

Supporting Information: Integrating $\beta\text{-Pb}_{0.33}\text{V}_2\text{O}_5$ Nanowires with CdSe Quantum Dots: Towards Nanoscale Heterostructures with Tunable Interfacial Energetic Offsets for Charge Transfer

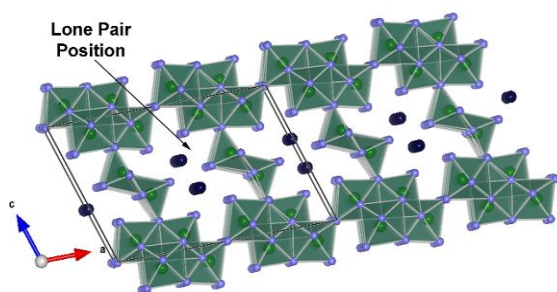


Figure S1. Crystal structure of $\beta\text{-Pb}_x\text{V}_2\text{O}_5$

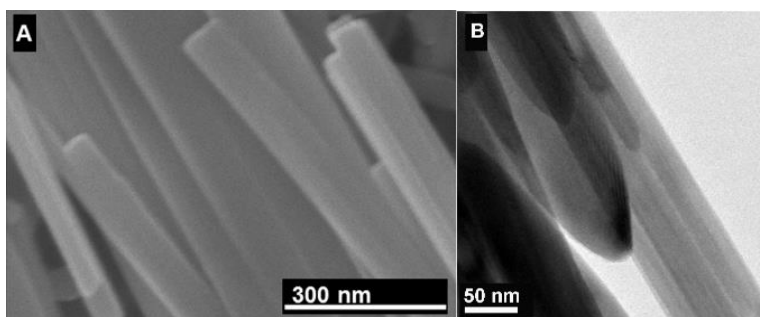


Figure S2. SEM image (A) and TEM image (B) of $\beta\text{-Pb}_x\text{V}_2\text{O}_5$ nanowires mixed with MP-CdSe QDs

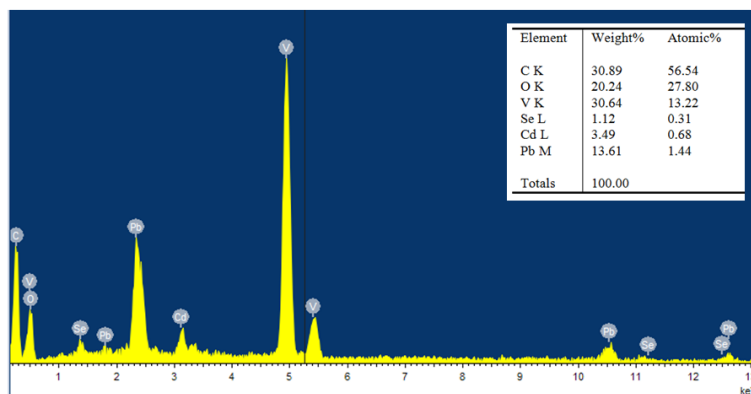


Figure S3. Representative EDS spectrum of $\beta\text{-Pb}_x\text{V}_2\text{O}_5$ nanowires mixed with Cys-CdSe QDs

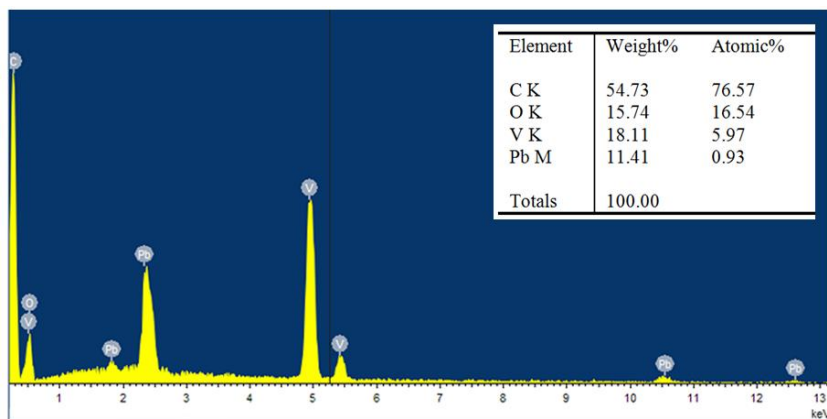


Figure S4. Representative EDS spectrum of β - $\text{Pb}_x\text{V}_2\text{O}_5$ nanowires mixed with MP-CdSe QDs

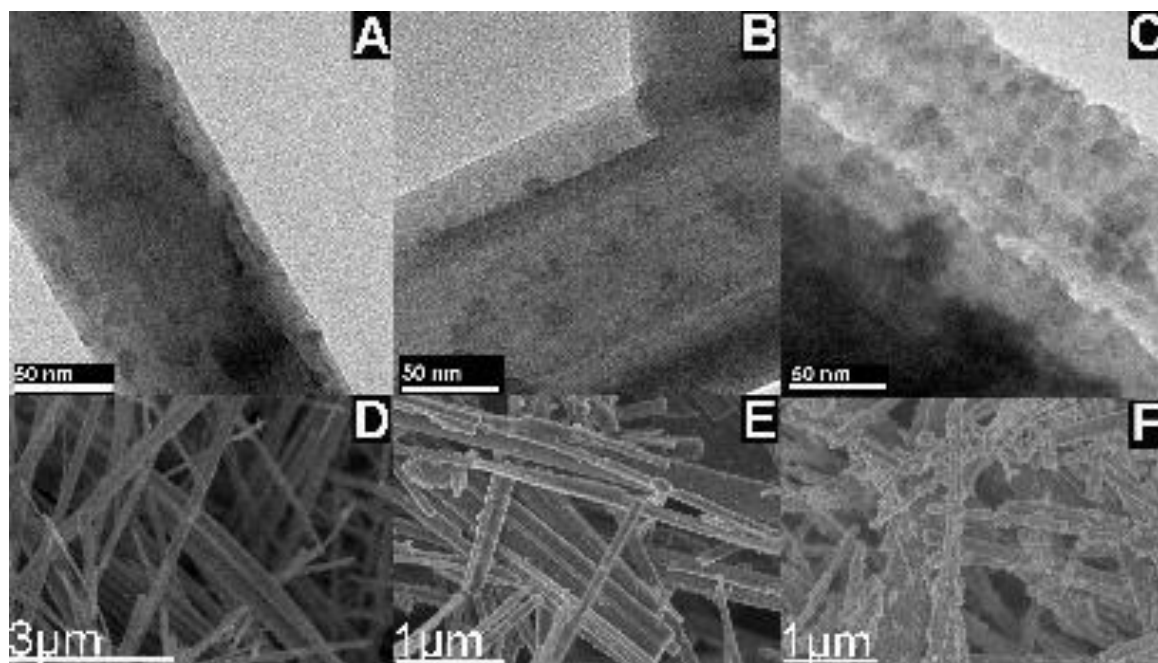


Figure S5. TEM (top) and SEM (bottom) images of β - $\text{Pb}_x\text{V}_2\text{O}_5$ nanowires treated *via* one SILAR cycle (A and D), two SILAR cycles (B and E), and four SILAR cycles (C and F).

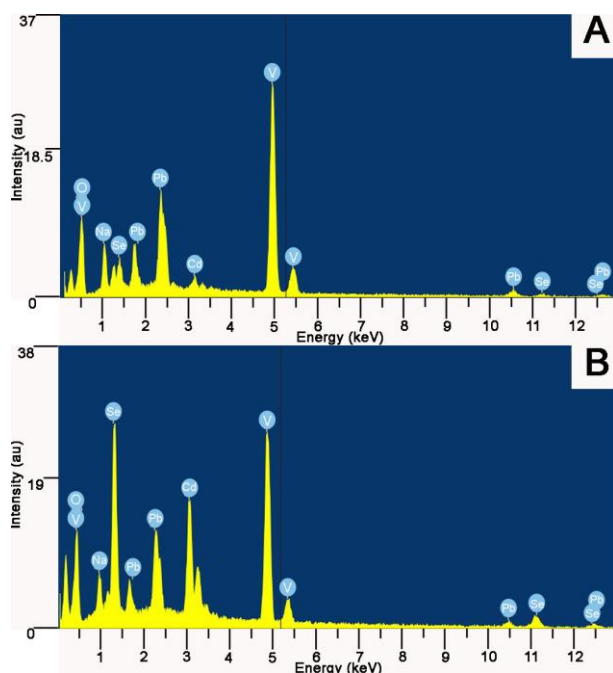


Figure S6. Representative ensemble EDS spectra for $\beta\text{-Pb}_x\text{V}_2\text{O}_5$ nanowires after A) one SILAR cycle and B) five SILAR cycles

Table S1: Calculated elemental concentrations of $\beta\text{-Pb}_x\text{V}_2\text{O}_5$ nanowires with increasing number of SILAR cycles. All concentrations are expressed as ratios of atomic concentrations.

	One cycle	Two cycles	Three cycles	Four cycles	Five cycles
Cd:Se	0.59:1	0.89:1	0.60:1	0.78:1	0.68:1
Cd:Se:V	0.078:0.17:2	0.18:0.15:2	0.16:0.26:2	0.70:0.90:2	0.76:1.14:2

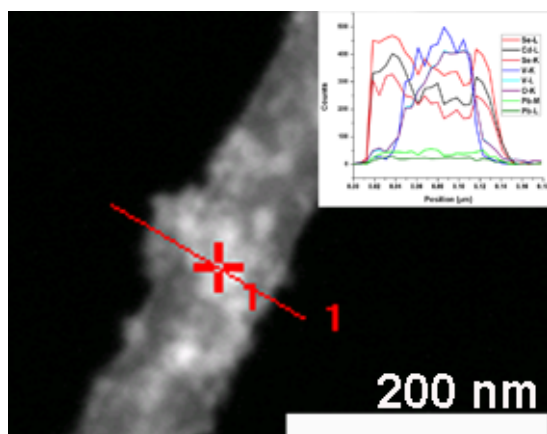


Figure S7. TEM image and corresponding EDS line scan acquired for $\beta\text{-Pb}_x\text{V}_2\text{O}_5$ nanowires coated with CdSe QDS *via* five SILAR cycles.

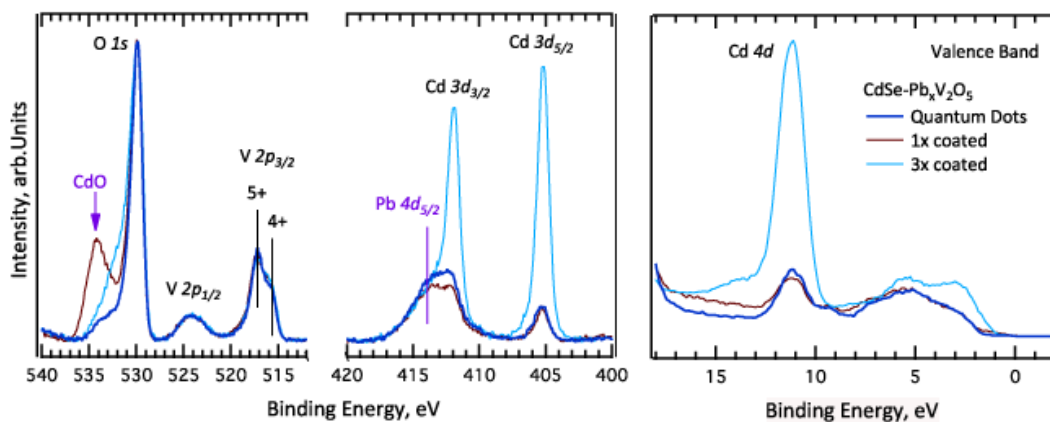


Figure S8. HAXPES spectra for β - $\text{Pb}_x\text{V}_2\text{O}_5$ nanowires functionalized with Cys-CdSe QDs displaying equivalent coverage and modification of the electronic structure as for one SILAR cycle.

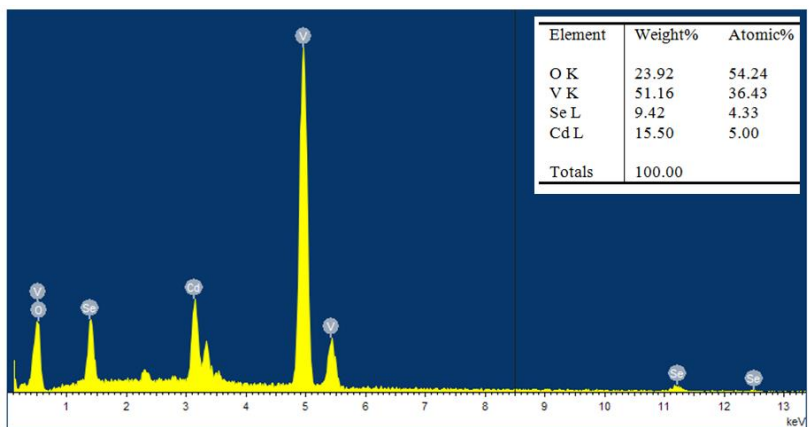


Figure S9. Representative EDS spectrum of V_2O_5 nanowires mixed with Cys-CdSe QDs

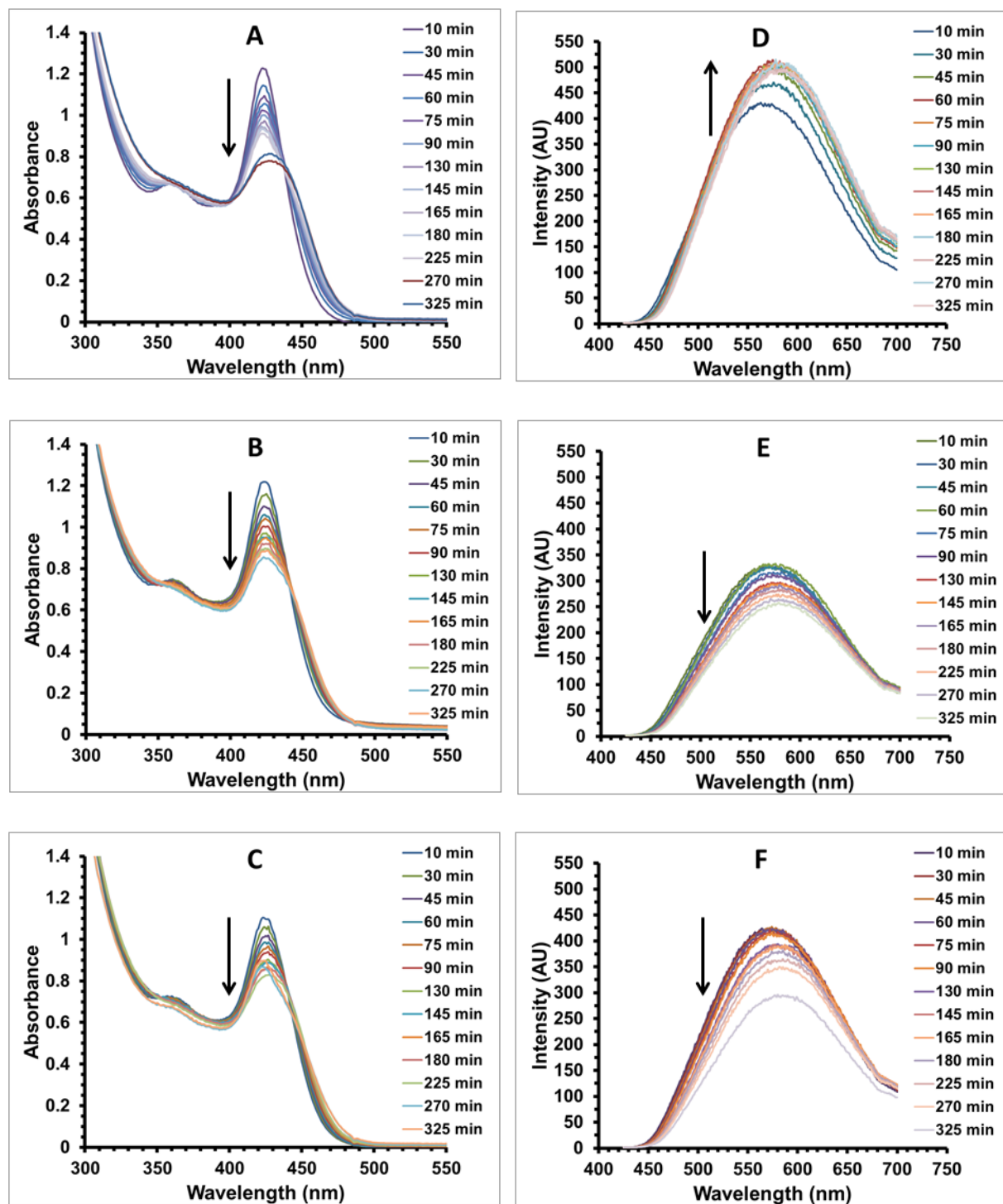


Figure S10. UV-Vis absorption (A, B, C) and steady-state emission (D, E, F) spectra of Cys-CdSe QDs as a function of elapsed time after sample preparation. The top spectra (A and D) correspond to free Cys-CdSe QDs with no nanowires added. The middle spectra (B and E) and bottom spectra (C and F) correspond to Cys-CdSe QDs mixed with β - $\text{Pb}_x\text{V}_2\text{O}_5$ and V_2O_5 nanowires, respectively.

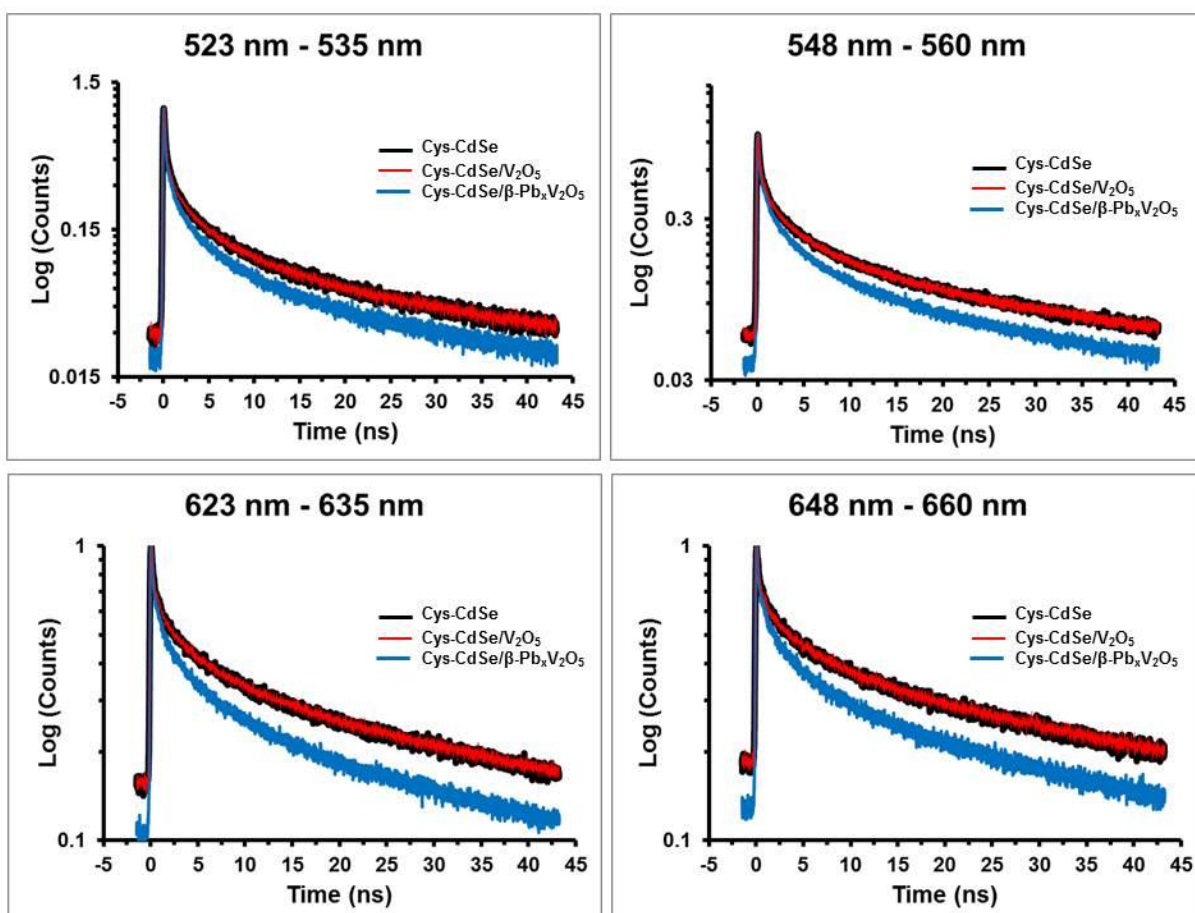


Figure S11. Representative time-resolved emission decay traces at various wavelengths within the steady-state emission band. All decay traces shown were acquired 75 min after samples were prepared.

Table S2. Fitting parameters from global analysis of time-resolved emission decay data at all reaction times for free Cys-CdSe QDs (S2-1), Cys-CdSe QDs combined with V₂O₅ nanowires (S2-2), and Cys-CdSe QDs combined with β -Pb_xV₂O₅ nanowires (S2-3).

Table S2-1. Free Cys-CdSe

Elapsed Time (min)	$\langle \tau \rangle_{\text{ave}}$ (ns)	τ_1 (ns)	f_1 (%)	τ_2 (ns)	f_2 (%)	τ_3 (ns)	f_3 (%)	χ^2
60	20.7	0.51 ± 0.04	3.3	3.8 ± 0.1	15.9	24.8 ± 0.2	80.9	1.089
75	20.8	0.49 ± 0.04	3.2	3.7 ± 0.1	15.7	24.9 ± 0.2	81.1	1.098
90	21.1	0.49 ± 0.04	3.1	3.7 ± 0.1	15.1	25.1 ± 0.2	81.8	1.094
130	21.2	0.49 ± 0.04	3.1	3.7 ± 0.1	15.3	25.3 ± 0.2	81.6	1.087
145	22.2	0.52 ± 0.04	3.1	3.9 ± 0.1	15.3	26.5 ± 0.2	81.6	1.081
165	22.2	0.50 ± 0.04	3.1	3.8 ± 0.1	15.1	26.4 ± 0.2	84.0	1.089
180	22.3	0.52 ± 0.04	3.1	3.9 ± 0.1	15.1	26.6 ± 0.2	81.0	1.072
225	22.6	0.51 ± 0.04	3.0	3.9 ± 0.1	14.9	26.9 ± 0.2	82.1	1.073
270	23.5	0.52 ± 0.05	3.0	3.3 ± 0.1	14.8	27.8 ± 0.2	82.2	1.051
325	23.0	0.51 ± 0.05	3.0	3.8 ± 0.1	14.4	27.2 ± 0.2	82.6	1.074

Table S2-2. Cys-CdSe combined with V₂O₅

Elapsed Time (min)	$\langle \tau \rangle_{\text{ave}}$ (ns)	τ_1 (ns)	f_1 (%)	τ_2 (ns)	f_2 (%)	τ_3 (ns)	f_3 (%)	χ^2
60	19.6	0.48 ± 0.04	3.8	3.6 ± 0.1	16.3	23.8 ± 0.2	80.0	1.087
75	21.3	0.51 ± 0.04	3.2	3.8 ± 0.1	15.5	25.5 ± 0.2	81.3	1.073
90	19.6	0.48 ± 0.04	3.8	3.6 ± 0.1	16.2	23.7 ± 0.2	80.1	1.081
130	19.5	0.47 ± 0.04	3.7	3.5 ± 0.1	16.0	23.5 ± 0.2	80.3	1.083
145	19.8	0.48 ± 0.04	3.8	3.6 ± 0.1	16.2	24.0 ± 0.2	80.0	1.077
165	19.2	0.46 ± 0.04	3.9	3.5 ± 0.1	15.2	23.3 ± 0.2	80.0	1.075
180	19.5	0.48 ± 0.04	4.0	3.5 ± 0.1	16.4	23.8 ± 0.2	80.0	1.071
225	19.1	0.47 ± 0.04	4.0	3.5 ± 0.1	16.6	23.3 ± 0.2	79.3	1.067
270	18.1	0.46 ± 0.04	4.3	3.3 ± 0.1	16.8	22.2 ± 0.2	78.9	1.007
325	16.0	0.46 ± 0.04	5.0	3.2 ± 0.1	19.1	20.2 ± 0.3	75.8	1.018

Table S2-3. Cys-CdSe combined with β -Pb_xV₂O₅

Elapsed Time (min)	$\langle \tau \rangle_{\text{ave}}$ (ns)	τ_1 (ns)	f_1 (%)	τ_2 (ns)	f_2 (%)	τ_3 (ns)	f_3 (%)	χ^2
60	16.6	0.48 ± 0.04	4.4	3.4 ± 0.1	18.2	20.7 ± 0.2	77.4	1.083
75	16.5	0.47 ± 0.04	4.4	3.3 ± 0.1	18.4	20.6 ± 0.2	77.2	1.088
90	16.8	0.48 ± 0.04	4.4	3.4 ± 0.1	18.4	20.9 ± 0.2	77.2	1.086
130	16.8	0.46 ± 0.04	4.5	3.4 ± 0.1	18.5	21.0 ± 0.2	76.9	1.085
145	16.6	0.47 ± 0.04	4.6	3.3 ± 0.1	18.3	20.8 ± 0.2	77.2	1.093
165	16.8	0.48 ± 0.04	4.7	3.4 ± 0.1	18.3	21.0 ± 0.2	77.0	1.067
180	16.8	0.48 ± 0.04	4.6	3.4 ± 0.1	18.7	21.1 ± 0.2	76.7	1.049
225	16.6	0.48 ± 0.04	4.5	3.3 ± 0.1	18.7	20.8 ± 0.2	76.7	1.066
270	16.6	0.47 ± 0.04	4.6	3.3 ± 0.1	18.6	20.8 ± 0.2	76.8	1.010
325	16.0	0.45 ± 0.04	4.8	3.2 ± 0.1	18.4	20.0 ± 0.2	76.8	1.025

Appendix S1. Emission quantum yield determination

The emission quantum yield (QY) of Cys-CdSe was determined using a rhodamine 101 dye (in ethanol) as a standard (QY = 1)¹. In order to eliminate any instrument variation, the same conditions were used to measure both Cys-CdSe and rhodamine 101 emission intensities. The excitation wavelength was 365 nm with excitation and emission slits set at 10 nm and 5 nm, respectively. Absorption spectra were obtained to ensure the absorbance at 365 nm was less than 0.15 to prevent re-absorption. A 400 nm longpass filter was placed in front of the emission slit to remove contributions from Rayleigh scattering of 730 nm light in the emission spectrum. Samples were placed in septa-sealed quartz cuvettes (1 cm pathlength) and purged with argon for a minimum of 15 min before emission measurement. The QY was calculated following the IUPAC formula²:

$$\Phi_{QDs} = \left[\frac{A_{dye} * F_{QDs} * \eta^2}{A_{QDs} * F_{dye} * \eta_o^2} \right] * \Phi_{dye}$$

where A_{dye} and A_{QDs} are the absorbances at 365 nm, F_{dye} and F_{QDs} are the integrated emission intensities over the entire spectra, η is the refractive index of water³, and η_o is the refractive index of ethanol³.

Appendix S2. Global fitting analysis of time-resolved emission data:

All decay traces were fit using a reconvolution procedure with multiexponential fit given by equation S1:

$$I(t) = \int_{-\infty}^t IRF(t') \sum_{i=1}^n A_i \exp\left(-\frac{t-t'}{\tau_i}\right) dt' \quad (S1)$$

where the total instrument response function is assumed to be the sum of \square pulses with amplitude $IRF(t')$ at time t' , $I(t)$ is emission intensity at time t , A_i is the amplitude of the i^{th} component, and τ_i is the lifetime of the i^{th} component. A global fitting procedure was used to find a single set of lifetimes that modeled the decay traces precisely at every wavelength for a given sample at a given reaction time. Out of the 16 decay traces corresponding to different ranges of emission wavelengths (i.e. different bins of the 16-channel photomultiplier tube), those having significant scattering or having maximum measured counts less than 1000 were not included in global fitting. Values of τ_i and $IRF(t')$ and the pulse period of laser were taken as fixed global parameters for each decay. Values of A_i , decay background, shift in $IRF(t')$ and intensity of scattering light were taken as variable non-global parameters. For each decay trace, an average lifetime for the decay was computed as:

$$\langle \tau \rangle = \frac{\sum_n (A_n \tau_n^2)}{\sum_n (A_n \tau_n)} \quad (S2)$$

The fractional intensity contribution of each component to the total decay was computed as:

$$f_n(\%) = \left(\frac{A_n \tau_n}{\sum_n A_n \tau_n} \right) \times 100 \quad (S3)$$

The quality of fits was assessed by analyzing the random scattering of residuals around zero and the associated reduced chi-square values (χ^2). In addition, autocorrelation plots were assessed to judge the quality of the fits. Values of χ^2 near to 1 with no apparent trends in residual and autocorrelation plots were assessed as good fits.

References

1. Karstens, T.; Kobs, K., Rhodamine B and rhodamine 101 as reference substances for fluorescence quantum yield measurements. *Journal of Physical Chemistry* **1980**, *84* (14), 1871-2.
2. Eaton, D. F., Reference Materials for Fluorescence Measurement. *Pure & Appl. Chem.* **1988**, *60* (7), 1107-1114.
3. Li, H.; Shih, W. Y.; Shih, W.-H., Synthesis and characterization of aqueous carboxyl-capped CdS quantum dots for bioapplications. *Industrial & Engineering Chemistry Research* **2007**, *46* (7), 2013-2019.