

## Electronic Supplementary Information

# Energy Transfer from Colloidal Nanocrystals to Strongly Absorbing Perovskites

Yasiel Cabrera,<sup>a ‡</sup> Sara M. Rupich,<sup>a ‡</sup> Ryan Shaw,<sup>b</sup> Benoy Anand,<sup>b</sup> Manuel de Anda Villa,<sup>b</sup>  
Rezwanur Rahman,<sup>a</sup> Aaron Dangerfield,<sup>a</sup> Yuri N. Gartstein,<sup>b</sup> Anton V. Malko,<sup>b</sup> Yves J.  
Chabal<sup>a\*</sup>

<sup>a</sup>Department of Materials Science & Engineering and <sup>b</sup>Department of Physics

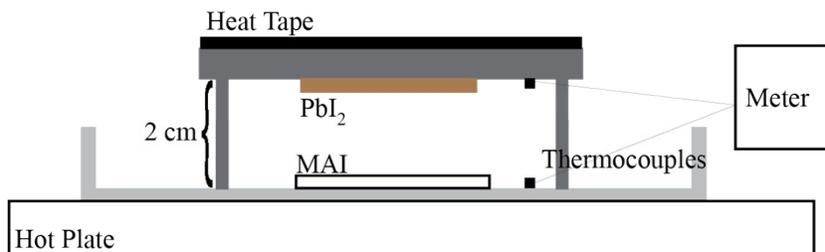
The University of Texas at Dallas, Richardson, TX 75080 USA

## Supplementary Methods

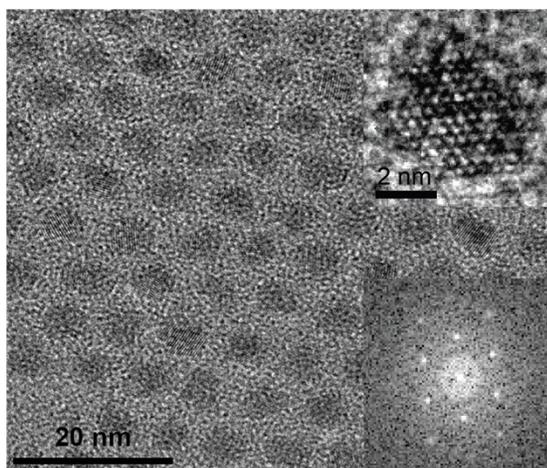
***In-situ* FTIR during ALD.** For these measurements, double-side-polished, float-zone grown Si (111) wafers (n-doped,  $\rho \sim 10\text{-}60 \text{ } \Omega \text{ cm}$ ) are cut into  $3.8 \times 1.5 \text{ cm}^2$  substrates to fit the sample holder in a home-built ALD reactor.<sup>1</sup> Substrates are cleaned and perovskite films grown as described in the main text. After cleaning and/or perovskite growth, the sample is loaded into the N<sub>2</sub>-purged ALD reactor, with a base pressure of  $\sim 10^{-4}$  Torr. To monitor perovskite stability and characterize the ALD process, the sample is loaded into the reactor, heated to 80 °C under N<sub>2</sub> gas and reference spectra are collected. For stability measurements, IR spectra are collected at 80°C as a function of time. For Al<sub>2</sub>O<sub>3</sub> growth, 20 TMA/D<sub>2</sub>O cycles are carried out. The precursor exposures are both 1s pulse for TMA ( $p = 390\text{mTorr}$ ) and 1s pulse for D<sub>2</sub>O ( $p = \sim 800 \text{ mTorr}$ ) at a deposition temperature of 80 °C with 10 min purges after each exposure, after which IR spectra are collected.

The IR absorption measurements are performed with a Thermo Nicolet 6700 infrared interferometer, equipped with a liquid-nitrogen cooled broadband mercury cadmium telluride (MCT-B) detector. A single-pass transmission at Brewster incidence ( $\sim 74^\circ$  to normal) is used to minimize substrate phonon absorption in the low frequency region ( $< 1000 \text{ cm}^{-1}$ ) and increase sensitivity of all components (parallel and perpendicular to the surface) of surface species. Manual gate valves are used to protect the potassium bromide (KBr) windows from the precursor gases during ALD cycles. The sample temperature is monitored with a K-type thermocouple spot-welded onto a tantalum clip firmly attached at the center of the long edge of the Si substrate.

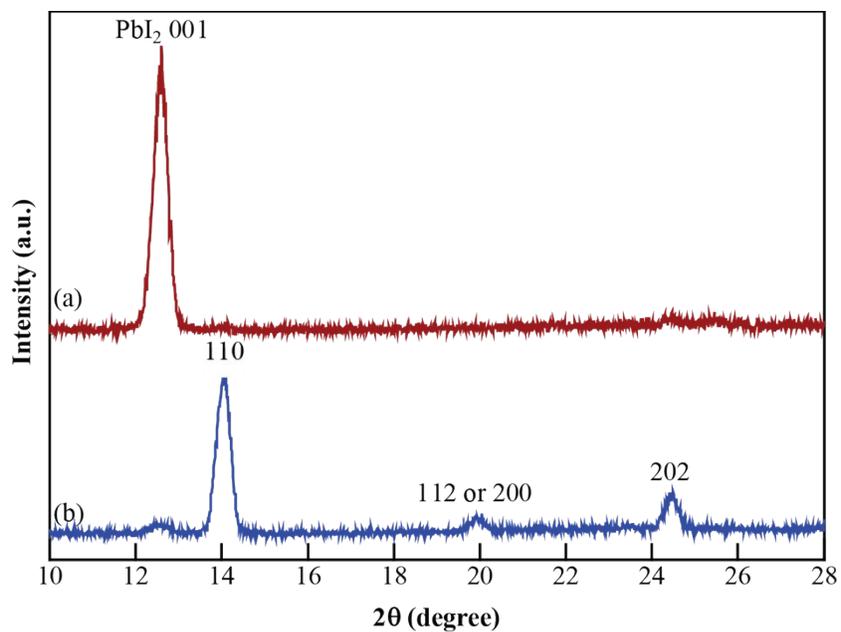
## Supplementary Figures



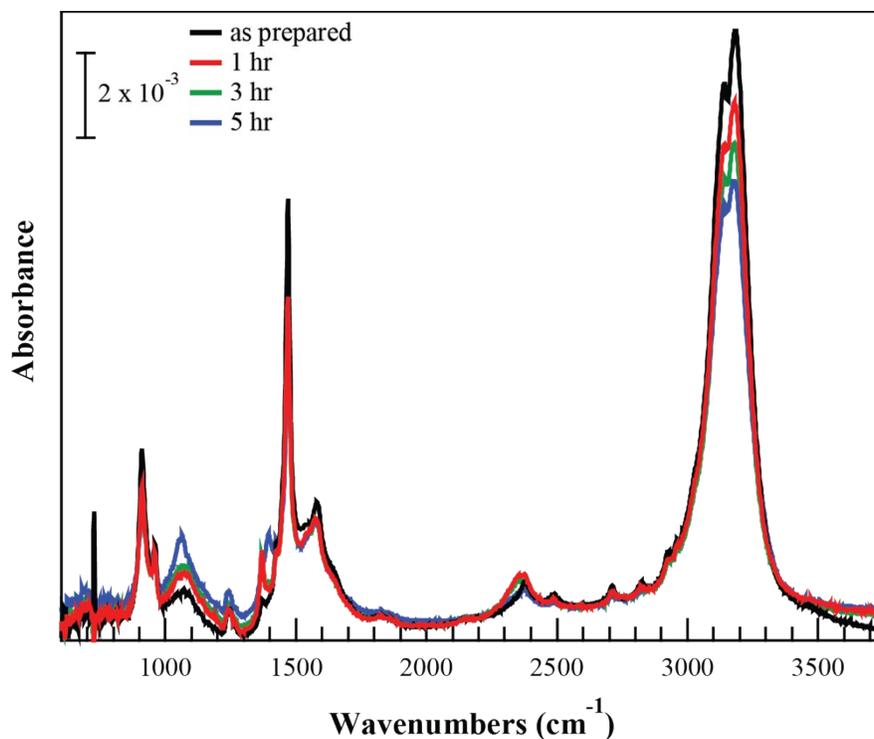
**Fig. S1.** Schematic of the home-built set-up for the conversion of PbI<sub>2</sub> to perovskite. A glass petri dish is placed on a hot plate on which a small amount of methyl ammonium iodide (MAI) is placed. The powder is surrounded by a 2 cm tall aluminum cylinder over which an aluminum plate is suspended. The PbI<sub>2</sub> film on glass is mounted to the bottom of the Al plate and centered over the MAI powder. Heat tape is attached to the top-side of the Al plate to control the substrate temperature. Thermocouples are attached to both the bottom glass plate and top aluminum plate to monitor the temperature. By adjusting the power to the hot plate and heat tape, the temperature of both plates was held at 160 °C during the conversion.



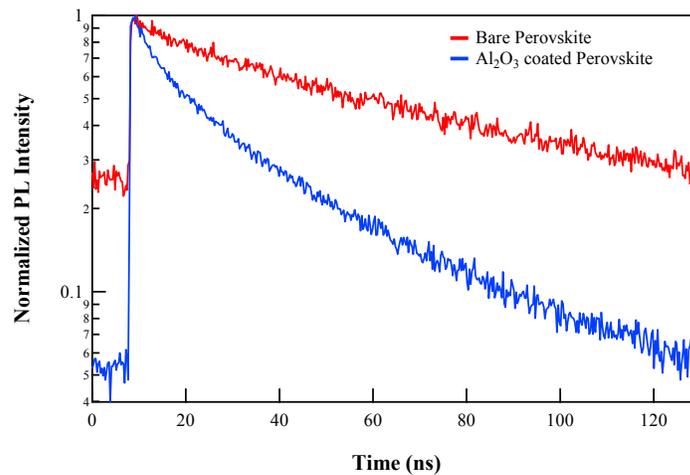
**Fig. S2.** TEM image of CdSe/ZnS NQDs. The upper inset is HRTEM image of a single NQD while the lower inset shows the FFT pattern of the NQD highlighting its crystallinity.



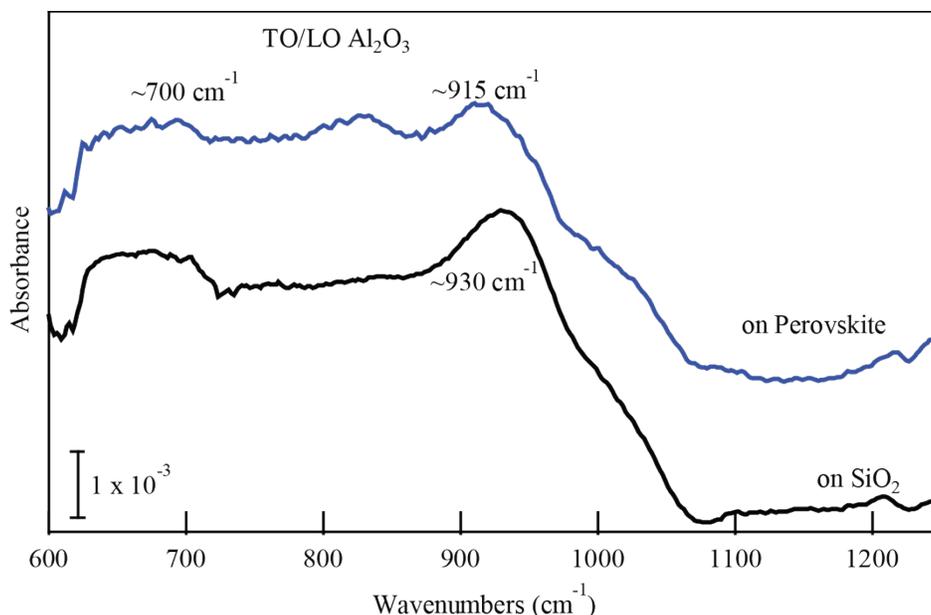
**Fig. S3.** XRD patterns of perovskite films after ALD at 80 °C where (a) 160 cycles of TMA/H<sub>2</sub>O and (b) 10 pulses of TMA followed by 160 cycles of TMA/H<sub>2</sub>O were deposited. The peaks at 14°, 19°, and 24.5° correspond to the orthorhombic perovskite phase while the peak at 12.5° corresponds to the 001 phase of PbI<sub>2</sub>.



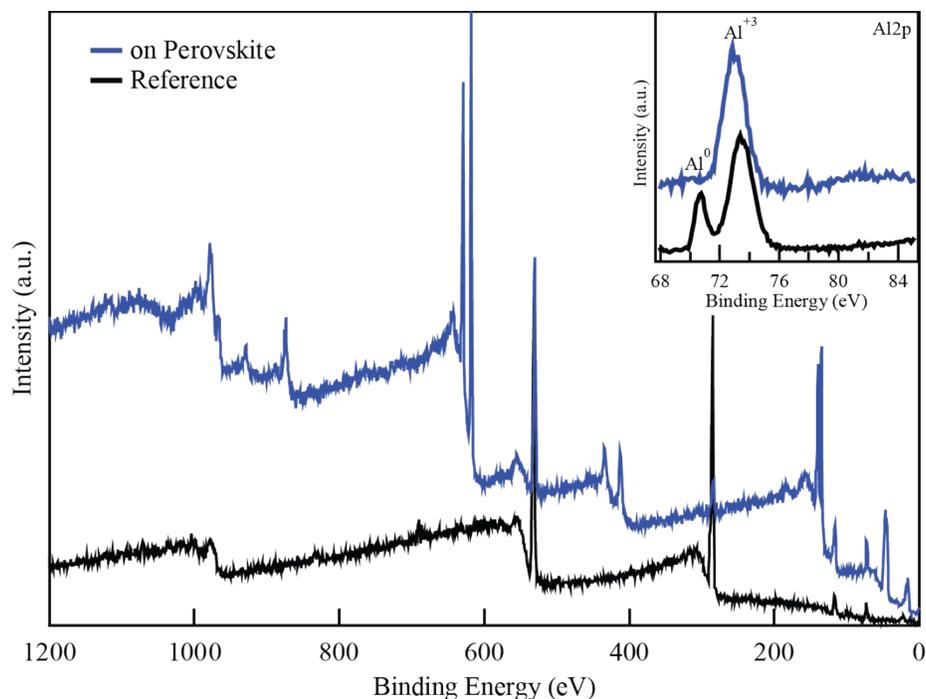
**Fig. S4.** FTIR spectra of the lead halide perovskite as a function of annealing time at 80 °C. A decrease in the intensity of the  $\text{CH}_x/\text{NH}_x$  stretching modes ( $2600 - 3570 \text{ cm}^{-1}$ ) is observed with time indicating sample degradation. After 3 hours at  $80^\circ\text{C}$ , the intensity of these modes decreased  $\sim 20\%$  indicating that the majority of the sample remained in the perovskite phase.



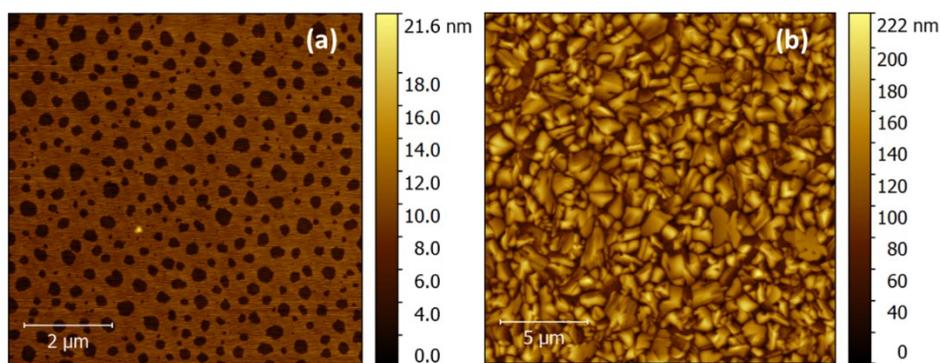
**Fig. S5.** PL lifetimes of perovskite with and without an  $\text{Al}_2\text{O}_3$  overlayer.



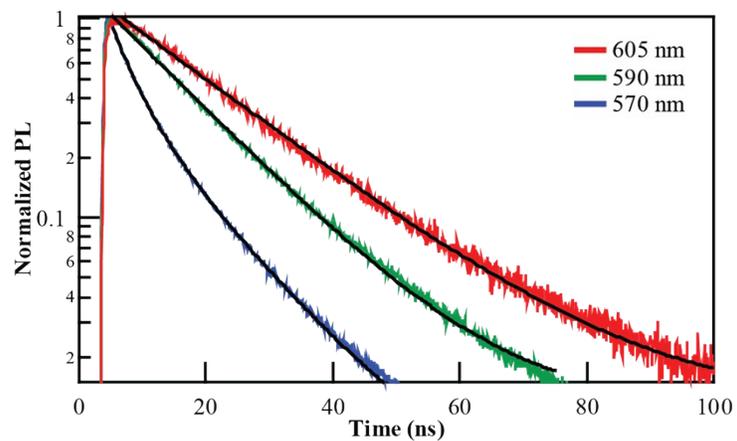
**Fig. S6.** Transmission IR spectra of Al<sub>2</sub>O<sub>3</sub> grown from 10 pulses TMA followed by 20 TMA/D<sub>2</sub>O cycles on perovskite and SiO<sub>2</sub> substrates. The total absorbance after 20 cycles is calculated by referencing the last spectra to the starting substrate. After 20 cycles, the appearance of the TO/LO phonon modes are visible indicative of Al<sub>2</sub>O<sub>3</sub> growth. Note that the LO mode for the Al<sub>2</sub>O<sub>3</sub> grown on the perovskite is at slightly lower frequency (915 rather than 930 cm<sup>-1</sup>) than for Al<sub>2</sub>O<sub>3</sub> on SiO<sub>2</sub>, indicating poorer uniformity (smaller domains) on the perovskite presumably due to the perovskite surface roughness. However, the integrated areas of the TO/LO phonon modes for both samples are within 5% of each other indicating that Al<sub>2</sub>O<sub>3</sub> grew at the same average rate on both SiO<sub>2</sub> and perovskite surfaces.



**Fig. S7.** XPS spectrum of Al<sub>2</sub>O<sub>3</sub> grown from 20 cycles TMA and D<sub>2</sub>O on the perovskite (blue). A reference Al<sub>2</sub>O<sub>3</sub> spectrum taken from the native oxide layer on aluminum (black). Inset, Al2p region in which the reference sample confirms the presence of Al<sup>3+</sup>. In addition to the Al and O peaks due to the Al<sub>2</sub>O<sub>3</sub>, other peaks are visible in the perovskite sample corresponding to the presence of Pb, I, and C from perovskite layer since Al<sub>2</sub>O<sub>3</sub> layer is very thin.



**Fig. S8.** AFM image of (a) a monolayer of NQD spun-cast on glass and (b) perovskite prepared at 160 °C for 90 min. The perovskite film has a root mean square roughness of ~32 nm.



**Figure S9.** PL lifetimes of a close packed monolayer of NQDs as a function of wavelength. Due to spectral diffusion due to ET between neighboring NQDs of different sizes, NQDs with longer emission wavelengths exhibit slower decays.

### Supplemental References

1. J. Kwon, M. Dai, M. D. Halls, E. Langereis, Y. J. Chabal and R. G. Gordon, *J. Phys. Chem. C*, 2009, **113**, 654-660.