

Supporting Information

Quantum Confinement-Tunable Ultrafast Charge Transfer at the PbS Quantum Dot and PCBM Fullerene Interface

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Experimental section

Chemicals

Lead(II) oxide powder (PbO, 99%), Oleic acid (OA, technical grade 90%), and Bis(trimethylsilyl) sulfide (TMS, 95% purity) were purchased from J. T. Baker, Alpha Aesar, and Acros Organics respectively. 1-Octadecene (ODE, technical grade 90%), toluene (anhydrous, 99.8%), octane (anhydrous, $\geq 99\%$), acetone (ACS reagent, $\geq 99.5\%$), methanol (HPLC grade, $> 99\%$), 1,2-dichlorobenzene (HPLC grade, 99%), and phenyl-C61-butyric acid methyl ester (PCBM, $> 99\%$ purity) were purchased from Sigma-Aldrich. ODE was degassed by pumping at 80 °C overnight before use, while the other chemicals were used as received without further purification.

Synthesis and Solution Preparation

The synthesis was performed in a single, three-neck, round bottom flask with Schlenk line setting. PbS QDs were synthesized using lead oleate and TMS as precursors in ODE as a non-coordinating solvent, according to known methods.¹ Lead oleate was prepared by pumping the mixture of PbO and OA at 80 °C for 16 h. The resulting solution was stirred vigorously under nitrogen for about 30 min, while being heated to certain temperatures ranging between 80°C - 160 °C depending on the required QD size. Inside a glovebox, the sulfur precursor was prepared by mixing TMS with ODE. This mixture was rapidly injected into the reaction flask at the required injection temperature (i.e. 80 °C for smaller QDs and 160 °C for larger QDs). After TMS injection, slow cooling was allowed to facilitate size focusing and help narrowing the size distribution. Once 35 °C was reached, acetone was injected to isolate the oleate-capped PbS QDs by precipitating them from solution. The precipitate was washed twice with toluene/acetone as solvent/antisolvent mixture, followed by redispersing in toluene. Then, the washing procedure was repeated twice again with toluene/methanol mixture, and finally dissolved in octane. The stock solutions in octane were then diluted with 1,2-dichlorobenzene, or alternatively PCBM in 1,2-dichlorobenzene, while maintaining an OD of 0.1 at the first exciton absorption peak within a 2 mm path length cuvette.

Time-Resolved Absorption Experiments

In this study, Ultrafast Systems Helios UV-NIR femtosecond transient absorption spectroscopy system was used to measure the samples. Helios is equipped with CMOS VIS and InGaAs NIR spectrometers covering the range of 350-800 nm with 1.5 nm resolution at 9500 spectra/s and range of 800-1600 nm with 3.5 nm resolution at 7900 spectra/s, respectively. The probe beam is provided by Spectra-Physics Spitfire Pro 35F-XP regenerative femtosecond amplifier which produces 35fs pulses at 800 nm with 4 mJ of energy per pulse. A small portion ($\approx 60 \mu\text{J}$) of the Spitfire output is routed via a delay line, adjustable pinholes, focusing lens, and variable neutral density filter to a crystal for white light continuum (WLC) generation; and further to the sample via a focusing mirror. Two crystals are available to cover VIS and NIR ranges. A computer controlled delay line is used to vary the delay between the pump and probe pulses that allow transient absorption measurements within a 3.3 ns time window. 1 mJ of the Spitfire output is used to pump TOPAS-C two stage parametric amplifier equipped with frequency mixing stages and non-collinear difference frequency generator that allows tuning from 236 to 12000 nm. TOPAS-C output beam is routed via adjustable pinholes, variable neutral density filter, depolarizer, chopper wheel and focusing lens to excite the sample. Pump and probe beams are overlapping spatially and temporally in the sample. Probe beam is collected by the spectrometer via collimating and focusing lenses, and wave pass filters to attenuate the white light around the Spitfire fundamental at 800 nm. All transient absorption experiments were carried out at room temperature.

The Global fit is the Surface Explorer (SX) global fit. It is a commercial software (Ultrafast Systems LLC, Sarasota, FL 34234, USA). In this type of analysis, (wavelength, time) data matrix is corrected for the chirp of the super-continuum probe pulse and the time zero is adjusted for the real time zero using the coherent signal from the solvent. First step of global fit is singular value decomposition (SVD) of data matrix into principal components. Then, during global fit itself SX uses exponential decay kinetics as fit functions for the Principal kinetics. These fit functions are the same as in single kinetics resonant fit (Fit kinetic item in kinetics menu). This step gives us times: t_0 , t_{IRF} and component lifetimes, optimal to fit all principal kinetics. Then SX determines the amplitudes of the components that best fit the 2D surface in all points. For each wavelength these amplitudes are different, but lifetimes are the same. For more information,

please see SX manual (sections 7 Fitting Kinetics, 8 Principal components via SVD, 9 Global Fit).

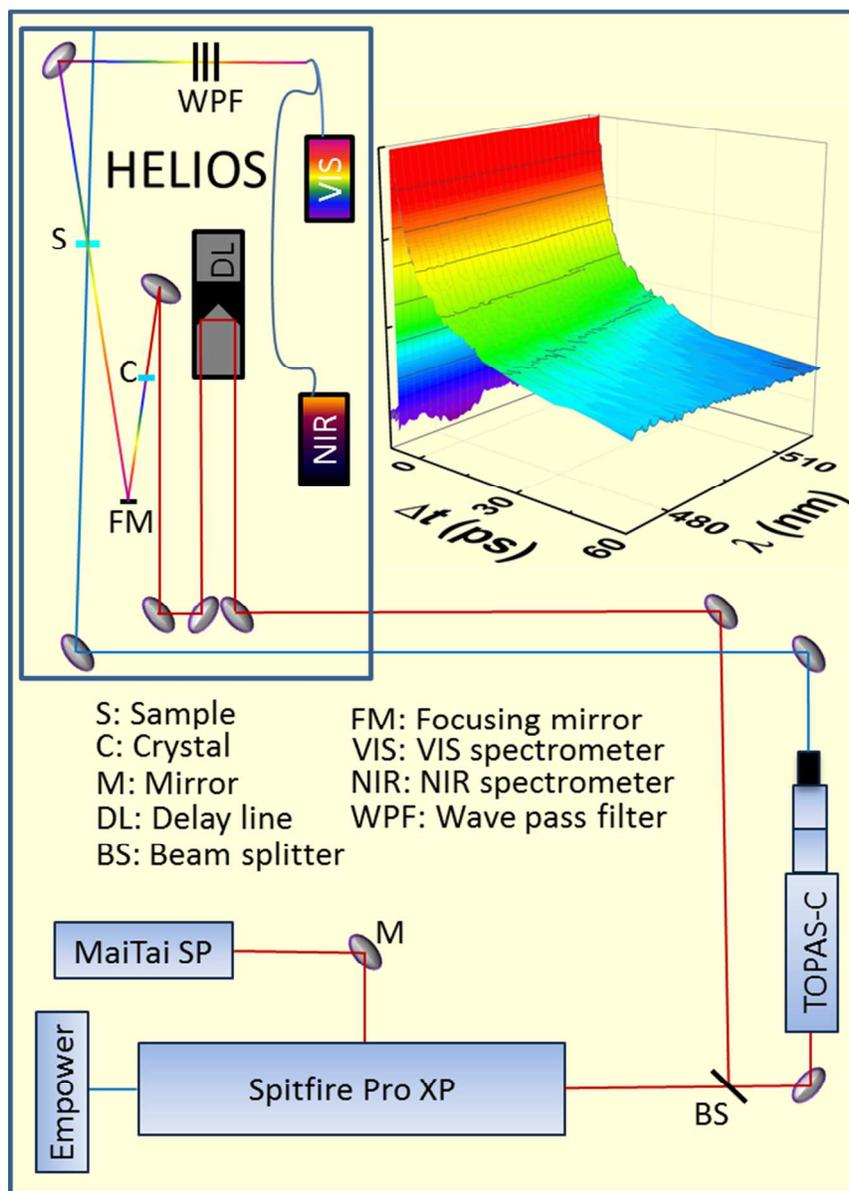


Figure S1: The experimental setup of femtosecond transient absorption spectroscopy showing the integration of the ultrafast Helios UV-NIR spectrometers (Ultrafast systems, FL, USA) with both Spitfire Pro 35F-XP regenerative amplifier (Spectra physics) and TOPAS-C two-stage parametric amplifier.

Supporting Results

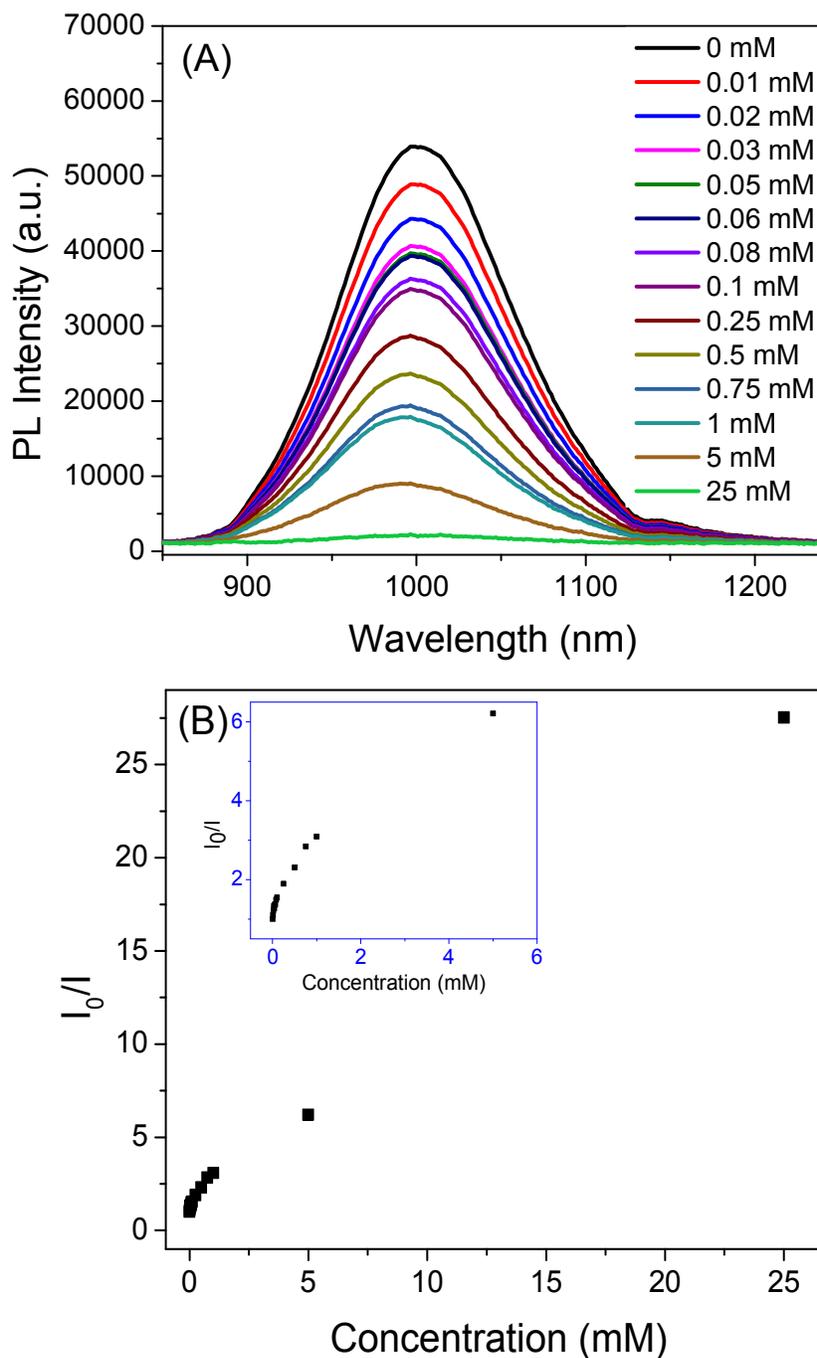


Figure S2: a) Photoluminescence spectra of PbS-880 upon the addition of a larger range of PCBM concentrations (0.01-25mM), in 1,2-dichlorobenzene. b) Stern-Volmer (SV) plot for PbS-880 and PCBM system revealed a deviation from linearity at low PCBM concentrations as clarified in the inset.

Table S1. PL intensity of PbS-880 and PbS-1320 solutions upon the addition of 0 mM, 1mM and 5mM concentrations of PCBM.

PCBM concentration (mM)	PL Intensity I_{PL} (arb. units)
PbS-880	
0	60910
1	20841
5	10213
PbS-1320	
0	30660
1	27943
5	27242

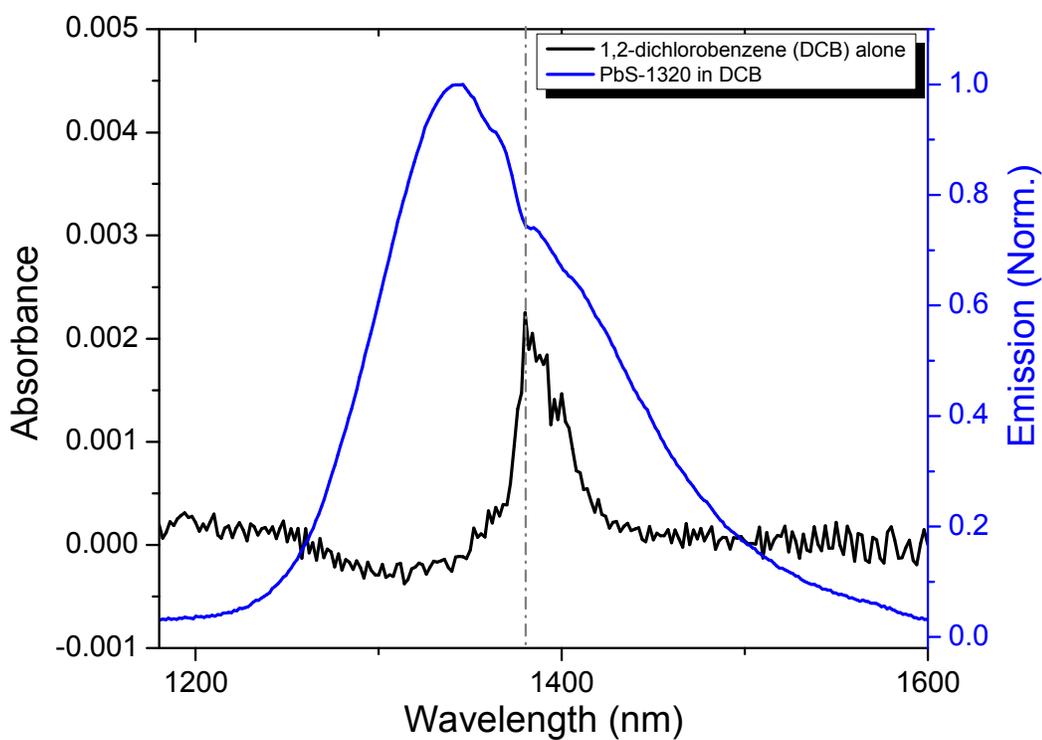


Figure S3: The absorbance of 1,2-dichlorobenzene (DCB) reveals a peak at 1380 nm, which corresponds to the dip observed in the PL spectra of solutions of PbS-1320. Similar spectroscopic features had been also observed for QDs in other solvents.^{2,3}

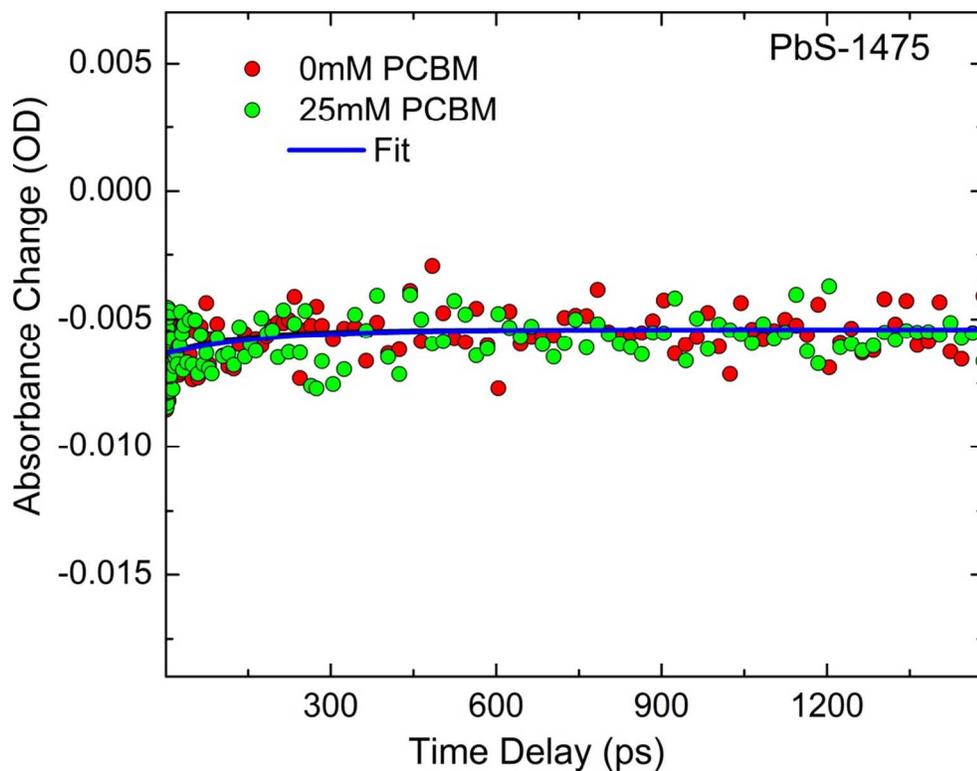


Figure S4: The kinetics of the ground state bleach recovery of PbS-1470 at 0 and 25 mM PCBM reveal that the dynamics behavior lacks both the fast and slow components, demonstrating that all the size contribution here is inactive for electron transfer to PCBM. This evidence further supports the fact that ET can be tuned by quantum confinement effects in the PbS QDs.

References:

- (1) Hines, M. A.; Scholes, G. D. *Adv. Mater. (Weinheim, Ger.)* **2003**, *15*, 1844.
- (2) Knowles, K. E.; Malicki, M.; Weiss, E. A. *J. Am. Chem. Soc.* **2012**, *134*, 12470.
- (3) Peterson, M. D.; Holbrook, R. J.; Meade, T. J.; Weiss, E. A. *J. Am. Chem. Soc.* **2013**, *135*, 13162.