Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Hot Exciton Cooling and Multiple Exciton Generation in PbSe Quantum Dots

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1. Transient absorption setup

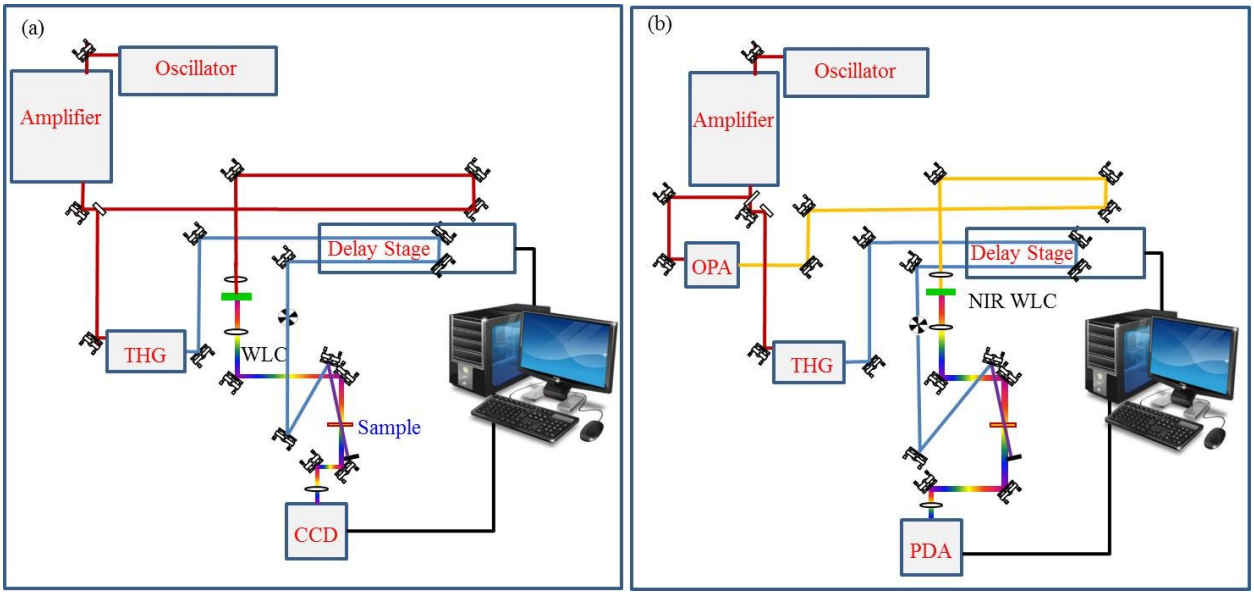

Figure S1: Transient absorption setup for (a) Visible and (b) NIR regions. OPA: Optical parametric amplifier, THG: Third harmonic generation, WLC: white light continuum, CCD: charge coupled device and PDA: photo-diode array.

2. Particle size distributions

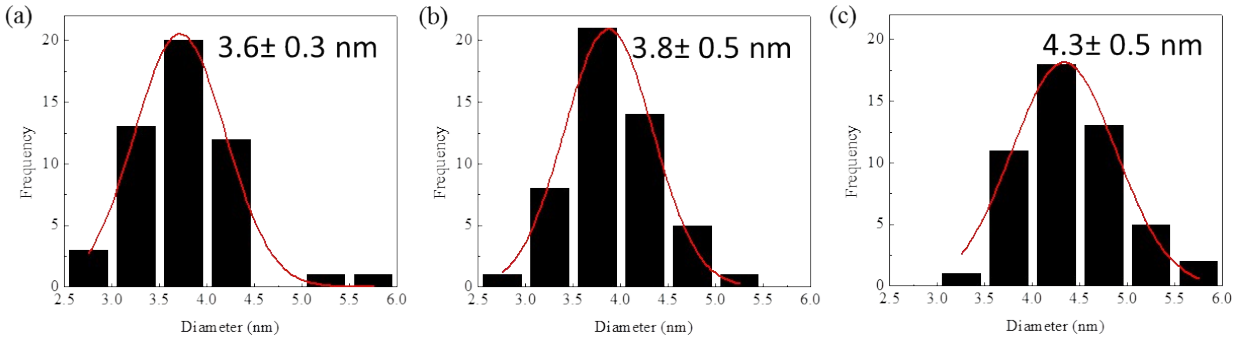

Figure S2: Particle size distribution of PbSe (a) QD_1, (b) QD_2 and (c) QD_3. Red solid line is Gaussian fitting of the histograms.

3. Absorption spectra and their second derivative

The absorption spectrum (black line) and its second derivative (blue line) of QD_2 and QD_3 are shown in Figure S3. The first dip of the second derivative of absorption spectra (~ 1200 nm in QD_2 and 1300 nm in QD_3) corresponds to a first excitonic peak in absorption spectra and is defined as 1S-1S transition. Another dip is observed around 600 nm for all the samples, which is assigned to the Σ transition.

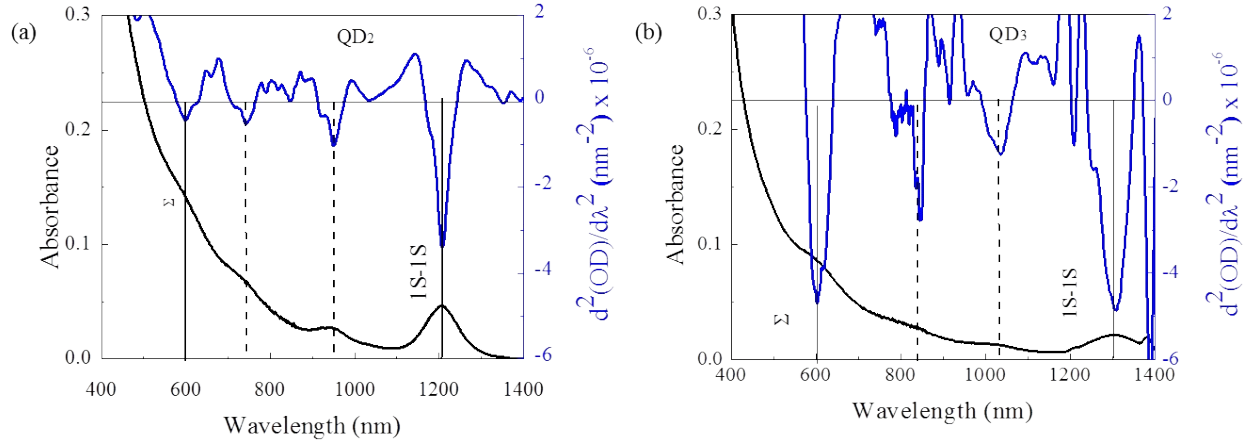

Figure S3: Absorption spectra (black line) and its second derivative (blue) for (a) QD_2 and (b) QD_3

4. NIR TA spectra

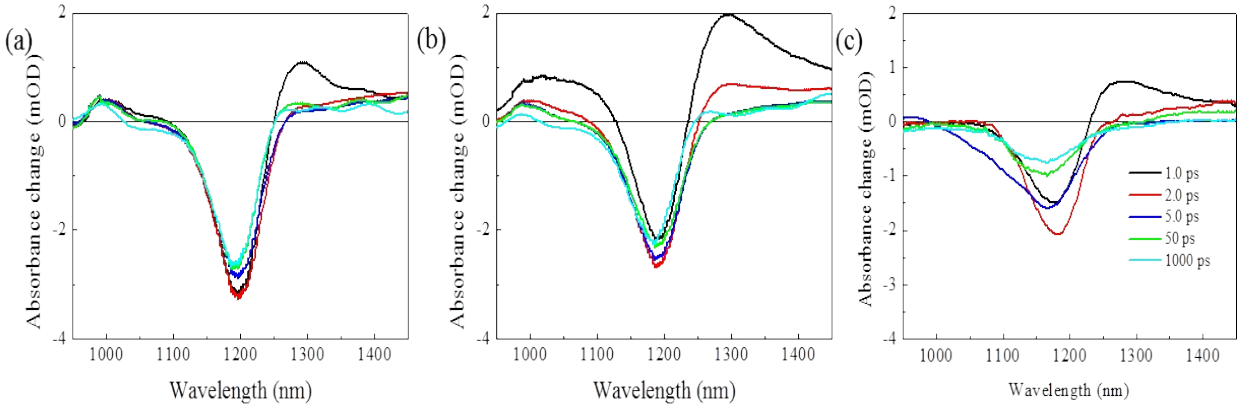

Figure S4. NIR TA spectra of PbSe QD_2 at pump wavelengths of (a) 800 nm, (b) 400 nm and (c) 267 nm

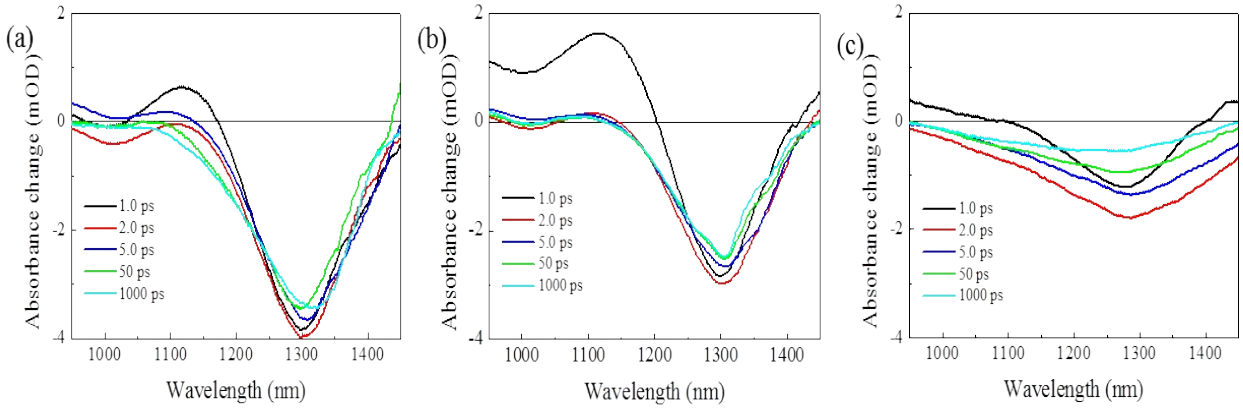

Figure S5. NIR TA spectra of PbSe QD_3 at pump wavelengths of (a) 800 nm, (b) 400 nm and (c) 267 nm

5. Fluence-dependent transient kinetics

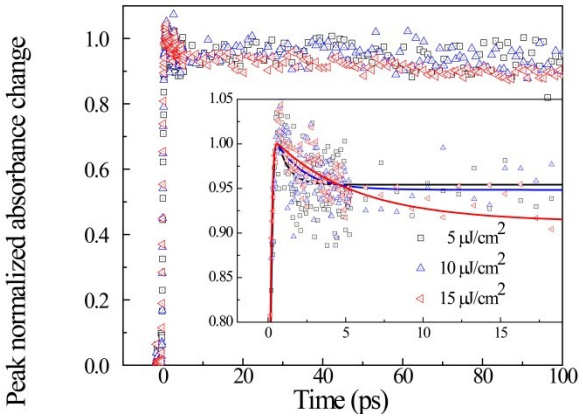

Figure S6: QD_1: Peak normalized kinetics probed at 1100 nm, with 800 nm excitation wavelength and pump at different fluencies. Inset is the zoom in the first 20 ps. Symbols are data points and solid lines are bi- exponential curve fitting lines.

6. MEG QY in PbSe QDs

Tail normalized TA dynamics of QD_2 with probe wavelength of 1200 nm and QD_3 with probe wavelength of 1300 nm for different pump wavelengths are shown in Figure S7 (a) and S7 (b) respectively. Measured QY for QD_2 and QD_3 is shown in table 1 in the main text.

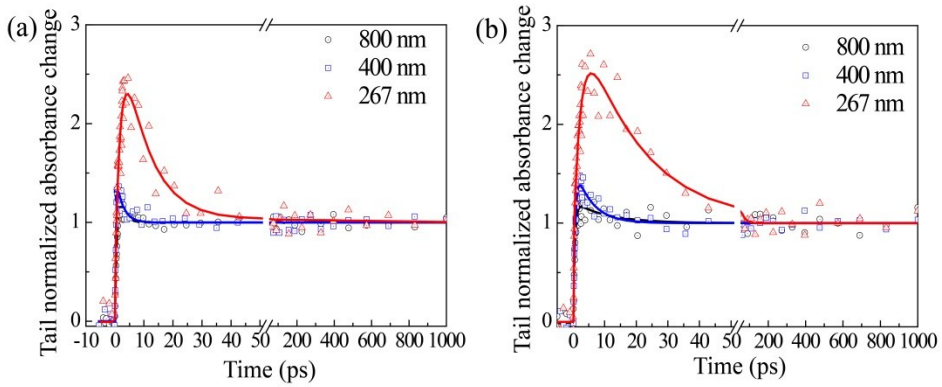

Figure S7: Tail normalized kinetics with pumping wavelengths of 800 (black circle), 400 (blue square) and 267 nm (red triangle) of (a) QD_2 with 1200 nm probe wavelength and (b) QD_3 with 1300 nm probe wavelength. Symbols are data points and solid lines are bi- exponential curve fitting lines.

MEG QY of PbSe QDs as a function of hν/Eg is shown in figure S8. Three excitation energies are used to excite PbSe QDs samples. MEG QY values below the 2Eg are not considered for the analysis. Here, we see the trend that MEG QY of smaller sized QDs is higher than the larger sized QDs at given hν/Eg, which is consistent with the literature.

6. Visible TA spectra

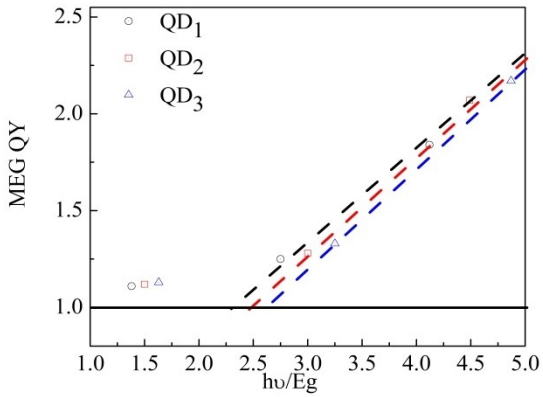

Figure S8. MEG QY of PbSe QD_1 (black circles), QD_2 (red squares) and QD_3 (blue triangles) as function of hν/Eg. Dash lines are guide to eye.

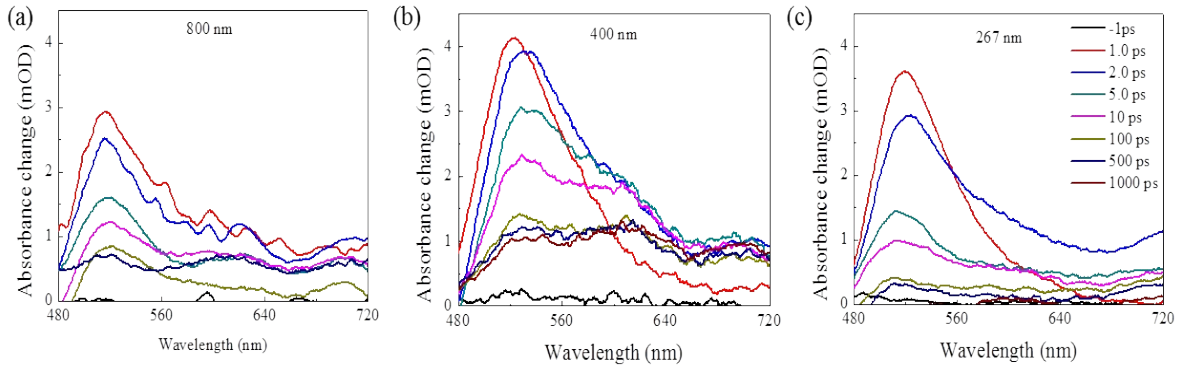

Figure S9: TA spectra of QD_1 at pump wavelengths of (a) 800 nm, (b) 400 nm and (c) 267 nm

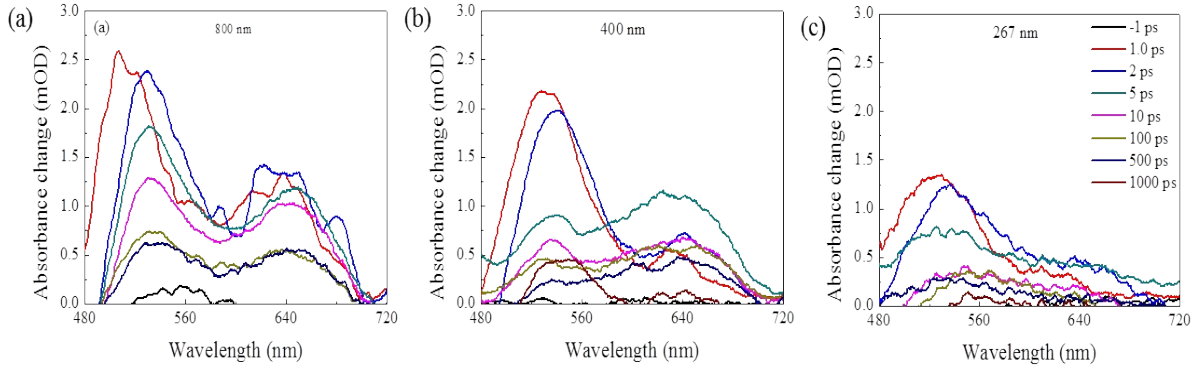

Figure S10: TA spectra of QD_2 at pump wavelengths of (a) 800 nm, (b) 400 nm and (c) 267 nm

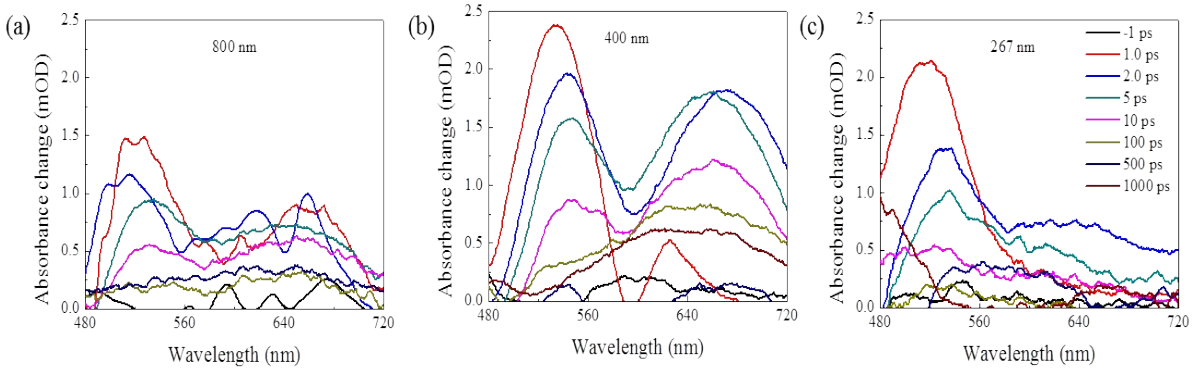

Figure S11: TA spectra of QD_3 at pump wavelengths of (a) 800 nm, (b) 400 nm and (c) 267 nm

TA kinetics

TA kinetics probed at 525 nm, 650 nm and using pump wavelengths of 800 nm, 400 nm and 267 nm are shown in figure S12 (a), (b) and (c) for QD2 and figure S13 (a), (b) and (c) for QD3 respectively.

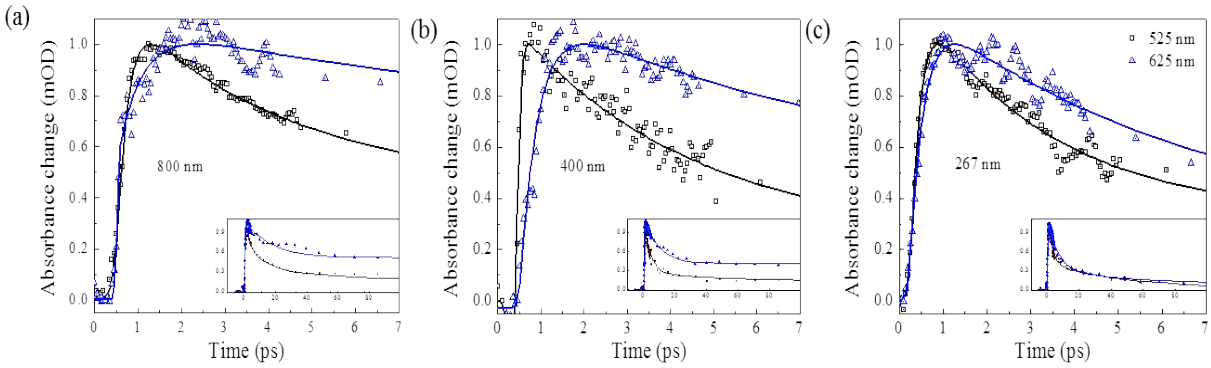

Figure S12:TA kinetics of QD_2 at probe wavelengths 525 nm (black) and 650 nm (blue) at (a) 800 nm pump, (b) at 400 nm pump and (c) at 267 nm pump. Inset of figures shows kinetics at long delays. Symbols are data points and solid lines are bi- exponential curve fitting

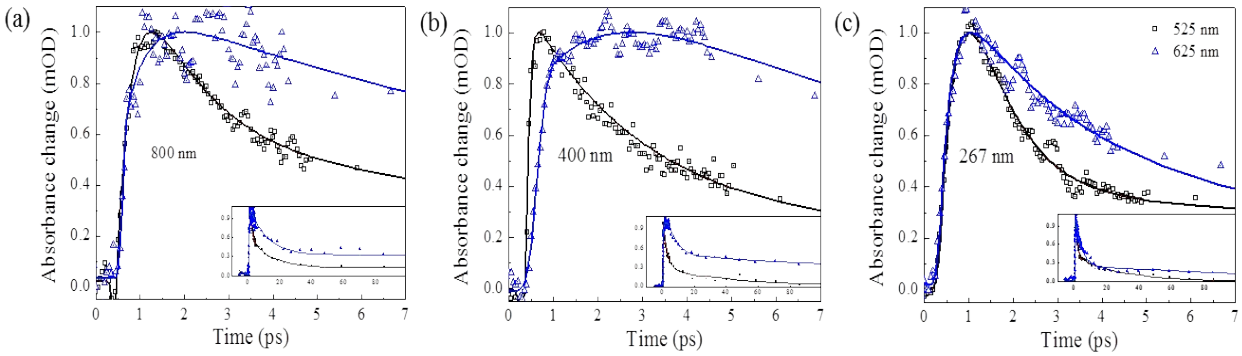

Figure S13: TA kinetics of QD_3 at probe wavelengths 525 nm (black squires) and 650 nm (blue triangles) at (a) 800 nm pump, (b) at 400 nm pump and (c) at 267 nm pump. Inset of figures shows kinetics at long delays. Symbols are data points and solid lines are bi- exponential curve fitting

7. MEG QY measurement above the band gap

Figure S14 shows the tail normalized TA dynamics of QD1 at 525 nm probe, for different pump wavelengths. Similar to the table 1 of the main text, (A/B)525 ratio (A/B ratio with 525 nm probe wavelength) for QD1, QD2 and QD3 with excitations wavelengths of 800 nm, 400 nm and 267 nm were measured from data in Figure S14 and shown in table S1.

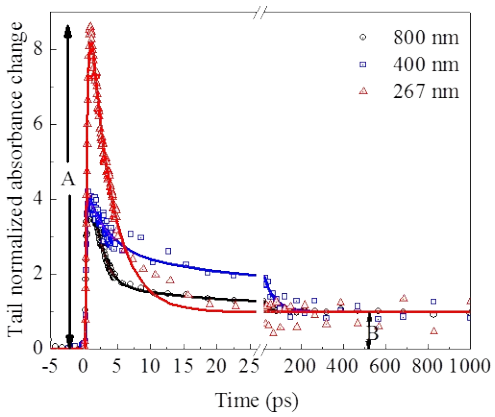

Figure S14: Tail normalized kinetics of QD_1 with probe wavelength of 525 nm and pumping wavelengths of 800 (black circle), 400 (blue square) and 267 nm (red triangle). Symbols are data points and solid lines are bi- exponential curve fitting. Inset of the figure shows kinetics at short delays.

Table S1: Peak to tail ratio $(A/B)_{525}$ of PbSe QD_1, QD_2 and QD_3 at 525 nm probe wavelength and at 800 nm, 400 nm and 267 nm pump wavelengths

Pump wavelength (nm)	$(A/B)_{525}$		
	QD_1	QD_2	QD_3
800	3.75	5	12
400	4.15	5.8	13.12
267	8.22	11.45	28.5

8. Absorption cross section calculation of PbSe QDs

Absorption cross sections values of PbSe QDs were calculated using the refractive index (n, k) values of the PbSe bulk material, following the equation 1.[1]

$$\sigma = \frac{\omega}{n_h c} V \left| f(\omega) \right|^2 (2 n_m k_m) \quad \text{* MERGEFORMAT (1)}$$

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Where ω is the excitation angular frequency, n_h is the refractive index of the host medium, c is the speed of light, V is the volume of the nanostructure, |f(ω)| is the local field factor defined as the ratio of the electric field inside to the outside of the nanostructure. n_m and k_m are the real and imaginary refractive index of the nanostructure. QDs can be considered as a sphere (radius R) of uniform dielectric medium (ε_m) in a host medium of dielectric constant ε_h. f(ω) for QDs can be calculated by solving the Laplace's equation.[2]

$$f(\omega) = \frac{3}{2 + \varepsilon_r} \quad \text{* MERGEFORMAT (2)}$$

$$\text{Therefore, } \sigma = 4\pi n_m k_m \frac{V}{n_h \lambda} \left| \frac{3}{2 + \varepsilon_r} \right|^2 \quad \text{* MERGEFORMAT (3)}$$

Where

$$\begin{aligned} \varepsilon_r &= \frac{\varepsilon_m}{\varepsilon_h} \\ \varepsilon_m &= \varepsilon_1 + i\varepsilon_2 = n_m^2 \\ n_m &= n + ik \\ \varepsilon_1 &= n^2 - k^2 \\ \varepsilon_2 &= i2nk \end{aligned} \quad \text{* MERGEFORMAT (4)}$$

$$\sigma = \frac{16}{3} \pi^2 nk \frac{R^3}{n_h \lambda} \left| \frac{3}{2 + \left(\frac{n_m}{n_h} \right)^2} \right|^2 \quad \text{* MERGEFORMAT (5)}$$

$$\sigma = 338.4nk \frac{R^3}{\lambda \left[\left(2 + \frac{n^2 - k^2}{n_h^2} \right)^2 + \frac{4n^2 k^2}{n_h^4} \right]} \quad \text{* MERGEFORMAT (6)}$$

n, k and n_h values are taken from the database.[3] Calculated absorption cross section spectra of PbSe QD_1, QD_2 and QD_3 are shown in figure S15. Absorption cross section values for pumping wavelengths are shown in table S2.

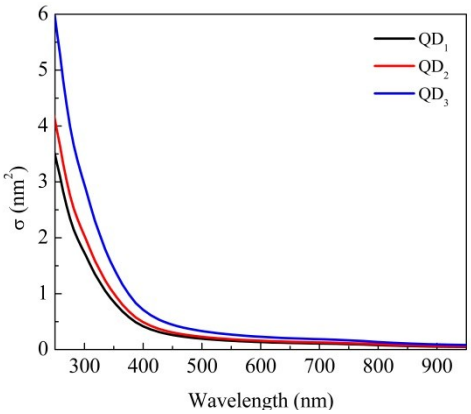

Figure S15: Absorption cross section of PbSe QD_1, QD_2 and QD_3.

Table S2: Absorption cross section of PbSe QDs for pumping wavelengths using bulk n and k values method.

σ_λ (10^{-16} cm^2)	QD_1	QD_2	QD_3
σ_{800}	7.8	9.2	13.4
σ_{400}	41.69	49.06	71.08
σ_{267}	257.56	303.06	439.13

References:

1 J. Giblin and M. Kuno, *J. Phys. Chem. Lett.*, 2010, **1**, 3340.

2 L. D. Landau, *Electrodynamics of Continuous Media*, Pergamon Press Ltd., 2 edn., 1984.

3 Refractive index of PbSe online, http://www.filmetrics.com/refractive-index-database/PbSe/Lead-Selenide (accessed October 2016).