Electronic Supporting Information

Consequences of Ligand Removal from CdSe Quantum Dots on Photocatalytic H_2 Production

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Materials and Methods

General Considerations. All chemicals and solvents were purchased from commercial sources and used without further purification unless otherwise noted. Acetonitrile used in the preparation of the Meerwein's Salt stock solution was dried on a Glass Contour Solvent Purification System (Pure Process Technology, LLC) and stored over activated 4 Å molecular sieves (Fisher Scientific) prior to use.

Characterization of CdSe QDs. For all absorption characterization, the QD samples were placed in a quartz cuvette with a 1-cm path length. A PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer was used to record all absorbance spectra. The concentrations of all QD stock solutions following all synthesis and ligand exchanges were calculated using the first excitonic absorbance transition as described by Yu et al.[1] Characterization via FTIR was collected with a Perkin Elmer Spectrum 3 FTIR with a diamond/ZnSe UATR mode. Characterization via ^{1}H NMR was collected on a Bruker 400 MHz spectrometer and analyzed in MestReNova. TEM imaging was executed on a ThermoFisher Talos F200i cold emission microscope at an accelerating voltage of 200 kV using -400 mesh ultrathin lacey carbon grids. QD diameters were determined through TEM imaging and sizing via ImageJ.

Synthesis of Oleic Acid (OA)-Capped CdSe QDs. To a dry 100 mL 3-neck round bottom flask with a stir bar, 0.514 g of cadmium oxide, 3 mL of oleic acid, and 10 mL of 1-octadecene was added. The flask was placed in a heating mantle and put under vacuum to degas for 30 minutes while stirring. After 30 minutes of degassing, the flask was placed under argon, a temperature probe was inserted into the solution through a septum on the neck of the flask, and heated to 260 °C. During this time, a selenium precursor was prepared by dissolving 0.680 g of selenium power in 10 mL of 1-octadecene and stirring continuously to thoroughly mix. Once at 260 °C, the flask was removed from the heating mantle, placed in a cork ring, and 1 mL of the selenium precursor was rapidly injected. This step should be very quick for optimal size distribution of the resulting QDs. Immediately after injection of the selenium precursor, a 10 second timer was started to allow for growth of the QDs. After 10 seconds, the flask was cooled to 210 °C, then slowly lowered into a water bath and cooled to room temperature. To wash the resulting QDs, the contents of the flask were distributed amongst six 50 mL centrifuge tubes and 45 mL of ethanol was added to each tube. The tubes were centrifuged at 5000 rpm for 15 minutes and the resulting clear supernatant was decanted and discarded. The orange pellet was dried under a N_2 stream and 5 mL of hexanes was added to each tube to disperse the pellet, then 45 mL of ethanol was added to each tube. Another round of centrifugation at 5000 rpm for 15 minutes was conducted and the supernatant was discarded once again. The resulting pellet was dried under a N_2 stream and dispersed and stored in minimal hexanes for future use.

MPA-CdSe Ligand Exchange Procedure. 0.563 g of tetramethylammonium hydroxide pentahydrate was dissolved in 31 mL of methanol and 193 µL of MPA was added. To a dry 100 mL 3-neck round bottom flask, 19 mL of this methanol solution was added, and this solution was placed under argon and stirred. The temperature was set to 45 °C and, while heating, 0.5 mL of a 388 µM solution of OA-CdSe QDs in hexanes was added to the flask dropwise while stirring. The syringe used to inject the QDs was rinsed once with hexanes to ensure complete transfer for the QDs to the flask. The reaction flask was refluxed at 45 °C while stirring for 45 minutes, resulting

in a transparent orange solution. Once the flask was allowed to cool to room temperature, the contents of the flask were distributed amongst four 50 mL centrifuge tubes and 35 mL of ethyl ether and 10 mL of ethyl acetate were added to each tube. The centrifuge tubes were centrifuged at 4500 rpm for 15 minutes and the resulting supernatant was decanted and disposed of. The orange pellet was dried under a N_2 stream and dispersed in minimal nanopure H_2O.

BF_4-CdSe Ligand Exchange Procedure. The BF_4-CdSe ligand exchange procedure was adapted from the reported exchange procedure from Chang et. al.[2] A 1 M stock solution of trimethyloxonium tetrafluoroborate (Meerwein's salt, MS) was prepared in 4 mL of acetonitrile inside a N_2 filled glovebox. The rest of the ligand exchange procedure was conducted outside of the glovebox in ambient conditions. A 50 μM solution of OA-CdSe QDs was prepared in 3 mL of chloroform. To this QD solution, a very minimal amount of DMF was added (~5 drops) and approximately 0.5 mL of the MS stock solution was added. The addition of MS to the QDs should result in a very cloudy opaque suspension. This solution was dispersed between two centrifuge tubes and centrifuged at 7000 rpm for 3 minutes. The supernatant was decanted and discarded, and the resulting orange pellet was dried under N_2 and dispersed in minimal DMF.

BF_4-CdSe Recapping Procedure. The recapping of BF_4-CdSe with MPA was adapted from a procedure reported by Chang et. al.[2] A stock solution of 0.5 mL MPA in 2 mL of methanol was prepared and adjusted to pH 11 with tetramethylammonium hydroxide pentahydrate. Aliquots of this solution (~600 μL) was added to a 50 μM solution of BF_4-CdSe in 1 mL of DMF until an opaque suspension was formed. Then, aliquots of methanol (~1 mL) was added to the suspension until the solution was transparent. This solution was stirred for 1 hour, then precipitated with excess acetone and centrifuged at 7000 rpm for 3 minutes. The resulting pellet was dispersed in minimal nanopure H_2O.

Sample Preparation for Photocatalysis. Stock solutions of MPA-CdSe QDs were prepared in H_2O and stock solutions of BF_4-CdSe QDs were prepared in DMF (see ligand exchange procedure for details). A 100 mL stock solution of 0.5 M ascorbic acid was prepared in water purified by a Millipore system and adjusted to the desired pH with minimal (< 5 mL) 5 M NaOH. In 40 mL scintillation vials, the components were added to achieve the desired concentrations – 1 μM CdSe, 0.5 M ascorbic acid – to reach a total volume of 5 mL. To account for the BF_4-CdSe QDs being stored in DMF, for each set of experiments, an appropriate amount of minimal DMF was added to any vials containing MPA-CdSe QDs to match the amount of DMF present in the samples containing BF_4-CdSe. For samples that contain additional MPA or the $[Mo_3S_{13}]^{2-}$ cocatalyst, stock solutions were prepared in water or 6:4 v/v ratio DMF:H_2O, respectively and the proper volumes were added to the scintillation vials. The vials were sealed with gas-tight septa and purged with 80%/20% N_2/CH_4 (Airgas) as an internal standard for 15 minutes by bubbling through the liquid and a further 5 minutes of purging in the headspace of each vial. The vials were placed in a custom-built temperature-controlled block connected to a Thermotek circulating water bath at 15 °C (or 30 °C) and illuminated through the base of the vials by 530 nm green light-emitting diodes (Philips LumiLED Luxeon Star Hex 700 mA LEDs mounted on 20 mm star-shaped CoolBases). A L30A thermal sensor and a Newport Power Meter (1918-C) were used to measure each LED's power individually before each experiment. Each LED power at 530 nm was adjusted to 10 mW ± 1 mW prior to each experiment. The block was mounted on a Thermo-Scientific MaxQ orbital shaker and set to shake continuously at 100 rpm for the duration of each experiment.

The amount of H_2 produced during the 72 hours of each experiment was determined by sampling the headspace via gas chromatography (GC) using a Shimadzu GC-2014 with a 5 Å molecular sieve column (30 m, 0.53 mm) and a thermal conductivity detector. Multiple time points were used for sample collection, including sampling after 1 hr, 2 hr, 4 hr, 6 hr, 8 hr, 24 hr, 48 hr, and 72 hr. The amount of H_2 evolved was quantified with a calibration curve using CH_4 as an internal standard. Uncertainty reported for H_2 generation is expressed as the standard deviation of multiple trials of each condition.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). QD samples were dried completely under vacuum and weighed out in vials. 2 mL of concentrated trace metal grade nitric acid was added, then the vials were placed in a boiling water bath at 95 °C for 1 hour to ensure total dissolution of the QDs. The digests were transferred to 50 mL polypropylene tubes and ultra-pure water was added to a final volume of 20 mL. The samples were diluted 100-fold, then analyzed for the desired elements by a Perkin Elmer 2000C ICP-OES. Calibrations were run at 2,4, 10, and 20 ppb for Cd and Se. Samples were run in KED mode at 4 mL min^{-1} helium flow.

Discussion of Apparent Quantum Yield (AQY) Calculation. The quantum yield for hydrogen production (ϕ_{H_2}) was calculated according to previous reports,[3] expressed as the amount of hydrogen produced over time relative to absorbed photons, as shown in Equation 1. To obtain power measurements of the vials without any QDs and in the presence of 1 µM CdSe QDs, a Newport power meter (Model 1918-C) was used. A P_{abs} of 0.0034 W was estimated for 1 µM CdSe.

$$\phi_{H_2} = 2\frac{k}{q_p} \qquad \textbf{(Equation 1)}$$

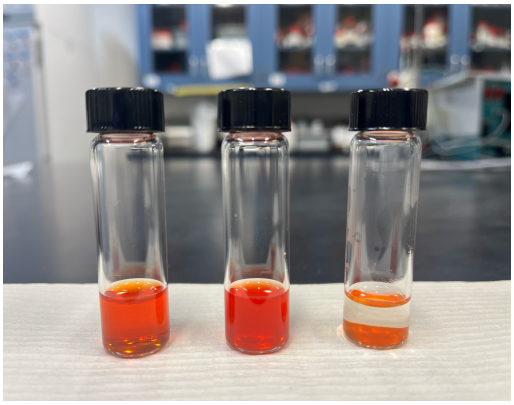

Figure S1: Solutions of **BF_4-CdSe** depicting degradation of sample over time. Examples of samples suspended in DMF and protected from light immediately following ligand stripping (left), after 2 weeks (middle), and 4 weeks (right).

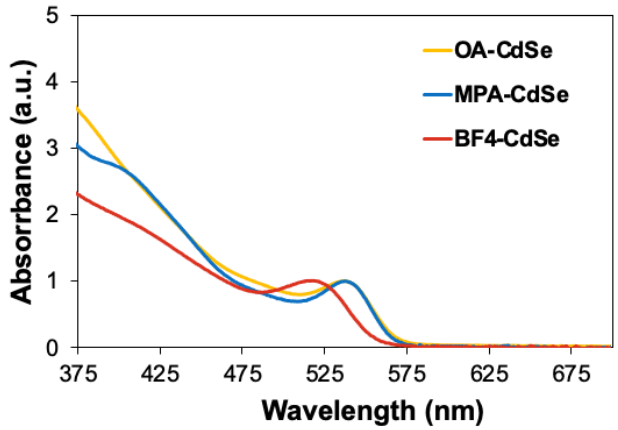

Figure S2: Absorption spectra of natively synthesized **OA-CdSe** (hexanes), ligand-exchanged **MPA-CdSe** (H_2O), and ligand-stripped **BF_4-CdSe** (DMF).

Table S1: ICP-OES analysis of **MPA-CdSe** and **BF_4-CdSe** before photocatalysis and corresponding ratios of Cd to Se.

SAMPLE ID	ppb element		
	Cd	Se	Cd:Se
MPA-CdSe	1.05×10^8	6.19×10^7	1.7:1
BF_4-CdSe	4.08×10^7	3.07×10^7	1.3:1

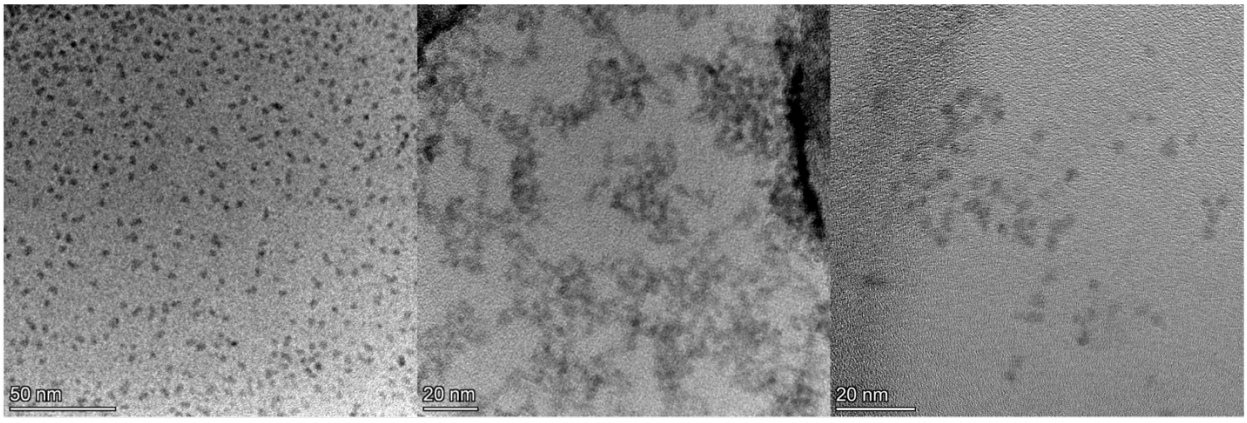

Figure S3: Transmission electron microscopy (TEM) micrographs of **OA-CdSe** (left), **BF_4-CdSe** (middle) and **Recapped MPA-CdSe** (right) QDs. **OA-CdSe** QDs have a diameter of 3.9 ± 0.5 nm. **BF_4-CdSe** QDs have a diameter of 3.6 ± 0.5 nm. **Recapped MPA-CdSe** QDs have a diameter of 3.5 ± 0.4 nm. We note that the shape of the QDs do not change after ligand removal or recapping.

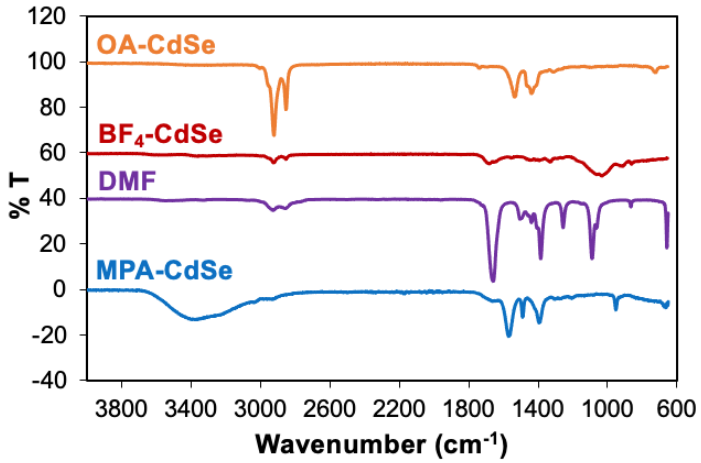

Figure S4: Fourier-Transform Infrared (FT-IR) spectra of natively synthesized **OA-CdSe**, ligand removed **BF_4-CdSe**, DMF, and **MPA-CdSe**, collected in ATR mode. **OA-CdSe** were evaporated from hexanes, **BF_4-CdSe** were precipitated from DMF with chloroform ($CHCl_3$), and **MPA-CdSe** were evaporated from methanol. In the **BF_4-CdSe** spectrum, we note the presence of the characteristic BF_4^- resonance around 1000 cm^{-1} as reported previously by Chang et. al.[2] In the **MPA-CdSe** spectrum, we note the lack of a distinctive S-H peak around 2600 cm^{-1}, confirming binding to the QD surface via the thiol functional group. This is consistent with previous reports.[4,5]

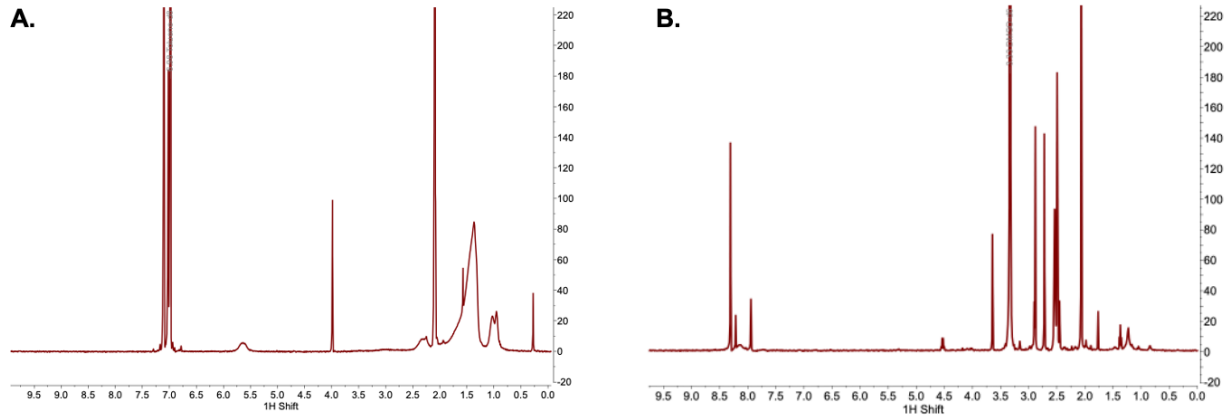

Figure S5: ^{1}H NMR spectrum of A) **OA-CdSe** in toluene-d_8 and B) **BF_4-CdSe** in DMSO-d_6. In the **BF_4-CdSe** spectrum, we note the lack of residual bound oleic acid (~5.6 ppm) following ligand removal.

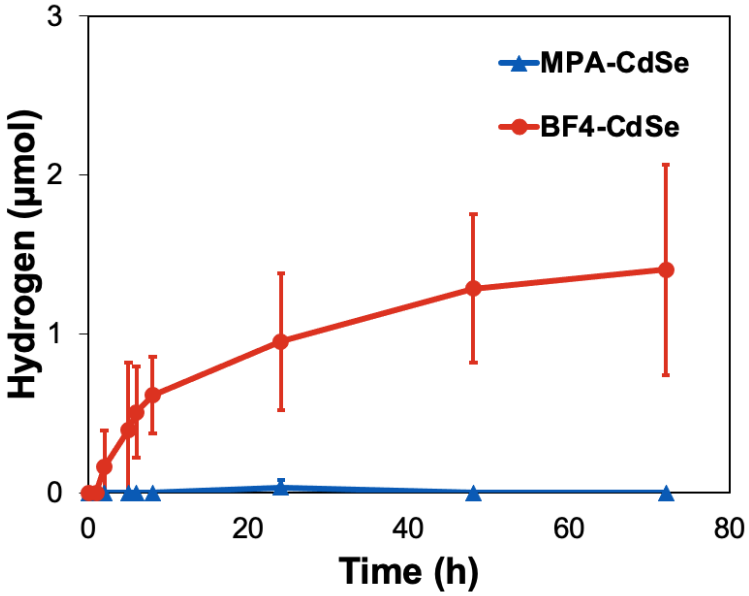

Figure S6: H_2 produced (µmol) over 72 hours from 1 µM **MPA-** or **BF_4-CdSe** QDs in 0.1 M Na_2SO_3 in water at pH 7. All samples irradiated with 530 nm light and kept at 15 ˚C.

Table S2: µmoles of H_2, turnover numbers (TONs) with respect to QD, and apparent quantum yield (ϕ_{H_2}) of **MPA-CdSe** and **BF_4-CdSe** at various pH values after 72 hours under photocatalytic conditions (1 µM CdSe, 0.5 M AA in water, irradiated with 530 nm light and kept at 15 ˚C).

	CdSe					
	MPA-CdSe			BF_4-CdSe		
pH	µmol H_2	TON_{QD}	ϕ_{H_2}	µmol H_2	TON_{QD}	ϕ_{H_2}
3.0	9 ± 0.8	1900 ± 160	0.46 ± 0.04%	3 ± 0.20	500 ± 40	0.15 ± 0.01%
3.5	43 ± 3	8600 ± 500	2.20 ± 0.15%	6 ± 0.04	1300 ± 7	0.31 ± 0.002%
4.0	161 ± 18	32000 ± 3600	8.25 ± 0.92%	15 ± 2	3100 ± 330	0.77 ± 0.10%
4.5	81 ± 12	16000 ± 2300	4.15 ± 0.62%	17 ± 1	3400 ± 240	0.87 ± 0.05%
5.0	45 ± 20	8900 ± 3400	2.31 ± 1.03%	40 ± 5	8200 ± 980	2.05 ± 0.26%
5.5	21 ± 30	4300 ± 5500	1.08 ± 1.54%	22 ± 4	4300 ± 810	1.13 ± 0.21%
6.0	4 ± 10	700 ± 120	0.21 ± 0.51%	10 ± 3	1900 ± 650	0.51 ± 0.15%
7.0	0 ± 0	0 ± 0	-	8 ± 1	1700 ± 260	0.41 ± 0.05%

Table S3: µmoles of H_2, turnover numbers (TONs) with respect to QD, and apparent quantum yield (ϕ_{H_2}) of **MPA-CdSe** and **BF_4-CdSe** with various amounts of added MPA after 72 hours under photocatalytic conditions (1 µM CdSe, 0.5 M AA in water, irradiated with 530 nm light at 15 ˚C).

	MPA-CdSe			BF_4-CdSe		
	µmol H_2	TON_{QD}	ϕ_{H_2}	µmol H_2	TON_{QD}	ϕ_{H_2}
QD Alone	110 ± 4	21000 ± 820	5.64 ± 0.21%	23 ± 2	4500 ± 420	1.18 ± 0.10%
10 µM MPA	110 ± 30	22000 ± 6900	5.64 ± 1.54%	61 ± 10	12000 ± 2200	3.13 ± 0.51%
50 µM MPA	42 ± 30	8400 ± 5500	2.15 ± 1.54%	60 ± 2	12000 ± 340	3.08 ± 0.10%

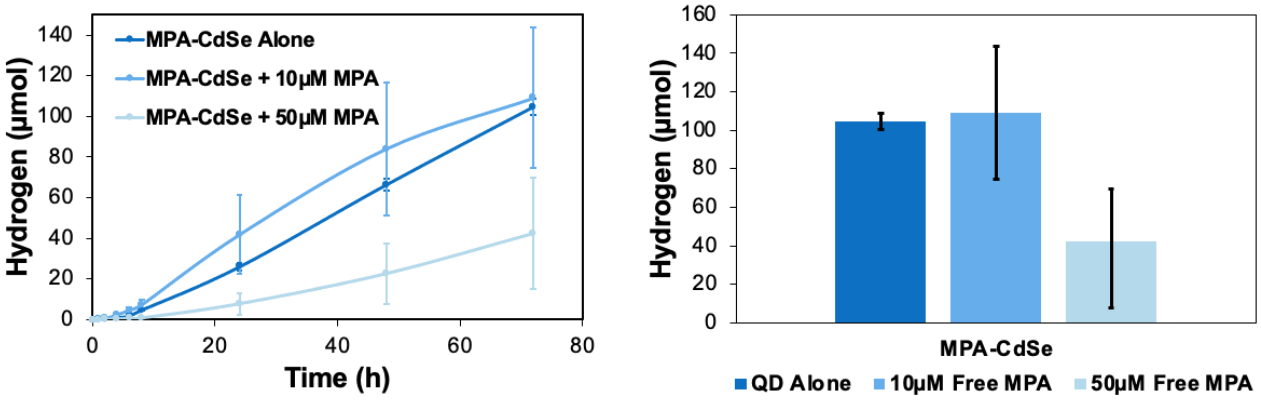

Figure S7: H_2 produced (µmol) over 72 hours (left) and total H_2 produced (µmol) after 72 hours (right) from 1 µM **MPA-CdSe** QDs in 0.5 M ascorbic acid in water at pH 4.5 with 10 µM and 50 µM added free MPA. All samples irradiated with 530 nm light and kept at 15 ˚C.

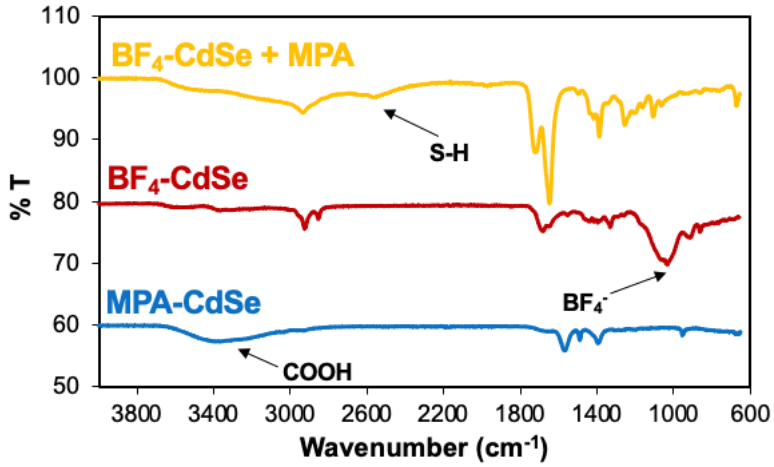

Figure S8: FT-IR spectra of **BF_4-CdSe** with added MPA ligand compared against **BF_4-CdSe** and **MPA-CdSe**, collected in ATR mode. **BF_4-CdSe** samples were precipitated from DMF with chloroform ($CHCl_3$), and **MPA-CdSe** were evaporated from methanol. We note the disappearance of the characteristic BF_4^- anion in the **BF_4-CdSe + MPA** spectrum, suggesting dynamic displacement of the anion with MPA. The S-H peak of MPA is visible ~2600 cm^{-1} suggesting MPA is not statically bound to the ligand-removed QD but rather interacts in a dynamic fashion with the nanocrystal.

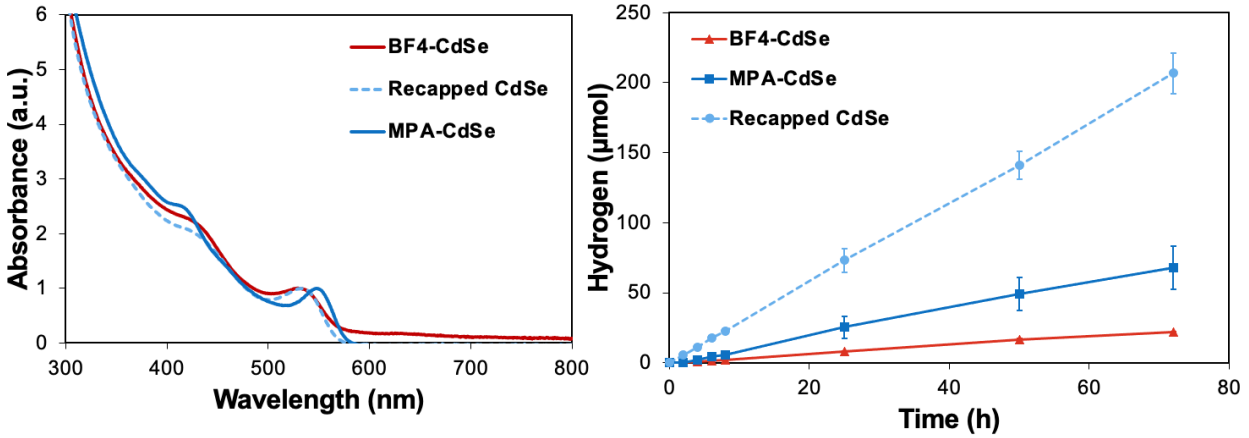

Figure S9: Absorbance spectra (left) and time-course photocatalytic H_2 production (right) of **BF_4-CdSe**, **MPA-CdSe**, and recapped CdSe (**BF_4-CdSe** capped with MPA). Absorbance spectra of **BF_4-CdSe** collected in DMF, **MPA-CdSe** and recapped CdSe collected in H_2O. Photocatalysis shows H_2 produced (µmol) over 72 hours from 1 µM **MPA-**, **BF_4-CdSe**, and recapped CdSe QDs in 0.5 M ascorbic acid in water at pH 4.5. All samples irradiated with 530 nm light and kept at 15 ˚C.

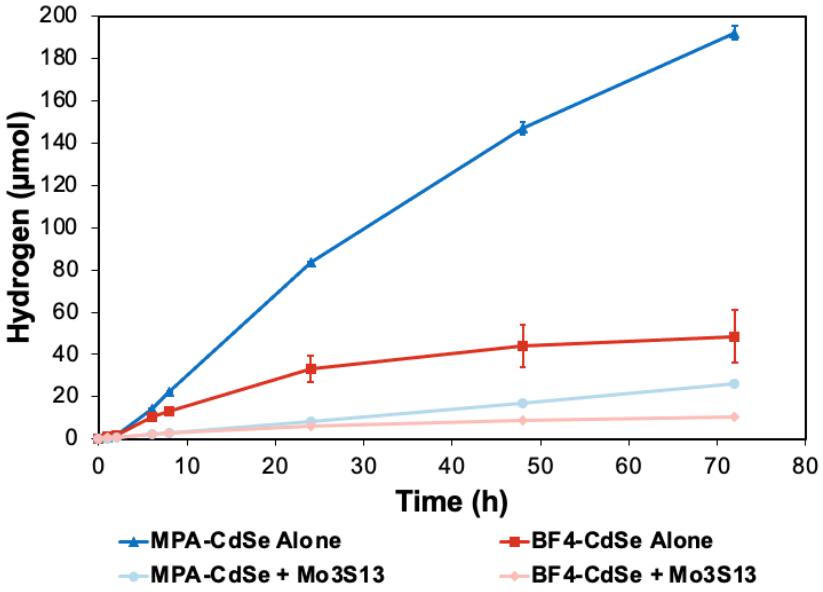

Figure S10: H_2 produced (µmol) over 72 hours from 1 µM **MPA-** and **BF_4-CdSe** QDs in 0.5 M ascorbic acid in water at pH 4.5 with the addition of 1 µM **$[Mo_3S_{13}]^{2-}$**. All samples irradiated with 530 nm light and kept at 15 ˚C.

Table S4: µmoles of H_2, turnover numbers (TONs) with respect to **$[Mo_3S_{13}]^{2-}$**, and apparent quantum yield (ϕ_{H_2}) of **MPA-CdSe** and **BF_4-CdSe** with and without cocatalyst after 72 hours under photocatalytic conditions (1 µM CdSe, 0.5 M AA in DMF:H_2O (6:4 v/v ratio), irradiated with 530 nm light and kept at 31 ˚C).

	MPA-CdSe			BF_4-CdSe		
	µmol H_2	TON_{cat}	ϕ_{H_2}	µmol H_2	TON_{cat}	ϕ_{H_2}
QD Alone	13 ± 5	2600 ± 910	0.67 ± 0.26%	33 ± 2	6700 ± 450	1.69 ± 0.10%
1 µM $[Mo_3S_{13}]^{2-}$	16 ± 9	3300 ± 1800	0.82 ± 0.46%	104 ± 8	20900 ± 1600	5.33 ± 0.41%

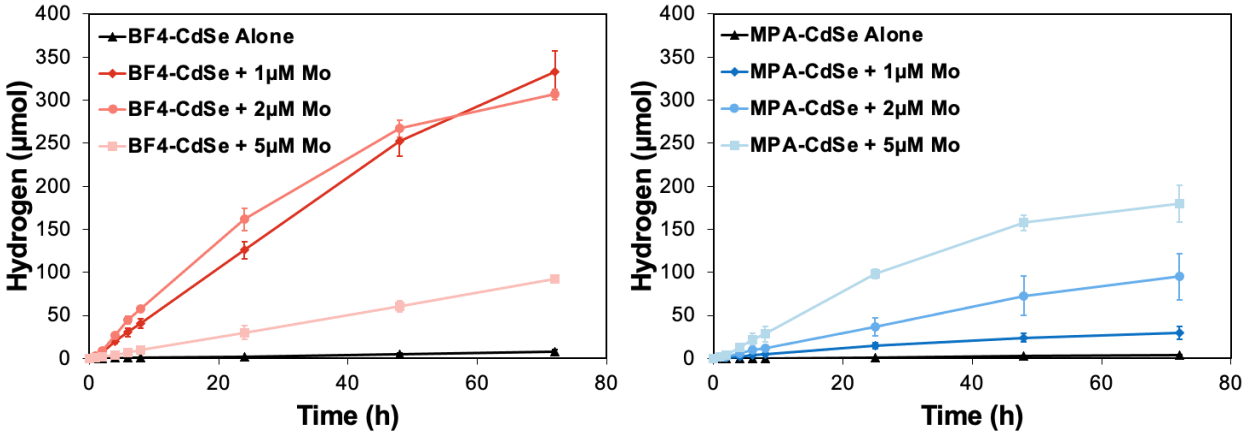

Figure S11: H_2 produced (μmol) over 72 hours from 1 μM **BF_4-CdSe** (left) and **MPA-CdSe** (right) QDs in 0.5 M ascorbic acid in DMF:H_2O (6:4) with the addition of 1, 2, and 5 μM **$[Mo_3S_{13}]^{2-}$**. All samples irradiated with 530 nm light and kept at 31 ˚C.

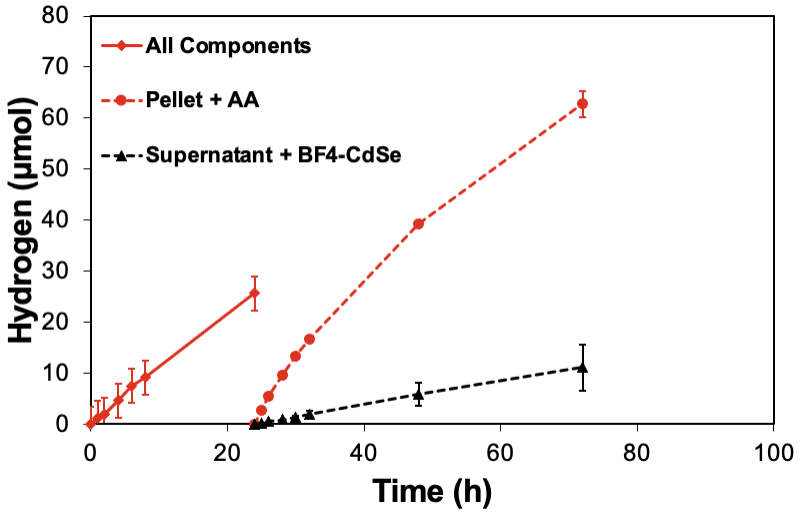

Figure S12: H_2 produced (μmol) from 1 μM **BF_4-CdSe** QDs with 1 μM **$[Mo_3S_{13}]^{2-}$** in 0.5 M ascorbic acid in DMF:H_2O (6:4 v/v ratio). After 24 hours, the pellet and supernatant were separated. To the pellet, fresh 0.5 M ascorbic acid in DMF:H_2O (6:4 v/v ratio) was added. To the supernatant, 1 μM of fresh **BF_4-CdSe** was added. All samples irradiated with 530 nm light and kept at 31 ˚C. Pellet and supernatant separation and replenishment experiment was modeled by that previously reported by our group.[6]

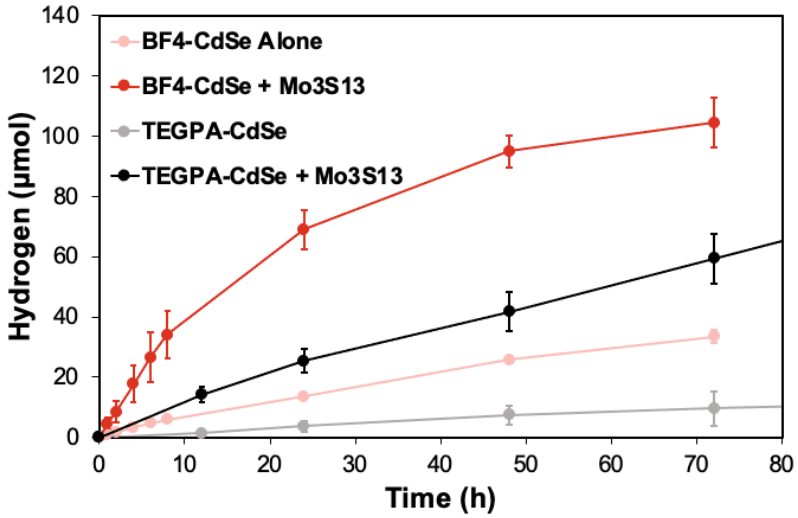

Figure S13: H_2 produced (µmol) over 72 hours from 1 µM **BF_4-CdSe** QDs in 0.5 M ascorbic acid in DMF:H_2O (6:4) with the addition of 1 µM **$[Mo_3S_{13}]^{2-}$**. Compared against previously reported data of **TEGPA-CdSe** QDs in 0.8 M ascorbic acid in DMF:H_2O (6:4) with the addition of **$[Mo_3S_{13}]^{2-}$** to show differences in initial rates of H_2 production.[6] All samples irradiated with 530 nm light and kept at 31 ˚C.

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