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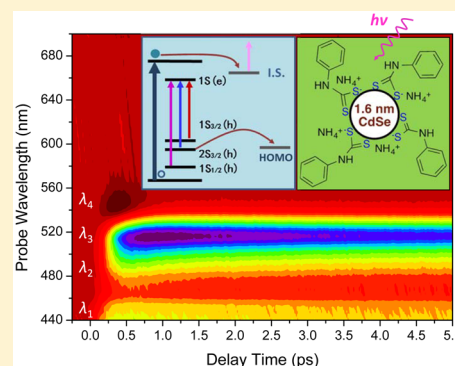
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Molecule-like CdSe Nanoclusters Passivated with Strongly Interacting Ligands: Energy Level Alignment and Photoinduced Ultrafast Charge Transfer Processes

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S Supporting Information

ABSTRACT: Semiconductor nanoclusters (SCNCs) are promising electronic materials for use in solid-state device fabrication, where device efficiency is strongly controlled by charge generation and transfer from SCNCs to their surroundings. In this paper we report the excited-state dynamics of molecule-like 1.6 nm diameter CdSe SCNCs, which are passivated with the highly conjugated ligand phenyldithiocarbamate. Femtosecond transient absorption studies reveal subpicosecond hole transfer ($\tau \approx 0.9$ ps) from a SCNC to its ligand shell based on strong electronic interaction and hole delocalization, and subpicosecond hot electron transfer ($\tau \approx 0.2$ ps) to interfacial states created by charge separation. A series of control experiments were performed by varying SCNC size (1.6 nm vs 2.9 nm) and photon energy of the pump laser (388 nm vs 490 nm) as well as addition of electron quencher (benzoquinone) and hole quencher (pyridine), which rules out alternative mechanisms and confirms the critical role of energy level alignment between the SCNC and its passivating ligands. Understanding such charge carrier transfer dynamics across the SCNC–organic molecule interface is very important to various physical phenomena such as hot carrier relaxation and multiple exciton generation, which together could aid in the design of high-efficiency solar cells and photocatalysts.



1. INTRODUCTION

Efficient charge transfer (CT) across the semiconductor quantum dot (QD)–surface ligand interface is crucial in enhancing the performance of ligand-passivated QDs in many potential applications such as solar cells,^{1–6} light-emitting diodes,^{7–10} and other optoelectronic devices.^{11–14} Commonly used long alkyl chain-containing surface-passivating ligands hinder CT processes. To improve such processes, various dye molecules were used to modify the QD's surface, and ultrafast spectroscopy techniques were implemented to study the electron transfer (ET) or hole transfer (HT) dynamics.^{15–17} It was shown that both the ET and HT processes depend on the structural parameters of the QDs such as size, composition, chemical nature of the surface-passivating ligands, and electronic interaction between QDs and ligands.^{14,18–28} Compared to the amount of information available on excited-state dynamics of metal chalcogenide QDs, the scientific knowledge concerning ultrasmall semiconductor nanoclusters (SCNCs, <2.0 nm in diameter) is very limited^{28,29} and mostly focused on theoretical calculation.^{30–33} To the best of our knowledge, no report is available studying the dynamics of both ET and HT across the ultrasmall SCNC–surface ligand interface.

Ultrasmall SCNCs bridge the gap between small molecules and QDs with discrete highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital energy levels.^{34–36} In QDs a low percentage of atoms occupy the surface and the variety of surface facets leads to inhomogeneous composition, which results in precise information on the electronic structure and dynamics remaining elusive. In contrast, 1.6 nm diameter Cd₃₄Se₃₄ SCNCs, also known as “magic-size” clusters, contain nearly 80% surface atoms,^{37–39} and thus their surface structure is expected to have profound effects on their photophysical properties. Atomically precise, ultrasmall SCNCs therefore have much better ability to provide quantitative information about ET and HT dynamics than traditionally studied QDs through appropriate selection of surface-passivating ligands, which induce a strong SCNC–ligand interaction. Recently, Weiss and co-workers^{40,41} and our group⁴² have shown that attaching phenyldithiocarbamate (PDTC) ligands to CdSe QDs, and SCNCs, respectively, reduced the optical bandgap due to expansion of the hole wave function outside of the inorganic

Received: October 11, 2014

Revised: December 9, 2014

Published: January 8, 2015

core to the ligand monolayer. This expansion is from interfacial orbital mixing due to strong interaction between the SCNC and its ligands.^{43,44} We have shown nearly a 2-fold higher reduction of the optical bandgap of CdSe SCNCs in comparison to QDs, presumably due to their very small size.

In this paper we report for the first time the study of excited-state dynamics of PDTC-passivated 1.6 nm diameter CdSe SCNCs conjugates. We observed a subpicosecond time scale for both ET and HT processes when the SCNCs were excited at a photon energy much larger than the optical bandgap. We explored the dynamics by selectively changing the excitation energy and nanocluster size to prove that interfacial orbital mixing and formation of interfacial states promoted the hole transfer and hot electron transfer from the SCNC core to the PDTC ligand monolayer. Furthermore, appropriate energetic alignment between SCNC orbitals and PDTC molecular orbitals (MOs) is critical to the observed ultrafast ET and HT processes. Understanding such excited-state dynamics could open up new avenues for the design of new ligands as well as new SCNC–ligand conjugates that will exhibit fast charge separation and slow recombination, which have great potential to increase the efficiency of solar cells prepared from them.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Ligand-Passivated SCNCs. Materials.

Cadmium chloride (CdCl_2 , 99.9%), selenium (pellets, 99.9%), dodecylamine (DDA, 98%), 1-hexanethiol (95%), carbon disulfide (CS_2 , 99.9%), aniline (99%), trioctylphosphine oxide (TOPO, 95%), trioctylphosphine (TOP, 90%), hexadecylamine (HDA, 98%), cadmium stearate, toluene (HPLC grade), acetonitrile (HPLC grade), chloroform (HPLC grade), hexane (HPLC grade), methanol (HPLC grade), sure seal dichloromethane (DCM) (>99%), and concentrated ammonium hydroxide (NH_4OH) (ACS grade) were purchased from Sigma-Aldrich and used without further purification. Organic solvents were purged with N_2 for 30 min prior to use.

Synthesis of Phenylthiocarbamate Ligands. Phenylthiocarbamate (PDTC) ligand was prepared according to a literature procedure.⁴⁵ Briefly, 82.0 mmol of CS_2 was added dropwise over 30 min to 41.0 mmol of aniline dispersed in 30 mL of concentrated NH_4OH at 0 °C. The solution was stirred under N_2 overnight. The resulting products for each aniline derivative appeared as suspended solids that ranged in color from yellow to white to gray. These products were washed with cold chloroform and dried under vacuum overnight. The PDTC ligand was stored in the dark before use. The products were characterized by ^1H NMR spectroscopy and electrospray ionization–mass spectrometry.

Synthesis of CdSe Nanoclusters. 1.6 diameter CdSe SCNCs $[(\text{CdSe})_{34}]$ were synthesized using our published procedure with slight modification.⁴⁶ Briefly, in a 100 mL two-neck round-bottom flask, 0.140 g of CdCl_2 mixed with 5 mL of DDA at 30 °C until all solid dissolved. The optically clear solution was cooled to room temperature, and 10 mL of nitrogen-purged toluene was added before the addition of the selenium precursor. Selenium precursor was prepared separately by dissolving 0.06 g of freshly ground selenium powder in a mixture of 785 μL of DDA and 215 μL of 1-hexanethiol at 30 °C under N_2 . After addition of the selenium precursor, the reaction was stirred under N_2 at 40 °C for 2 h. After 2 h, a stable absorption peak was observed, and the SCNCs were precipitated by the dropwise addition of nitrogen-purged

acetonitrile. The yellow solid was collected by centrifugation. The precipitation step was repeated for two more times. Finally, the solid was dried with N_2 and stored in the glovebox for further optical characterization and surface modification.

The CdSe QDs were synthesized according to literature procedure.⁴⁰ 1.0 M trioctylphosphine selenide (TOPSe) solution was prepared inside the glovebox. Briefly, 0.165 mmol of cadmium stearate, 5.02 mmol TOPO, and 8.03 mmol of HDA were loaded in a 100 mL three-neck round-bottom flask, and the mixture was heated at 320 °C under nitrogen until an optically clear solution was appeared. At this point 1.0 mL of TOPSe was injected, and the reaction temperature was maintained at 290 °C. When the QDs displayed an absorption maximum at 541 nm, the reaction mixture was quenched by adding 10 mL of chloroform. CdSe QDs were purified by adding methanol. The purified product was stored inside the glovebox. According to an empirical formula,⁴⁷ CdSe QDs displaying a 541 nm band-edge absorption peak have a diameter of 2.9 nm. The size distribution of CdSe QDs used in the present work, as determined by a TEM image, is 2.9 ± 0.2 nm.

Ligand Exchange Reaction. The ligand exchange reaction was performed according to our published procedure.⁴² Briefly, all samples were prepared inside a nitrogen-filled glovebox and reactions were carried out in a Schlenk line. 0.19 mmol of DDA-coated CdSe SCNCs was dissolved in 10 mL of DCM in a 25 mL two-neck round-bottom flask followed by addition of 0.39 mmol of PDTC ligand. The biphasic reaction mixture was vigorously stirred at room temperature for 48 h. After the reaction mixture displayed its stable lowest energy absorption maximum, it was centrifuged, dried under reduced pressure, and stored inside a glovebox. The PDTC-passivated samples were stable at least a month inside the glovebox. The PDTC-passivated CdSe SCNCs were completely soluble in DCM.

2.2. Transient Absorption Spectroscopy. The transient absorption (TA) spectroscopy system⁴⁸ uses a regeneratively amplified mode-locked Ti:sapphire laser system (Clark-MXR, wavelength = 775 nm, pulse duration $\lesssim 150$ fs, pulse energy ~ 1 mJ at 1 kHz repetition rate). For the present TA experiment, pump sources with two different wavelengths were used: (i) second harmonics of the amplifier output (388 nm) by frequency doubling in a BBO crystal and (ii) output at 490 nm from a noncollinear optical parametric amplifier (NOPA), which was pulse-compressed to ~ 30 fs pulse duration. Output from the femtosecond laser amplifier (775 nm) was split and used to pump the doubling crystal, the NOPA, and a 3 mm thick sapphire plate to generate supercontinuum white light (420–1600 nm) used as the probe source. Pulse energy of the pump light was attenuated to below 0.15 μJ . PDTC-passivated CdSe SCNCs in DCM were contained in a 1 mm thick quartz cuvette. The white-light probe beam was focused into the cuvette, while the pump beam was defocused to ensure the coverage of the probe beam in a noncollinear geometry. After the sample, the pump beam was blocked by a diaphragm, while transmission of the white-light probe beam was refocused onto the entrance slit of a spectrometer. It was then dispersed by a curved grating and detected by a linear array CMOS detector in the wavelength range of 430–730 nm. When 490 nm pump beam was used, an edgepass filter was used to clean the residual pump beam radiation. The delay time between pump and probe pulses (Δt) was variable by moving a retroreflector on a computer-controlled translation stage which reflects the pump beam. An optical chopper revolving at 500 Hz, half of the

repetition rate of the femtosecond laser, was used to modulate the pump beam, and the TA signal was recorded as the change in optical density with pump beam blocked and unblocked:

$$\Delta OD(\Delta t, \lambda) = -\log \left[\frac{I^*(\Delta t, \lambda)}{I_0(\lambda)} \right] \quad (1)$$

where I^* and I_0 are the probe beam transmission at each delay time with the preceding pump beam unblocked and blocked, respectively. Group velocity dispersion in the TA spectrum $\Delta OD(\Delta t, \lambda)$ was corrected using a power law function

$$\Delta t(\lambda) = \Delta t_0 + A|\lambda - \lambda_0|^p \quad (2)$$

in which Δt_0 is the delay time at λ_0 , a reference wavelength. The parameters Δt_0 , A , λ_0 , and p were determined in fitting selected time zeros.

3. RESULTS AND DISCUSSION

3.1. Data Analysis and Exciton Dynamics. Previously, we have shown that functionalization of ultrasmall CdSe SCNC surface with conjugated ligand PDTCs allowed excitonic hole delocalization.⁴² It was observed that maximum delocalization took place for smaller (1.6 nm diameter) CdSe SCNCs because of matching between the energy levels of the SCNC and PDTC ligand orbitals. The delocalization of strongly confined holes to the ligand monolayer resulted in excitonic band gap reduction. The wavelength of the first excitonic transition of the PDTC-passivated CdSe SCNCs was determined in UV-vis absorption measurement to be around 504 nm (Figure 1),⁴² corresponding

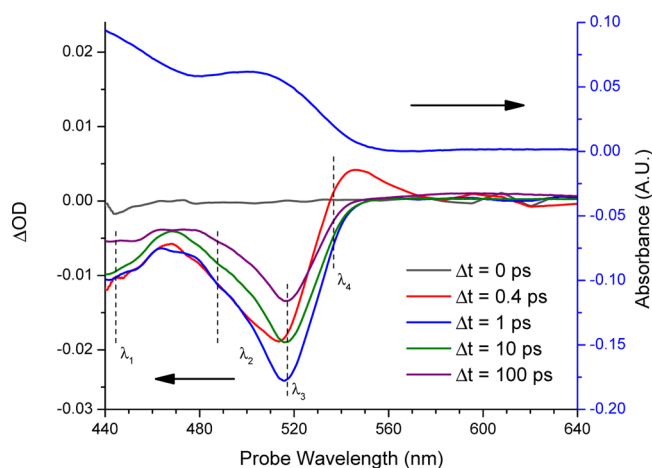


Figure 1. Steady-state absorption spectrum (top) and TA spectra at different pump–probe delay times (bottom) of PDTC-passivated CdSe SCNCs ($d = 1.6$ nm). Vertical dashed lines indicate the center wavelengths of TA spectra. Note that maximum of the positive PA signal is red-shifted from λ_4 to ~ 545 nm due to strong influence by the negative PB signal at λ_3 .

to a bandgap of $\Delta E_g \approx 2.46$ eV. Based on the previous experimental and theoretical results of Norris et al.,⁴⁹ absorption at different wavelengths can be assigned to different excitonic transitions, which are better resolved in the TA spectrum (Figure 1). The 388 nm pump source (photon energy = 3.20 eV, i.e., 0.74 eV above bandgap) excites the $1P(e) - 1P_{1/2}(h)$ and $1P(e) - 1P_{3/2}(h)$ excitonic transitions, probably with contamination from the $1S(e) - 2S_{1/2}(h)$ transition. In the short wavelength region, the TA spectrum shows negative photobleaching (PB) signal with three partially resolved peaks

at $\lambda_1 = 445$ nm ($h\nu = 2.79$ eV), $\lambda_2 = 488$ nm ($h\nu = 2.54$ eV), and $\lambda_3 = 517$ nm ($h\nu = 2.40$ eV) that can be assigned to $1S(e) - 1S_{1/2}(h)$, $1S(e) - 2S_{3/2}(h)$, and $1S(e) - 1S_{3/2}(h)$ transitions, respectively (Figure 2).^{4,15,50–52} The PB signal at all three

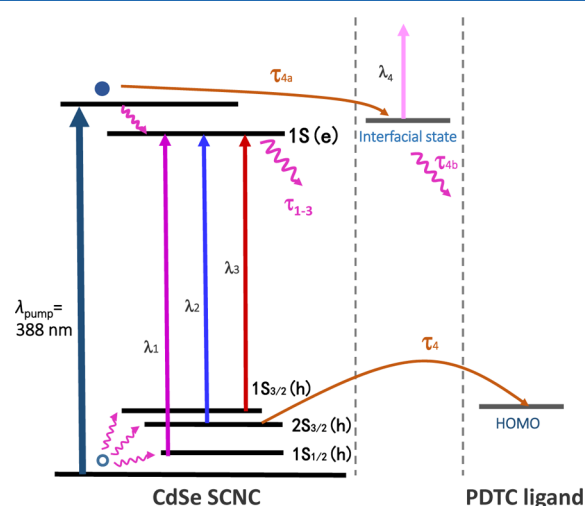


Figure 2. Energy diagram and photoinduced processes in the CdSe SCNC–PDTC conjugate. Arrows mark the pump wavelength and the center wavelengths in TA spectra (Figure 1). Wavy arrows and curved arrows indicate relaxation and CT processes, respectively.

wavelengths is attributed to filling of the $1S(e)$ electron state following photoexcitation of the $1P(e) - 1P(h)$ transition that generates excitons and subsequent electron and hole relaxation. The exciton bleach recovery kinetics at these wavelengths are therefore similar to one another (Figure 3a) and can be fit using a multiexponential decay function with time constants of $\tau_1 = 632$ ps, $\tau_2 = 23$ ps, and $\tau_3 = 2.7$ ps (see section 3.2 for details).

To better understand the underlying dynamics and interpret the observed ultrafast kinetics, control TA experiments with electron and hole quenchers^{53,54} were also performed. Benzoquinone (BQ) was added into the solution to quench electrons in photoexcited CdSe SCNCs. The aforementioned fast decay components ($\tau_3 = 2.7$ ps, $\tau_2 = 23$ ps) were significantly accelerated while the slow component ($\tau_1 = 632$ ps) was much less affected (Figure 4a–c). In comparison, when pyridine, a hole quencher, was added, the change of fast kinetics was insignificant at 455 nm and undetectable at 488 and 517 nm (Figure 4a–c). This confirms the previous observation that the exciton bleach signal is dominated by electrons rather than holes.²⁰ The slow and fast components are attributed to exciton recombination at the band edge^{55,56} and electron transfer to the passivating ligands, respectively.^{15,17}

Detailed comparison between the exciton bleach recovery kinetics at these three peak wavelengths reveals a unique fast decay component at λ_2 with a decay constant of $\tau_4 \sim 900$ fs (Figure 3b). The possibility of TA signal from the DCM solvent or PDTC ligands at λ_2 has been ruled out by negative results in control experiments using these samples. Subpicosecond PB recovery process was previously observed in TA spectra of CdSe QDs^{57,58} and was attributed to electron relaxation following exciton generation. However, it was detected at the wavelength corresponding to the $1P(e) - 1P_{3/2}(h)$ transition, which is out of the detection range of the present experiment. At such wavelength, the growth of the PB signal in the delay time window of 0 to 400 fs was assigned to

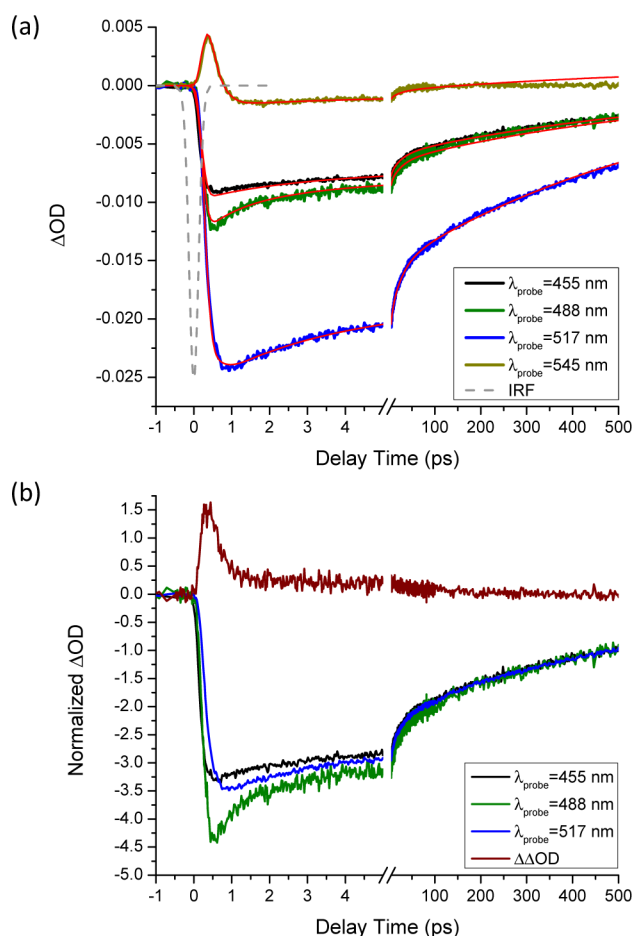


Figure 3. (a) Ultrafast kinetics of the CdSe SCNC–PDTC conjugate at four peak wavelengths of the TA spectra. The dashed gray line represents instrument response function (IRF). The thin red lines are simulation using parameters determined in global fitting (Table 1). (b) Ultrafast kinetics normalized to their slow decay component at long delay time. The positive trace ($\Delta\Delta OD$) is subtraction of normalized kinetics at 488 nm from that at 517 nm, which unravels the hole transfer as described in the text.

the relaxation of electrons from higher energy levels to the 1P state, whereas the recovery of the PB signal ($\tau = 540$ fs) was assigned to 1P to 1S electron relaxation and is complementary to a secondary growth ($\tau = 530$ fs) at the wavelength of 1S(e)–1S_{3/2}(h) transition. In the present work of CdSe SCNC–PDTC ligand conjugates, the subpicosecond PB recovery process was observed at λ_2 exclusively, corresponding to the 1S(e)–2S_{3/2}(h) transition. Electron relaxation is therefore unlikely to be the underlying mechanism.

Because transients at λ_1 , λ_2 , and λ_3 share the same electron state, the observed difference in the bleach recovery kinetics can only be explained by different dynamics involving the hole states. λ_2 is the center wavelength of the 1S(e)–2S_{3/2}(h) transition. The subpicosecond decay component is therefore attributed to hole transfer from the 2S_{3/2}(h) level of the CdSe SCNC to the HOMO level of the PDTC ligand. According to previous effective mass approximation calculation⁵⁹ and electrochemical measurements,^{60–62} the valence band edge of 1.6 nm CdSe SCNCs would be $E_b = -6.16$ eV. The HOMO energy of PDTC is calculated to be ~ -6.15 eV.⁴¹ This energetic alignment between the valence band of SCNC and the HOMO of PDTC enhances the possibility of strong interfacial orbital

mixing and formation of hybrid orbitals (Figure 2). Thus, strongly confined hole wave functions of ultrasmall CdSe SCNCs can expand beyond the inorganic core boundary to the ligand monolayer through hybrid orbitals. Coupling and hybridization between the lowest-energy hole states of CdSe SCNC and the ground state of PDTC ligand is therefore expected,^{40,41,63} which facilitates exciton relaxation and hole transfer.³¹ Although PB signal due to state filling that involves three hole states (1S_{3/2}, 2S_{3/2}, 1S_{1/2}) were detected, only hole transfer from the 2S_{3/2}(h) state was observed. This is probably due to the larger extension of the 2S_{3/2}(h) orbital of the CdSe SCNC and hence better overlap with the HOMO of the PDTC ligand (Figure 2). It is worth noting that for CdSe QDs, the PB signal in the TA spectra is mainly due to the photoexcited electrons residing in the lowest energy 1S(e) state, whereas the contribution of holes is usually insignificant.²⁰ The observation of hole transfer in the present experiment on SCNCs is attributed to the relatively high excitation energy and the relatively large energy separation between hole states due to the ultrasmall size of the SCNCs.

In the longer wavelength region, the TA spectrum of CdSe SCNC–PDTC conjugates possesses a positive photoabsorption (PA) signal centered at $\lambda_4 = 536$ nm ($h\nu = 2.31$ eV, see Figure 1). The PDTC molecule does not have absorption at 388 nm (Figure S.1), and no TA signal of PDTC in DCM was observed. Previously, positive signals in QD systems in the long wavelength region were assigned to exciton–exciton interactions (in CdSe QDs, $r \sim 5.7$ nm)^{20,57} or to absorption of charged free radicals resulted from electron transfer (in CdSe/CdS QD–MV²⁺ conjugates).⁵⁴ In order to unravel the underlying mechanism of the PA signal, TA spectroscopy was applied to investigate the photoinduced dynamics of 1.6 nm diameter CdSe SCNCs passivated by dodecylamine (DDA) ligands, which, unlike PDTC ligands, are not strongly coupled to the CdSe cores because of mismatch of the energy levels. TA spectrum of DDA-passivated CdSe SCNCs (Figure S.2) is dominated by broad PA signal in the longer wavelength region (>460 nm). The PB signal due to state filling is almost completely out of the detection range of the array detector although weak negative signal at the shorter wavelength edge of the detection range (~ 450 nm) was observed. The ultrafast dynamics of the PA signal can be fit to a biexponential decay with time constants much longer than 1 ps. A similar broad and long-lived PA signal was previously observed for ligand-protected QDs^{15,17} and was attributed to red-shifted 1S–1S excitonic transitions due to exciton–exciton interaction. This PA signal of DDA-coated CdSe SCNCs, however, is significantly different from the PA signal that was observed for CdSe SCNC–PDTC ligand conjugates, which is much narrower in the wavelength domain and is of subpicosecond time scale. Exciton–exciton interaction is, therefore, unlikely to be the underlying mechanism of the PA signal centered at λ_4 .

The positive TA signal cannot be attributed to radical cations either: Its subpicosecond time scale is too short compared to that of the radical cation signal (on the order of 100 ns as reported previously⁵⁴). Moreover, unlike the PA signal of radical cations,⁵⁴ the positive signal of the CdSe SCNC–PDTC conjugate at ~ 545 nm did not disappear when the electron quencher BQ was added (Figure 4d). It is therefore attributed to new charge transfer states (CTs) created by charge separation across the SCNC–ligand interface. CTs are usually formed within 0.1 ps,^{64–66} which is consistent with the observation of the present experiment. They are then populated

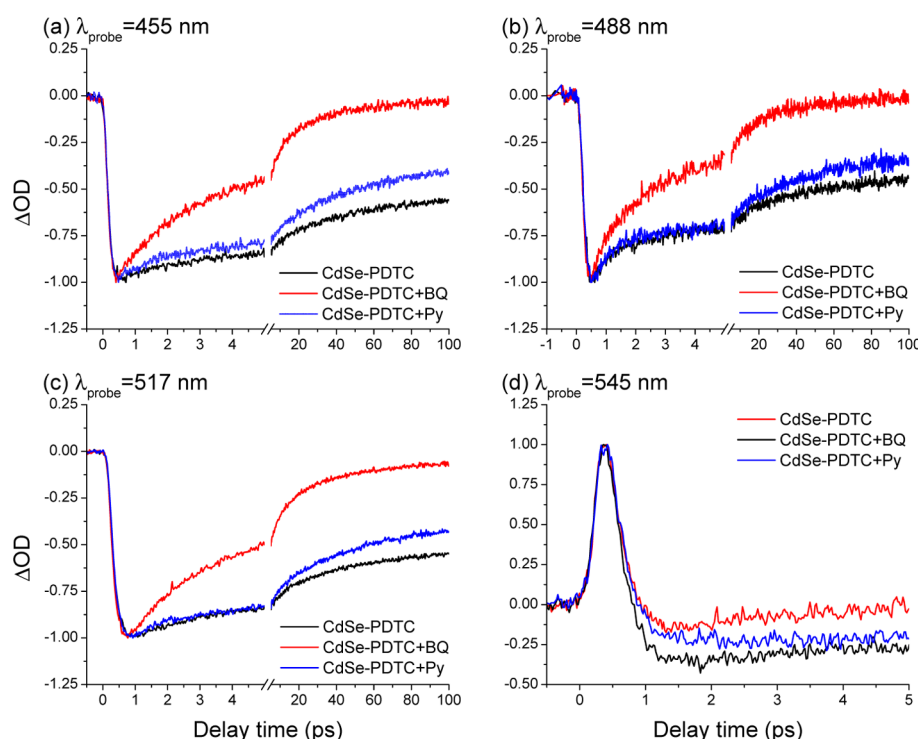


Figure 4. Ultrafast kinetics of PDTC-passivated 1.6 nm CdSe SCNCs at four wavelengths with benzoquinone (BQ) as electron quencher and pyridine (Py) as hole quencher. The three kinetics at each wavelength are normalized to their maximum ΔOD .

via hot electron transfer upon photoexcitation of 388 nm. No positive signal was observed when lower pump photon energy was used (for instance, $\lambda = 490$ nm; see Figure 5). Such a

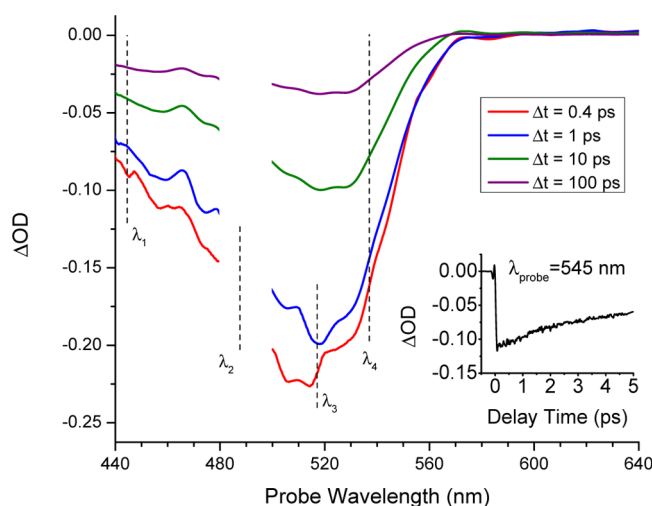


Figure 5. TA spectra of PDTC-passivated 1.6 nm CdSe SCNCs with 490 nm pump wavelength. Note the absence of positive signal in the long wavelength region. Inset shows decay kinetics at 545 nm.

comparison suggests that the interfacial CTSs involved in the observed hot electron transfer process are above the conduction band edge of CdSe SCNCs, which facilitates strong electronic coupling and allows hot electron transfer to PDTC ligands. Energy level alignment by itself, however, does not ensure hot electron transfer. Following excitation by high-energy photons, hot charge carrier transfer is in competition with and may be outrun by relaxation processes. Observation of subpicosecond hot electron transfer in the SCNC–PDTC

conjugates in the present experiment implies that the hot electron transfer rate is comparable to that of the relaxation processes. This is attributed to large energy spacing between electron states of the inorganic core and the well-engineered nanocluster–surface ligand interface that removes electron trap states, both of which slow down electron cooling.

Time evolution of the PA signal can be well-simulated using a two-step consecutive reaction model, in which the intensity of PA matches the population of the interfacial states (see section 3.2 for details). The growth of the PA signal (with rate constant $k_{4a} = 5.37 \text{ ps}^{-1}$) corresponds to hot electron transfer to the interfacial state, while its decay ($k_{4b} = 5.45 \text{ ps}^{-1}$) may be attributed to ultrafast recombination and relaxation processes.

Electronic coupling between the orbitals of the CdSe SCNCs and the passivating ligands depends on their energy level structures. Modification of either SCNCs or ligands can therefore affect the CT processes. Previously, we have shown that exciton delocalization in CdSe SCNC decreased as its size was increased.⁴² Based on this observation, different TA signals are expected for QDs. To further explore the ultrafast hole and electron transfer processes, we varied the sizes of nanocrystals, while PDTC surface coating remained unchanged. Indeed, when PDTC passivated CdSe QDs with $d = 2.9 \text{ nm}$ and $E_g = 2.15 \text{ eV}$ ($\lambda = 578 \text{ nm}$, see Figure S.3 for steady-state absorption spectrum) were used to investigate the excited state dynamics, different TA spectra were observed (Figure 6). The positive signal in the long-wavelength region is significantly weaker compared to that of the 1.6 nm CdSe SCNCs. The subpicosecond decay component at λ_2 (with time constant τ_4) is almost absent. Such observation supports the attribution of the PA signal at λ_4 to charge transfer rather than exciton–exciton interaction because magnitude of the PA and PB signal due to exciton–exciton interaction is insensitive to the size of QDs or SCNCs.⁵⁸ Moreover, it suggests that both hot electron

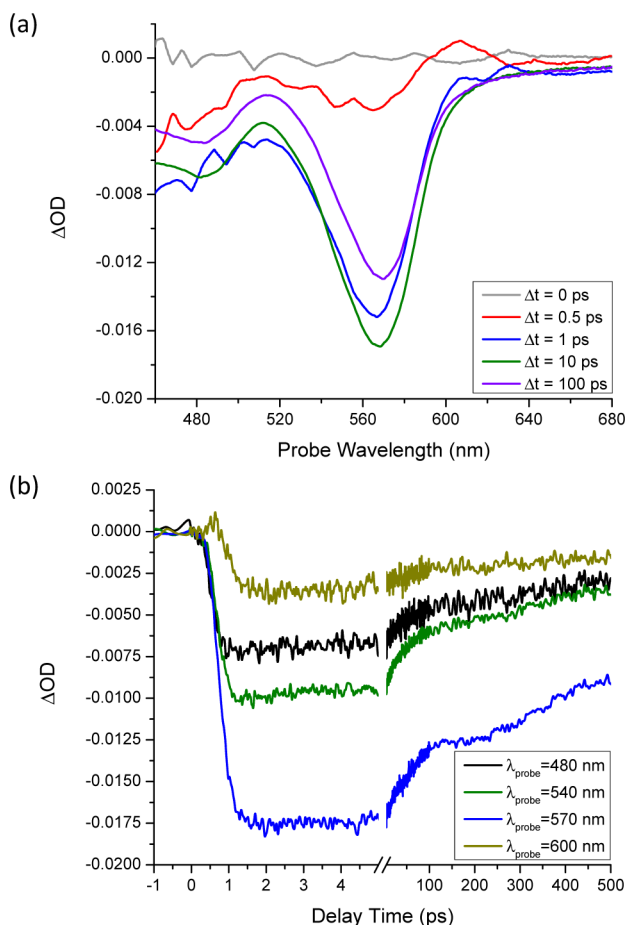


Figure 6. (a) TA spectra of the CdSe QD-PDTC conjugate with $d = 2.9$ nm and bandgap $E_g = 2.15$ eV ($\lambda = 578$ nm) at different pump-probe delay times. (b) Ultrafast kinetics at four wavelengths of the TA spectra.

and hole transfer processes are sensitive to energy level alignment.

3.2. Global Fitting. To unravel the exciton dynamics and derive quantitative information about charge transfer processes, experimentally obtained 3D TA spectra were fit to a model that takes into account ultrafast processes at all four center wavelengths:

$$\Delta OD(\lambda, \Delta t) = \left\{ \sum_{i=1}^3 \left[A_i(\lambda) \frac{\sum_{j=1}^{3 \text{ or } 4} \gamma_j e^{-\Delta t/\tau_j}}{\sum_{j=1}^{3 \text{ or } 4} \gamma_j} \right] + A_4(\lambda) \left[\frac{k_{4a}}{k_{4b} - k_{4a}} (e^{-k_{4a}\Delta t} - e^{-k_{4b}\Delta t}) \right] \right\} \otimes \text{IRF}(\Delta t) \quad (3)$$

In the wavelength domain, the spectral profile was simulated by a multipeak Gaussian line shape. Each component can be written as

$$A_i(\lambda) = \frac{Y_i}{\sigma\sqrt{2\pi}} e^{-(1/2)[(\lambda-\lambda_i)/\sigma]^2} \quad (4)$$

with $i = 1-4$ and where λ_i 's are the center wavelengths of absorption. The ultrafast kinetics at $\lambda_1 \sim \lambda_4$ were then fit to eq 3 simultaneously. At $\lambda_1 \sim \lambda_3$, the exciton dynamics are fit to multiexponential decay with three (at λ_1 and λ_3) or four (at λ_2)

components with different weights (γ_j) and time constants (τ_j). At λ_4 the positive PA signal is fit to a two-step consecutive reaction model (the second term in the curly brackets in eq 3). In simulating the 3D TA spectra, ultrafast kinetics are convolved with instrument response function:

$$\text{IRF}(t) = \frac{Y_{\text{IRF}}}{\sigma_{\text{IRF}}\sqrt{2\pi}} e^{-(1/2)(t/\sigma_{\text{IRF}})^2} \quad (5)$$

with $\sigma_{\text{IRF}} = 127$ fs. To save computation time, convolution was performed only in the region of $\Delta t = -0.5$ to 5 ps. A small positive offset had to be added to $A_4(\lambda)$ to compensate the strong influence by the negative signal at λ_3 .

Experimentally obtained TA spectra of 1.6 nm CdSe SCNC-PDTC conjugates were simulated using eq 3 and time constants, among other parameters, were determined in a global fit. The fit ultrafast kinetics are shown in Figure 3 while fit TA spectra in the wavelength domain are compared to experimental ones in Figure 7. The fit parameters are listed in Table 1.

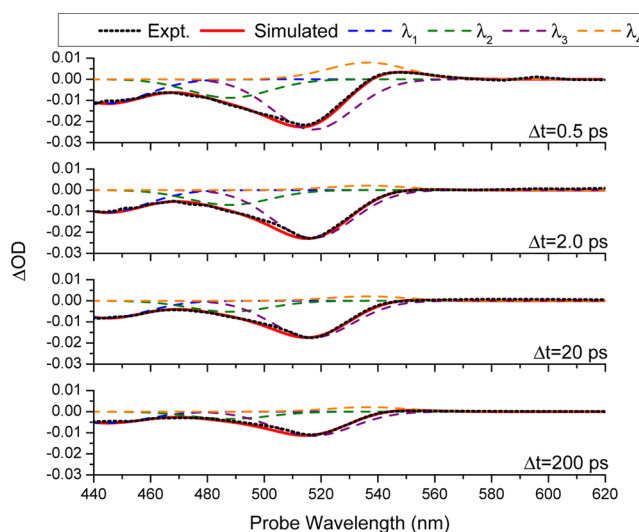


Figure 7. Simulation of PDTC-passivated 1.6 nm CdSe SCNCs with 388 nm pump wavelength using parameters determined in the global fit (Table 1). Dotted lines are the experimental spectra. Solid red lines are simulated spectra. Dashed lines are components of TA spectra at different peak wavelengths: $\lambda_1 = 445$ nm, $\lambda_2 = 488$ nm, $\lambda_3 = 517$ nm, and $\lambda_4 = 536$ nm.

4. CONCLUSIONS

In conclusion, we have studied the excited-state CT dynamics in molecule-like CdSe SCNCs coated with conjugated PDTC ligands. Subpicosecond PA signal was detected at a wavelength that is longer than the 1S-1S excitonic transition. PB recovery dynamics were observed at the wavelengths of three excitonic transitions that involve the 1S electron state. In addition, an extra subpicosecond PB recovery process is distinguishable at the 1S(e)-2S_{3/2}(h) transition wavelength. Control experiments have been carried out in order to unravel the underlying mechanism for the subpicosecond PA and PB processes. Based on the experimental results, it is unlikely that the subpicosecond dynamics are due to exciton-exciton interaction and the electron relaxation process. The subpicosecond PA and PB recovery processes are attributed to hot electron transfer (ET) and hole transfer (HT) from the CdSe SCNC core to the

Table 1. Parameters Determined in Fitting the TA Spectra

λ_1	λ_2	λ_3	λ_4	(in nm)
445	488	517	536	
Y_1	Y_2	Y_3	Y_4	
-0.43	-0.38	-0.92	1.37	
τ_1	τ_2	τ_3	τ_4	(in ps)
632	23	2.7	0.9	
γ_1	γ_2	γ_3	γ_4	
1 (fixed)	0.32	0.32	0.62	
k_{4a}	k_{4b}			(in ps ⁻¹)
5.37	5.45			
σ				(in nm)
14				
σ_{IRF}				(in fs)
127				

ligand monolayer, respectively. The HT process is subject to strong interfacial orbital mixing and formation of hybrid orbitals between the valence band orbitals of SCNC and the HOMO of the PDTC ligands,^{40,41,43} while the subpicosecond ET process is attributed to hot electrons transferred to interfacial CTSs following photoexcitation using 388 nm pump source.

The present investigation will provide important guidelines in the preparation of highly efficient electronic materials for the design of optoelectronic devices as follows: (1) Various types of QDs are commonly used as sensitizers in photovoltaic cells where fast transfer and stabilization of photoexcited holes are extremely important to preventing photovoltaic surface corrosion. From the TA analysis we observed a fast HT from the 2S hole level of CdSe SCNC to the HOMO level of PDTC ligand. Therefore, appropriate ligand passivation of both QDs and SCNCs will provide a better understanding of the interfacial hole transfer dynamics, which will allow us to enhance the long-term stability of photovoltaics. (2) Capturing hot electrons before they relax to the band edge (“electron cooling”) can increase the efficiency of photovoltaic devices.⁶⁷ The positive signal observed in the long-wavelength region is not only size dependent but also influenced by pump photon energy. Absorption of 388 nm photons populate the conduction band of SCNCs with hot electrons,^{68,69} which are transferred to the interfacial states before relaxing to the conduction band edge because of the strong interfacial electronic interaction between the CdSe SCNC and PDTC. Extraction of hot electrons will likely outpace intraband electron cooling, which has a subpicosecond time constant.⁷⁰ This is important for enhancement of the efficiency in photovoltaic applications. (3) Because of the large electronic level spacing—couple of hundred meV as has been calculated in the literature,^{49,71,72} as well as determined by the measured TA peak wavelengths—the hot carrier cooling of our strongly confined 1.6 nm CdSe SCNCs is much slower than in QDs,²¹ which makes possible the observation of HT and hot electron transfer signals in the TA spectrum. The carrier cooling phenomenon is strongly correlated with multiple exciton generation (MEG)^{73–75} and if the cooling rate is slower than the MEG rate, one will be able to generate a large photocurrent in SCNC-based photovoltaic cells.⁶ Taken together, we believe that passivating the surface of ultrasmall SCNCs with highly conjugated organic ligands containing various chemical substituents that both participate in strong electronic coupling

and create a larger number of interfacial hybrid orbitals will provide better control over the manipulation of rates of hot electron and hole transfer, intraband cooling, and carrier recombination and thus facilitate the fabrication of highly efficient photovoltaic devices.

■ ASSOCIATED CONTENT

§ Supporting Information

TA spectrum of DDA-coated CdSe SCNCs; absorption spectra of PDTC in water and 2.9 nm diameter CdSe QDs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Y.X., B.P., and J.L. gratefully acknowledge the financial support of the Department of Energy via its EPSCoR grant (DE-FG02-07ER46375). B.P. and J.L. acknowledge financial support from the University of Louisville. R.S. and M.B.T. acknowledge IUPUI startup funds.

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