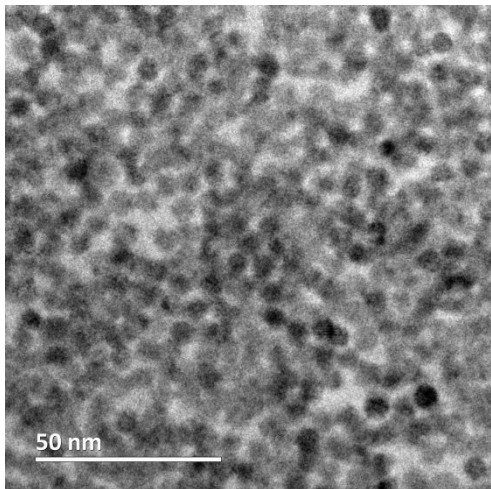


Figure S4: Atomic Force Microscope image of an imperfect region in the optimized blade coated film (a) Height profile of the measured red line (b)

a



b

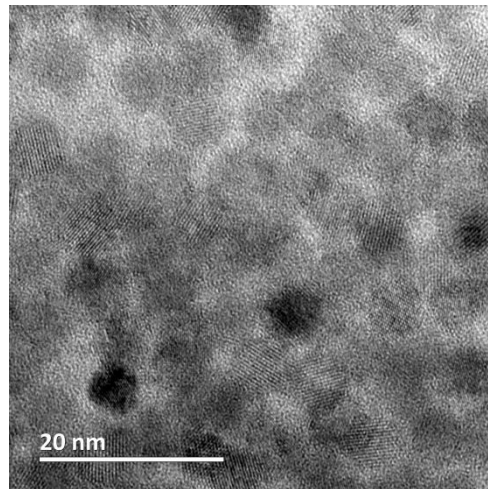


Figure S5: Transmission Electron Images of exchanged SWIR-CQDs dispersed in the quaternary solvent mixture. TEM magnification is shown with a scale bar of 50 nm (a) and 20 nm (b).

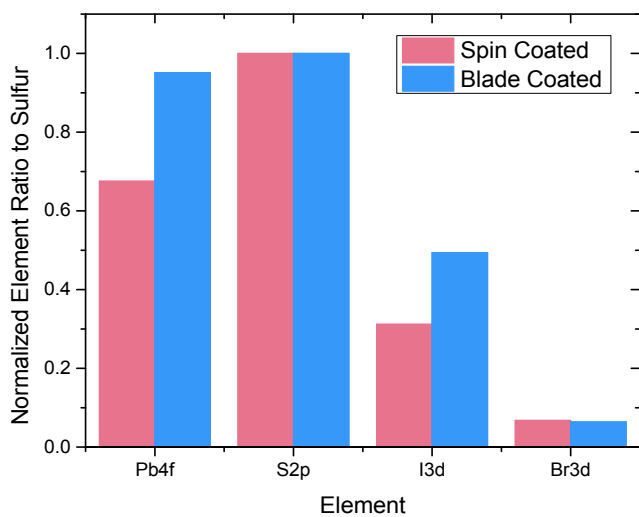


Figure S6: XPS ratios of different films normalized to the integrated S 2p signal.

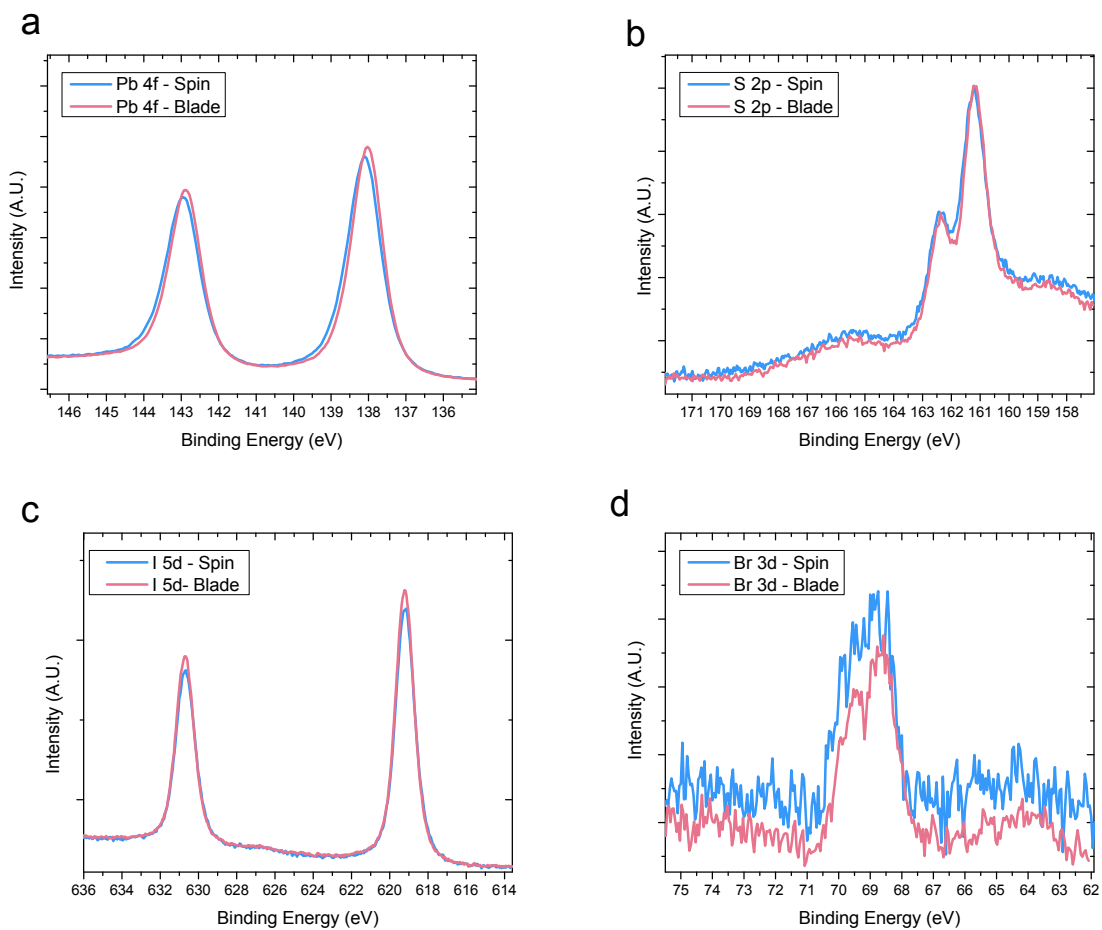


Figure S7: XPS spectra of CQD films for Pb 4f (a), S 2p (b), I 5d (c), and Br 3d (d).

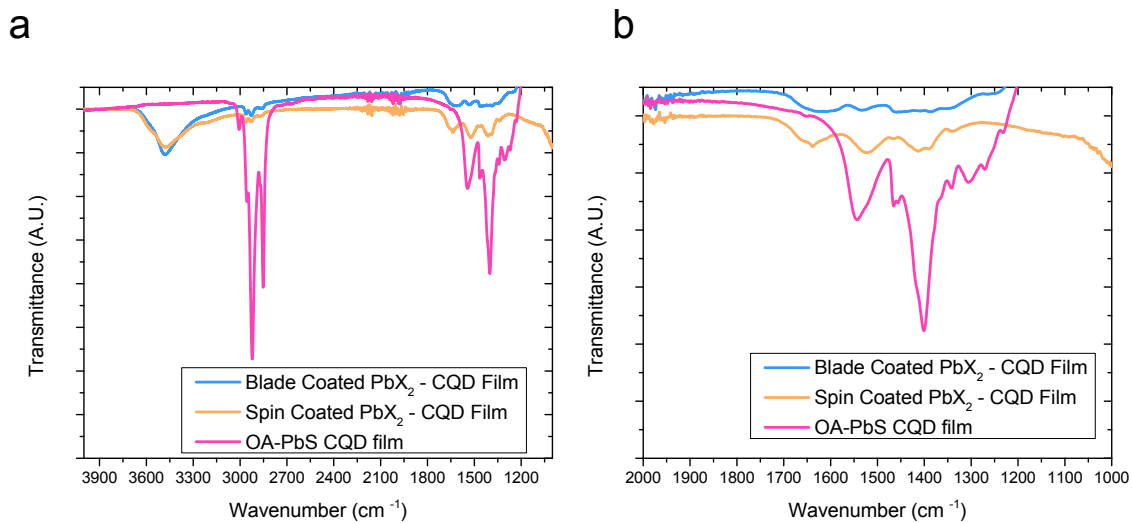


Figure S8: FTIR of blade coated PbX₂-PbS films, spin coated PbX₂-PbS films, and oleic acid capped PbS CQD films. Full FTIR spectra (a) zoomed in region between 2000 cm⁻¹ to 1000 cm⁻¹ (b)

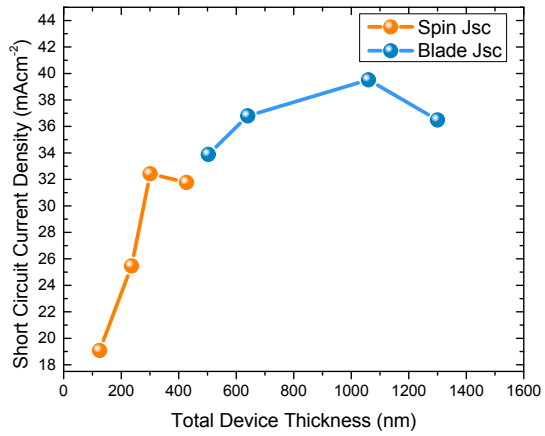
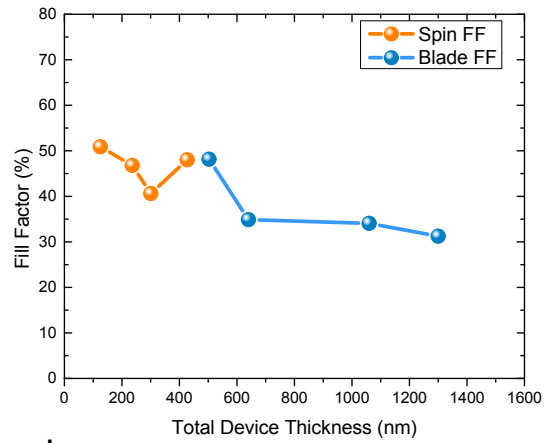
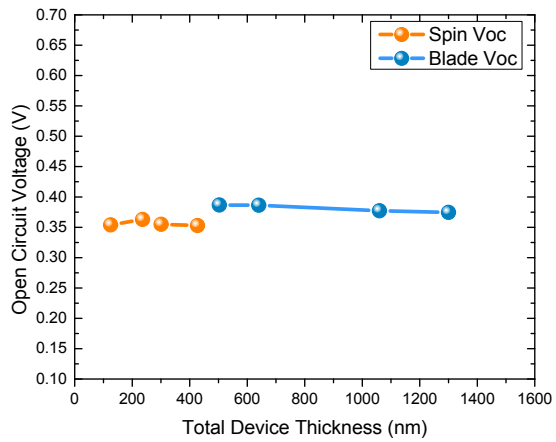
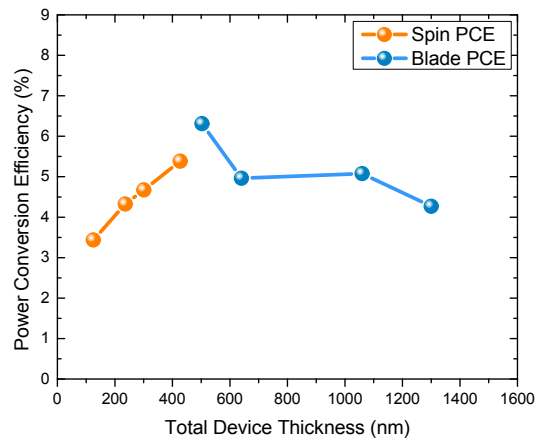
a**b****c****d**

Figure S9: Full solar harvesting solar cell parameters with varying thicknesses for Jsc (a) FF (b) Voc (C) and PCE (D)

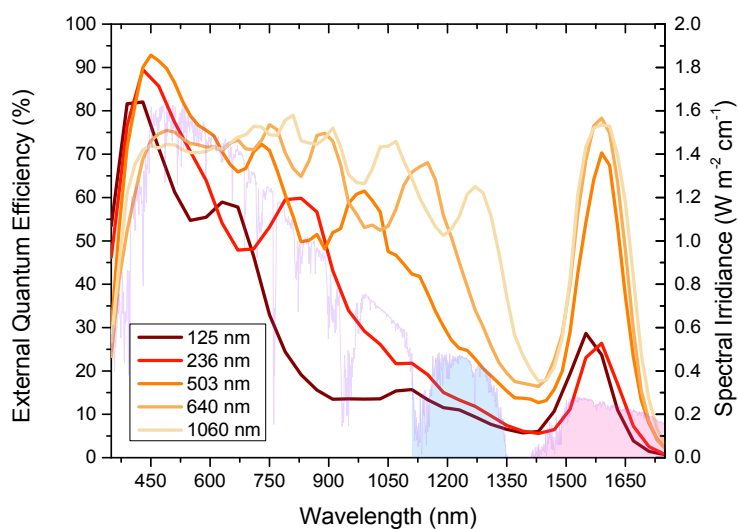


Figure S10: External Quantum Efficiency spectra for IR CQD solar cells made with different thicknesses overlaid on top of the AM1.5G spectrum. 1100 nm filtered IR regions in the AM1.5G spectrum are highlighted in light blue and light pink.

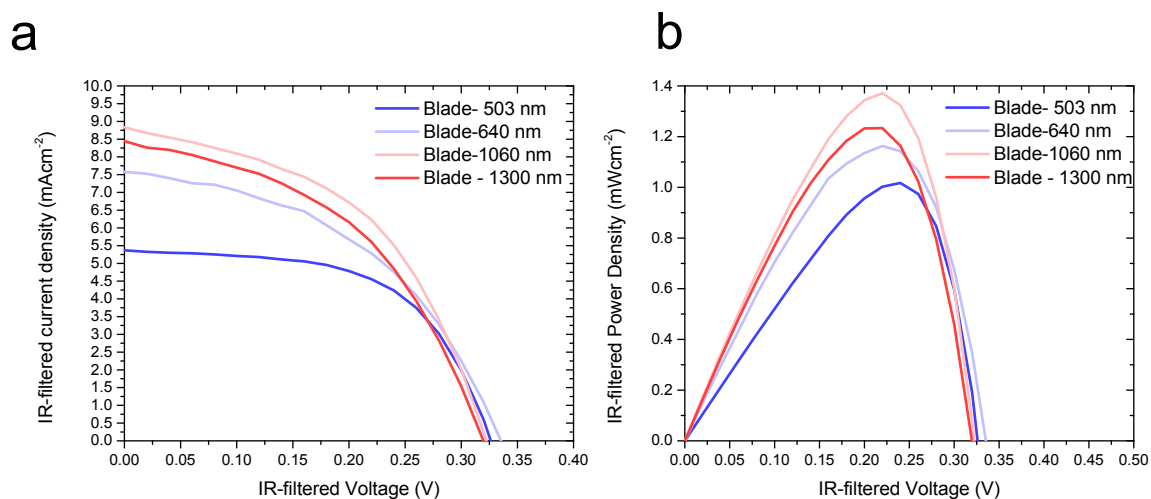


Figure S11: IR-JV curves for blade-coated CQD devices. The shape of the JV indicates that FF diminishes gradually with increasing thickness (a) The power density curves move gradually to lower voltages as thickness increases, indicative of the mild diminution in FF (b)

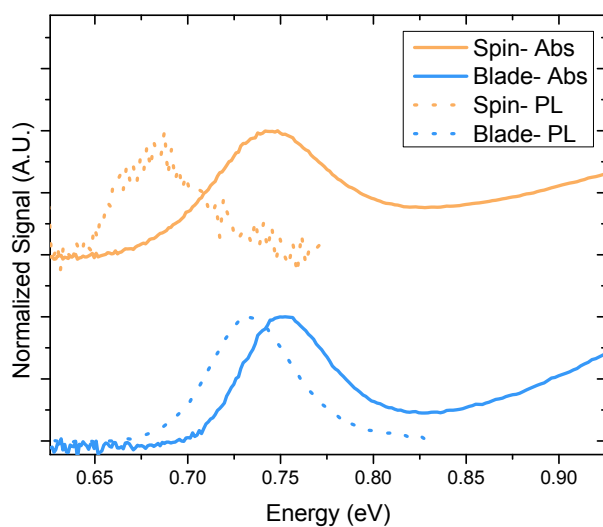


Figure S12: Absorbance and photoluminescence plots comparing spin and blade coated films.

References

- (1) Killilea, N.; Wu, M.; Sytnyk, M.; Yousefi Amin, A. A.; Mashkov, O.; Spiecker, E.; Heiss, W. Pushing PbS/Metal-Halide-Perovskite Core/Epitaxial-Ligand-Shell Nanocrystal Photodetectors beyond 3 μm Wavelength. *Adv. Funct. Mater.* **2019**, *29* (14), 1–7.
- (2) Baek, S. W.; Jun, S.; Kim, B.; Proppe, A. H.; Ouellette, O.; Voznyy, O.; Kim, C.; Kim, J.; Walters, G.; Song, J. H.; et al. Efficient Hybrid Colloidal Quantum Dot/Organic Solar Cells Mediated by near-Infrared Sensitizing Small Molecules. *Nat. Energy* **2019**, *4* (11), 969–976.
- (3) Lan, X.; Voznyy, O.; García De Arquer, F. P.; Liu, M.; Xu, J.; Proppe, A. H.; Walters, G.; Fan, F.; Tan, H.; Liu, M.; et al. 10.6% Certified Colloidal Quantum Dot Solar Cells via Solvent-Polarity-Engineered Halide Passivation. *Nano Lett.* **2016**, *16* (7), 4630–4634.
- (4) Fan, J. Z.; Andersen, N. T.; Biondi, M.; Todorović, P.; Sun, B.; Ouellette, O.; Abed, J.; Sagar, L. K.; Choi, M.; Hoogland, S.; et al. Mixed Lead Halide Passivation of Quantum Dots. *Adv. Mater.* **2019**, *31* (48), 1–8.