Supporting Information

Probing Perovskite Photocatalysis. Interfacial Electron Transfer between CsPbBr$_3$ and Ferrocene Redox Couple

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1. Experimental

a. Chemicals:

Lead (II) bromide (PbBr₂, Alfa Aesar, 99.999%), cesium carbonate (Cs₂CO₃, Alfa Aesar, 99.9%), oleic acid (Sigma Aldrich, technical grade, 90%), oleylamine (Sigma Aldrich, technical grade, 70%), 1-octadecene (1-ODE, Sigma Aldrich, 90%), hexane (Sigma Aldrich, 95%), acetone (Fischer, HPLC grade), dichloromethane (Sigma Aldrich, anhydrous, >99.8%, contains 40-150 ppm amylene as stabilizer), didodecyldimethyl ammonium bromide (DDAB, Sigma Aldrich, 98%), methyl acetate (Sigma Aldrich, anhydrous, 99.5%), ethyl acetate (Sigma Aldrich, anhydrous, 99.8%), ethanol (Sigma Aldrich, anhydrous, 200 proof), ferrocene (Fc⁰, Sigma Aldrich, 98%), ferrocenium hexafluorophosphate (FcPF₆ or Fc⁺, Sigma Aldrich, 97%), are used as received from the supplier.

b. Synthesis of CsPbBr₃ nanocrystals (NCs) and ligand exchange:

Synthesis of CsPbBr₃ NCs was adapted from a previously reported procedure. The steps are listed as follows:

Cs-Oleate Preparation Procedures:

Cs-Oleate was prepared by mixing 0.3693 g (1.13 mmol) of Cs₂CO₃, 3.379 mL (10.71 mmol) of oleic acid, and 3.621 mL (11.32 mmol) of 1-octadecene in a 25 mL round bottom flask (flask 1). The mixture was degassed at 80° C for 1 hour.

CsPbBr₃ NC Synthesis Procedures:

To a 50 mL three neck round bottom flask (flask 2) was added 6 mL (19.05 mmol) of oleic acid, 6 mL (18.76 mmol) of 1-octadecene, and 0.828 g (2.26 mmol) of PbBr₂, followed by degassing for 1 hour at 80° C. After one hour, the temperature was raised to 170°C (while still under vacuum). While flask 2 is ramping to 170°C, flask 1 is set to 150°C (all while under vacuum). Once at 170°C, flask 2 has added to it 6 mL (18.24 mmol) of oleylamine (while still under vacuum). The reaction mixture was then put under a nitrogen environment. Simultaneously, flask 1 was put under a nitrogen atmosphere. After both solutions were brought up to temperature, 4 mL of Cs-Oleate from flask 1 were added to flask 1 with a heated syringe. The mixture was then immediately placed into an ice bath until it reached a temperature of ~65° C.

Workup:

Step 1: Purification of OLAC/OLAM-ligated NCs:

All of the product was spun down with an addition of ~ 5 mL of ODE to clean the reaction flask and get all of the product into a 45 mL centrifuge tube. The product was spun down for 7000 rpm for 10 minutes.

The supernatant was discarded, and the pellet was kept and washed with exactly 2 mL of hexane and 2 mL of MeOAc (note: the pellet is not re-dispersed in hexane before MeOAc addition; 2 mL of both are
This solution was spun down at 7000 rpms for 10 minutes and the supernatant was again discarded.

The pellet was fully re-suspended in hexane. The hexane solution is quite turbid and cloudy. Thus, the solution was spun down at 4000 rpms for 5 minutes. The pellet was discarded, and the colloidal-stable supernatant was kept. The product should be highly colored but completely transparent with no turbidity.

The nanocrystals were then diluted to a concentration of ~6 µM.

**Step 2: DDAB ligand exchange**

To perform exchange native OLAC/OLAM ligands to DDAB, the procedures of Kovalenko et al. were followed\(^2\). Toluene, purified NCs in hexane, and the 0.05 M solution of DDAB in toluene were added together in a ratio of 1:1:0.4 by volume.

The solution was stirred for 1 hour to allow exchange to occur.

**Step 3: Purification of DDAB-CsPbBr\(_3\) NCs**:

After ligand exchange, the reaction mixture had added to it ethyl acetate in a ratio of 1:1.2 by volume. The sample was then centrifuged at 7800 rpm for 5 minutes. The supernatant is kept, and acetone is added to the supernatant at a ratio of 1:10 acetone:supernatant, and the solution spun once more at 7800 rpm for 5 minutes. The pellet is kept and redispersed in hexane and the supernatant is discarded.

c. **Preparation of Fc\(^+\) Stock Solutions:**

9.9 mg of FcPF\(_6\) (Fc\(^+\)) was added to a 20 mL scintillation vial, along with 10 mL of N\(_2\)-sparged DCM. The solution was sonicated for 1 hour, forming a 6 mM stock solution. To avoid any dilution effects, 10 µL was chosen as the injection volume of Fc\(^+\) stock for each concentration investigated (2.5 – 20 µM). Separate stock solutions for each desired concentration were made by diluting the main stock. For steady state photolysis, 50 µL of a 6 mM stock was injected into the cuvette, as concentrations above 6 mM Fc\(^+\) in DCM are not well dissolved.

Note: special care is needed to keep Fc\(^+\) stocks fresh, as Fc\(^+\) is susceptible to moisture-induced degradation evidenced by a color change from blue to green. All stock solutions were remade each day, and when not in use during the day the solutions were stored in a glovebox.

d. **Steady State Photolysis:**

To a 1 cm path length quartz cuvette was added 2.4 mL of a 37.5 nM stock solution of DDAB-CsPbBr\(_3\) NCs in sparged hexane and 0.6 mL of sparged DCM (total volume of 3 mL with NC concentration of 30 nM). 100 µM Fc\(^+\) was injected into the cuvette and an absorption spectrum was recorded. Irradiation was performed at an irradiance of 75 mW/cm\(^2\) utilizing a broadband white light source with a 415 nm long pass filter (see Figure S3 for lamp output).
e. **Instrumentation:**

All steady state absorption measurements are carried out on a Varian Cary 50 bio spectrophotometer.

Photoluminescence measurements were performed on a Horiba Jobin Yvon Fluorolog 3 spectrophotometer.

Time-resolved photoluminescence decay (PL decay) was performed using a Horiba Jobin Yvon time correlated single photon counting (TCSPC) system, utilizing an IBH DataStation Hub for timing and a nanoLED laser for excitation (370 nm).

Femtosecond transient absorption measurements were performed on a Clark MR-2010 laser system (775 nm fundamental, 1 mJ/pulse, FWHM = 150 fs, repetition rate of 1 kHz) with detection software from Ultrafast Systems (Helios). The fundamental beam was split 95/5, where 95% of the beam is frequency-doubled to 387 nm for the pump and the remaining 5% is sent to a computerized optical delay stage and then focused onto a CaF₂ crystal to generate the white-light continuum probe pulse. The pump beam was sent through an iris of known diameter and the power was modulated via a neutral density wheel to keep the power density at ~ 8 µJ/cm² for these experiments.

Nanosecond Laser Flash Photolysis (NsLFP) measurements were done utilizing the 3rd harmonic of a Nd:YAG laser (355 nm) with approximately 15 ns pulsewidth and a 10 Hz repetition rate. A 1000 W Xe lamp (Hanovia) was pulsed via a Sorensen Power Supplies pulser and was used as a monitoring beam. The light that passed through the sample was sent through a monochromator and detected with a PMT which is recorded by a 1 GHz LeCroy oscilloscope.

For steady-state photolysis experiments, a Fiber-Lite Model 190 fiber optic illuminator (Dolan-Jenner Industries, INC.) was used with an USHIO 10.8 V 30 W halogen bulb (see Figure S5 for spectral output).
To highlight the need for ligand exchange to didodecyldimethyl ammonium bromide (DDAB), and to highlight the lack of a clear absorption signature of Fc\(^0\) upon direct reduction, an oleic acid (OLAC) and oleylamine (OLAM) stock solution was added stepwise to a 200 µM Fc\(^+\) solution to monitor the reduction of Fc\(^+\). Figure S1 (A) shows the gradual loss of Fc\(^+\) absorbance at 625 nm, which is made clear in panel (B) in the difference absorbance spectrum. Thus, native OLAM, even in the presence of OLAC, must be replaced with DDAB in order to deconvolute amine reduction and photoreduction.

Additionally, it should be noted that the absorption of the reduced product Fc\(^0\) cannot be well resolved despite direct reduction of Fc\(^+\) with OLAM. For reference, a Fc\(^0\) absorption spectrum is shown in (f) of panel (A). Despite the amine reduction from OLAM, there is not a clear signal of Fc\(^0\) absorption, likely due to the convolution of the scattering profile of the sample. Thus, progress of the reduction reaction is better studied through loss of Fc\(^+\) absorption at ~ 625 nm.
Figure S2. CsPbBr₃ emission monitored at 509 nm using continuous excitation at 430 nm (6 µW) from the spectrofluorometer. All spectra track the emission at CsPbBr₃ λ_{max} (509 nm). PL intensity of CsPbBr₃ NCs continually irradiated at 509 nm is shown on (A) the 150 minute timescale and (B) the 16 hour timescale in deaerated 20/80 DCM/hexane solvent.

Table S1. Kinetic analysis of photoluminescence decay of CsPbBr₃ interacting with Fc⁺, corresponding to Figure 3 in the main text. All decay traces were fit to biexponential decay functions.
Figure S3. Spectrum of broad band white light used for steady state photolysis experiments. A 415 nm long pass filter was used in front of the lamp to attenuate UV light.

Figure S4. Dark study of CsPbBr$_3$ NCs and Fc$^*$. (A) Absorption spectra of deaerated solution containing 30 nM CsPbBr$_3$ + 100 $\mu$M Fc$^*$ (a) before and (g) after 60 minutes without irradiation, with intermediate spectra taken every 10 minutes. (B) Zoomed region between 530 nm and 800 nm, indicating lack of significant absorption change in the region where Fc$^*$ absorbs. (C) Difference absorption change in the 530-800 nm window from (B) shows only a slight change in absorption, possibly due to reduction from residual amine ligands (leftover oleylamine).
3. References:
