Supporting Information for:

Tuning Intermediate-Band Cu$_3$VS$_4$ Nanocrystals from Plasmonic-like to Excitonic via Shell-Coating

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Content list:

Figures S1-S9

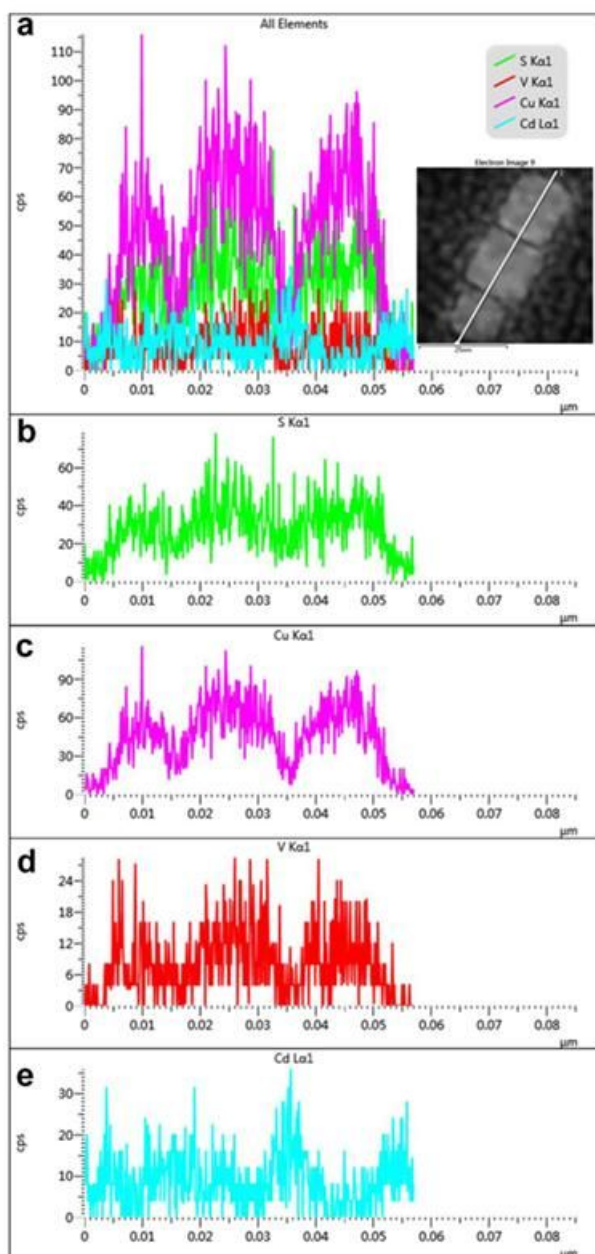Kinetics fitting in Cu$_3$VS$_4$/CdS-RhB complexes

Figure S1. Line-scan elemental mapping for CVS/CdS NCs. (a) plots of the counts for elemental Cu (magenta), V (red), Cd (cyan) and S (green) along the line drawn in the inset. (b-e) Individual plots of the counts for elemental S (b), Cu (c), V (d), and Cd (e).
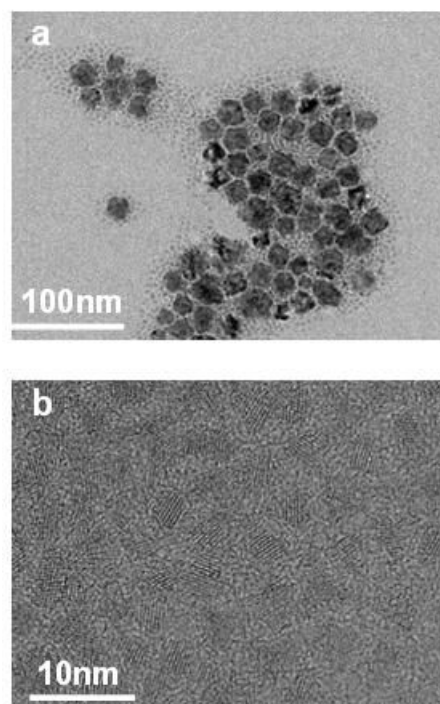
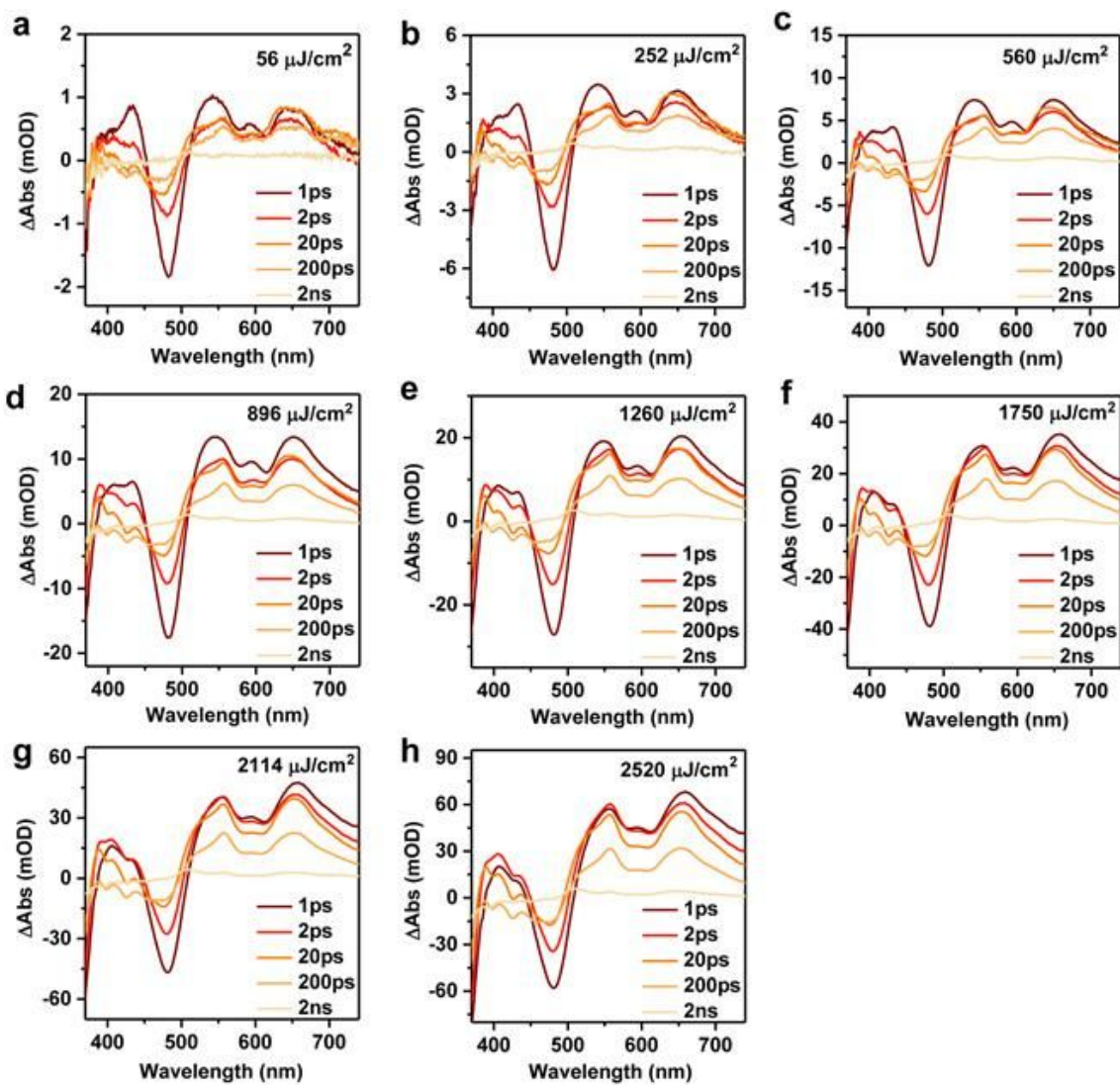**Figure S2.** (a) TEM image of CVS/CdS NCs. (b) HRTEM image of scattered CdS NCs of the image in (a).

Figure S3. TA spectra of CVS NCs probed at indicated time delays following various excitation fluences from 56 to 2520 µJ/cm². The pump wavelength is 350 nm.
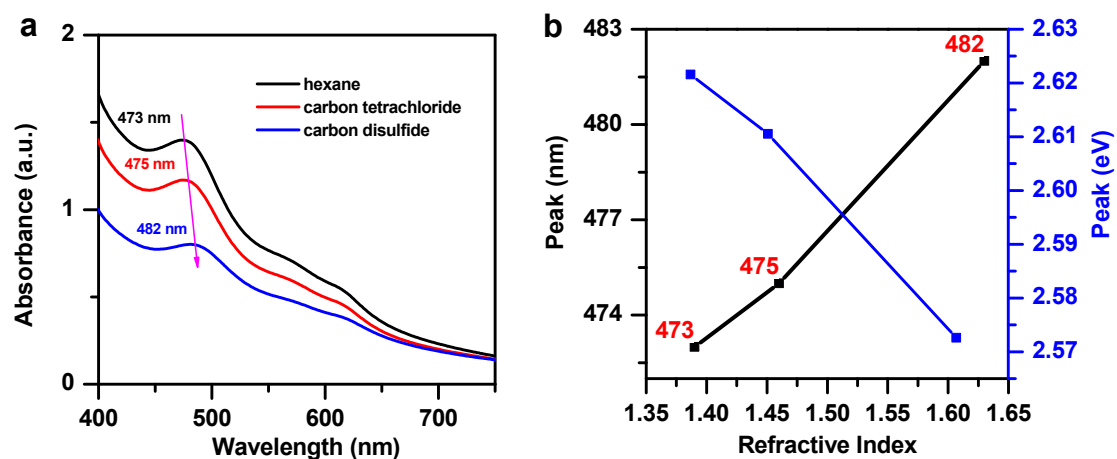
Figure S4. (a) Absorption spectra of CVS NCs dispersed in different solvents indicated in the legends. (b) Resonance peak positions in wavelength (left) and in energy (right) as a function of solvent refractive index.
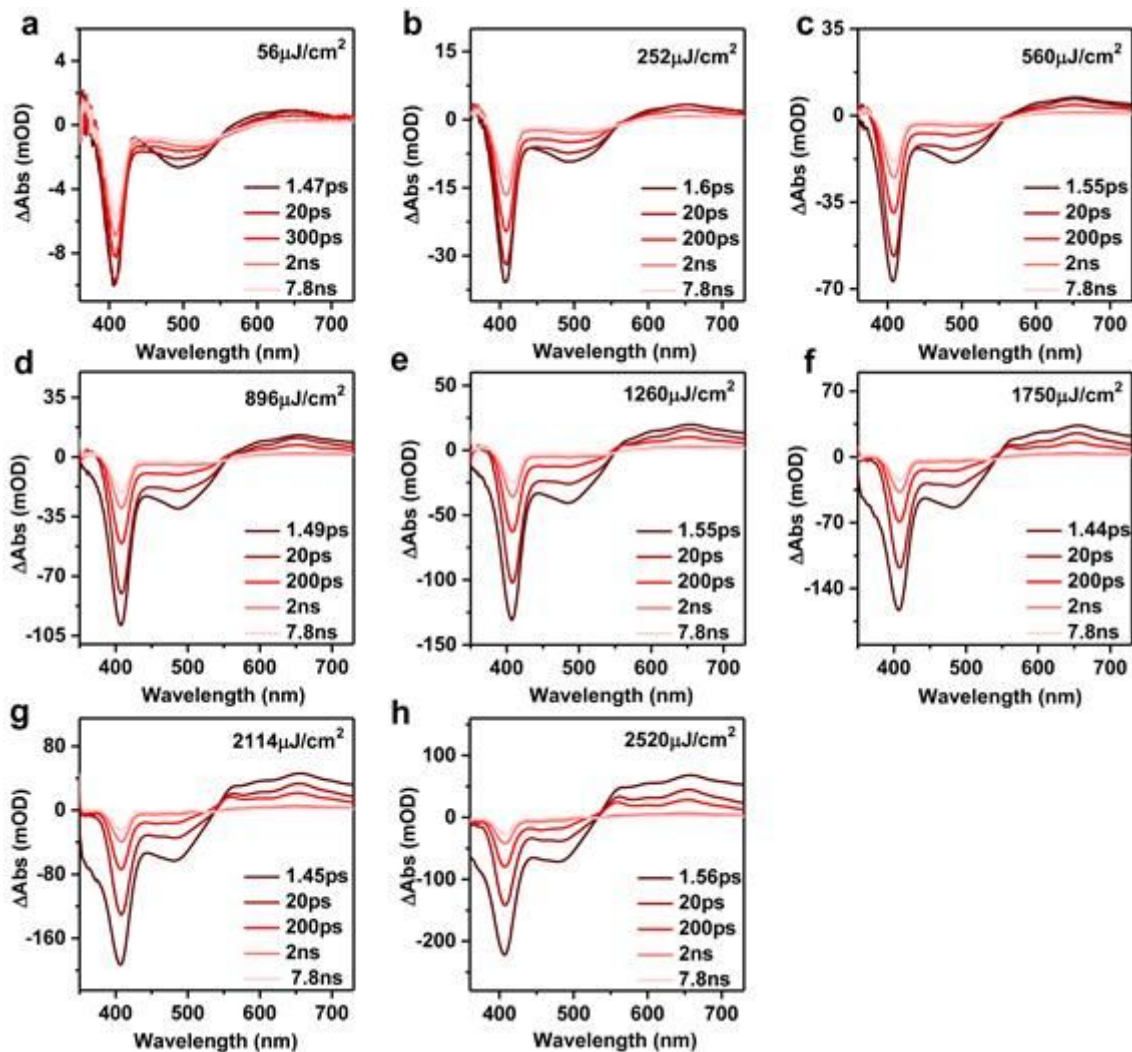
Figure S5. TA spectra of CVS/CdS NCs probed at indicated time delays following various excitation fluences from 56 to 2520 µJ/cm². The pump wavelength is 350 nm.
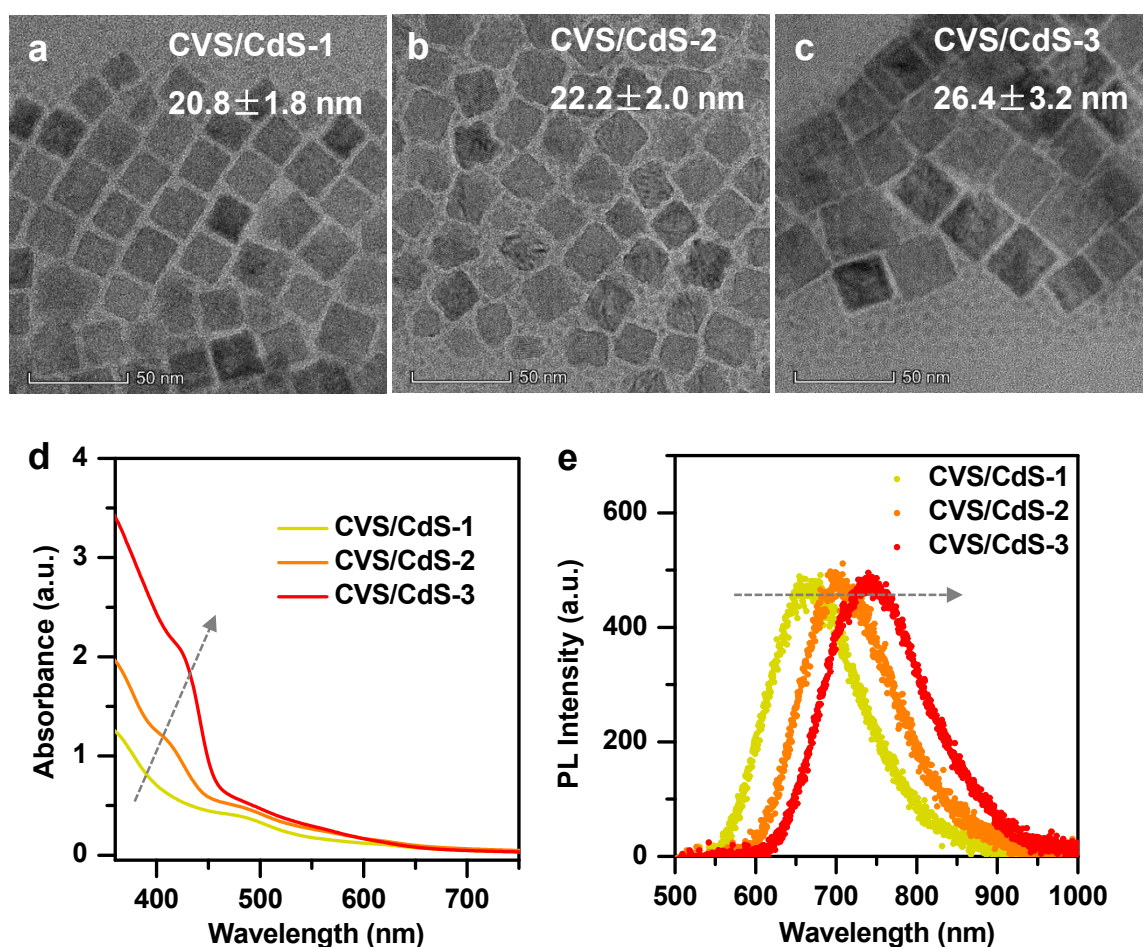
Figure S6. (a-c) TEM images of three CVS/CdS core/shell samples with the same core size of 16.1 nm and different shell thicknesses increasing from ~2.0 to 5.2 nm. (d) Absorption and (e) PL spectra of the CVS/CdS samples. The spectral changes with increasing shell thickness are indicated by gray dashed arrows in the figures.
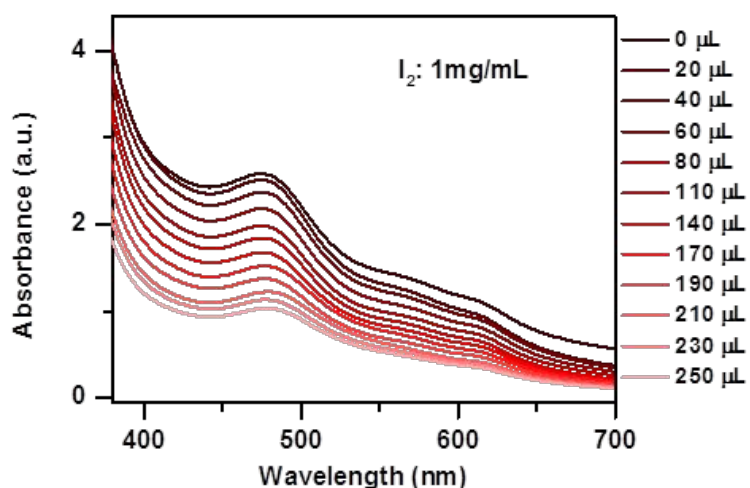
Figure S7. Absorption spectra of CVS NCs with increasing amount of I_2 added. The I_2 molecules are dissolved in chloroform and the concentration is 1 mg/mL. Note that even larger amounts of I_2 were not used because of the characteristic absorption of I_2 at 510 nm that can interfere with the resonance peaks of CVS NCs.
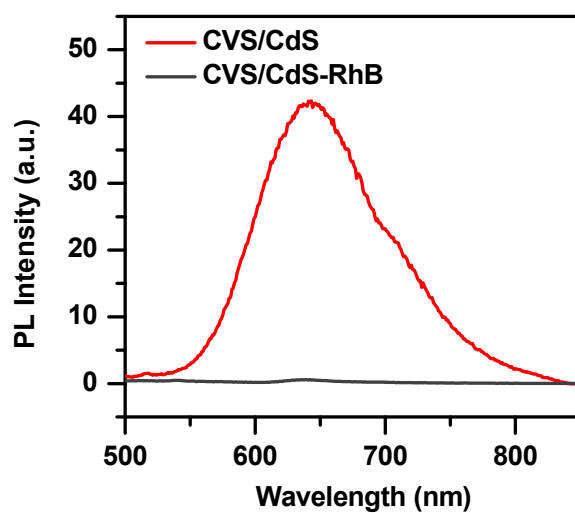

Figure S8. PL spectra of CVS/CdS NCs with (black) and without (red) surface-functionalized RhB molecules.
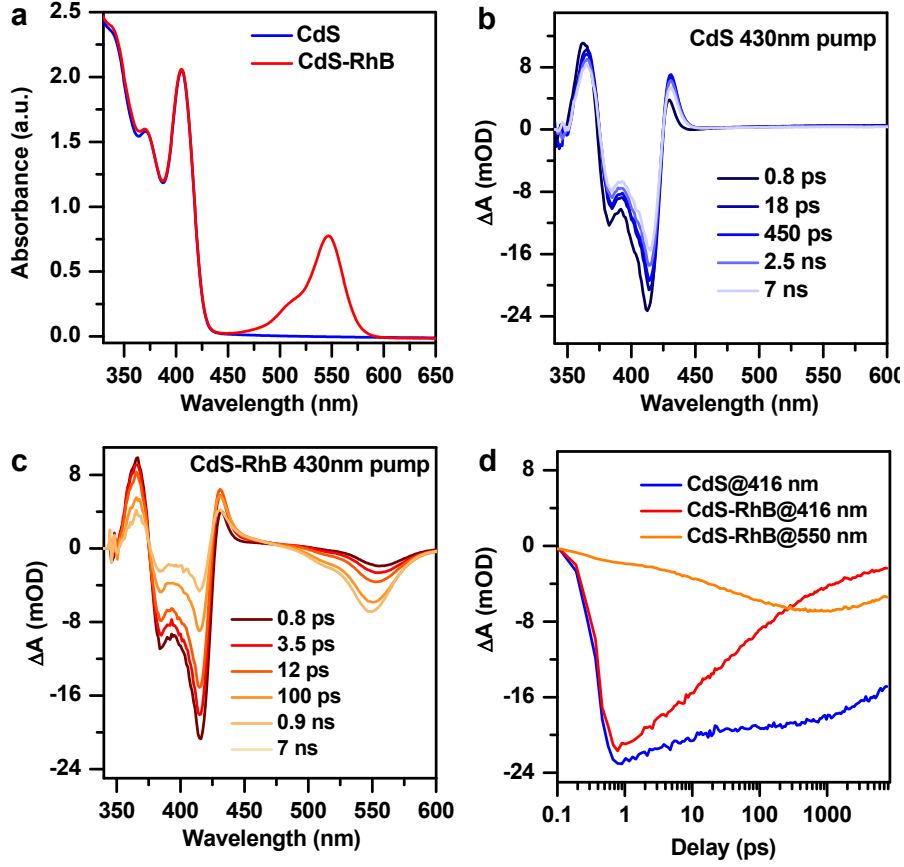
Figure S9. (a) Absorption spectra of CdS NCs with (black) and without (red) surface-functionalized RhB molecules. (b,c) TA spectra of free CdS NCs (b) and CdS-RhB complexes (c) at indicated delays following the excitation by 430 nm pump pulses. (d) TA kinetics probed at 416 nm for free CdS NCs (blue) and at 416 nm (red) and 550 nm (orange) for CdS-RhB complexes.

Kinetics fitting in Cu_3VS_4/CdS-RhB Complexes.

The kinetics of the NC bleaches probed at 398 and 475 nm, which are isosbestic points where the charge separated states (NC^+-RhB^-) have no signals, can be fitted with the following two-exponential decay function:

$$S(t)_{NC} = S(0)_{NC} \cdot \sum_{i=1}^{2} A_i e^{-t/\tau_{ET,i}} \tag{S1},$$

where $S(0)_{NC}$ is the initial signal amplitude and $\tau_{ET,i}$ and A_i are the time constant and amplitude of the ith component.

The kinetics of the RhB bleach probed at 562 nm is slightly more complicated due to the overlap between NC bleach and RhB bleach at this wavelength. We first find out the ratio between the bleach amplitude at 562 nm and 475 nm in free NCs (C) and assume that C is the same in NC-RhB complexes. By doing so, the kinetics at 562 nm can be expressed as:

$$S(t)_{562nm} = C \cdot S(0)_{NC} \cdot \sum_{i=1}^{2} A_i e^{-t/\tau_{ET,i}} + S_{RhB}\left(1 - \sum_{i=1}^{2} A_i e^{-t/\tau_{ET,i}}\right) \qquad (S2),$$

where S_{RhB} is the full signal amplitude of the RhB bleach after electron transfer. Note that because charge recombination is slow we have ignored it by assuming infinitely slow recombination in eq. S2. Using the same set of $\tau_{ET,i}$ and A_i parameters, we simultaneously fit the kinetics of NC bleach and the kinetics at 562 nm. The fitting parameters are listed in Table S1. The average ET time ($\tau_{ET, ave}$) is calculated as:

$$\tau_{ET,ave} = \sum_{i=1}^{2} A_i \tau_{ET,i} \bigg/ \sum_{i=1}^{2} A_i \qquad (S3).$$

Table S1. Fitting parameters for TA kinetics

$\tau_{ET,1}$ (ps)	A_1 (%)	$\tau_{ET,2}$ (ps)	A_2 (%)	$\tau_{ET,ave}$ (ps)
6.7±0.7	25.9±3.5	1.2±0.1	74.1±3.1	2.6±0.3