Electronic Supplementary Information for:

The role of surface functionalization in quantum dot-based photocatalytic CO_2 reduction: balancing efficiency and stability

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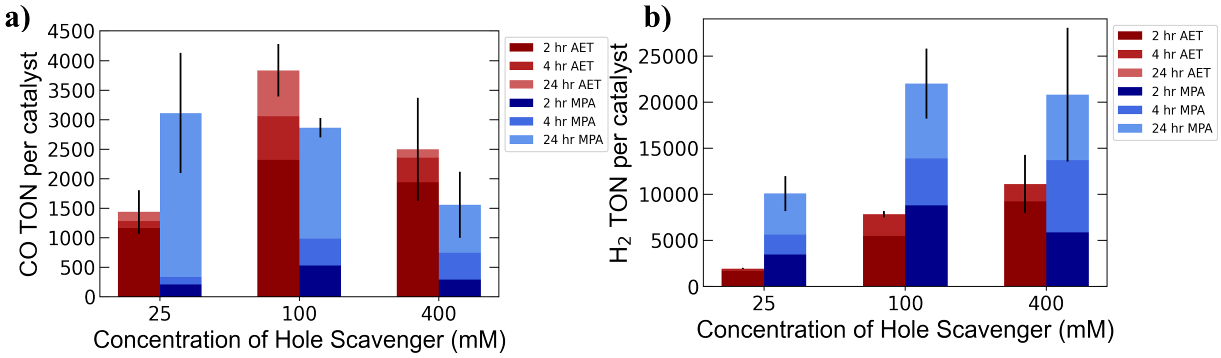

Figure S1. Comparing (a) CO TON and (b) H_2 TON for both AET and MPA QDs. Note that (a) is the same as main text Figure 1b. Photocatalysis experiments were performed in triplicate on 2.0 mL aqueous solutions of 0.4 µM ZnSe QDs and 0.4 µM Co-TPP, irradiated with 400 nm LEDs.

Varying NaAsc and TEOA concentrations with AET QDs

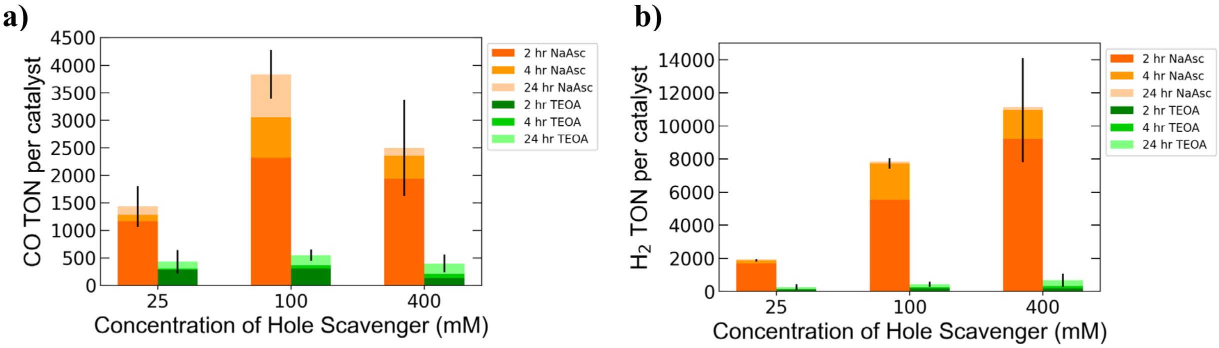

Figure S2. (a) CO TON and (b) H_2 TON for AET QDs with NaAsc and TEOA at varying concentrations. Note that (a) is the same as main text Figure 1d. Photocatalysis experiments were performed in triplicate on 2.0 mL aqueous solutions of 0.4 µM ZnSe QDs and 0.4 µM Co-TPP, irradiated with 400 nm LEDs.

Experiments with a mixture of hole scavengers and AET QDs

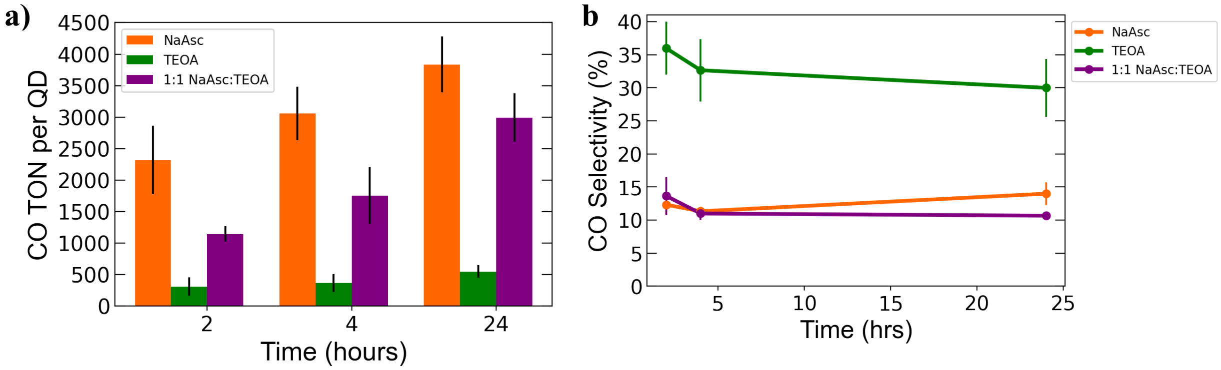

Figure S3. (a) CO TON and (c) selectivity for AET QDs with TEOA, NaAsc, or a mixture of both hole scavengers. The mixture produced both low selectivites and lower yields, and was therefore not pursued further. Photocatalysis experiments were performed in triplicate on 2.0 mL aqueous solutions of 0.4 μM ZnSe QDs, 0.4 μM Co-TPP, and 100 mM total hole scavenger and were irradiated with 400 nm LEDs.

Long duration experiments comparing AET and MPA

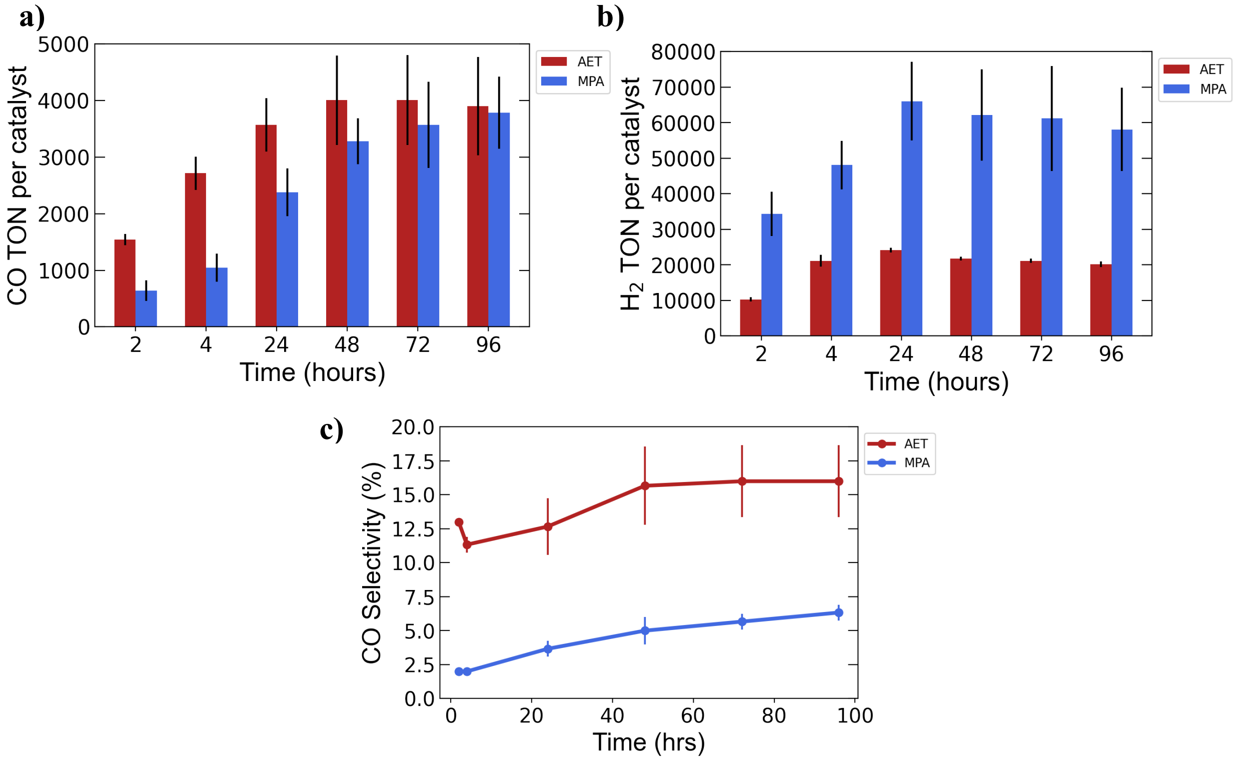

Figure S4. (a) CO TON, (b) H_2 TON, and (c) selectivity for AET and MPA QDs in four-day photocatalysis experiments. Note that (a) is the same as main text Figure 2a. Photocatalysis experiments were performed in triplicate on 2.0 mL aqueous solutions of 0.4 μM ZnSe QDs and 0.4 μM Co-TPP, irradiated with 400 nm LEDs.

Varying catalyst concentration with AET QDs

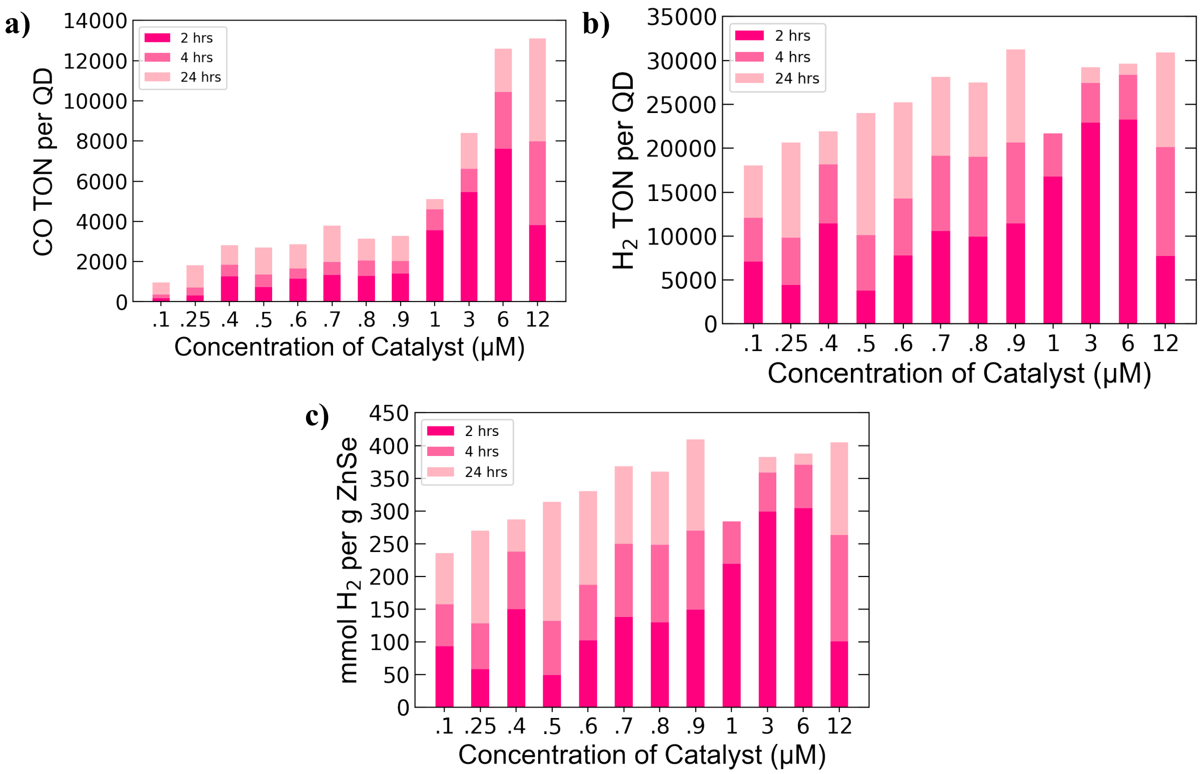

Figure S5. (a) CO TON per QD, (b) H_2 TON per QD, and (c) mmol H_2 produced per gram of ZnSe. These data are complimentary to those presented in Figure 4. Photocatalysis experiments were performed on 2.0 mL aqueous solutions of 0.4 μM ZnSe QDs and 50 mM NaAsc, irradiated with 400 nm LEDs.

Calculations of TON, selectivity, and mmol CO per gram ZnSe

Peak integrations on GC chromatograms were calculated using the PeakSimple program and compared to calibration values to determine mole percent of H_2 and CO in reaction vials. Measured percentages were typically in the 0 – 3 % range. Assuming a 22 mL volume and ideal gas behavior, percentages could be converted to molar quantities. In the best performing samples ~10 μmol of CO were produced and up to 60 μmol of H_2 were produced. Turnover numbers were computed using the following equations: $CO\ TON = \frac{mol\ CO\ produced}{mol\ Co{-}TPP\ catalyst}$ and $H_2\ TON = \frac{mol\ H_2\ produced}{mol\ Co{-}TPP\ catalyst}$. In certain instances, we have also reported TON per QD. Selectivity was calculated using the following equation: $CO\ selectivity = \frac{mol\ CO}{mol\ H_2 + mol\ CO}$.

To calculate the mmol CO produced per gram of ZnSe QDs, we had to calculate the total mass of QDs. The 3.6 nm diameter was used to calculate a volume ($\sim 2.4*10^{-20}$ cm^3) per QD and then a mass ($\sim 1.3*10^{-19}$ g) per QD using the density of ZnSe (5.27 g cm^{-3}). The number of QDs per reaction (0.8 nmol) was then used to determine the total mass per reaction (~61 μg ZnSe), which could be used with CO quantities to determine mmol CO per gram ZnSe.

Table of results

Table S1. Summary of photocatalysis experimental results. ZnSe QDs were present at a concentration of 0.4 μM for all samples. Errors are provided only for data collected in triplicate.

Ligand	Hole Scavenger (mM)	Catalyst (μM)	CO TON per catalyst	H_2 TON per catalyst	CO Selectivity (%)	Time (h)
AET	NaAsc (25)	0.4	$(1.2 \pm 0.4)*10^3$	$(1.7 \pm 0.5)*10^3$	18 ± 3	2
			$(1.3 \pm 0.4)*10^3$	$(2.0 \pm 0.3)*10^3$	17 ± 3	4
			$(1.4 \pm 0.4)*10^3$	$(1.88 \pm 0.08)*10^3$	20. ± 4	20
AET	NaAsc (50)	0.1	$0.72*10^3$	$2.84*10^4$	2	2
			$1.44*10^3$	$4.8*10^4$	3	4
			$3.84*10^3$	$7.2*10^4$	5	20
AET	NaAsc (50)	0.25	$0.48*10^3$	$7.04*10^3$	6	2
			$1.104*10^3$	$1.568*10^4$	7	4
			$2.88*10^3$	$3.36*10^4$	8	20
AET	NaAsc (50)	0.4	$1.3*10^3$	$1.1*10^4$	10	2
			$1.8*10^3$	$1.8*10^4$	9	4
			$2.8*10^3$	$2.2*10^4$	11	20
AET	NaAsc (50)	0.5	$0.592*10^3$	$3.04*10^3$	16	2
			$1.12*10^3$	$8.*10^3$	12	4
			$2.16*10^3$	$1.92*10^4$	10	20
AET	NaAsc (50)	0.6	$0.733*10^3$	$5.2*10^3$	13	2
			$1.133*10^3$	$9.333*10^3$	10	4
			$1.933*10^3$	$1.6667*10^4$	10	20
AET	NaAsc (50)	0.7	$0.743*10^3$	$6.286*10^3$	11	2
			$1.143*10^3$	$1.0857*10^4$	9	4
			$2.171*10^3$	$1.6000*10^4$	12	20
AET	NaAsc (50)	0.8	$0.65*10^3$	$4.950*10^3$	11	2
			$1. *10^3$	$9.5*10^3$	10	4
			$1.550*10^3$	$1.4*10^4$	10	20
AET	NaAsc (50)	0.9	$0.622*10^3$	$4.889*10^3$	11	2
			$0.889*10^3$	$9.333*10^3$	9	4
			$1.467*10^3$	$1.3778*10^4$	9	20
AET	NaAsc (50)	1	$1.44*10^3$	$6.8*10^3$	18	2
			$1.84*10^3$	$8.8*10^3$	18	4
			$2.04*10^3$	$8.4*10^3$	20	20
AET	NaAsc (50)	3	$0.733*10^3$	$3.067*10^3$	19	2
			$0.880*10^3$	$3.6*10^3$	19	4
			$1.12*10^3$	$3.867*10^3$	22	20
AET	NaAsc (50)	6	$0.507*10^3$	$1.533*10^3$	25	2
			$0.667*10^3$	$1.867*10^3$	27	4
			$0.867*10^3$	$2.*10^3$	30	20
AET	NaAsc (50)	12	$0.127*10^3$	$0.257*10^3$	33	2
			$0.267*10^3$	$0.667*10^3$	28	4
			$0.433*10^3$	$1.033*10^3$	30	20

AET	NaAsc (100)	0.4	$(2.3 \pm 0.5)*10^3$	$(5.5 \pm 1.8)*10^3$	12.3 ± 1.5	2
			$(3.1 \pm 0.4)*10^3$	$(7.9 \pm 1.4)*10^3$	11.3 ± 1.3	4
			$(3.8 \pm 0.5)*10^3$	$(7.7 \pm 0.3)*10^3$	14.0 ± 1.7	20
			$(4.0 \pm 0.8)*10^3$	$(21.7 \pm 0.6)*10^3$	15.7 ± 2.7	48
			$(4.0 \pm 0.8)*10^3$	$(21.1 \pm 0.6)*10^3$	16.0 ± 2.6	72
			$3.9 \pm 0.9)*10^3$	$(20.2 \pm 0.8)*10^3$	16.0 ± 1.6	96
AET	NaAsc (400)	0.4	$(1.9 \pm 0.8)*10^3$	$(9 \pm 3.)*10^3$	6.3 ± 1.1	2
			$(2.4 \pm 0.7)*10^3$	$(11.1 \pm 2.2)*10^3$	6.7 ± 0.6	4
			$(2.5 \pm 0.9)*10^3$	$(11 \pm 3.)*10^3$	6.7 ± 0.6	20
AET	TEOA (25)	0.4	$(2.8 \pm 1.1)*10^2$	$(1.6 \pm 0.7)*10^2$	39. ± 16	2
			$(3.1 \pm 1.2)*10^2$	$(1.35 \pm 0.27)*10^2$	42. ± 5	4
			$(5.1 \pm 2.1)*10^2$	$(2.6 \pm 1.7)*10^2$	37. ± 7	20
AET	TEOA (100)	0.4	$(3.1 \pm 1.5)*10^2$	$(1.9 \pm 1.2)*10^2$	36. ± 4	2
			$(3.7 \pm 1.4)*10^2$	$(2.7 \pm 1.5)*10^2$	33 ± 5	4
			$(5.5 \pm 1.0)*10^2$	$(4.4 \pm 1.5)*10^2$	30. ± 4	20
AET	TEOA (400)	0.4	$(1.3 \pm 0.5)*10^2$	$(2.0 \pm 0.5)*10^2$	17.7 ± 2.1	2
			$(2.1 \pm 0.9)*10^2$	$(3.3 \pm 1.4)*10^2$	17.3 ± 1.6	4
			$(4.0 \pm 1.6)*10^2$	$(7 \pm 4)*10^2$	17.0 ± 2.6	20
AET	NaAsc (50) + TEOA (50)	0.4	$(1.15 \pm 0.13)*10^3$	$(7.4 \pm 1.7)*10^3$	13.7 ± 2.9	2
			$(1.8 \pm 0.5)*10^3$	$(14 \pm 3)*10^3$	11.0 ± 1.0	4
			$(3.0 \pm 0.4)*10^3$	$(25.5 \pm 1.5)*10^3$	10.7 ± 0.6	20
MPA	NaAsc (25)	0.4	$(2.1 \pm 0.5)*10^2$	$(3.5 \pm 0.6)*10^3$	2. ± 0	2
			$(3.4 \pm 1.3)*10^2$	$(5.6 \pm 2.3)*10^3$	2. ± 0	4
			$(3.1 \pm 1.0)*10^3$	$(10.1 \pm 1.9)*10^3$	10. ± 4	20
MPA	NaAsc (100)	0.4	$(5.4 \pm 2.3)*10^2$	$(9 \pm 3)*10^3$	2. ± 0	2
			$(10 \pm 3)*10^2$	$(14 \pm 4)*10^3$	2. ± 0	4
			$(2.86 \pm 0.17)*10^3$	$(22 \pm 4)*10^3$	4.3 ± 0.6	20
			$(3.3 \pm 0.4)*10^3$	$(6.2 \pm 1.3)*10^4$	5.0 ± 1.0	48
			$(3.6 \pm 0.8)*10^3$	$(6.1 \pm 1.5)*10^4$	5.7 ± 0.6	72
			$(3.8 \pm 0.6)*10^3$	$(5.8 \pm 1.2)*10^4$	6.3 ± 0.6	96
MPA	NaAsc (400)	0.4	$(3 \pm 3)*10^2$	$(6 \pm 6)*10^3$	6 ± 8	2
			$(7 \pm 4)*10^2$	$(14 \pm 6)*10^3$	1.3 ± 0.6	4
			$(1.6 \pm 0.6)*10^3$	$(21 \pm 7)*10^3$	2.3 ± 0.6	20

Table of control experiments

Table S2. Summary of control experiments demonstrating that all components were required to produce significant CO. It is worth highlighting that the QDs by themselves do produce significant H_2. We believe that in this case, the ligand or surface Se atoms may be acting as the sacrificial reductants.

Control	NaAsc (mM)	Co-TPP (μM)	AET QD (μM)	CO TON per QD	CO TON per cat.	H_2 TON per QD	H_2 TON per cat.	CO Selectivity (%)	Time (h)
No light	100	0.4	0.4	0	0	220	220	0	2
				0	0	250	250	0	4
				0.38	0.38	200	200	0.002	20
No CO_2	100	0.4	0.4	60.	60.	$4.1*10^3$	$4.1*10^3$	1	2
				180	180	$8.8*10^3$	$8.8*10^3$	2	4
				520	520	$7.8*10^3$	$7.8*10^3$	6	20
No QDs	100	1	-	-	23	-	0.69	10	2
					48		1.7	8	4
					120		4.9	7	20
No catalyst	100	-	0.4	110	-	$4.5*10^3$	-	2	2
				270		$6.8*10^3$		4	4
				880		$8.1*10^3$		10	20
No hole scavenger	-	1	1	31	31	$1.5*10^3$	$1.5*10^3$	2	2
				58	58	$1.8*10^3$	$1.8*10^3$	3	4

Transient absorption data and fits

Transient spectra for AET QDs

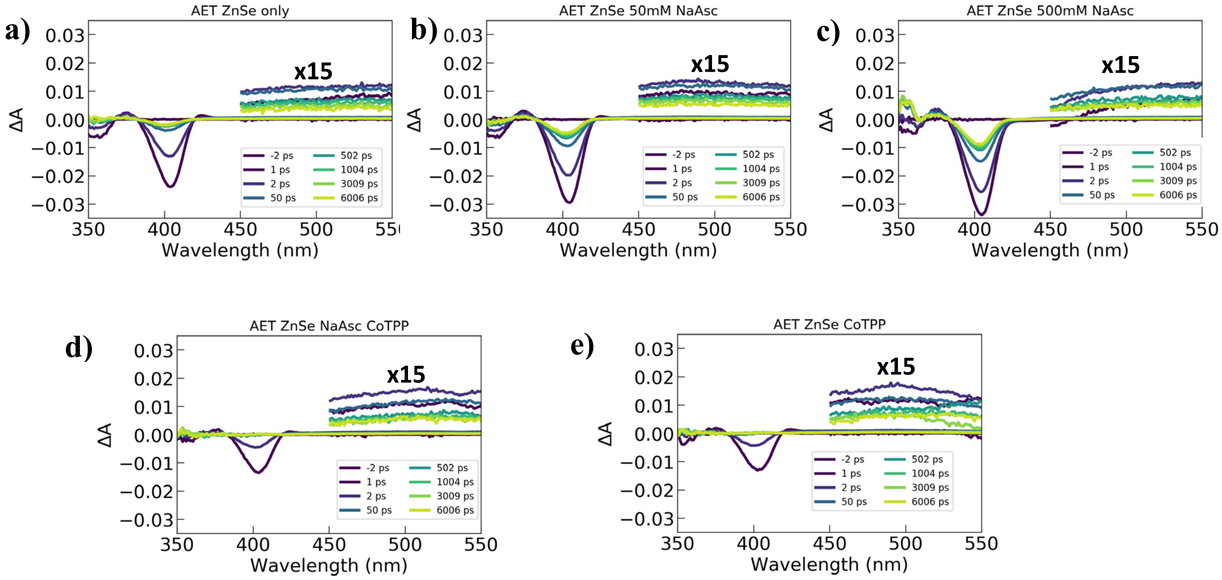

Figure S6. Transient spectra for AET QDs excited at 350 nm. (a) 6 µM AET ZnSe QDs in water, (b) 6 µM AET ZnSe QDs with 50 mM NaAsc in water, (c) 6 µM AET ZnSe QDs with 500 mM NaAsc in water, (d) 5 µM AET ZnSe QDs with 5 µM Co-TPP in water, (e) 5 µM AET ZnSe QDs with 5 µM Co-TPP and 50 mM NaAsc in water.

Transient spectra for MPA QDs

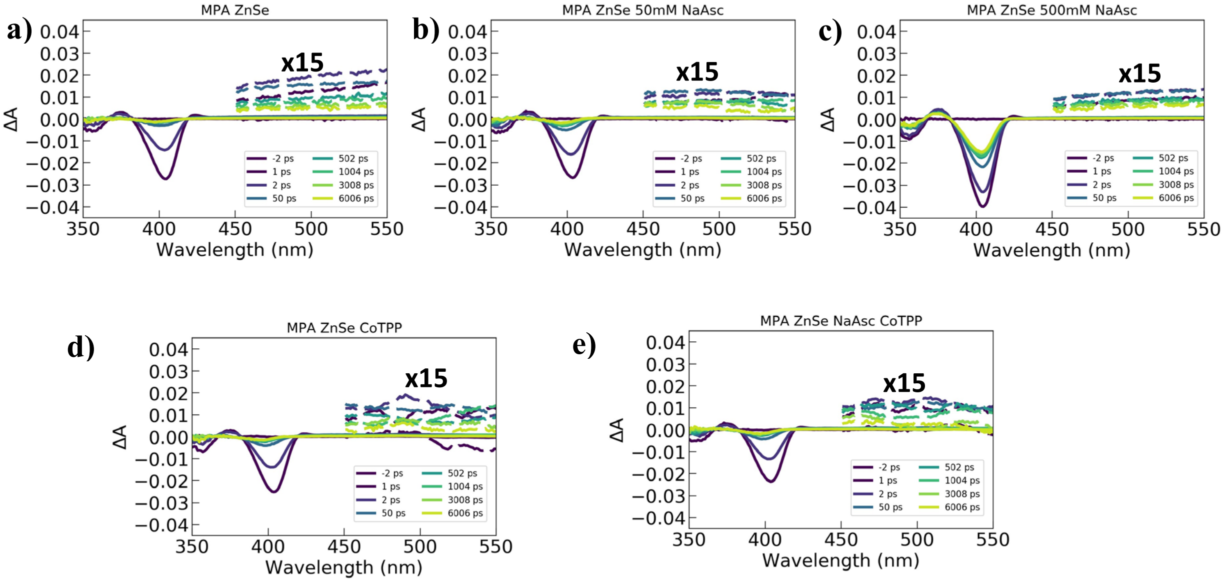

Figure S7. Transient spectra for MPA QDs excited at 350 nm. (a) 6 µM MPA ZnSe QDs in water, (b) 6 µM MPA ZnSe QDs with 50 mM NaAsc in water, (c) 6 µM MPA ZnSe QDs with 500 mM NaAsc in water, (d) 5 µM MPA ZnSe QDs with 5 µM Co-TPP in water, (e) 5 µM MPA ZnSe QDs with 5 µM Co-TPP and 50 mM NaAsc in water.

Trapped carrier dynamics

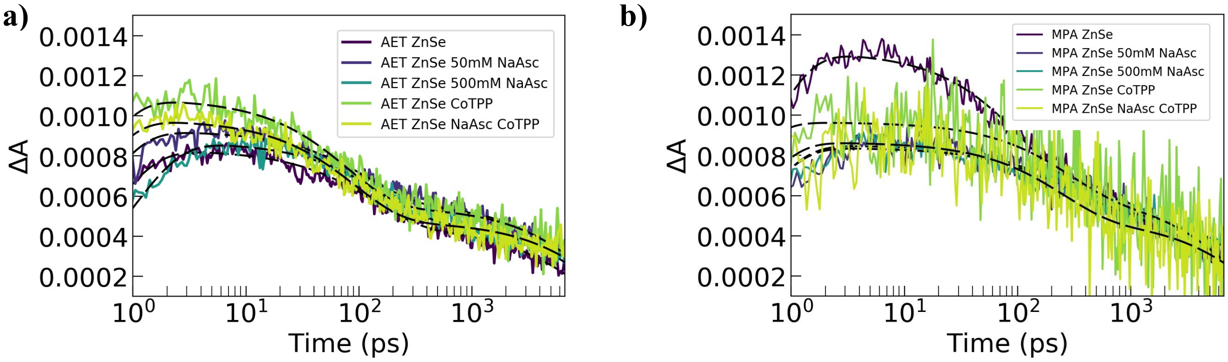

Figure S8. Kinetic traces for the broad photoinduced absorption feature (collected at 500 nm) for (a) AET QDs and (b) MPA QDs. Multi-exponential fits (dashed black lines) are overlaid.

Table S3. Fitting parameters for kinetic traces shown in Figure S8. Data were fit to multi-exponential functions that contain both an exponential rise and a bi-exponential decay. All times are in picoseconds.

Sample	A_1	τ_1	A_2	τ_2	A_3	τ_3
MPA ZnSe	0.00061	0.54	1.10	110	1.10	5800
MPA ZnSe 50mM NaAsc	0.00074	0.50	0.43	290	0.72	12000
MPA ZnSe 500mM NaAsc	0.00095	0.47	0.31	260	0.58	15000
MPA ZnSe CoTPP	0.00053	0.27	0.70	270	1.10	8800
MPA ZnSe NaAsc CoTPP	0.00083	0.41	0.47	250	0.57	11000
AET ZnSe	0.00043	0.62	0.89	130	1.00	9100
AET ZnSe 50mM NaAsc	0.00083	0.47	0.43	120	0.68	11000
AET ZnSe 500mM NaAsc	0.00072	1.00	0.54	160	0.67	12000
AET ZnSe CoTPP	0.00025	0.39	2.10	79	2.10	12000
AET ZnSe NaAsc CoTPP	0.00049	0.38	1.00	91	0.97	14000

Data were fit to tri-exponential functions of the form $\Delta A(t) = A_1 * \left(1 - e^{-\frac{t}{\tau_1}}\right) * \left(A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}}\right)$