Supporting Information

Dual Nature of the Excited State in Organic-Inorganic Lead Halide Perovskites

Kevin G. Stamplecoskie[1], Joseph S. Manser[2], and Prashant V. Kamat*[,1,2]

Radiation Laboratory

University of Notre Dame

Notre Dame, Indiana 46556, United States

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[1] Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

[2] Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States

*Corresponding author: Prashant V. Kamat (pkamat@nd.edu)

Experimental Details

Methylammonium iodide synthesis. CH_3NH_3I was synthesized by dropwise addition of aqueous HI (Alfa Aesar, 57%) into methylamine (Sigma Aldrich, aqueous, 40%) under stirring at 0 °C. After allowing the solution to stir for two hours, the solvent was removed by rotary evaporation. The yellow-white crystals were washed three times by sonication in diethyl ether, filtered, and dried overnight under vacuum to yield white crystals of CH_3NH_3I.

$CH_3NH_3PbI_3$ film preparation for optical measurements. Borosilicate glass slides were rinsed with detergent, sonicated in ethanol for 15 min, and subjected to oxygen plasma treatment for 5 min prior to mesoporous alumina deposition. Alumina films were cast onto the clean glass slides by spin coating a 4 wt% colloidal suspension of Al_2O_3 in 2-propanol (Sigma Aldrich, 20 wt% in 2-propanol, <50 nm) at 5000 rpm for 30 s (2000 rpm/s ramp rate). The films were then dried at 150 °C for 1 h. The $CH_3NH_3PbI_3$ precursor solution was prepared by dissolving stoichiometric quantities of CH_3NH_3I and PbI_2 (Alfa Aesar, 99.9985%) in *N,N*-dimethylformamide at 150 mg/ml to obtain the desired optical density for transmittance measurements. The yellow-colored solution was stirred at 70 °C for 1 h prior to perovskite film deposition. The precursor solution was loaded onto the alumina films and spin cast at 2000 rpm for 30 s (1000 rpm/s ramp rate). For the as-deposited samples, no further treatment was carried out, while for the annealed samples, the films were placed on a hot plate at 100 °C for 20 min to form the dark brown $CH_3NH_3PbI_3$ perovskite. Perovskite film deposition and annealing were carried out in a dry nitrogen atmosphere (≤10 ppm H_2O).

Optical characterization. For steady-state absorption spectra of solutions and films, a Cary 50 UV-vis absorption spectrometer was used. Transient absorption measurements were performed using a Clark laser with a 775 nm fundamental pulsed at 1 kHz with 130 fs FWHM pulse durations. The fundamental is split to generate a white light probe by focusing through a Ti-sapphire crystal. For 387 nm excitation, the second harmonic of the 775 nm is generated and used to excite samples. Transient absorption spectra are recorded as a difference between probe signals with/without a pump pulse, and the delay between pump and probe is controlled to generate spectra at varied times following excitation. For optical characterization of solid-

state samples, the as-deposited and annealed films were placed in sealable quartz cuvettes and evacuated for at least 30 min prior to all measurements.

Structural characterization. A Bruker D8 Advance Davinci powder X-ray diffractometer was used to record diffraction patterns of the precursor powder and thin film samples. For measurement of the precursor components, CH_3NH_3I and PbI_2 powders were deposited on quartz substrates. Thin film samples were prepared by depositing a 400 mg/ml stoichiometric precursor solution of CH_3NH_3I and PbI_2 in *N,N*-dimethylformamide onto a mesoporous alumina substrate. Processing of the thin film samples for structural characterization was done in the same manner as the optical samples detailed above.

Details of Kinetic Analysis

A biexponential equation of the form $y = y_0 + A_1 \exp(-x/\tau_1) + A_2 \exp(-x/\tau_2)$ was used to fit the normalized excited state decay kinetics of the solution and solid-state samples. The coefficients A_1 and A_2 represent the weighted contribution of each exponential component to the overall kinetics, and τ_1 and τ_2 are the time constants of the two exponential decay elements. The average lifetime at the specified spectral position for film samples was calculated using the equation $< \tau > = A_1\tau_1 + A_2\tau_2$.
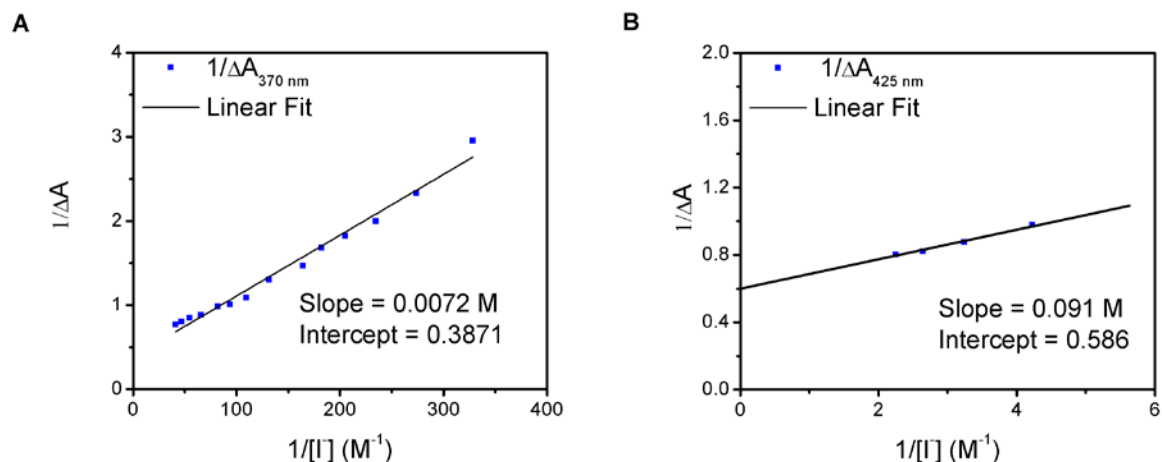
Figure S1. Benesi-Hildebrandt plot for obtaining the association constant for iodine ions with Pb^{2+}, monitored at 370 nm (A) and 425 nm (B) for each of the corresponding plumbate complexes.
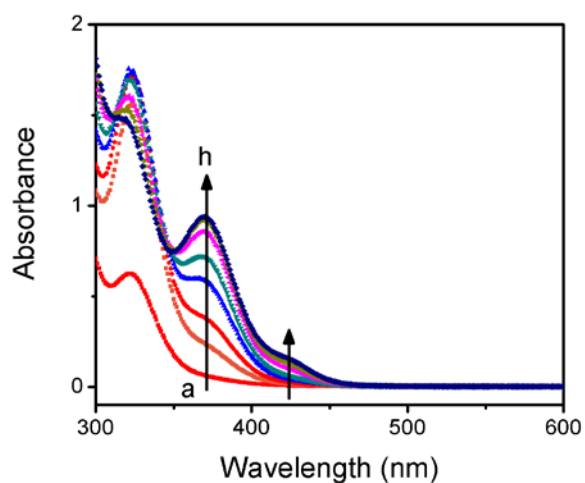

Figure S2. Absorption spectra of 200 μM PbI_2 in dimethylformamide with increasing potassium iodide concentrations of, a) 0 mM, b) 3.7 mM, c) 7.5 mM, d) 15 mM, e) 22 mM, f) 37 mM, g) 52 mM and h) 67 mM.
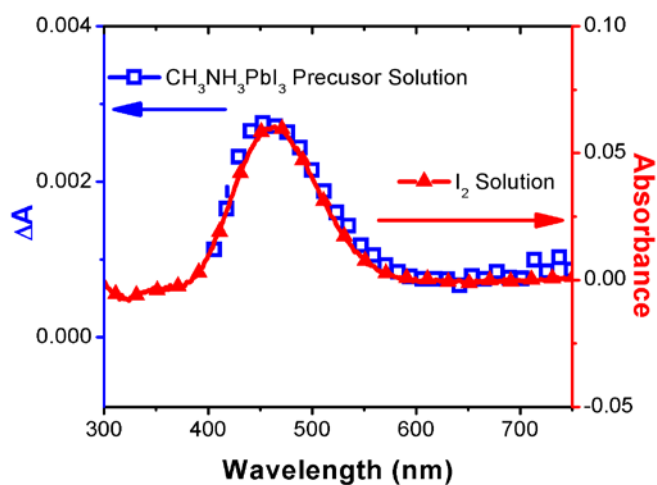
Figure S3. Transient absorption spectrum of $CH_3NH_3PbI_3$ precursor solution after 387 nm femtosecond pulsed excitation, overlapped with an absorption spectrum of I_2 in dimethylformamide.
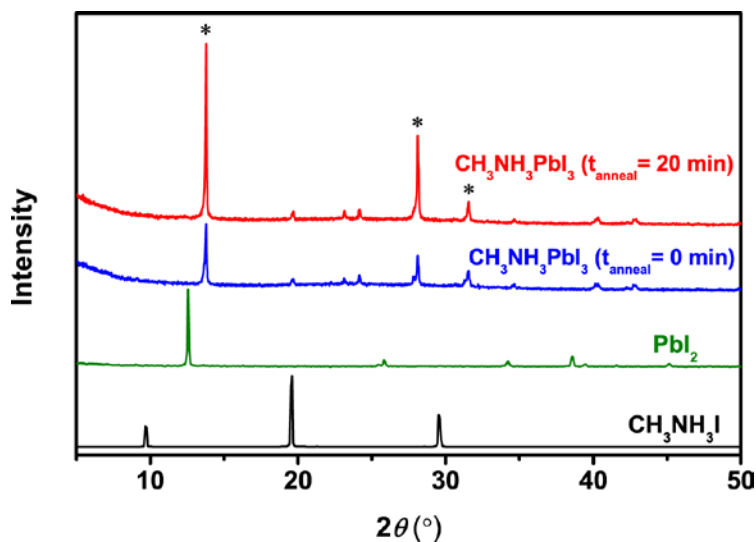

Figure S4. XRD spectra of the precursor powders CH_3NH_3I (black trace) and PbI_2 (green trace), along with spectra of the as-deposited perovskite film on alumina scaffold before annealing (blue trace) and after 20 minutes of annealing at 100 °C (red trace). * indicates prominent reflections of the tetragonal phase of $CH_3NH_3PbI_3$ at 2θ = 13.8°, 28.1°, and 31.6°.
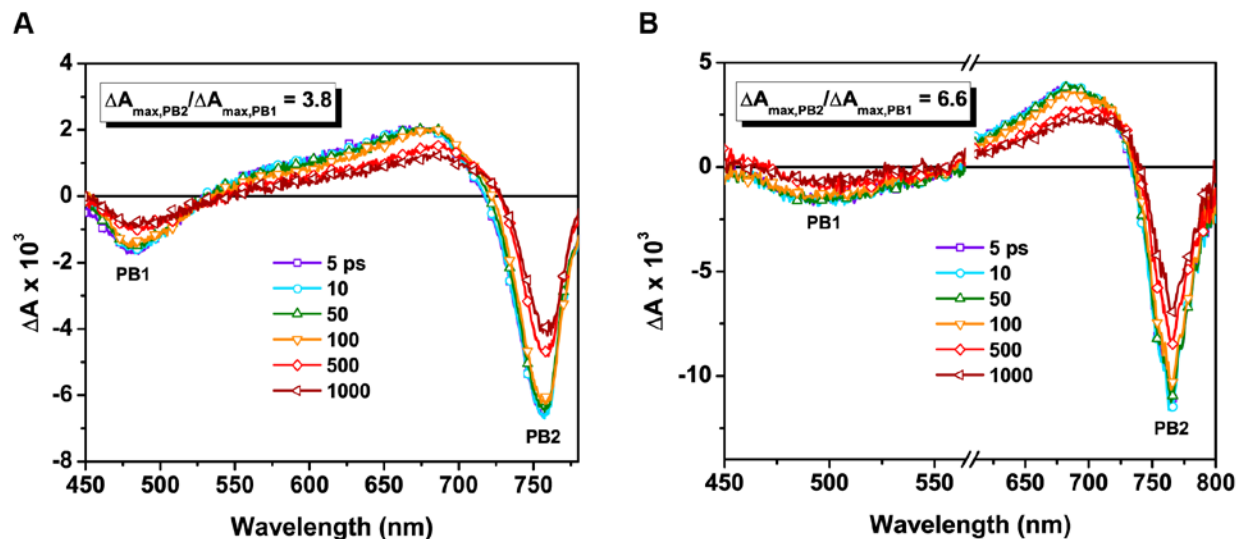
Figure S5. Comparison of the ratio of the photoinduced bleaches (PB1 and PB2) in the $CH_3NH_3PbI_3$ excited state spectrum following (A) 387 nm and (B) 590 nm femtosecond pulsed laser excitation. The larger PB2/PB1 bleaching ratio with the 590 nm pump pulse demonstrates increased excitation of the lower energy transition. Pump power in both measurements was 1.5 mW/cm².