Charge Transfer Dynamics in Cadmium Chalcogenide Quantum Dots based Heterostructures

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This work is dedicated to my parents.

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I love you both.

कर्मण्येवाधिकारस्ते मा फलेषु कदाचन।
मा कर्मफलहेतुभूतस्ते सऽसऽचर्येऽक्षणे॥ नमः

- Shrimad Bhagavad Gita
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Abstract

Quantum confinement effects in semiconductor nanocrystals or quantum dots (QDs) give rise to unusual electronic properties such as, size dependent bandgaps, high molar absorptivities and in some cases, hot carrier extraction and multi-exciton generation, which makes them suitable to harvest solar energy. Competition between charge transfer and electron-hole recombination determines the efficiency of charge separation and thus the performance of QDs based electronic devices. Compared to the bulk semiconductors, surface of QDs significantly affects the opto-electronic properties of QDs due to high surface to volume ratios. The difference in the chemical environment of the surface atoms with that of bulk results in mid-gap states which can trap photoexcited charge carriers. This dissertation explores the role of these surface states in charge transfer and draws comparisons with charge transfer from band edge states.

Mesoporous titanium oxide (TiO$_2$) is often used as the electron extracting component in dye sensitized and QDs based solar cells. CdSe QDs were assembled on TiO$_2$ nanoparticles (NPs) using linker assisted assembly (LAA) approach and electron transfer was studied from band edge and surface states of CdSe QDs to TiO$_2$ NPs using steady-state and time-resolved spectroscopy. Electron transfer was found to be 2-3 times faster from band edge states as compared to surface states, consistent with driving force dependent electron transfer. Well passivated core/shell CdSe/ZnS QDs showed improved electron transfer performance to TiO$_2$ despite the presence of a spatial and energetic barrier of ZnS shell.

Ill-defined features of CdSe QDs-TiO$_2$ donor-acceptor systems such as driving force, surface coverage of QDs on TiO$_2$, distance between donor and acceptor renders it difficult to study fundamental aspects of charge transfer. Molecular acceptors, on the other hand, have well defined energy levels and surface coverage of these acceptors can be easily quantified using various
analytical techniques. We studied hole transfer dynamics in well passivated chloride treated CdTe QDs tethered to molecular hole acceptors ferrocenylhexanethiol (FcC₆SH). ¹H NMR spectroscopy allowed for facile quantification of surface coverage of FcC₆SH on CdTe QDs. Chloride treated CdTe QDs were found to undergo effective ligand exchange with FcC₆SH resulting in at least 10 times higher coverage of FcC₆SH as compared to untreated as-synthesized CdTe QDs. Higher coverage of molecular acceptor on chloride treated CdTe QDs provided multiple hole transfer pathways which facilitated highly efficient (~99%) hole transfer.

Oleate capped CdE QDs (E = S, Se and Te) were ligand exchanged with FcC₆SH to unravel the hole transfer dynamics from band edge and surface states of CdE QDs to molecular hole acceptors. Trends in rate constant of hole transfer from band edge and surface states were consistent with driving force dependent hole transfer. Hole transfer to surface bound thiolates was found to be much slower for CdSe and CdS QDs, and absent in CdTe QDs, precluding the possibility of sequential hole transfer from QDs to thiolates to ferrocene.

Finally, charge separation in a novel type II heterostructure was studied using ns and ps timescale transient absorption spectroscopy where V₂O₅ NWs were interfaced with CdE QDs using successive ionic layer adsorption and reaction (SILAR) and LAA approach. Type II band offsets between the NWs and QDs resulted in localization of electrons in NWs and holes in QDs. All V₂O₅/CdE heterostructures showed ultrafast charge transfer and long-lived charge separated state, which can be potentially very useful for photocatalysis and solar energy harvesting.
Chapter I

Introduction to the Electronic Properties of Quantum Dots
Quantum dots (QDs) are semiconductor nanocrystals which show size-dependent optical and electronic properties. QDs are not only intriguing to study for fundamental basic science but also have found useful applications in QD based solar cells, photocatalysts, LEDs, imaging probes, and field effect transistors (FETs).

In a bulk semiconductor, the large number of atoms results in molecular orbitals having very similar energies, which form a continuum of electronic states (or bands). Bonding interactions (σ) between the atomic orbitals form the basis of the valence band (VB), and similarly anti-bonding interactions (σ*) form the basis of the conduction band (CB) (Figure 1.1). At 0 K, VB is completely filled with electrons and CB is completely empty. The energetic gap between the VB and CB is called the electronic bandgap (E_g) and is a characteristic of the material. Materials having bandgap between ~0.3-3.8 eV are considered as semiconductors.¹

At temperatures above 0 K, electrons in the VB may gain enough thermal energy to be excited into the CB. This electronic transition from VB to CB is analogous to the transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) in molecules and can also be achieved with infrared, visible and low-energy ultraviolet radiation at room temperature. The excitation of an electron from VB to CB leaves a positive charge vacancy (also known as hole) in the VB. In bulk semiconductors, the charge carriers (electrons and holes) can form a bound state when they approach each other in space. This bound electron-hole pair is called a Wannier exciton and can be treated as hydrogen atom-like bound state. The physical
distance between the electron and hole in a bulk exciton is called Bohr exciton radius ($a_B$) and can be expressed as:

$$a_B = \frac{\hbar^2 \varepsilon}{e^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$

(1.1)

where $\hbar$ is reduced Planck’s constant, $\varepsilon$ is the dielectric coefficient of the semiconductor material, and $m_e^*$ and $m_h^*$ are the effective masses of electron and hole respectively. The values of $m_e^*$ and $m_h^*$ are computed from the dispersion of CB and VB of semiconductor material near the respective band edges and are a measure of how fast the particle (electron or hole) accelerates in an applied electric field. For cadmium chalcogenide semiconductors, the values of $m_e^*$ are
typically much smaller than the values of $m_h^*$.\(^1\) When the size of a semiconductor becomes comparable to or smaller than the Bohr exciton radius, quantum confinement effects become dominant. The confinement of charge carriers within the QD’s volume results in discrete energy levels within the CB and VB of QDs rather than continuum of states observed in bulk semiconductors. The shared features of QDs with molecules and bulk semiconductors renders them intriguing to study to understand the link between quantum and bulk phenomena.

QDs are typically quasi-spherical semiconductor nanocrystals, and the quantum confinement effects in QDs can be understood by a “particle-in-a-sphere” model.\(^2\) Application of this model to QDs was developed in detail by Brus, Efros and others\(^3\)–\(^5\), and is summarized in the following paragraphs. In this model, the particle is assumed to be confined in a sphere of radius $R$ with zero potential inside and infinite potential outside the sphere. Solving the Schrodinger equation for this system yields the following wavefunction:

$$\Phi_{n,l,m}(r, \theta, \phi) = C \frac{j_l(k_{n,l} r) Y_l^m(\theta, \phi)}{r}$$

where $C$ is a normalization constant, $Y_l^m(\theta, \phi)$ is a spherical harmonic and $j_l(k_{l,n} r)$ is the $l$th order spherical Bessel function. The corresponding energies are:

$$E_k = \frac{\hbar^2 k_{n,l}^2}{2m}$$

where $k_{n,l} = \alpha_{n,l}/R$, where $\alpha_{n,l}$ is the $n^{th}$ root of the $l^{th}$ order spherical Bessel function. The electronic states of this system are characterized by quantum numbers $n$ (1,2,3..), $l$ (s,p,d...) and $m$. The energy is proportional to $1/R^2$ and therefore, is strongly dependent on the size of the sphere. However, to realize a more realistic model for QDs, several refinements have to be made to the previously discussed model. For instance, the sphere is filled with atoms and therefore the potential
inside the sphere cannot be uniformly zero. The periodic potential introduced by the atoms can be incorporated by using the effective mass approximation where electrons and holes behave as free particles with effective masses \( m_e^* \) and \( m_h^* \) respectively. Then, the energies of the CB and VB in QDs can be estimated as:

\[
E_k^c = \frac{\hbar^2 k^2}{2m_e^*} + E_g \tag{1.4}
\]
\[
E_k^v = -\frac{\hbar^2 k^2}{2m_h^*} \tag{1.5}
\]

where, \( E_g \) is the bulk bandgap of semiconductor material. Thus, the energy required for a transition from VB to CB becomes:

\[
\Delta E = E_k^c - E_k^v \tag{1.6}
\]

\[
\Delta E = E_g + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \tag{1.7}
\]

However, the refined model still has not taken the Coulombic interactions between the bound electron and hole into account. Since Coulombic interaction scales with \( 1/R \), while the energies of electrons and holes scale with \( 1/R^2 \), the size-confinement effects dominate in the small semiconductor nanocrystals. Therefore, in strong confinement regime, the charge carriers can be treated as free particles in a sphere, and the Coulombic interaction term \((-E_c)\) can simply be added as a first-order correction to the energies of electron-hole pair. Thus,

\[
\Delta E = E_g + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - E_c \tag{1.8}
\]
The lower effective mass of electron as compared to hole results in significant size dependence of CB as compared to the VB in QDs. Figure 1.2 shows the optical absorption spectra of different sizes of CdSe QDs. The Bohr radius for bulk CdSe is 5.6 nm.\textsuperscript{6} As the size of the QDs increases, the first-excitonic peak shifts to longer wavelengths (lower energies), consistent with quantum confinement effects as explained above.

**Figure 1.2:** Absorption spectra of CdSe QDs of different sizes.
Core vs Surface States

QDs exhibit high surface-to-volume ratios because of their nanoscale dimensionality. Since the surface constitutes a significant fraction of a QD, the properties of surface can affect the electronic and optical properties of QDs significantly. In cadmium chalcogenide QDs (CdE where E= S, Se or Te), the electronic structure of QDs can be qualitatively understood by MO theory (Figure 1.3), where the VB of QDs have predominant contributions from fully filled E^2- valence shell p orbitals and CB from the unfilled 5s Cd^{2+} orbitals. The higher density of states near the VB edge as compared to the CB edge is due to the 6-fold degeneracy of p orbitals versus 2 fold degeneracy of s orbital.

Figure 1.3: Simplified molecular orbital diagram of CdSe QDs.
The coordination environment near the surface of QDs is considerably different than that of bulk semiconductors. For example, in CdSe QDs, the atoms in the \{111\} and \{100\} planes are triply and doubly coordinated, respectively, as compared to the QD core where each atom is coordinated to four neighboring atoms.\textsuperscript{7-12} These under-coordinated atoms are often known as “dangling bonds,” and the molecular orbitals corresponding to these atoms lie energetically between the CB and VB of QDs (Figure 1.4). These midgap states are known as “trap states” or “surface states” and can trap photogenerated electrons or holes resulting in fast non-radiative recombination of electrons and holes. The unpassivated Cd atoms result in the formation of electron trap states, and similarly unpassivated Se atoms result in hole trap states.

**Figure 1.4:** Simplified molecular orbital diagram of CdSe QDs with surface trap states.
The electronic transitions to trap states are known to have negligible oscillator strengths; therefore, direct observation of trap states by absorption spectroscopy is difficult. However, in some cases, the trapped charge carriers can still recombine radiatively and give rise to a broad low energy emission band (Figure 1.5). Traditionally, the origin of this broad band has been attributed to a distribution of electron and hole trap states.\textsuperscript{13-15} However, recent studies by Kambhampati et al. have challenged this view based on their temperature-dependent photoluminescence studies on a myriad of QD systems and a simple observation that the trap-state photoluminescence (PL) peak is typically red-shifted by 300-550 meV relative to the band-edge PL peak, which is much larger than the thermal energy available at room temperature, and therefore the exchange between the core excitonic states and surface states should not be possible.\textsuperscript{10, 16-17} They explained their experimental observations by treating the trap state as a quantized charge-transfer state (see section 1.5) coupled to the excitonic state via a high-frequency intramolecular vibrational mode with high electron-phonon coupling and a low-frequency classical solvent mode (Figure 1.5). At low temperature, electron transfer (ET) occurs mostly via tunneling of electrons through the activation barrier. However, at higher temperature, ET is activated thermally when electrons obtain enough thermal energy to cross the activation barrier. Interestingly, they were able to simulate their experimental data by incorporating only one surface state.
Figure 1.5. Three models for core excitonic and surface emission in QDs and respective simulated emission data. (a,b) Standard deep trap state model with a distribution of trap states within the bandgap explains the broad and redshifted nature of surface emission but is unable to account for temperature dependence of core/surface PL ratio. (c,d) Classical ET picture, which is able to describe the temperature dependence but unable to describe spectral features of surface emission band. (e,f) Semi-classical Marcus-Jortner ET picture, which is able to describe both the temperature dependence and spectral features of surface emission band. Reproduced with permission from reference 13, American Physical Society.

Traditionally, removal of trap states has been deemed desirable as trap states result in increased non-radiative recombination and thus decreased photoluminescence quantum yields (PLQY) of QDs. Also, trapping of charge carriers can result in irreversible loss of potential energy which in turn results in poor performance of photovoltaic devices. Ligands on the surface of QDs play the
role of surfactants, stabilizing QD dispersions in a variety of solvents, and also provide effective surface passivation for QDs. When ligands bind to the surface metal and chalcogen atoms through various anchoring groups, the mixing between the frontier ligand orbitals and unpassivated surface atoms can result in the formation of new molecular orbitals which are within the VB and CB manifolds, thus cleaning the bandgap of surface states (Figure 1.6)\(^{18}\). Effective surface passivation is often achieved by growing a thick inorganic shell or various atomic ligand passivation techniques.

**Figure 1.6:** Simplified molecular orbital diagram showing the role of surface ligands in passivating trap states in CdSe QDs
Surface Chemistry of QDs

The earlier reports on synthesis of cadmium chalcogenide QDs were based on the pyrolysis of organometallic reagents by injection into a hot coordinat{ing solvent (later studies showed that the solvent was non-coordinating).\textsuperscript{19} The cadmium precursor was prepared by decomposition of dimethylcadmium in tri-n-octyl phosphine oxide (TOPO) at high temperature, and the chalcogenide precursor was prepared by adding chalcogen powder to tri-n-octyl phosphine (TOP). The injection of chalcogenide precursor to cadmium precursor at high temperature (~300 °C) resulted in formation of QDs. Since TOP and TOPO were the only solvents used, earlier structural models of cadmium chalcogenide QDs were based on a stoichiometric core (equal number of cadmium and chalcogen atoms) with surface Cd atoms bound to TOPO and surface Se bound to TOP. This hypothesis was corroborated by \textsuperscript{31}P nuclear magnetic resonance (NMR) spectroscopy studies conducted by Beccerra and coworkers.\textsuperscript{20} However, later reports in early 2000s showed many inconsistencies in the TOPO model. The QDs’ composition was found to be almost always rich in metal as compared to chalcogen.\textsuperscript{21-26} Also, different batches of TOPO resulted in compositional inconsistencies in synthesized QDs. For example 90% TOPO resulted in QDs with a high metal-to-chalcogenide ratio, whereas 99% TOPO yielded QDs closer to stoichiometric, though still metal rich.\textsuperscript{24,27} Moreover, pure recrystallized TOPO did not yield any QDs unless phosphonic acids were added externally to the cadmium precursor.\textsuperscript{28-29} Detailed compositional analysis of technical grade TOPO revealed the presence of phosphonic and phosphinic acid impurities in TOPO.\textsuperscript{28,30-31} More \textsuperscript{31}P NMR studies revealed that the peaks observed in NMR spectra arose from bound phosphonic acid and its anhydride, confirming that the earlier assignment by Becerra et. al. was incorrect.\textsuperscript{32} Closer inspection of the ligand shell of oleate-capped CdSe QDs revealed that the ratio between bound oleate and excess cadmium was 2:1, resulting in charge-
neutral QDs. A ligand-exchange study of oleate-capped CdSe QDs with phosphonates and thiols revealed that the oleate ligands can be displaced in a 1:1 ratio by incoming ligands.

**Figure 1.7:** Covalent bond classification of surface ligands in metal chalcogenide nanocrystal.

In light of these studies on the surface chemistry of QDs, a new model for surface ligation of QDs was proposed by Owen et al., where the authors adapted Green’s classification of covalent bonds to characterize ligand shells and the surface-modification reactions of QDs. The ligands were broadly characterized as X-type (1 electron donor), L-type (2 electron donor) and Z-type (2 electron acceptors). In this new model, the QD’s core is seen as charge neutral (equal number of metal and chalcogen atoms), where the surface chalcogen is bonded to neutral Z-type CdX2 ligands and surface metal is bonded to L-type ligands (Figure 1.7). A distinct feature of this model treats
the outer CdX₂ complex as labile based on the studies conducted by Owen et al.\textsuperscript{36,38} The reactions of QDs with different types of ligands can be described as shown in Figure 1.8.

Figure 1.8: Various surface-modification reactions for metal chalcogenide QDs.

**Photophysics of Charge Carriers within QDs**

Following photoexcitation, the electrons and holes can undergo various relaxation and recombination pathways. The hot electrons and holes can either relax very quickly (~0.1-1 ps) to CB edge and VB edge, respectively, or become trapped (~1-10 ps) in the surface states, also known as hot carrier trapping.\textsuperscript{17} In the absence of charge acceptors, the thermalized carriers at the band edges can either recombine (~10 ns) radiatively or non-radiatively, or can get trapped at the surface (cold carrier trapping), where they are in a thermodynamic equilibrium with core excitons. The
trapped electrons/holes can also recombine with delocalized holes/electrons radiatively or non-radiatively (~10-1000 ns) to give rise to a red-shifted surface state (also known as trap state) emission band, which can be typically observed in fluorescence spectra of CdS QDs and sometimes in CdSe QDs.\textsuperscript{39} The trapped electron can also recombine with the trapped hole; however, the highly localized nature of trapped electrons and trapped holes would result in very poor overlap between electron and hole wavefunctions and therefore should be highly improbable.

Presence of a charge acceptor in the vicinity of QDs provides additional deactivation pathways for the photoexcited charge carriers. Now, apart from recombination, excitonic and trapped electrons/holes can be transferred to charge acceptors. The competition between the charge-separation rate and charge-recombination rate determines the efficiency of charge separation and is central for the operation of QD-based electronic devices. Charge-transfer processes can be described in simple reaction parameters and are explained in detail in the next section.
Figure 1.9: Various photophysical processes in metal chalcogenide QDs. (a) Photoexcitation of an electron from deep in the VB to deep in CB, (b) fast interband vibrational relaxation (0.1-10 ps) of electron and hole to respective band edges by phonon emission, (c) hot carrier trapping, (d) cold carrier trapping, (e) core electron-hole recombination (radiative and non-radiative), (f) recombination between a trapped hole and a delocalized electron, (g) recombination between a trapped electron and a delocalized hole, (h) recombination between a trapped electron and a trapped hole at the surface of QDs.
**Theory of Charge Transfer (Marcus Theory)**

Marcus Theory was used initially to characterize ET in small molecules, but lately has been used to describe charge transfer in a variety of complex systems including QD-based donor-acceptor (D-A) heterostructures. Marcus Theory simplifies the ET process as crossing of two parabolas representing the potential energy surfaces of the reactants (D-A) and products (D\(^+\)-A\(^-\)) along a common reaction coordinate (Figure 1.10).\(^{40}\) This common reaction coordinate constitutes the differences in the vibrational and polarization energy of reactant and product states arising in the molecules and solvent. The ordinate is free energy rather than potential energy to take into account the density of states and electronic structure of reactants and products. The activation barrier \(\Delta G^\neq\) can be calculated by straightforward algebra by assuming simple parabolic potential energy surfaces with similar dispersion for reactants and products:

\[
\Delta G^\neq = \frac{1}{4\lambda} (\lambda + \Delta G^0)^2
\]  

where \(\Delta G^0\) is the driving force of ET and is mathematically equal to the difference in free energy corresponding to the equilibrium configuration of products and reactants, and \(\lambda\) is the reorganization energy, defined as the energy required by the reactants to acquire the same equilibrium configuration as products without going through the ET process.

For classical ET, the rate constant of ET (\(k_{\text{ET}}\)) can be calculated simply as the rate of crossing the top of activation barrier and can be expressed using Arrhenius relationship as:

\[
k_{\text{ET}} = A \exp\left(\frac{-(\lambda + \Delta G^0)^2}{4\lambda k_B T}\right)
\]
**Figure 1.10:** (a) Classical Marcus ET picture depicting ET process as crossing of potential energy surfaces of reactants (D-A) and products (D'-A') along a common reaction coordinate, (b) Semiclassical Marcus Jortner ET picture allowing quantum mechanical tunneling through the activation barrier along with classical crossing of activation barrier (reproduced with permission from reference 36, American Chemical Society).

where $k_B$ is the Boltzmann constant and $A$ is a prefactor which depends on the frequency of crossing the top of activation barrier. Based on the relative values of $\Delta G^0$ and $\lambda$, ET can be categorized into 3 regions, namely normal region ($|\Delta G^0| < \lambda$), barrierless region ($|\Delta G^0| = \lambda$), and inverted region ($|\Delta G^0| > \lambda$), as shown in Figure 1.11. The rate constant is expected to increase with an increase in driving force. However, at large driving forces, the rate constant is expected to decrease due to a positive activation barrier. Experimentally, the existence of inverted region could not be confirmed experimentally for some time, as ET at driving forces greater than reorganization energy becomes diffusion-limited in intermolecular ET donor-acceptor systems.
Normal Region (\(\Delta G^0 < \lambda\))

Barrierless Region (\(\Delta G^0 = \lambda\))

Inverted Region (\(\Delta G^0 > \lambda\))

**Figure 1.11:** Various regions of ET according to classical Marcus ET Theory: (a) Normal, (b) barrierless, and (c) inverted Marcus region.

However, in 1986, Closs and Miller studied intramolecular ET in donor-spacer-acceptor systems and experimentally confirmed the existence of inverted region.\(^{41}\) Thus, Marcus Theory was able to explain ET in a broad range of complex systems in simple reaction parameters as explained in equation 1.10.

One of the major limitations of classical Marcus Theory was the deviation of experimental ET rate at low temperature from the predicted rate. Classical Marcus Theory predicts a vanishing rate constant as temperature approaches zero; however, experimentally-calculated \(k_{ET}\) for the biological system *Chromatium vinosum* shows non-zero and temperature-independent \(k_{ET}\) at low temperatures.\(^{42}\) This and few other limitations in classical Marcus Theory arise because it is assumed that the barrier must be crossed.

As an improvement, Marcus Jortner ET Theory incorporated quantum mechanical tunneling through the activation barrier.\(^{43}\) The extent of tunneling through the barrier is proportional to the vibrational overlap between the reactant and product states. Assuming harmonic oscillator
potential energy surfaces, the new $k_{ET}$ expression then can be expressed from Fermi’s golden rule as:

$$k_{ET} = \frac{2\pi}{\hbar} |\langle R|H|P\rangle|^2 |\langle r_{vib}|p_{vib}\rangle|^2 \delta(E_R - E_P)$$  \hspace{1cm} (1.11)

where $|\langle R|H|P\rangle|$ is the electronic matrix element that mixes the donor and acceptor states, $|\langle r_{vib}|p_{vib}\rangle|$ is the vibrational overlap matrix of the vibrational modes of reactants and products coupled to ET and $\delta(E_R - E_P)$ is the difference in density of states between the reactants and products.

In classical ET, the rate constant is assumed to be affected by medium-frequency modes corresponding to the polarization changes in external medium, which is a reasonable assumption at higher temperature. However, high-frequency modes corresponding to vibrations within the inner sphere (intramolecular) become important at low temperatures, as they can participate in tunneling. In the semi-classical ET treatment by Jortner, the high-frequency intramolecular vibrational modes are characterized by mean frequency $\omega$ and an effective electron-phonon coupling strength $S$ (also known as Huang-Rhys parameter), whereas the low frequency solvent modes are treated classically contributing $\lambda_0$ to the overall reorganization energy. Thus, the semi-classical expression for rate constant of ET becomes:

$$k_{ET} = \frac{2\pi}{\hbar} H_{RP}^2 \left( \frac{1}{4\pi\lambda_0 k_B T} \right)^{\frac{1}{2}} \sum_{\nu'} e^{-\frac{\lambda_0}{\lambda_0 k_B T}} \exp \left( -\frac{(\lambda_0 + \nu' \omega + \Delta G^0)^2}{4\lambda_0 k_B T} \right)$$  \hspace{1cm} (1.12)

This rather complicated-looking expression can be understood easily. The expression in front of the summation represents the frequency of ET in the absence of the barrier, which includes the electronic matrix element of the reactant and product states, $H_{RP}$, and classical density of states. The term under summation is the Frank Condon factor which includes the sum over all possible
vibrational overlap integrals between the initial reactant vibrational level \( \nu \) and final product vibrational level \( \nu' \). The exponential term represents the population having the energy required to undergo ET with energy conservation. The sum is dominated by the reaction channels for which 

\[ |\Delta G^0| \sim \lambda_0 + \nu' \hbar \omega, \]

equivalent to barrierless ET in classical ET picture.

Marcus Jortner ET Theory has been used extensively to explain ET in molecular systems at low temperatures, ET in inverted region, trapping of photoexcited charge carriers at the surface of QDs, and charge transfer in QD based heterostructures.

**Charge Transfer in QD Donor-Acceptor Assemblies**

Separation of charge carriers following photoexcitation is important to harvest solar energy in QD-based devices and photocatalysis. In order to utilize solar energy effectively, charge separation must outcompete electron-hole recombination. There has been a plethora of experimental work studying charge transfer in QD based donor-acceptor heterostructures. Some of these studies are briefly discussed here to provide context for the experimental work discussed in other chapters in this dissertation.

**Driving Force Dependent CT**

Driving force \( (\Delta G^0) \) primarily constitutes the energy difference between the donor and acceptor electronic states. Given no or negligible change in reorganization energy, \( k_{ET} \) is expected to increase with an increase in driving force in normal Marcus region. For driving forces higher than the reorganization energy, \( k_{ET} \) is expected to decrease in the inverted Marcus region as explained in section 1.5.
Tvrda et al. studied ET in heterostructures consisting of CdSe QDs donors and metal oxide acceptors using ultrafast transient absorption spectroscopy (Figure 1.12).\textsuperscript{44} Driving force of ET was manipulated by using a series of different sized CdSe QDs and different metal oxides (TiO\textsubscript{2}, SnO\textsubscript{2} and ZnO). The trends in ET were consistent with driving force-dependent ET in the normal Marcus region. However, no inverted region was observed as the driving force was increased systematically. The absence of inverted region was rationalized by considering a continuum of accepting states in the CB of metal oxides such that ET occurs in the normal region only.

\textbf{Figure 1.12:} Schematic energy diagram of ET from different sizes of CdSe QDs to different metal oxides (left) and experimental rate constant of ET for QD-metal oxide heterostructures as a function of driving force (reproduced with permission from reference 44, Proceedings of the National Academy of Sciences).

Watson et al. explored the role of excitonic and surface states in ET from CdSe QDs covalently attached to TiO\textsubscript{2} nanoparticles in mixed dispersions using time-resolved emission spectroscopy (detailed study in chapter 2).\textsuperscript{45-46} These studies showed that the electrons were transferred from both band-edge and trap states; however, the rate constant of ET was approximately 3-4 times higher for ET from band-edge states as compared to trap states, consistent with driving force-dependent ET.
Even though QDs can be readily incorporated onto metal oxides, and QDs-TiO$_2$ based heterostructures are an important component of QD-based solar cells, such systems are not necessarily ideal models for studying fundamental charge transfer. The complications arise due to metal oxides having a continuum of accepting states and therefore unclear driving forces of ET. Moreover, multiple QDs can attach to a single metal oxide nanoparticulate, directly or via single or multiple spacers, which can affect electronic coupling between donors and acceptors. Recently, various groups have shown that the observed rate constant of charge transfer increases linearly with average number of acceptors attached to the surface of QDs.$^{47-52}$

$$k_{CT,obs} = Nk_{CT,int} \quad (1.13)$$

where $k_{CT,obs}$ and $k_{CT,int}$ are the observed and intrinsic rate constant of charge transfer respectively, and $N$ is the average number of acceptors per QD.

Deconvolution of the intrinsic rate constant of charge transfer from the observed rate constant of charge transfer is very difficult in QDs-metal oxide based heterostructures. Molecular acceptors, on the other hand, have well-defined HOMO-LUMO energetics; therefore, the driving force of charge transfer can be calculated more easily. Moreover, the average number of acceptors bound to a single QD can be quantified using a variety of techniques such as 1-H NMR, transient absorption spectroscopy, etc.
Lian et al. studied driving force dependent ET from a series of differently-sized cadmium chalcogenide (CdS, CdSe and CdTe) QDs adsorbed to a variety of molecular dyes (anthraquinone, methyl viologen and methylene blue) using ultrafast transient absorption spectroscopy (Figure 1.13). The authors did not observe the Marcus inverted region as driving force was increased systematically. They invoked a new mechanism, “Auger assisted electron transfer,” to explain their experimental results in which the photoexcited hole is strongly coupled to ET, which gives rise to a continuum of product states. The expression for rate constant of ET then becomes the summation of individual $k_{ET}$ for all possible reaction channels, keeping the overall rate constant of ET high in the classical Marcus inverted region.

$$k_{AET}(R) = \sum_i \frac{2\pi}{\pi} |H_{AET}(R, E_{h,i})|^2 \left(\frac{1}{4\pi\lambda_0 k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{(\lambda_0 + \Delta\epsilon(R, E_{h,i}))^2}{4\lambda_0 k_B T}\right)$$  \hspace{1cm} (1.14)
Alivisatos et al. studied driving force-dependent hole transfer from core/shell CdSe/CdS QDs covalently attached to functionalized molecular ferrocene.\textsuperscript{48} The cyclopentadiene rings on ferrocene were functionalized with electron-withdrawing and electron-donating substituents to modulate the oxidation potential of functionalized ferrocenes. The surface coverage of bound ferrocene on the surface of QDs was calculated from 1-H NMR, and the intrinsic rate constant of hole transfer was deconvoluted from the overall rate constant of hole transfer. No inverted region was observed as the driving force of hole transfer was increased systematically. The trends were qualitatively explained by invoking Auger-assisted hole transfer wherein hole transfer was strongly coupled to the photoexcited electron in CB of QDs.

**Figure 1.14:** Schematic diagram of hole transfer from core/shell CdSe/CdS QDs covalently tethered to substituted ferrocene derivatives (left) and experimental intrinsic rate constant of hole transfer as a function of driving force. Reproduced with permission from reference 48, American Chemical Society.

**Electronic Coupling-Dependent CT**

The rate constant expression in equation 1.12 is predicted to vary with the square of the electronic coupling matrix \( H_{RP} \). As the distance between donor and acceptor increases, the electronic coupling between the donor and acceptor decreases due to exponential falloff of charge-carrier wavefunctions. Therefore, \( H_{RP} \) is predicted to decrease exponentially with increasing distances.
between donor and acceptor. Assuming that the distance dependence of the solvent motion barrier is negligible, $k_{CT}$ can be rewritten as:

$$k_{CT} = k_0 \exp(-\beta d)$$  \hspace{1cm} (1.15)$$

where $k_0$ is the rate constant of charge transfer when donor and acceptor are in close contact with each other, $\beta$ is the damping coefficient, and $d$ is the physical distance between donor and acceptor.

Electronic coupling-dependent CT has been explored in a myriad of QD based donor-acceptor heterostructures by either changing the distance between QDs donor and acceptor by using spacer of different length in D-B-A systems\textsuperscript{53-54} or by changing the insulating shell thickness in core/shell QDs donor-acceptor heterostructures.\textsuperscript{49, 52, 54-58} Dibbell et al. studied distance-dependent ET in QDs covalently attached to TiO$_2$ nanoparticles using mercaptoalkanoic acids of varying length.\textsuperscript{53} ET injection yields were found to decrease as the length of linker was increased systematically. Ding et al. studied hole transfer from core/shell CdSe/CdS QDs to covalently-attached molecular ferrocene as a function of shell thickness, linker length and the number of bound acceptors per QD.\textsuperscript{49} The intrinsic rate constant of hole transfer was found to decrease exponentially with damping coefficients of (0.24±0.025) Å$^{-1}$ for CdS shell thickness and (0.24±0.025) Å$^{-1}$ for aliphatic linker length, consistent with equation 1.15.

**Thesis Overview**

This dissertation is focused on characterizing charge transfer in QDs-metal oxide, QDs-molecular acceptors and QDs/nanowires (NWs) heterostructures. Chapter 2 includes a detailed study on characterizing the role of band edge states and surface states in ET from CdSe QDs to TiO$_2$. Furthermore, ET characteristics have been compared and contrasted with core only CdSe QDs and
core/shell CdSe/ZnS QDs, where core/shell QDs show more efficient ET in absence of surface states, despite having a spatial and energetic barrier due to the presence of ZnS shell.

Chapter 3 builds on improving the system studied in chapter 2, wherein chloride treated CdTe QDs are tethered to molecular hole acceptors ferrocenylhexanethiol (FcC₆SH), with well defined driving force and surface coverage of hole acceptors. Chloride treatment, not only passivates the surface of QDs (without growing a thick insulating shell), but also allows for better surface coverage of hole acceptors as compared to as-synthesized untreated CdTe QDs.

Chapter 4 revisits the ideas discussed in chapter 2 and chapter 3, where hole transfer from band edge states and surface states of a variety of cadmium chalcogenide QDs (CdE, where E = S, Se and Te) covalently attached to molecular hole acceptors (FcC₆SH) is discussed in detail.

Finally, chapter 5 includes a detail charge transfer characterization in a novel type II CdE/V₂O₅ NWs heterostructures using transient absorption (TA) spectroscopy. Detailed TA study shows ultrafast exciton dissociation and long-lived charge-separated state, where electrons and holes are localized in V₂O₅ NWs and CdE QDs respectively.
References


Chapter II

Photoinduced Electron Transfer from Quantum Dots to TiO$_2$: Elucidating the Involvement of Excitonic and Surface States

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Introduction

The unusual electronic structure of quantum dots (QDs) renders them intriguing as absorbers of light and donors of excited charge carriers for solar energy conversion.\textsuperscript{1-4} QDs have size-dependent band gaps and band-edge potentials and high molar absorption coefficients.\textsuperscript{5-8} They can undergo slow charge-carrier cooling or multiexciton generation, potentially enabling the extraction of hot or multiple charge carriers.\textsuperscript{9-17} Additionally, the electronic structure of QDs is influenced by adsorbed capping ligands, which can passivate surfaces and determine energies of surface-localized electronic states.\textsuperscript{18-20} Relaxation of electrons and holes into surface states irreversibly dissipates potential energy and decreases the driving force of interfacial charge transfer. Therefore, to extract charge carriers from QDs before they relax into surface states is important from the standpoint of maximizing rates of charge transfer and efficiencies of solar cells and photocatalysts.

We and others have reported spectroscopic studies of excited-state electron transfer (ET) from cadmium chalcogenide QDs to molecularly-tethered metal oxide semiconductor nanoparticles (NPs) and thin films.\textsuperscript{21-32} Such ET processes are central to the operational mechanism of QD-sensitized solar cells, the reported power-conversion efficiencies of which have increased dramatically.\textsuperscript{33-34} Rate constants of ET ($k_{et}$) on the orders of $10^7$ to $10^{12}$ s\textsuperscript{-1} have been measured, and $k_{et}$ has been shown to depend on driving force, the properties of molecular linkers, the size and crystallinity of QDs, the composition and electronic structure of the metal oxide substrate, and the mechanism by which QDs are deposited onto the substrate.\textsuperscript{25-32}

Despite the significant effort to characterize ET from QDs to metal oxides, the mechanism of ET, and specifically the question of whether electrons are extracted from
excitonic or surface states of QDs remains largely unexplored. This question is timely given the renewed interest in the nature of surface states. The broad and highly Stokes-shifted emission often exhibited by QDs has been taken as evidence for distributions of surface-localized states within the band gap, into which electrons and holes might relax before recombining at energies much less than the bandgap. Such states might be associated with unpassivated or ligand-bound atoms at surfaces of QDs.\textsuperscript{18, 35} Khambampati and coworkers recently proposed an alternative interpretation.\textsuperscript{20, 36-39} They argued that the so-called trap-state emission from QDs, hereafter referred to as surface emission, can be accounted for by a single surface electronic state rather than a distribution of mid-gap states.\textsuperscript{36-38} Notably, a semiclassical treatment of ET from excitonic states to a surface state accounts for the temperature-dependent intensities of band-edge and surface emission.\textsuperscript{18, 36-38} This new insight into the electronic structure of QDs has significant implications regarding mechanisms by which photogenerated electrons are transferred from QDs to acceptors.

Our research group reported that electrons could be extracted from both excitonic and surface states of QDs.\textsuperscript{24} In this article, we report the results of an in-depth spectroscopic characterization of the dynamics and mechanism of ET from core-only CdSe QDs and core/shell CdSe/ZnS QDs to molecularly-tethered TiO\textsubscript{2} NPs. Our results reveal (1) that both excitonic and surface states of core-only QDs were active in ET and (2) that the ZnS shell prevented the trapping of electrons in surface states and the transfer of holes to adsorbed ligands but did not decrease the rate constant or efficiency of ET to TiO\textsubscript{2}. Thus, the core/shell CdSe/ZnS QDs were superior to core-only CdSe QDs in two significant respects. Our results highlight the mechanistic complexity of excited-state ET at QD-containing
interfaces, the role of surface states in such processes, and the attractiveness of core/shell QDs as sensitizers of TiO$_2$.

**Experimental**

**Materials**

Cadmium oxide (CdO), 3-mercaptopropionic acid (MPA), tri-$n$-octylphosphine (TOP) (90%), tri-$n$-octylphosphine oxide (TOPO) (98%), and 1-tetradecylphosphonic acid (TDPA) (98%) were obtained from Alfa Aesar. Titanium(IV) isopropoxide and silica LUDOX dispersion (30% by weight in water) were purchased from Sigma Aldrich. Zirconium(IV) $n$-propoxide was obtained from TCI. Selenium powder was obtained from Puratronic. Ethanol (EtOH) (200 proof) was obtained from Decon Labs. Toluene and methanol (MeOH) were obtained from Fisher Scientific. Toluene dispersions of core/shell CdSe/ZnS QDs (QD540-OS Pure Core) were purchased from NOMCorp. All reagents were used as received.

**Syntheses of metal oxide NPs**

Titania (TiO$_2$) colloids were prepared following the method of Robel et al.$^{40}$ Titanium(IV) isopropoxide (0.20 mL, 0.66 mmol) was added dropwise to 10 mL of EtOH with vigorous stirring under Ar atmosphere. ZrO$_2$ colloids were prepared by using an analogous method.$^{21}$ Zirconium(IV) $n$-propoxide (0.21 mL, 0.66 mol) was added dropwise to 10 mL of EtOH with vigorous stirring under Ar atmosphere. Dispersions of metal oxide NPs were diluted by adding 10 mL of toluene. The as-synthesized TiO$_2$ and ZrO$_2$ dispersions were stable for several hours. A fresh batch of metal oxide dispersions was prepared before each spectroscopic measurement.
Synthesis of CdSe QDs

Toluene dispersions of CdSe QDs were prepared using the method reported by Peng and Peng.\textsuperscript{41} Selenium powder (0.206 g, 2.60 mmol) and TOP (10 mL) were combined in an Ar atmosphere in a glovebox, and the solution was sealed with a rubber septum and then transferred to a fume hood. The solution was stirred at room temperature until it turned colorless. CdO (0.206 g, 1.60 mmol) was added to TOPO (15.1 g, 39.1 mmol) and TDPA (0.892 g, 3.20 mmol) in a separate three-neck flask. The flask was heated to 300 °C under constant stirring until the cadmium-containing mixture became colorless. The solution was allowed to cool to 270 °C, at which point the selenium-containing solution was swiftly injected into the cadmium-containing mixture. Growth of CdSe QDs was evidenced by a change of the color of the mixture from pale yellow to orange to red. When the desired particle size was reached, the mixture was removed from heat and the reaction was quenched. To separate CdSe QDs from excess organic ligands (TOPO, TOP, and TDPA), nonsolvent/solvent washing was used. QDs were first flocculated by addition of MeOH, and the precipitate was isolated by centrifugation. The QDs were then resuspended in toluene. This washing procedure was repeated at least three times.

Spectroscopy

Mixed dispersions containing QDs and MPA and/or TiO\textsubscript{2} or ZrO\textsubscript{2} NPs were prepared as described in Appendix S1 in the Supporting Information. Briefly, the concentration of QDs was identical for all dispersions. The concentration of MPA was 0.1 mM for dispersions of core-only CdSe QDs containing MPA and was 1.5 mM for dispersions of core/shell CdSe/ZnS QDs containing MPA. The higher concentration of MPA in the dispersions containing CdSe/ZnS QDs corresponded to the threshold concentration above which
adsorption-induced changes in the intensity of emission from QDs saturated, as described below. The concentration of TiO$_2$ or ZrO$_2$, in formula units, was 6.6 mM for all dispersions containing metal oxide NPs.

UV/vis absorption spectra were obtained with an Agilent 8453 diode array spectrophotometer. Steady-state emission spectra were acquired with a Varian Cary Eclipse fluorimeter with excitation at 440 nm. Time-resolved photoluminescence (TRPL) decay traces were obtained with a Becker and Hickl Tau-130 time-correlated single photon counting (TCSPC) setup. The setup consisted of a pulsed diode laser (BDL 445 SMC) emitting monochromatic pulses at 445 nm with pulse-width of 40-90 ps (full width at half maximum (FWHM)) at 1 mW power and 50 MHz repetition rate. The laser could be operated at 3 different repetition rates (1 MHz, 20 MHz, and 50 MHz). All time-resolved measurements were made at 1 MHz repetition rate to avoid re-excitation of samples before decaying completely to the baseline. A delay cable equivalent to 50 ns was employed in the sync channel, and the time-to-amplitude converter (TAC) was fixed to 50 ns to acquire decay traces corresponding to the first 50 ns of decay to achieve higher time resolution. QD-containing dispersions were housed in a four-sided quartz cuvette with a path length of 1 cm. Emission was collected at 90° to the excitation beam and focused into a polychromator coupled to a 16-channel photomultiplier tube (PML 16-C). Each channel corresponded to a 12.5 nm window in the wavelength regime. All time-resolved measurements were obtained at magic angle conditions by placing a polarizer in the emission channel at 54.7° to the polarization of the excitation beam. A 460 nm long-pass
Figure 2.1. Absorbance spectrum (solid line) and normalized emission spectrum (dashed line) of a dispersion of core-only CdSe QDs in toluene.

A neutral density filter was placed in the emission channel before the polychromator to minimize scattering of the excitation light from samples. A neutral density filter was used to adjust the intensity of the excitation beam such that the probability of detection of a photon per excitation pulse was less than 0.01. TRPL decay traces were obtained over 1024 time bins with time resolution of 48.8 ps. Decay traces were collected over 500 s for band-edge emission (485-580 nm) and 2000 s for surface emission (610-735 nm). The instrument response function
(IRF) was acquired by using a light-scattering suspension of silica LUDOX and measuring a decay trace at the excitation wavelength. At a laser gain of 20% and a detector gain of 90%, FWHM for the IRF was approximately 240 ps. TRPL decay traces were fitted using Fluofit software by Picoquant.

**Results and discussion**

**Our strategy to quantify ET with emission spectroscopy**

Excited-state ET from QDs to TiO$_2$ NPs competes with trapping and electron-hole recombination and results in dynamic quenching of emission from the QDs.$^{21, 24, 40, 43}$ Thus, steady-state and time-resolved emission measurements are a useful but indirect method for quantifying the ET processes of interest. TCSPC with multichannel detection was particularly apt for this study because it enabled independent and simultaneous characterization of ET from excitonic and surface states.

We prepared mixed dispersions of QDs (core-only CdSe or core/shell CdSe/ZnS), MPA, and/or TiO$_2$ or ZrO$_2$ NPs using conditions established previously by our group and others.$^{21, 24, 40}$ It is well-established that MPA can tether core-only CdSe QDs and core/shell CdSe/ZnS QDs to TiO$_2$ or ZrO$_2$ via coordination of its terminal thiol group to the QD and its terminal carboxyl group to the metal oxide.$^{40, 44-45}$ Thus, we anticipated the formation of QD-MPA-TiO$_2$ or QD-MPA-ZrO$_2$ assemblies within the mixed dispersions. The conduction band edge potential of ZrO$_2$ is nearly 1 V more negative than that of bulk CdSe.$^{46-49}$ Therefore, ET from photoexcited CdSe QDs to ZrO$_2$ NPs was thermodynamically unfavorable, and ZrO$_2$ NPs served as inert substrates for control experiments. MPA alone can quench the emission from QDs by accepting photogenerated
holes.\textsuperscript{21, 24, 50-52} Additionally, TiO$_2$ and ZrO$_2$ NPs can quench emission from QDs via ET (for TiO$_2$ only) and/or via changes in the local concentration or interfacial charge distribution in the vicinity of QDs upon immobilization on the NPs.\textsuperscript{24} To account for these possible quenching mechanisms, we measured steady-state and time-resolved emission from QDs alone, from dispersions of QDs with MPA (hereafter referred to as QD/MPA dispersions), from mixed dispersions of QDs and metal-oxide NPs (QD/TiO$_2$ and QD/ZrO$_2$ dispersions), and from mixed dispersions containing QDs, MPA, and metal-oxide NPs (QD-MPA-TiO$_2$ and QD-MPA-ZrO$_2$ dispersions). The concentration of QDs was equal in all dispersions. This approach enabled us to determine whether ET within QD-MPA-TiO$_2$ assemblies caused additional quenching beyond the contributions from MPA or TiO$_2$ alone and beyond the extent of quenching within QD-MPA-ZrO$_2$ assemblies.

**Electron transfer from core-only CdSe QDs**

**Electronic spectra.** Core-only CdSe QDs exhibited a first excitonic absorption band with wavelength of maximum absorbance ($\lambda_{\text{max}}$) of 500 nm (Figure 2.1). The average diameter of the QDs was estimated to be 2.35 nm using the empirical equation reported by Yu et al.\textsuperscript{6} The optical band gap of the core-only CdSe QDs was estimated to be 2.39 eV from the $x$-intercept of a linear fit to the low-energy tail of a plot of the square of absorbance vs wavenumber (Figure S2.1 in Supporting Information). The core-only CdSe QDs exhibited a band-edge emission band centered at 520 nm, with FWHM of ~29 nm (1100 cm$^{-1}$), and a broad surface emission band centered at 750 nm (Figure 2.1).

**Steady-state emission quenching.** Steady-state emission spectra were obtained for mixed dispersions containing core-only CdSe QDs, MPA, and/or metal oxide NPs, as a function of time after mixing. Experiments were performed in triplicate for each type of
dispersion. Amounts of quenching were quantified as emission-quenching percentages (\(\%Q\)), which equal \([(I_0 - I)/I_0] \times 100\), where \(I_0\) is the intensity of emission at a given wavelength from dispersions of QDs alone and \(I\) is the intensity of emission from a quencher-containing dispersion. Normalized emission intensities at the band-edge and surface emission maxima from a representative experiment are plotted as a function of time in Figure S2.2 in Supporting Information. At a given equilibration time, the addition of TiO\(_2\) or ZrO\(_2\) NPs to CdSe QDs quenched the emission of CdSe QDs to a similar extent (Figures 2.2 and S2.2). Values of \(\%Q\) for band-edge and surface emission were \(~30\%\) and \(~10\%\), respectively. The emission spectral profile did not change upon addition of metal oxide NPs. Addition of MPA to CdSe QDs resulted in \(~80\%\) quenching of band-edge emission, whereas surface emission was quenched by \(~40\%\) (Figures 2.2 and S2.2). Preferential quenching of band-edge emission by MPA is consistent with a hole-transfer mechanism, as the driving force for the transfer of holes from the valence band edge of CdSe QDs to the thiolate of adsorbed MPA is greater than that for the transfer of holes from surface-localized states at higher energies. QD-MPA-TiO\(_2\) and QD-MPA-ZrO\(_2\) dispersions were characterized to evaluate additional quenching of emission resulting from the
Figure 2.2. Emission spectra of the following dispersions containing core-only CdSe QDs: QDs alone (1, black), QD/ZrO₂ (2, orange), QD/TiO₂ (3, blue), QD/MPA (4, red), QD-MPA-ZrO₂ (5, green), and QD-MPA-TiO₂ (6, purple). *Inset:* Emission spectra of the same dispersions, zoomed in and normalized to the intensity at the surface-emission maximum. Spectra were acquired 45 min after preparation of mixed dispersions.

formation of tethered assemblies and ET. Notably, emission from QD-MPA-TiO₂ dispersions was quenched to a much greater extent than emission from QD-MPA-ZrO₂ dispersions (Figures 2.2 and S2.2). Band-edge emission was quenched by ~95% for QD-MPA-TiO₂ dispersions and ~88% for QD-MPA-ZrO₂ dispersions relative to dispersions of free CdSe QDs. Surface emission was quenched by ~89% for QD-MPA-TiO₂ dispersions and ~38% for QD-MPA-ZrO₂ dispersions. We attribute the additional quenching of emission in the case of QD-MPA-TiO₂ dispersions to ET from QDs to TiO₂, as explained...
above and consistent with prior reports.\textsuperscript{21-22, 24} Finally, the spectral profile of the surface emission band was nearly invariant for the different dispersions containing core-only CdSe QDs (inset to Figure 2.2). The lack of shifting or narrowing of this band is consistent with the possibility of a single surface electronic state, or a very narrow distribution, rather than a broad distribution of electron-trap states that might promote ET with varying rate constants and efficiencies and would therefore be quenched to varying degrees.

**Time-resolved emission measurements.** To investigate the dynamics and efficiency of excited-state ET, TRPL measurements were carried out on mixed dispersions using TCSPC. Decay traces were fitted to the following equation using a multi-exponential reconvolution method:

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

(2.1)

where \(t\) is time, \(I(t)\) is intensity, \(A_i\) is amplitude of the \(i^{th}\) component, \(\tau_i\) is lifetime of the \(i^{th}\) component and \(IRF(t')\) is the instrument response function. The goodness of fit was evaluated by the distribution of residuals (differences between data and fit) around zero and
Figure 2.3. TRPL decay traces and corresponding fits for band-edge emission (a) and surface emission (b) from the following dispersions containing core-only CdSe QDs: QDs alone (1, grey), QD/MPA (2, red), QD-MPA-ZrO$_2$ (3, green), and QD-MPA-TiO$_2$ (4, purple). IRF (5, yellow) was used in reconvolution.
by chi-square values. Chi-square values of 0.95-1.40 were considered acceptable. An additional exponential component was added if it resulted in significant improvement in chi-square values and the plots of residual as a function of time. Although a long-pass filter was placed in the emission channel to minimize light scattering, some scattering was still measured in all decay traces. The effect of scattered light was taken into account while fitting decay traces. Single, double and triple-exponential reconvolution fits, along with corresponding residuals and chi-square values, for band-edge and surface emission from all samples are in Figure S2.3 of Supporting Information. For all samples containing CdSe core-only QDs, triexponential reconvolution yielded the highest-quality fits for both band-edge and surface emission. Triexponential decay kinetics formally implies the existence of three populations of fluorophores, each with single-exponential decay kinetics. Multiexponential decay kinetics are common for dispersions of cadmium chalcogenide QDs, with inherent heterogeneities in size and surface chemistry, and have been attributed to decay through multiple states.24,29,53-55 Our values of $A_i$ and $\tau_i$ from fits to representative emission decay traces within the band-edge and surface emission bands are compiled in Table S2.3 in Supporting Information for dispersions containing core-only CdSe QDs. Intensity-weighted average lifetimes ($\langle \tau \rangle$) were calculated as follows:24,43,56-58

$$\langle \tau \rangle = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$  \hspace{1cm} (2.2)

Decay traces were obtained at different wavelengths throughout the band-edge and surface emission bands. Representative decay traces and fits are shown in Figure 2.3 for band-edge emission (513 nm) and surface emission (622 nm) from core-only CdSe QDs alone and from each of the mixed dispersions containing core-only CdSe QDs. Values of $\langle \tau \rangle$ from decay traces at the band-edge emission maximum and at 622 nm, within the
surface emission band, are in Table 2.1. Values of $\langle \tau \rangle$ for wavelengths throughout the band-edge and surface emission bands are compiled in Tables S2.4 and S2.5 in Supporting Information. Values of $\langle \tau \rangle$ at 513 nm (at the band-edge emission maximum) and at 722 nm (at slightly higher energy than the surface emission maximum) for free core-only CdSe QDs were $(26.5 \pm 0.4)$ ns and $(50 \pm 3)$ ns, respectively (Tables S2.4 and S2.5). Values of $\langle \tau \rangle$ varied by less than 12% across the band-edge emission band, whereas $\langle \tau \rangle$ within the surface emission band ranged from approximately 43 ns to approximately 61 ns and varied non-monotonically with wavelength. For QD/MPA dispersions, the value of $\langle \tau \rangle$ at the band-edge emission maximum of 513 nm was $(26.8 \pm 0.8)$ ns (Table S2.4). Thus, quenching of band-edge emission upon addition of MPA to core-only CdSe QDs was either static or non-time resolvable (within the laser pulse). The value of $\langle \tau \rangle$ at 513 nm for QD-MPA-ZrO$_2$ dispersions was $(22.2 \pm 0.9)$ ns (Table S2.4). The decrease of $\langle \tau \rangle$, which arose from an increase of $A_2$ and decreases of $\tau_2$ and $\tau_3$ (Table S2.3), indicates a slight acceleration of excited-state decay upon incorporation of the core-only CdSe QDs into assemblies in the absence of ET.$^{24}$ The value of $\langle \tau \rangle$ at 513 nm for QD-MPA-TiO$_2$ dispersions was $(4.7 \pm 0.4)$ ns. The approximately five-fold decrease of $\langle \tau \rangle$ was caused primarily by (1) an increase of $A_1$, the preexponential factor corresponding to the fastest component of decay, by approximately 30%, (2) decreases of $A_2$ and $A_3$, indicating decreased contributions of the slower components of decay, and (3) an approximately three-fold decrease of $\tau_3$, the slowest lifetime (Table S2.3). The decrease of $\langle \tau \rangle$ confirms the presence of an additional excited-state deactivation pathway for QD-MPA-TiO$_2$ dispersions, which we attribute to ET from excitonic states of photoexcited CdSe QDs to TiO$_2$ NPs. This ET-induced dynamic

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quenching is consistent with the enhanced quenching of steady-state band-edge emission (Figure 2.2).

**Table 2.1.** Values of $\langle \tau \rangle$ at the band-edge and surface emission maxima of QD-MPA-ZrO$_2$ and QD-MPA-TiO$_2$ dispersions and corresponding values of $k_{et}$ and $\eta_{et}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\langle \tau \rangle$ QD-MPA-ZrO$_2$ (ns)</th>
<th>$\langle \tau \rangle$ QD-MPA-TiO$_2$ (ns)</th>
<th>$k_{et}$ (s$^{-1}$)</th>
<th>$\eta_{et}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>core-only CdSe QDs (band-edge)</td>
<td>22.2 ± 0.9</td>
<td>4.7 ± 0.4</td>
<td>$(1.7 \pm 0.2) \times 10^8$</td>
<td>79 ± 2</td>
</tr>
<tr>
<td>core-only CdSe QDs (trap-state)</td>
<td>34 ± 2</td>
<td>10 ± 2</td>
<td>$(7 \pm 2) \times 10^7$</td>
<td>71 ± 6</td>
</tr>
<tr>
<td>core/shell CdSeZnS QDs (band-edge)</td>
<td>15.1 ± 0.2</td>
<td>4.2 ± 0.2</td>
<td>$(1.7 \pm 0.1) \times 10^8$</td>
<td>72 ± 1</td>
</tr>
</tbody>
</table>

Similar results were obtained for surface emission from core-only CdSe QDs (Figure 2.3b). Values of $\langle \tau \rangle$ at 622 nm (within the surface emission band) for dispersed QDs alone, QD/MPA dispersions, QD-MPA-ZrO$_2$ dispersions, and QD-MPA-TiO$_2$ dispersions were $(48 \pm 2)$ ns, $(45 \pm 3)$ ns, $(34 \pm 2)$ ns, and $(10 \pm 2)$ ns, respectively (Table S2.5). The significantly decreased value of $\langle \tau \rangle$ for QD-MPA-TiO$_2$ dispersions relative to QD-MPA-ZrO$_2$, which arose primarily from an increase of $A_j$ and 0.5-to-2.5-fold decreases of the three lifetimes (Table S2.3), is indicative of ET from surface states of CdSe QDs to TiO$_2$ NPs, consistent with the enhanced quenching of steady-state surface emission (Figure 2.2).

**Mechanism, dynamics, and efficiency of ET.** The measured additional component of dynamic quenching of both band-edge and surface emission from CdSe-MPA-TiO$_2$ dispersions relative to CdSe-MPA-ZrO$_2$ dispersions provides compelling evidence that
electrons were transferred from both excitonic and surface states of the QDs to TiO₂. Thus, the data provide new insight into the mechanisms of excited-state interfacial ET within QD-containing heterostructures. Dynamics of ET were extracted from time-resolved emission data. Rate constants of ET from excitonic or surface states of QDs to TiO₂ NPs were estimated as follows, assuming that ET is the only additional deactivation pathway in QD-MPA-TiO₂ assemblies as compared to QD-MPA-ZrO₂ assemblies and that the rate constants for all other competing excited-state deactivation processes are identical in QD-MPA-TiO₂ and QD-MPA-ZrO₂ assemblies:²¹-²²,²⁹,⁴³

\[ k_{et} = \frac{1}{\langle \tau \rangle_{\text{CdSe-MPA-TiO}_2}} - \frac{1}{\langle \tau \rangle_{\text{CdSe-MPA-ZrO}_2}} \] (2.3)

Equation 2.3 is derived in Appendix S2.2 in Supporting Information. Any differences in the rate constants of competing deactivation processes, upon substitution of TiO₂ for ZrO₂, would introduce error into our estimation of \( k_{et} \). Importantly, the intensity of surface emission in TRPL decay traces reached the maximum within the instrument response (Figure 2.3b), indicating that photogenerated electrons had already equilibrated into a distribution of excitonic and surface states. Therefore, ET from excitonic states did not affect measured dynamics of surface emission decay, enabling the use of equation 2.3 to estimate rate constants of ET from surface states. Values of \( k_{et} \) extracted from measured TRPL decay traces for dispersions containing core-only CdSe QDs are summarized in Tables 2.1, S2.4, and S2.5.
Dynamics of ET from excitonic states of core-only CdSe QDs to TiO$_2$ NPs varied with emission wavelength. Values of $k_{et}$ decreased by approximately two-fold from $(2.5 \pm 0.8) \times 10^8$ s$^{-1}$ at 487 nm, near the high-energy threshold of band-edge emission, to $(1.1 \pm 0.3) \times 10^8$ s$^{-1}$ at 558 nm, near the low-energy tail of band-edge emission (Table S2.3). This effect may have arisen from differences in the driving force for ET, assuming that variation of the size of QDs and the energies of their excitonic states contributed in part to the breadth of the band-edge emission band, and/or from differences in the electronic coupling between

**Figure 2.4.** Absorbance spectrum (solid line) and normalized emission spectrum (dashed line) of a dispersion of core/shell CdSe/ZnS QDs in toluene.
various states at or near the conduction band edge of the QDs and acceptor states of TiO$_2$. In contrast, values of $k_{et}$ for ET from surface states varied to a lesser extent and non-monotonically with emission wavelength (Table S2.5).

ET from excitonic states of core-only CdSe QDs to TiO$_2$ was 2-to-3-fold faster than ET from surface states. This difference in $k_{et}$ may have arisen from differences in the driving force of ET. Because excitonic states are at more negative potentials (higher energies) than surface states, the driving force is greater for ET from excitonic states than from surface states of QDs. Another possibility is that weaker electronic coupling between surface states of QDs and acceptor states of TiO$_2$ may have resulted in slower ET. Regardless of the mechanism, the irreversible dissipation of potential energy upon relaxation of electrons into surface states of QDs is generally undesirable, as it may influence both ET dynamics and the reducing potential of charge carriers for a range of light-initiated redox processes. Thus, a challenge is to extract electrons from QDs before they are trapped in surface states.

Efficiencies of ET ($\eta_{et}$) are ultimately more important than rate constants and can dictate the performance of QD-based photovoltaic devices and photocatalysts. To be efficient, ET must occur faster than competing electron-hole recombination processes. For photoinduced ET from QDs to TiO$_2$ NPs, $\eta_{et}$ can be extracted from measured TRPL decay traces and corresponding fits for QD-MPA-TiO$_2$ and QD-MPA-ZrO$_2$ dispersions:

$$\eta_{et} = \left(1 - \frac{(\tau)_{QD-MPA-TiO_2}}{(\tau)_{QD-MPA-ZrO_2}}\right) \times 100 \quad (2.4)$$

Equation 2.4 is derived in Appendix S2.2 in Supporting Information.

We calculated $\eta_{et}$ as a function of emission wavelength throughout the band-edge and surface emission bands. Results are summarized in Tables 2.1, S2.4, and S2.5. Values of $\eta_{et}$ calculated from TRPL decay traces within the band-edge emission band ranged from
approximately 82% to 71% and decreased with increasing emission wavelength. The decrease of \( \eta_{et} \) was associated with the two-fold decrease of \( k_{et} \) with increasing wavelength of band-edge emission; however, the decrease of \( \eta_{et} \) was mitigated by the increase of excited-state lifetime with wavelength of band-edge emission, as evidenced by the measured increase of \( \langle \tau \rangle \) with wavelength for QD-MPA-ZrO\(_2\) dispersions (Table S2.4). Values of \( \eta_{et} \) calculated from TRPL decay traces within the surface emission band ranged from approximately 64% to 76% and did not vary systematically with emission wavelength (Table S2.5).

In summary, our results and analysis reveal that electrons were transferred to TiO\(_2\) from both excitonic and surface states of core-only CdSe QDs. The involvement of surface states in ET is of fundamental interest and has potential implications for a range of QD-based photocatalyst and solar-cell architectures. Our measurements reveal that ET to TiO\(_2\) was most efficient from the highest-energy band-edge or excitonic states of the QDs and of similar efficiency from lower-energy excitonic states and throughout the distribution of surface states. The slight increase of \( \eta_{et} \) from the highest-energy excitonic states (at emission wavelengths less than 500 nm) is consistent with the higher driving force for ET and the measured values of \( k_{et} \), which were greatest at these short wavelengths. Increases of excited-state lifetime at longer wavelengths within the band-edge emission band and into the surface emission band largely compensated for the decrease of \( k_{et} \), such that \( \eta_{et} \) varied only minimally. Relaxation of electrons into surface states prior to their extraction from QDs is generally undesirable, as it results in irreversible dissipation of potential energy of charge carriers and corresponding decreases of the driving force of ET, \( k_{et} \), and \( \eta_{et} \). However, trapping of electrons in surface states impacted the efficiency of ET to TiO\(_2\) only

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minimally due to the aforementioned interplay between $k_{et}$ and excited-state lifetime in determining $\eta_{et}$.

**Electron transfer from Core/Shell CdSe/ZnS QDs**

**Electronic properties of the core/shell QDs.** Trapping of charge carriers can be avoided by using type-I core/shell QDs.\textsuperscript{60-61} To assess dynamics and efficiencies of ET from core/shell QDs to TiO$_2$, in the absence of trapping, we used commercially-available core/shell CdSe/ZnS QDs in similar spectroscopic studies as for core-only CdSe QDs. The oleylamine-capped core/shell CdSe/ZnS QDs exhibited a broad first excitonic absorption band centered at ~520 nm (Figure 2.4). The breadth of the absorption band indicated some leakage of exciton wave function into the ZnS shell.\textsuperscript{61} The optical band gap of the CdSe core in core/shell CdSe/ZnS QDs was estimated to be 2.26 eV (Figure S2.1). Thus, the band gap of the CdSe core of the core/shell QDs was approximately 0.13 eV less than that of the core-only CdSe QDs, indicating that the driving force for ET to TiO$_2$ was lower (by $\leq$ 0.13 eV) for the core/shell QDs. The core/shell CdSe/ZnS QDs were reported by the vendor to consist of CdSe cores with diameter of 2.5 nm coated with 3 monolayers (MLs) of ZnS shell. Assuming the thickness of 1 ML of ZnS to be 0.31 nm,\textsuperscript{61} on the basis of the wurtzite structure of ZnS, the diameter of the core/shell QDs was estimated to be 4.4 nm. Emission spectra of core/shell CdSe/ZnS QDs consisted predominantly of band-edge emission centered at ~540 nm with FWHM of ~43 nm (1400 cm$^{-1}$) (Figure 2.4). The broader band-edge emission of the core/shell CdSe/ZnS QDs, relative to the core-only CdSe QDs, is indicative of a larger distribution of particle sizes. The presence of a ZnS shell may also have broadened the band-edge emission.\textsuperscript{61} The absence of significant surface emission indicates that surface states were passivated by the ZnS shell.\textsuperscript{61}
Steady-state emission quenching. All samples containing core/shell CdSe/ZnS QDs, MPA, and/or metal oxide NPs were equilibrated for 2.5 h before spectroscopic measurements. The quantum yield of emission from dispersions of free CdSe/ZnS QDs decreased by 25-35% during this equilibration period, probably due to desorption of oleylamine capping ligands from the surface of QDs into the EtOH/toluene mixed solvent. Interestingly, the addition of MPA resulted in significant enhancement of emission from core/shell CdSe/ZnS QDs (Figure 2.5), in contrast to the quenching of emission from core-only CdSe QDs upon exposure to MPA (Figure 2.2). The quantum yield of emission from
CdSe/ZnS QDs within QD/MPA dispersions was unchanged during the equilibration period of 2.5 h (Figure S2.2c). The wide-band-gap ZnS shell apparently effectively confined photogenerated holes within the CdSe core, preventing their transfer to MPA. Therefore, no static or non-time-resolvable quenching of emission of CdSe/ZnS QDs was observed. The elimination of hole-transfer quenching by MPA is beneficial from the standpoint of photoinduced ET within QD-mpa-TiO$_2$ assemblies. The transfer of holes to MPA decreases the oxidizing potential of the holes, reduces the average separation between electrons (in TiO$_2$) and holes (on MPA rather than in the QD) in the charge-separated state, and additionally has the potential to oxidatively degrade MPA. Thiolated ligands have been shown to replace amine-bearing ligands from the surfaces of CdSe and CdSe/ZnS QDs.$^{52}$

The observed enhancement of steady-state emission from CdSe/ZnS QDs upon exposure to MPA (Figure 2.5) is consistent with a mechanism in which MPA displaces oleylamine from the surface of the QDs and passivates the surface more effectively. Due to the increased quantum yield of emission, we were able to use a higher concentration of MPA (1.5 mM) in experiments involving core/shell CdSe/ZnS QDs than in those involving core-only CdSe QDs.

TiO$_2$ NPs quenched emission from MPA-capped CdSe/ZnS QDs to a much greater extent than did ZrO$_2$ NPs (Figures 2.5, S2.2c). Values of $\%Q$, relative to QD/MPA dispersions, were ~90% for QD-mpa-TiO$_2$ dispersions and ~35% for QD-mpa-ZrO$_2$ dispersions. The greater quenching of emission by TiO$_2$ than ZrO$_2$ provides evidence that photoexcited CdSe/ZnS QDs transferred electrons to TiO$_2$.

**Time-resolved emission measurements.** TRPL data were acquired from 500 to 575 nm, throughout the band-edge emission band of the core/shell CdSe/ZnS QDs, for
Figure 2.6. TRPL decay traces and corresponding fits for band-edge emission from the following dispersions containing core/shell CdSe/ZnS QDs: QDs alone (1, grey), QD/MPA (2, red), QD-MPA-ZrO₂ (3, green), and QD-MPA-TiO₂ (4, purple). IRF (5, yellow) was used in reconvolution.

dispersions of free QDs, QD/MPA dispersions, and QD-MPA-TiO₂ and QD-MPA-ZrO₂ dispersions. TRPL decay traces were fitted using multi-exponential reconvolution (equation 2.1). The decay traces were modeled most accurately by triexponential fits with the exception of the decay traces corresponding to emission at 508 and 520 nm from QD-MPA-TiO₂ dispersions, for which biexponential reconvolution gave the best fits. Representative decay traces and fits for emission at 537 nm, near the band-edge maximum, are shown in Figure 2.6. Values of $\langle \tau \rangle$ are compiled in Table 2.1 (at the band-edge emission maximum) and Table S2.6 in the Supporting Information (at wavelengths throughout the
band-edge emission band). Representative values of $A_i$ and $\tau_i$ for the different dispersions containing core/shell QDs are in Table S2.7 in the Supporting Information. The enhancement of steady-state emission upon addition of MPA to core/shell CdSe/ZnS QDs (Figure 2.5) manifests as an increase of the emission lifetime in TRPL data (Figure 2.6). Values of $\langle \tau \rangle$ from decay traces at 537 nm increased from $(13.3 \pm 0.1)$ ns for dispersions of free CdSe/ZnS QDs to $(18.0 \pm 0.3)$ ns for QD/MPA dispersions (Table S2.6). Values of $\langle \tau \rangle$ for emission at 537 nm for QD-MPA-TiO$_2$ and QD-MPA-ZrO$_2$ dispersions were $(4.2 \pm 0.2)$ ns and $(15.1 \pm 0.2)$ ns, respectively (Table 2.1). The lower value of $\langle \tau \rangle$ for QD-MPA-TiO$_2$ dispersions was caused primarily by a nearly 3-fold increase of $A_f$, the preexponential factor for the fastest component of decay, and 2-to-2.5-fold decreases of the three lifetimes (Table S2.7). The significant additional dynamic quenching in QD-MPA-TiO$_2$ dispersions, relative to QD-MPA-ZrO$_2$ dispersions, confirms the presence of an additional excited-state deactivation pathway, which we attribute to ET from CdSe/ZnS QDs to TiO$_2$ NPs.

Dynamics and efficiency of ET. Values of $k_{et}$ and $\eta_{et}$ were calculated, using equations 2.3 and 2.4, from measured values of $\langle \tau \rangle$ for wavelengths throughout the band-edge emission band and are compiled in Table S2.6. Values of $k_{et}$ ranged from $(3.3 \pm 0.4) \times 10^8$ s$^{-1}$ at 500 nm to $(1.1 \pm 0.1) \times 10^8$ s$^{-1}$ at 575 nm. Because $\langle \tau \rangle$ of QD-MPA-ZrO$_2$ dispersions was essentially independent of emission wavelength (Table S2.6), the decrease of $k_{et}$ with increasing wavelength gave rise to a corresponding decrease of $\eta_{et}$. Calculated values of $\eta_{et}$ decreased from $(85 \pm 2)\%$ at 500 nm to $(66 \pm 3)\%$ at 575 nm (Table S2.6). The decreases of both $k_{et}$ and $\eta_{et}$ with increasing wavelength within the band-edge emission band are similar to those observed for core-only CdSe QDs (Table S2.4) and are logically attributed to variations of the driving force of ET and/or the interfacial electronic coupling.
ET from Core-Only vs. Core/Shell QDs

For the QD-MPA-TiO₂ assemblies that were the subject of this study, the measured values of $k_{et}$ and $\eta_{et}$ for ET from excitonic states were nearly identical (Tables 2.1, S2.4, and S2.6), despite the presence of the ZnS shell as an energetic and spatial barrier to ET in the case of the core/shell CdSe/ZnS QDs. This result is intriguing and stands in contrast to previous reports that rate constants of charge transfer from QDs to molecular and nanoparticulate acceptors decreased with the thickness of the shell. We speculate that the apparent insensitivity of $k_{et}$ and $\eta_{et}$ to the presence of the ZnS shell in our measurements arose from differences in the amount of MPA ligands adsorbed to QDs and the extent of cross-linking to TiO₂ NPs. Several factors may have contributed to these differences. First, the commercial core/shell CdSe/ZnS QDs were capped initially by oleylamine, which was more labile than the native capping ligands of the nominally TOPO-capped core-only CdSe QDs, as evidenced by the initial decrease of emission from the core/shell QDs as they equilibrated with surrounding solvent. The lability of oleylamine probably facilitated the attachment of MPA to the surface. Second, the surface area of the core/shell CdSe/ZnS QDs was approximately six-fold greater than that of the core-only CdSe QDs, assuming spherical particles, potentially enabling significantly higher saturation loadings of MPA on the core/shell QDs. Finally, the concentration of MPA in core/shell CdSe/ZnS QD-MPA-TiO₂ dispersions was 15-fold greater than in core-only CdSe QD-MPA-TiO₂ dispersions, as described above. Therefore, at equilibrium, the core/shell CdSe/ZnS QDs were probably cross-linked to TiO₂ NPs to a greater extent than were the core-only CdSe QDs, potentially increasing the fraction of QDs interfaced with TiO₂, the stability and persistence of such interactions, and the average interfacial electronic coupling. These effects would lead to an
increase in the value of $k_{et}$ extracted from TRPL decay traces. Alivisatos and coworkers recently reported a similar effect.\textsuperscript{67} They found that the presence of a CdS shell as charge-transfer barrier in type-I core/shell CdSe/CdS QDs coupled to adsorbed hole-accepting ferrocene derivatives could be compensated for by increasing the average number of adsorbed acceptors on the significantly higher surface area of core/shell CdSe/CdS QDs as compared to core-only CdSe QDs.\textsuperscript{67}

**Conclusions**

TRPL measurements have revealed new insight into the mechanisms and time scales of ET from photoexcited core-only CdSe and core/shell CdSe/ZnS QDs to molecularly-tethered TiO\textsubscript{2} NPs. Dynamic quenching of both band-edge and surface emission clearly indicates that electrons were transferred from both excitonic and surface states of core-only CdSe QDs to TiO\textsubscript{2} with $k_{et}$ of $10^7$-$10^8$ s\textsuperscript{-1}. Efficiencies of ET, which are more important than rate constants from the standpoint of converting incident irradiance into electrical power or chemical potential, were $\sim$66-85\% for ET from excitonic states and $\sim$64-76\% for ET from surface states. Thus, relaxation of electrons into surface states of core-only CdSe QDs did not greatly affect the efficiency of ET to TiO\textsubscript{2}. The 2-to-3-fold increase of $k_{et}$ for ET from excitonic states relative to ET from surface states probably arose from the increased driving force and/or differences in electronic coupling. More generally, trapping of electrons prior to their extraction from QDs is potentially undesirable, as it reduces the potential energy of the electrons.

Direct comparisons between the dynamics of ET from core-only CdSe QDs and core/shell CdSe/ZnS QDs are complicated by differences in their sizes, band gaps, and
driving forces for ET to TiO$_2$, as well as the extent of ligand-exchange and linker-assisted attachment to TiO$_2$. Nonetheless, our results reveal that type-I core/shell CdSe/ZnS QDs possess several advantages relative to core-only CdSe QDs as sensitizers of TiO$_2$. First, the ZnS shell minimized the trapping of electrons, as is well-established$^{60-61}$ and evidenced by the absence of surface emission (Figure 2.5). Second, the ZnS shell minimized the transfer of photogenerated holes to MPA, as evidenced by the absence of quenching of emission upon reaction of the QDs with MPA (Figures 2.5 and 2.6, Table S2.6). Third, the values of $k_{et}$ ($\sim$10$^8$ s$^{-1}$) and $\eta_{et}$ ($\sim$66-85%) for ET from excitonic states of core/shell QDs were nearly identical to those for ET from excitonic states of core-only QDs under our conditions. The presence of the ZnS shell as tunneling barrier to ET may have been offset by an increase in the number of linkages between the QDs and TiO$_2$, owing to their greater size and the increased surface loading of MPA. Our results provide mechanistic insight into the superior performance of Type-I core/shell QDs as excited-state electron donors.

**Acknowledgements**

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Electronic Supplementary Information

Photoinduced Electron Transfer from Quantum Dots to TiO$_2$: Elucidating the Involvement of Excitonic and Surface States

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Appendix S2.1. Detailed description of the preparation of samples for emission spectroscopy.

Appendix S2.2. Derivations of equations 3 and 4 for calculating rate constants of ET ($k_{et}$) and efficiencies of ET ($\eta_{et}$).

Figure S2.1. Normalized emission intensity as a function of equilibration time for dispersions containing core-only CdSe QDs measured at the band-edge maximum of 515 nm (a) and the surface maximum of 750 nm (b) and for dispersions containing core/shell CdSe/ZnS QDs measured at the band-edge maximum of 540 nm (c).

Figure S2.2. TRPL decay traces, instrument response function, multiexponential reconvolution fits, and corresponding residuals from representative measurements for each type of QD-containing dispersion at various wavelengths.

Table S2.3. Values of $\langle \tau \rangle$ within the band-edge emission band and corresponding values of $k_{et}$ and $\eta_{et}$ for dispersions containing core-only CdSe QDs.

Table S2.4. Values of $\langle \tau \rangle$ within the surface emission band and corresponding values of $k_{et}$ and $\eta_{et}$ for dispersions containing core-only CdSe QDs.

Table S2.5. Values of $\langle \tau \rangle$ within the band-edge emission band and corresponding values of $k_{et}$ and $\eta_{et}$ for dispersions containing core/shell CdSe/ZnS QDs.
Appendix S2.1. Preparation of Samples

The concentration of core-only CdSe QDs was equal in all mixed dispersions. The absorbance of the stock dispersion of CdSe QDs in 1:1 toluene/ethanol (by volume) at the first excitonic absorption maximum (500 nm) was approximately 0.15. Concentrations of the stock solution of MPA and the stock dispersions of metal oxides (in formula units) in 1:1 toluene/ethanol (by volume) were 1.5 mM and 33 mM, respectively. The mixed dispersions were prepared as follows:

Table S2.1. Compositions of mixed dispersions containing core-only CdSe QDs for spectroscopic analysis.

<table>
<thead>
<tr>
<th>Sample (core-only CdSe QDs)</th>
<th>Volume of stock QD dispersion (mL)</th>
<th>Volume of stock MPA solution (mL)</th>
<th>Volume of stock MO₂ dispersion (mL)</th>
<th>Volume of solvent (1:1 toluene/EtOH) (mL)</th>
<th>Total volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD alone</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>QD/ZrO₂</td>
<td>10</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>QD/TiO₂</td>
<td>10</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>QD/MPA</td>
<td>10</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>QD-MPA-ZrO₂</td>
<td>10</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>QD-MPA-TiO₂</td>
<td>10</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>15</td>
</tr>
</tbody>
</table>

For mixed dispersions containing core/shell CdSe/ZnS QDs, the absorbance of the stock dispersion of QDs at the first excitonic maximum (500 nm) was approximately 0.05. Concentrations of the stock solution of MPA and the stock dispersions of metal oxides (in formula units) in 1:1 toluene/ethanol (by volume) were 1.5 mM and 33 mM, respectively. The mixed dispersions were prepared as follows:
Table S2.2. Compositions of mixed dispersions containing core/shell CdSe/ZnS QDs for spectroscopic analysis.

<table>
<thead>
<tr>
<th>Sample (core/shell CdSe/ZnS QDs)</th>
<th>Volume of stock QD dispersion (mL)</th>
<th>Volume of stock MPA solution (mL)</th>
<th>Volume of stock MO₂ dispersion (mL)</th>
<th>Volume of solvent (1:1 toluene/EtOH) (mL)</th>
<th>Total volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD alone</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>QD/ZrO₂</td>
<td>20</td>
<td>0</td>
<td>6</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>QD/TiO₂</td>
<td>20</td>
<td>0</td>
<td>6</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>QD/MPA</td>
<td>20</td>
<td>4</td>
<td>0</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>QD-MPA-ZrO₂</td>
<td>20</td>
<td>4</td>
<td>6</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>QD-MPA-TiO₂</td>
<td>20</td>
<td>4</td>
<td>6</td>
<td>0</td>
<td>30</td>
</tr>
</tbody>
</table>
Appendix S2.2. Derivation of Equations 3 and 4 for Calculating Rate Constants of ET ($k_{ET}$) and Efficiencies of ET ($\eta_{et}$)

Excited states of core-only CdSe QDs or core/shell CdSe/ZnS QDs within QD-MPA-ZrO$_2$ assemblies can decay radiatively or non-radiatively, as ET is not feasible. If the decay is mono-exponential then

$$<\tau>_{QD-MPA-ZrO_2} = \frac{1}{k_r + k_{nr}}$$  \hspace{1cm} (S2.1)

where $k_r$ and $k_{nr}$ are rate constants of radiative and non-radiative relaxation, respectively. For QD-MPA-TiO$_2$ assemblies, in addition to the radiative and non-radiative deactivation pathways, ET is also feasible due to favorable interfacial band energetics. Therefore,

$$<\tau>_{QD-MPA-TiO_2} = \frac{1}{k_r + k_{nr} + k_{et}}$$  \hspace{1cm} (S2.2)

An expression for $k_{et}$ is derived by inverting equations 1 and 2 and taking the difference:

$$k_{et} = \left( \frac{1}{<\tau>_{QD-MPA-TiO_2}} - \frac{1}{<\tau>_{QD-MPA-ZrO_2}} \right)$$  \hspace{1cm} (2.3)

The efficiency of electron transfer equals number of electrons transferred to TiO$_2$ ($N_{et}$) divided by the total number of initial photoexcited QDs ($N_{total}$):

$$\eta_{et} = \frac{N_{et}}{N_{total}} \times 100$$  \hspace{1cm} (S2.4)

The ratio of $N_{et}$ to $N_{total}$ equals the ratio of $k_{et}$ to the sum of all rate constants of excited-state deactivation ($k_{total}$):

$$\frac{N_{et}}{N_{total}} = \frac{k_{et}}{k_{total}} = \frac{k_{et}}{k_r + k_{nr} + k_{et}}$$  \hspace{1cm} (S2.5)
Using equations S2, 3, and S5, equation S4 can be rewritten as

\[ \eta_{et} = \left( \frac{1}{\langle t \rangle_{QD - MPA - TiO_2}} - \frac{1}{\langle t \rangle_{QD - MPA - ZrO_2}} \right) \times < t >_{QD - MPA - TiO_2} \times 100 \]  
(S2.6)

Rearranging equation S6 yields

\[ \eta_{inj} = (1 - \frac{\langle t \rangle_{QD - MPA - TiO_2}}{\langle t \rangle_{QD - MPA - ZrO_2}}) \times 100 \]  
(2.4)
Fig. S2.1. Normalized emission intensity as a function of equilibration time for dispersions containing core-only CdSe QDs measured at the band-edge maximum of 515 nm (a) and the surface maximum of 750 nm (b) and for dispersions containing core/shell CdSe/ZnS QDs measured at the band-edge maximum of 540 nm (c). Graphs a and b contain representative data from one of three replicate measurements on such samples. Graph c contains averaged values from three measurements; error bars correspond to plus-or-minus one standard deviation relative to the average.
Fig. S2.2. Top graphs: TRPL decay traces (blue), IRF (red), and multiexponential reconvolution fits from eq. 1 (black) from representative measurements for each type of QD-containing dispersion at various wavelengths. Bottom graphs: corresponding residuals (data minus fit). Each set of graphs shows fits to monoexponential (left), biexponential (middle), and triexponential (right) functions. Corresponding chi-square values are in the insets.

Core-only CdSe QDs alone ($\lambda_{em} = 515$ nm):

Core-only CdSe QD/MPA ($\lambda_{em} = 515$ nm):
Core-only CdSe QD-MPA-ZrO₂ (\(\lambda_{em} = 515\) nm):

Core-only CdSe QD-MPA-TiO₂ (\(\lambda_{em} = 515\) nm):

Core-only CdSe QDs alone (\(\lambda_{em} = 622\) nm):
Core-only CdSe QD/MPA (λem = 622 nm):

Core only CdSe QD-MPA-ZrO₂ (λem = 622 nm):

Core-only CdSe QD-MPA-TiO₂ (λem = 622 nm):

Core/shell CdSe/ZnS QDs alone (λem = 540 nm):
Core/shell CdSe/ZnS QD/MPA ($\lambda_{em} = 540$ nm):

Core/shell CdSe/ZnS QD/MPA-ZrO$_2$ ($\lambda_{em} = 540$ nm):

Core/shell CdSe/ZnS QD/MPA-TiO$_2$ ($\lambda_{em} = 540$ nm):
**Table S2.3.** Values of $<\tau>$ within the band-edge emission band and corresponding values of $k_{et}$ and $\eta_{et}$ for dispersions containing core-only CdSe QDs.

<table>
<thead>
<tr>
<th>Emission wavelength ($\lambda_{em}$) (nm)</th>
<th>$&lt;\tau&gt;$ QD alone (ns)</th>
<th>$&lt;\tau&gt;$ QD-MPA (ns)</th>
<th>$&lt;\tau&gt;$ QD-MPA-ZrO$_2$ (ns)</th>
<th>$&lt;\tau&gt;$ QD-MPA-TiO$_2$ (ns)</th>
<th>$k_{et}\times10^8$ (s$^{-1}$)</th>
<th>$\eta_{et}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>487</td>
<td>27±1</td>
<td>25±2</td>
<td>18±3</td>
<td>3.2±0.9</td>
<td>2.5±0.8</td>
<td>82±6</td>
</tr>
<tr>
<td>500</td>
<td>27.1±0.6</td>
<td>26±1</td>
<td>21±1</td>
<td>4.0±0.6</td>
<td>2.0±0.4</td>
<td>81±3</td>
</tr>
<tr>
<td>513</td>
<td>26.5±0.4</td>
<td>26.8±0.8</td>
<td>22.2±0.9</td>
<td>4.7±0.4</td>
<td>1.7±0.2</td>
<td>79±2</td>
</tr>
<tr>
<td>525</td>
<td>28.4±0.6</td>
<td>26±1</td>
<td>22±1</td>
<td>6.0±0.9</td>
<td>1.2±0.3</td>
<td>73±4</td>
</tr>
<tr>
<td>538</td>
<td>29.5±0.9</td>
<td>31±2</td>
<td>24±2</td>
<td>7±1</td>
<td>1.1±0.3</td>
<td>71±5</td>
</tr>
</tbody>
</table>

**Table S2.4.** Values of $<\tau>$ within the surface emission band and corresponding values of $k_{et}$ and $\eta_{et}$ for dispersions containing core-only CdSe QDs.

<table>
<thead>
<tr>
<th>Emission wavelength ($\lambda_{em}$) (nm)</th>
<th>$&lt;\tau&gt;$ QD alone (ns)</th>
<th>$&lt;\tau&gt;$ QD+MPA (ns)</th>
<th>$&lt;\tau&gt;$ QD-MPA-ZrO$_2$ (ns)</th>
<th>$&lt;\tau&gt;$ QD-MPA-TiO$_2$ (ns)</th>
<th>$k_{et}\times10^7$ (s$^{-1}$)</th>
<th>$\eta_{et}$ (%)</th>
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<tbody>
<tr>
<td>610</td>
<td>43±1</td>
<td>39±2</td>
<td>42±3</td>
<td>15±3</td>
<td>4±2</td>
<td>64±8</td>
</tr>
<tr>
<td>622</td>
<td>48±2</td>
<td>45±3</td>
<td>34±2</td>
<td>10±2</td>
<td>7±2</td>
<td>71±6</td>
</tr>
<tr>
<td>635</td>
<td>45±2</td>
<td>44±2</td>
<td>37±2</td>
<td>13±3</td>
<td>5±2</td>
<td>65±8</td>
</tr>
<tr>
<td>647</td>
<td>45±2</td>
<td>42±2</td>
<td>41±2</td>
<td>14±2</td>
<td>5±1</td>
<td>66±5</td>
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<tr>
<td>660</td>
<td>48±2</td>
<td>47±2</td>
<td>45±3</td>
<td>11±2</td>
<td>7±1</td>
<td>76±5</td>
</tr>
<tr>
<td>672</td>
<td>53±2</td>
<td>52±3</td>
<td>46±3</td>
<td>11±1</td>
<td>7±1</td>
<td>76±3</td>
</tr>
<tr>
<td>685</td>
<td>57±2</td>
<td>47±3</td>
<td>45±3</td>
<td>11±1</td>
<td>7±1</td>
<td>76±3</td>
</tr>
<tr>
<td>697</td>
<td>61±4</td>
<td>56±4</td>
<td>41±3</td>
<td>11±1</td>
<td>7±1</td>
<td>73±3</td>
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<tr>
<td>710</td>
<td>56±3</td>
<td>55±4</td>
<td>49±4</td>
<td>13±2</td>
<td>6±1</td>
<td>74±5</td>
</tr>
<tr>
<td>722</td>
<td>50±3</td>
<td>44±3</td>
<td>46±4</td>
<td>12±2</td>
<td>6±2</td>
<td>74±5</td>
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</table>
Table S2.5. Values of $<\tau>$ within the band-edge emission band and corresponding values of $k_{et}$ and $\eta_{et}$ for dispersions containing core/shell CdSe/ZnS QDs.

<table>
<thead>
<tr>
<th>Emission wavelength ($\lambda_{em}$) (nm)</th>
<th>$&lt;\tau&gt;$ QD alone (ns)</th>
<th>$&lt;\tau&gt;$ QD+MPA (ns)</th>
<th>$&lt;\tau&gt;$ QD-MPA-ZrO2 (ns)</th>
<th>$&lt;\tau&gt;$ QD-MPA-TiO2 (ns)</th>
<th>$k_{et}/10^8$ (s$^{-1}$)</th>
<th>$\eta_{et}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>13.7±0.4</td>
<td>22±1</td>
<td>16.8±0.8</td>
<td>2.5±0.2*</td>
<td>3.3±0.4</td>
<td>85±2</td>
</tr>
<tr>
<td>513</td>
<td>13.8±0.2</td>
<td>18.3±0.5</td>
<td>14.9±0.3</td>
<td>3.1±0.2</td>
<td>2.6±0.2</td>
<td>80±1</td>
</tr>
<tr>
<td>525</td>
<td>13.3±0.2</td>
<td>18.0±0.4</td>
<td>14.4±0.6</td>
<td>3.5±0.1</td>
<td>2.2±0.1</td>
<td>76±1</td>
</tr>
<tr>
<td>537</td>
<td>13.3±0.1</td>
<td>18.0±0.3</td>
<td>15.1±0.2</td>
<td>4.2±0.1</td>
<td>1.7±0.1</td>
<td>72±1</td>
</tr>
<tr>
<td>550</td>
<td>14.0±0.2</td>
<td>18.4±0.4</td>
<td>15.5±0.3</td>
<td>4.8±0.1</td>
<td>1.4±0.1</td>
<td>69±1</td>
</tr>
<tr>
<td>563</td>
<td>15.0±0.3</td>
<td>21.0±0.6</td>
<td>16.8±0.4</td>
<td>5.7±0.2</td>
<td>1.2±0.1</td>
<td>66±2</td>
</tr>
<tr>
<td>575</td>
<td>16.7±0.6</td>
<td>22±1*</td>
<td>18±0.7*</td>
<td>6.3±0.5</td>
<td>1.1±0.1</td>
<td>66±3</td>
</tr>
</tbody>
</table>

* biexponential fits.
References


Chapter III

Highly Efficient Hole Transfer from Chloride Treated CdTe Quantum Dots to Covalently Tethered Molecular Acceptors
**Introduction**

QDs exhibit size-dependent band gaps\(^1\,^2\) and high molar absorptivities\(^4\,^6\) and have been shown to undergo hot electron transfer\(^7\,^8\) and multiexciton generation\(^9\,^{12}\) under certain conditions. These properties render QDs intriguing materials for solar energy conversion and photocatalysis. Separating photogenerated electrons and holes before they recombine enables the potential energy of these charge carriers to be exploited in subsequent charge-transfer processes. The surface chemistry of QDs can dramatically affect interfacial charge transfer. As-synthesized colloidal QDs are often surrounded by long insulating aliphatic ligands, which effectively passivate the surface of QDs and also provide colloidal stability in non-polar solvents. Incomplete passivation of the surface of QDs can give rise to surface states at energies within the band gap. Such mid-gap surface states can trap photogenerated charges, resulting in a loss of potential energy. Surface states can be passivated by growing a wide-bandgap inorganic shell over the core of QDs.\(^{13\,\,15}\) However, the presence of such a shell creates a spatial and energetic barrier for charge-transfer processes.\(^{16\,\,18}\) Recently, small ligands such as halides, sulfides, thiocyanates, and tetrafluoroborates have been shown to passivate effectively the surfaces of QDs in the absence of a thick inorganic shell.\(^{19\,\,29}\) Page et al. treated CdTe QDs with chloride, which engendered high stability in air, near-unity fluorescence quantum yields, and nearly monoexponential fluorescence decays.\(^{21}\) Greaney et al. reported that the trap-state landscape of CdSe QDs could be controlled by treating with cadmium halides.\(^{22}\) Bawendi et al. reported that the treatment of PbS QDs with iodide led to record efficiencies of 8.55% for colloidal QD-based solar cells.\(^{24}\)

The long insulating aliphatic ligands of as-synthesized QDs make it difficult to extract charges from photoexcited QDs. Therefore, ligands on the surface of QDs are often exchanged
with smaller molecules and tethered charge acceptors to extract charges efficiently from photoexcited QDs. Wide-bandgap semiconductors such as TiO$_2$, SnO$_2$ and ZnO have been sensitized extensively with QDs by using small bifunctional linkers such as 3-mercaptopropionic acid (MPA) to extract electrons from photoexcited QDs.$^{18,30-39}$ The mesoporous structure of these metal oxides allows higher loading of sensitizers. Also, easy incorporation of metal oxides into photovoltaic devices and their excellent charge-transport properties make metal oxides ideal as electron acceptors.$^{40-42}$ However, characterizing charge transfer within such assemblies is difficult, as multiple QDs can tether to a single metal oxide particulate via direct adsorption or via single or multiple covalent linkages. Moreover, a single metal oxide acceptor has a continuum of accepting electronic states and can accept more than one electron per particle.$^{39}$ The inherent complexity of such a system makes it difficult to quantify fundamental aspects of the charge-transfer process.

Alternatively, to gain insight into the mechanism of charge transfer process, QDs are often tethered to small molecular acceptors which have well-defined energetic structure and can accept just one charge carrier at a time. Since multiple molecular acceptors can bind to the surface of a single QD, they can provide multiple pathways for charge transfer to occur from photoexcited QDs to molecular acceptors. If that all of these charge-transfer pathways are additive, or, equivalently, if charge-transfer is first order with respect to the adsorbed charge acceptor, then the overall effective rate constant of charge transfer ($k_{CT}$) can be written as,$^{43-47}$

$$k_{CT} = Nk_{ct}$$  \hspace{1cm} (3.1)

Where $N$ is the average number of bound acceptors per QD and $k_{CT}$ is the intrinsic rate constant of charge transfer for a QD attached to one single acceptor.
Recently, $^1$H NMR spectroscopy has been used increasingly to quantify ligand exchange at the surfaces of QDs. Alivisatos and coworkers studied hole-transfer processes in CdSe/CdS core/shell QDs tethered to the molecular hole acceptor FcC$_6$SH and its derivatives. The distinct peaks of FcC$_6$SH bound to the surface of QDs in $^1$H NMR spectra allowed facile quantification of the average number of FcC$_6$SH per QD. Alivisatos and coworkers showed that, even for CdSe QDs overcoated with seven monolayers of CdS shell, holes could be efficiently extracted from the photoexcited CdSe core. However, a damping coefficient of (0.24 ± 0.025) Å$^{-1}$ was reported, and the presence of hole-trapping thiolates at the surface of QDs added complexity.

Inspired by the work of Alivisatos and coworkers and by the aforementioned reports of chloride treatment of QDs, we have studied hole-transfer dynamics in chloride-treated CdTe QDs bound to FcC$_6$SH. Our goal was to improve hole-transfer efficiency by eliminating the need for a thick inorganic shell over QD core and by avoiding the trapping of holes by thiolates and the corresponding loss of potential energy. Our results are reported in this manuscript. We found that chloride treatment resulted not only in effective passivation of QDs but also in almost ten-fold higher loading of FcC$_6$SH relative to untreated CdTe QDs. The higher loading of FcC$_6$SH resulted in almost 99% efficient hole transfer from photoexcited CdTe QDs to FcC$_6$SH.

**Experimental**

**Materials.** Cadmium Oxide (CdO) and tri-$n$-octyl phosphine (TOP, 98%) were purchased from Alfa Aesar. Tellurium powder (200 mesh, 99.8%), tetrade-cylphosphonic acid (TDPA, 99%), anhydrous cadmium chloride (CdCl$_2$, 99.99%), 1-hexanethiol (HT, 95%) and 6-
(ferrocenyl)hexanethiol (FcC$_6$SH) were purchased from Sigma Aldrich. HPLC grade solvents such as benzene, acetonitrile, chloroform and acetone were purchased from Fisher Scientific. Deuterated chloroform (CDCl$_3$) for NMR measurements was purchased from Cambridge Isotope Laboratories, Inc. All reagents were used as received.

**Synthesis of CdTe QDs.** TDPA-capped CdTe QDs were synthesized following the procedure of Wang et. al.$^{15}$ Briefly, tellurium powder (0.128 g, 1 mmol) and TOP (5 mL) were combined in an Ar atmosphere, and the solution was sealed with a rubber septum and then transferred to a fume hood. The tellurium-containing mixture was heated to 210 °C under constant stirring, at which point 5 mL octadecene was injected to the mixture. CdO (0.128 g, 1 mmol) was added to TDPA (0.7 g, 2.5 mmol) and octadecene (20 mL) in a separate three-neck flask. The flask was heated to 315 °C under Ar atmosphere with constant stirring till the cadmium-containing mixture became colorless. The solution was allowed to cool to 290 °C, at which point the tellurium-containing solution was swiftly injected into the cadmium-containing mixture. Growth of CdTe QDs was monitored by a change of color of the mixture from yellow to orange to dark red. When the desired particle size was reached, the mixture was removed from heat, and the reaction was quenched. The QD-containing mixture was allowed to cool to 60 °C, and approximately 40 mL of 1:1 v/v hexane/methanol solution was added to the mixture to extract CdTe nanocrystals from the byproducts and the unreacted precursors. The hexane layer was separated, and CdTe QDs were flocculated by addition of acetone and were dried under Ar atmosphere. The dried CdTe QDs were stored inside a glovebox in Ar atmosphere until further use.

**Chloride Treatment of CdTe QDs.** Untreated CdTe QDs underwent chloride treatment following the procedure of Page et al.$^{21}$ Briefly, a 0.33 M stock solution of CdCl$_2$ was
prepared by dissolving anhydrous CdCl$_2$ (0.3 g, 1.6 mmol) and TDPA (0.033 g, 0.12 mmol) in oleylamine (5 mL). The solution was degassed at 100 °C for 30 min and cooled to 60 °C under Ar atmosphere. The untreated CdTe QDs were dispersed in 20 mL CHCl$_3$ in a separate flask, and the solution was heated to 60 °C under constant stirring in Ar atmosphere for 30 min. A predetermined amount of CdCl$_2$ stock solution, equivalent to 96 Cl$^-$ ions per square nanometer of surface area of CdTe QDs (Supporting Information, Appendix S1), was quickly injected to the QD dispersion in CHCl$_3$. The reaction was allowed to proceed for 15 min. A visible change in color of solution from dark red to bright red, indicating improved quantum yield (QY) of emission, was observed. The heat was removed after 15 min, and the reaction was quenched. The chloride-treated QDs were flocculated by addition of acetone and then dried inside a glovebox under Ar atmosphere before being used in dispersions for spectroscopic measurements.

**Methods.** Three different sets of mixed dispersions were prepared as described in Appendix S3 in Supporting Information: (1) chloride-treated CdTe QDs and FcC$_6$SH; (2) untreated CdTe QDs and FcC$_6$SH and, (3) chloride-treated CdTe QDs and HT. The concentration of CdTe QDs was identical for all dispersions, and the concentration of FcC$_6$SH and HT was varied systematically from 0 μM to 170 μM.

UV/vis absorption spectra were obtained with an Agilent 8453 spectrophotometer. Steady-state emission spectra were acquired with a Varian Cary Eclipse fluorimeter with excitation at 500 nm. Time-resolved photoluminescence (TRPL) decay profiles were obtained with a Becker and Hickl Tau-130 time-correlated single photon counting (TCSPC) setup. The setup consisted of a diode laser (BDL 445 SMC) emitting monochromatic pulses at 445 nm with pulse-width of 40-90 ps (full width at half maximum (FWHM)) at power of 1 mW and repetition rate of 50 MHz. The laser could be operated at three different repetition rates (1 MHz, 20 MHz and 50 MHz). All time-
resolved measurements except for samples containing chloride treated CdTe QDs and FcC₆SH were made at 1 MHz repetition rate to avoid re-exciting samples before they decayed completely to the baseline. A delay cable equivalent to 50 ns was employed in the sync channel. The time-to-amplitude converter (TAC) was fixed to 50 ns to acquire decay profiles corresponding to the first 50 ns of decay, in order to achieve higher time resolution. The relatively short lifetimes (< 2 ns) of dispersions containing chloride-treated CdTe QDs and FcC₆SH allowed for time-resolved measurements to be acquired at higher repetition rate (20 MHz). QD-containing dispersions were housed in a four-sided quartz cuvette with a path length of 1 cm. Emission was collected at 90° to the excitation beam and focused into a polychromator coupled to a 16-channel photomultiplier tube (PML 16-C). Each channel corresponded to a 12.5 nm window in the wavelength regime. All time-resolved measurements were obtained at magic angle conditions by placing a polarizer in the emission channel at 54.7° relative to the polarization of the excitation beam. A 460 nm long-pass filter was placed in the emission channel before the polychromator to minimize scattering of the excitation light from samples. A neutral density filter was used to adjust the intensity of the excitation beam such that the probability of detection of a photon per excitation pulse was less than 0.01. TRPL decay traces were obtained over 4096 time bins with time resolution of 12.2 ps. Decay profiles were collected over 600 s and 50 s for measurements conducted at repetition rates of 1 MHz and 20 MHz, respectively. The instrument response function (IRF) was acquired by using a light-scattering suspension of silica LUDOX and measuring a decay profile at the excitation wavelength. At a laser gain of 20% and a detector gain of 90%, FWHM for the IRF was approximately 250 ps. TRPL decay traces were fitted using Fluofit software by Picoquant.

¹H NMR spectra of CdTe QDs-containing dispersions with micromolar concentrations were measured with an Inova 500 MHz instrument. The preparation of samples containing
chloride-treated or untreated CdTe QDs and FcC₆SH or HT is described in Appendix S4 in the Supporting Information. Benzene was used as an internal reference to enable the quantitative estimation of surface coverage of FcC₆SH on CdTe QDs. Briefly, 100 μL of 10 mM benzene in CDCl₃ and 600 μL of a QD-containing dispersion in CDCl₃ were added to an NMR tube, and an NMR spectrum was acquired. NMR spectra were integrated over 256 scans and 512 scans, respectively, for dispersions containing chloride-treated and untreated CdTe QDs. ¹H NMR spectra were processed using ACD Spectrus Processor software by ACD/Labs.

**Results and Discussion**

**An Approach to Quantify Hole Transfer as a Function of the Number of Adsorbed Hole Acceptors.** The transfer of holes from photoexcited QDs to the covalently-bound hole acceptor FcC₆SH competes with the intraband electron-hole recombination and results in dynamic quenching of emission.⁴³,⁵¹,⁵³ FcC₆SH binds to the surface of cadmium chalcogenide QDs via thiol anchoring group.⁴³⁻⁴⁴,⁵¹,⁵³ We prepared mixed dispersions containing either chloride-treated or untreated CdTe QDs and FcC₆SH, at varying concentrations, and acquired steady-state emission and time-resolved emission spectra to quantify hole transfer from photoexcited QDs to FcC₆SH. Alivisatos and coworkers performed cyclic voltammetry measurements on FcC₆SH and CdSe/CdS nanorods and estimated a driving force of approximately 850 meV for hole transfer from the CdSe core to FcC₆SH.⁴³,⁵¹ The valence band edge of bulk CdTe lies approximately 700 meV above that of bulk CdSe.⁵⁴ On the basis of these bulk band-edge potentials of CdTe and CdSe QDs and measured HOMO of FcC₆SH, a thermodynamic driving force of approximately 150 meV can be estimated for hole transfer from the valence band of photoexcited CdTe QDs to the HOMO of FcC₆SH. Special caution was taken while preparing these donor-acceptor assemblies to assure
that there was minimal or no overlap between the emission of CdTe QDs and the absorption of FcC₆SH, thereby eliminating the possibility of Forster resonance energy transfer (FRET). Additionally, the optical bandgap of the CdTe QDs used in this study is approximately 2 eV, on the basis of the absorption onset, and the HOMO-LUMO gap of ferrocene is approximately 2.7 eV. Thus, the possibility of electron transfer from photoexcited CdTe QDs to FcC₆SH can be neglected, as the LUMO of ferrocene lies at higher energy than the conduction band edge of CdTe QDs. Thiolates adsorbed to cadmium chalcogenide QDs can quench emission by trapping holes from photoexcited QDs. To account for this possibility, control experiments were conducted on mixed dispersions containing chloride-treated CdTe QDs and hexanethiol. Finally, the average number of bound FcC₆SH per QD was estimated by ¹H NMR measurements (SI, Appendix S5) on samples containing chloride-treated or untreated CdTe QDs, FcC₆SH and benzene (internal reference) in deuterated chloroform. Absorption spectra of mixed dispersions containing chloride treated or untreated CdTe QDs and FcC₆SH were acquired subsequently after NMR measurements. Concentration of QDs in mixed dispersions were calculated by estimating the extinction coefficient of QDs at the first excitonic peak of chloride treated or untreated CdTe QDs according to Yu et al..

**Electronic Spectra of CdTe QDs.** The untreated TDPA-capped CdTe QDs exhibited a first excitonic absorption band with wavelength of maximum absorbance (λₘₐₓ) of 580 nm (Figure 3.1a). The average diameter of the untreated QDs was estimated to be 3.5 nm using the empirical equation reported by Yu et. al. The untreated CdTe QDs exhibited a band edge emission centered at 591 nm with full width at half maximum (FWHM) of approximately 117 meV. Chloride-treated CdTe QDs exhibited very similar absorption and emission features as untreated QDs. The first excitonic absorption peak and band edge emission maximum for chloride treated QDs was blue-
shifted by approximately 1-2 nm and 3-5 nm respectively. The lack of significant changes of excitonic features following chloride treatment suggests that the treatment did not affect the size or energetics of the QDs significantly.21 Chloride treatment on several batches of QDs resulted in enhancement of the quantum yield of emission from (4.3 ± 1.9)% to (51.5 ± 2.5)% (SI Figure S3.1). In order to examine the effect of chloride treatment on charge-recombination dynamics, time-resolved decay profiles were acquired for chloride-treated and untreated CdTe QDs at their respective emission maxima (Figure 3.1b). The acquired decay profiles were fitted with a triexponential reconvolution procedure according to equation 2.

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

(3.2)

where \( t \) is time, \( I(t) \) is intensity, \( A_i \) is amplitude of the \( i^{th} \) component, \( \tau_i \) is lifetime of the \( i^{th} \) component and \( IRF(t') \) is the instrument response function. The goodness of fit was evaluated by the distribution of residuals (differences between data and fit) around zero and by chi-square values. Chi-square values of 0.95-1.20 were considered as good fits. An additional exponential component was added if it resulted in significant improvement in chi-square values and residual plots. Intensity-weighted average lifetimes (\( \langle \tau \rangle \)) were calculated as follows:32-34, 57

\[ \langle \tau \rangle = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \]  

(3.3)

The average lifetime for untreated CdTe QDs was calculated to be (20.1±0.4) ns with three individual lifetime components of (22.6 ± 0.5) ns, (3.1 ± 0.1) ns and (0.3 ± 0.03) ns contributing (91 ± 5)%, (7 ± 1)%, and (2 ± 1)% to the overall emission intensity. The average lifetime for chloride-treated CdTe QDs was reduced to (18.2 ± 0.5) ns with lifetime components of (19.5 ± 0.2) ns, (4.8 ± 0.3) ns, and (0.5± 0.07) ns contributing (92 ± 5)%, (7 ± 1)%, and (1 ± 1)% to the
overall emission intensity. Approximately 6-18 fold enhancement in fluorescence QY and nearly monoexponential excited state decays following chloride treatment is consistent with effective surface passivation of CdTe QDs.

$^1$H NMR spectroscopy was used to characterize the surface of chloride-treated and untreated CdTe QDs (Figure 3.1c). The $^1$H NMR spectrum of untreated CdTe QDs contains broad resonances in the aliphatic region (0.7-3.0 ppm) which were assigned to bound TDPA and bound TOP. Following chloride treatment of CdTe QDs, broad resonances were observed at around (5.3-5.4) ppm and (2.7-3.0) ppm, apart from the bound TDPA and TOP resonances in the aliphatic region. Given their similarity to resonances in the $^1$H NMR spectrum of free oleylamine, these broad resonances were logically assigned to bound oleylamine. Page et al. have previously shown the presence of chlorine and nitrogen at the surface of the chloride-treated CdTe QDs using X-ray photoelectron spectroscopy. They attributed the improved air stability, near unity quantum yield, and nearly monoexponential decays of chloride-treated CdTe QDs to chloride passivation of the surface of the QDs.$^{21}$ Anderson et al. recently showed that primary amines (RNH$_2$) effectively displaced native L-type tri-$n$-butyl phosphine (TBP) ligands from the surface of cadmium chloride-treated CdSe QDs and increased the photoluminescence quantum yield (PLQY) by more than 1000-fold.$^{25}$ We suggest that the high quantum yield and near-monoexponential PL decays following chloride treatment result from efficient surface passivation by a mixture of L-type (oleylamine), X-type (Cl$^-$ and TDPA$^-$), and Z-type ([Cd(TDPA)$_n$]$^{(2-n)\text{+}}$ and [CdCl$_n$]$^{(2-n)\text{+}}$) ligands.$^{48}$
Figure 3.1. (a) UV-Vis and steady state emission spectra, (b) time-resolved emission spectra of as synthesized (untreated) CdTe QDs (black) and chloride treated CdTe QDs (red), (c) 1H-NMR spectra of untreated CdTe QDs (blue), chloride treated CdTe QDs (red) and oleylamine (black) in CDCl₃.

**Emission Quenching of Chloride-Treated CdTe QDs by FcC₆SH.** Steady-state emission spectra were acquired for mixed dispersions containing chloride-treated CdTe QDs and FcC₆SH as a function of time after mixing. Experiments were performed in triplicate for each type of dispersion. Normalized emission intensities at the band-edge emission maxima are plotted as a function of time in Figure S3.2 in Supporting Information. The emission intensities for various samples were normalized to the emission intensity for dispersions containing no FcC₆SH at the first measurement (20 mins after mixing, from here on referred as I₀). The samples equilibrated after approximately 2 h, except for the dispersion containing no FcC₆SH for which emission intensity increased by (1.5 ± 0.05) times as compared to I₀ over 2 hours. The percentage quenching of emission (%Q) on addition of FcC₆SH was quantified as [(I₀ – I)/I₀]×100, where I is the intensity of emission normalized from a given quencher-containing dispersion. The addition of FcC₆SH to
chloride-treated CdTe QDs quenched the emission of photoexcited CdTe QDs by (98.7 ± 0.3)% as concentration of FcC₆SH was increased from 0 to 170 μM, consistent with hole transfer from chloride-treated CdTe QDs to FcC₆SH.

Time-resolved emission decay traces were acquired for all samples to probe the dynamics of hole transfer from photoexcited chloride-treated CdTe QDs to FcC₆SH. Representative decay profiles and corresponding tri-exponential reconvolution fits for all dispersions at emission maxima are shown in Figure S3.3 in Supporting Information. Average lifetimes for mixed dispersions containing varying concentration of FcC₆SH were calculated from fits according to equation 3 and are tabulated in Table 3.1. The addition of FcC₆SH to chloride-treated CdTe QDs resulted in dynamic quenching of emission, as average lifetime decreased from (18.2 ± 0.6) ns to (0.33 ± 0.05) ns with concentration of FcC₆SH increasing from 0 to 170 μM. The approximately 55-fold decrease of ⟨τ⟩ confirms the presence of an additional deactivation pathway, which can be assigned logically to hole transfer from valence band of photoexcited chloride-treated CdTe QDs to the HOMO of FcC₆SH. Assuming that hole transfer is the only additional deactivation pathway in FcC₆SH-containing dispersions relative to dispersions of free CdTe QDs, and that the rate constants of radiative and non-radiative recombination in chloride-treated CdTe QDs did not change following ligand exchange with FcC₆SH, the overall rate constant of hole transfer (kₜₜ) and efficiency of hole transfer (ηₜₜ) were calculated as follows:³³-³⁴,⁵⁸

\[
k_{HT} = \frac{1}{\langle \tau \rangle_{QD\ alone}} - \frac{1}{\langle \tau \rangle_{QD+FcC6SH}} \tag{3.4}
\]

\[
\eta_{HT} = (1 - \frac{\langle \tau \rangle_{QD\ alone}}{\langle \tau \rangle_{QD+FcC6SH}}) \times 100 \tag{3.5}
\]
where \( \langle \tau \rangle_{\text{QD alone}} \) and \( \langle \tau \rangle_{\text{QD+FcC6SH}} \) are average lifetimes of dispersions containing QDs only and dispersions containing both QDs and FcC6SH, respectively. For the mixed dispersion containing highest concentration of FcC6SH (170 μM), \( k_{HT} \) and \( \eta_{HT} \) were calculated to be \((98.2 \pm 0.3\%) \) and \((3.0 \pm 0.4) \times 10^9 \text{ s}^{-1} \), respectively (Table 3.1).

**Table 3.1.** Values of average number of bound FcC6SH per QD (\( N_{\text{FcC6SH}} \)), \( \langle \tau \rangle \), \( k_{HT} \) and \( \eta_{HT} \) for mixed dispersions containing: (1) chloride-treated CdTe QDs and FcC6SH; (2) untreated CdTe QDs and FcC6SH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[FcC6SH] dispersion (μM)</th>
<th>( N_{\text{FcC6SH}} )</th>
<th>( \langle \tau \rangle ) (ns)</th>
<th>( k_{HT} ) (s(^{-1}))</th>
<th>( \eta_{HT} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>18.2 ± 0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chloride treated CdTe QDs + FcC6SH</td>
<td>17</td>
<td>27 ± 6</td>
<td>1.15 ± 0.05</td>
<td>((8.2 \pm 0.4) \times 10^8)</td>
<td>93.7 ± 0.3</td>
</tr>
<tr>
<td>34</td>
<td>48 ± 5</td>
<td>0.71 ± 0.04</td>
<td>((1.4 \pm 0.1) \times 10^9)</td>
<td>96.1 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>86 ± 14</td>
<td>0.44 ± 0.04</td>
<td>((2.2 \pm 0.2) \times 10^9)</td>
<td>97.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>116 ± 7</td>
<td>0.41 ± 0.04</td>
<td>((2.4 \pm 0.3) \times 10^9)</td>
<td>97.8 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>198 ± 5</td>
<td>0.33 ± 0.05</td>
<td>((3.0 \pm 0.4) \times 10^9)</td>
<td>98.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Untreated CdTe QDs + FcC6SH</td>
<td>0</td>
<td>0</td>
<td>20.3 ± 0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>170</td>
<td>26 ± 6*</td>
<td>8.7 ± 0.5</td>
<td>((6.5 \pm 0.7) \times 10^7)</td>
<td>57.0 ± 3.1</td>
<td></td>
</tr>
</tbody>
</table>

*upper limit of \( N_{\text{FcC6SH}} \)

After spectroscopic measurements, the mixed dispersions were flocculated to separate unbound FcC6SH from bound FcC6SH. The total number of bound FcC6SH per QD was calculated for each dispersion using \(^1\)H NMR spectroscopy (SI Appendix S3.5). Figure 3.3b compares the \(^1\)H
spectra of the supernatant following flocculation of mixed dispersions containing chloride-treated CdTe QDs and FcC₆SH (170µM) (red), the precipitate containing QDs bound to FcC₆SH (blue) and unflocculated mixed dispersions containing QDs and FcC₆SH (170µM) (black). The sharp peaks in the red spectrum correspond to free oleylamine (5.3 ppm, m, 2H and 2.7 ppm, t, 2H) and free FcC₆SH (4.1 ppm, s, 5H and 4.05 ppm, m, 4H). The absence of sharp peaks in the blue spectrum confirms that oleylamine and FcC₆SH were bound to the surface of chloride-treated CdTe QDs. Figure 3.3a shows ¹H NMR spectra of mixed dispersions containing chloride-treated CdTe QDs and FcC₆SH after flocculation. The increased intensity of bound FcC₆SH peaks on increasing the concentration of FcC₆SH in mixed dispersions indicates increase in surface coverage of FcC₆SH.
Figure 3.2. (a) UV-Vis spectra, (b) steady state emission spectra and (c) time-resolved emission spectra with tri-exponential fits of mixed dispersions containing chloride treated CdTe QDs and FcC₆SH.

Resonances associated with protons in benzene (7.36 ppm) were used as a reference to quantify the average number of bound FcC₆SH per QD. The concentration of QDs was calculated
from absorption spectra of mixed dispersions after $^1$H NMR measurements. Based on the $^1$H NMR and absorption spectra of mixed dispersions, the average number of bound FcC$_6$SH increased from $(27 \pm 6)$ to $(198 \pm 5)$ as the concentration of FcC$_6$SH in mixed dispersions increased from 17 to 170 μM. The increased absorbance from 400 nm to 500 nm (Figure 3.2a) is consistent with an increase in the average number of bound FcC$_6$SH with increasing concentration of FcC$_6$SH.

The value of $k_{HT}$, extracted from time-resolved emission measurements, and the average number of bound FcC$_6$SH, calculated from $^1$H NMR measurements, were plotted as shown in Figure 3.4. The uncertainties in $k_{HT}$ values were calculated by propagation of error from three different experimental runs along with the uncertainties in fitting of decay profiles from each measurement. Uncertainties in $N_{FcC6SH}$ were also calculated from three different runs. Our estimation of the concentration of QDs from absorption spectra and estimation of bound FcC$_6$SH using the internal reference (benzene) are potential sources of error in calculation of $N_{FcC6SH}$. The experimentally-determined values of $k_{HT}$ increase with $N_{FcC6SH}$. Increasing the number of bound FcC$_6$SH per QD provides additional hole-transfer pathways for the photoexcited QDs which enables hole transfer to compete more efficiently with electron-hole recombination. Assuming that all bound FcC$_6$SH contribute equally to hole transfer and that individual hole-transfer events are additive in nature, the overall hole transfer process can be thought as a sum of ‘$N$’ ($N = N_{FcC6SH}$) intrinsic hole-transfer pathways with intrinsic rate constant of hole transfer $k_{ht}$, where $k_{ht}$ is defined as the rate constant of hole transfer for a system having one FcC$_6$SH (acceptor) bound per QD (donor). Alternatively,

$$k_{HT} = N_{FcC6SH} \times k_{ht}$$

(5)
Not all adsorbed FcC₆SH molecules on the surface of QDs will necessarily contribute to photoinduced hole transfer; therefore, some non-linearity in $k_{HT}$ vs $N_{FcC6SH}$ can be expected.⁴⁶ Also, as the concentration of FcC₆SH in mixed dispersions increased to 170 μM, the average lifetimes (~300 ps) became closer to the FWHM of the IRF (~250ps); therefore, even small variations in the values of calculated $\langle \tau \rangle_{QD+Fcc6SH}$ would result in huge variations in $k_{HT}$ (equation 4). However, given the relatively low standard deviations in the values of $k_{HT}$, from three measurements, the non-linear behavior of $k_{HT}$ with $N_{FcC6SH}$ at higher coverages probably arose because of inability of all adsorbed FcC₆SH molecules to participate in hole transfer from photoexcited chloride treated QDs. Therefore, the multiple deactivation pathways provided by multiple adsorbed hole acceptors at the surface of chloride treated QDs may not be purely additional in nature as assumed before.
Figure 3.3. (a) 1H NMR spectra of mixed dispersions containing chloride treated CdTe QDs and FcC₆SH in CDCl₃ after flocculation with acetonitrile, (b) 1H NMR spectra of mixed dispersion containing chloride treated CdTe QDs and FcC₆SH (170 µM): after flocculation of mixed dispersions with acetonitrile containing bound FcC₆SH and bound oleylamine (blue), supernatant of mixed dispersion flocculated with acetonitrile containing free FcC₆SH and free oleylamine (red), mixed dispersion evaporated under vacuum containing free and bound FcC₆SH and oleylamine (blue).

1H NMR spectra of mixed dispersions also showed distinct and broadened resonance attributed to oleylamine. The resonances corresponding to 5.5 ppm were used to quantify average number of bound oleylamine per QDs for all mixed dispersions containing chloride treated CdTe QDs and FcC₆SH. The average number of bound oleylamine seemed to vary non-monotonically as concentration of FcC₆SH (bound and free) increased from 0 to 170 µM. The average number of bound oleylamine were calculated as (756 ± 95) from triplicate measurements on all mixed dispersions containing chloride treated CdTe QDs and different concentration of FcC₆SH. The apparent invariation of bound oleylamine with linear increase in bound FcC₆SH indicates that
FcC₆SH did not undergo ligand exchange with oleylamine ligands. The absence of resonances corresponding to free TDPA in 31P NMR spectrum of supernatants obtained followed by ligand exchange of FcC₆SH with chloride treated CdTe QDs confirms that FcC₆SH didn’t displace any TDPA from the surface of CdTe QDs. Therefore, we suggest that FcC₆SH undergoes X-type ligand exchange with labile chlorides at the surface of chloride treated CdTe QDs.

**Figure 3.4.** Plot of overall rate constant of hole transfer ($k_{HT,obs}$) as a function of average number of bound FcC₆SH per QD ($N_{FcC6SH}$).

**Emission Quenching of Untreated CdTe QDs by FcC6SH.** Emission-quenching experiments were also conducted for untreated CdTe QDs. Steady-state emission spectra were acquired as a function of time after preparing mixed dispersions of untreated CdTe QDs and FcC₆SH. Emission intensities, normalized to the initial emission intensity for dispersion containing untreated CdTe QDs alone, at band-edge emission maxima are plotted as a function of time in Figure S3.2 in Supporting Information. Samples equilibrated after approximately 2 h, except for
the dispersion containing no FcC₆SH for which the emission intensity increased by \((1.9 \pm 0.2)\)-fold. The addition of FcC₆SH to untreated CdTe QDs resulted in quenching of emission (Figure 3.5b). The steady-state emission was quenched by \((44 \pm 5\)% as the concentration of FcC₆SH increased from 0 to 170 μM. Emission decay profiles were acquired for all mixed dispersions at the band-edge emission maximum and are plotted in Figure 3.5c with corresponding tri-exponential reconvolution fits. The addition of FcC₆SH to untreated CdTe QDs resulted in dynamic quenching of emission. Average lifetimes decreased from \((20.3 \pm 0.8)\) ns to \((8.7 \pm 0.5)\) ns as the concentration of FcC₆SH was increased from 0 to 170 μM. The quenching of emission of untreated CdTe QDs upon addition of FcC₆SH is consistent with the transfer of holes from photoexcited CdTe QDs to FcC₆SH.
Figure 3.5. (a) UV-Vis spectra, (b) steady state emission spectra and (c) time-resolved emission spectra with tri-exponential fits of mixed dispersions containing as-synthesized untreated CdTe QDs and FcC₆SH.
\(^1\)H NMR spectra were acquired for all mixed dispersions containing untreated CdTe QDs and FcC\(_6\)SH. These mixed dispersions did not flocculate upon addition of acetonitrile as was the case for chloride-treated CdTe QDs. Instead, the mixed dispersions were dried under vacuum and then washed with acetonitrile. Even after three washings, some resonances from residual free FcC\(_6\)SH were observed in \(^1\)H NMR spectra of dispersions containing untreated CdTe QDs and FcC\(_6\)SH. Broadening of the peak around 4.1 ppm (Figure S3.4 in Supporting Information) were attributed to bound FcC\(_6\)SH. Overlapping of the signals from free and bound FcC\(_6\)SH in NMR spectra precluded the accurate quantification of bound FcC\(_6\)SH per QD. An upper limit of (26±6) bound FcC\(_6\)SH per QD was estimated from the integrated intensities of cyclopentadienyl protons (3.95-4.12 ppm) in the \(^1\)H NMR spectrum (Figure S3.4) of a mixed dispersion containing untreated CdTe QDs and maximum concentration (170 \(\mu\)M) of FcC\(_6\)SH. We note that the actual number of bound FcC\(_6\)SH on the surface of untreated CdTe QDs might be even lower considering no discernible changes in absorbance of mixed dispersions containing untreated CdTe QDs and FcC\(_6\)SH (Figure 3.5a). The smaller number of bound FcC\(_6\)SH molecules per untreated QD, relative to chloride-treated QDs, is consistent with the less-efficient quenching of emission (Figure 3.5). Additionally, the absorption spectra of mixed dispersions following \(^1\)H NMR measurements reveal no visible red shift of first excitonic absorption peak, or any increase in absorbance, in the wavelength region 400-500 nm, consistent with the very low coverage of bound FcC\(_6\)SH.

The low coverage of bound FcC\(_6\)SH on untreated CdTe QDs can be explained by the inability of thiols to displace strongly-bound phosphonates efficiently.\(^49\) Chloride treatment of CdTe QDs resulted in an almost 10-fold increase in the extent of ligand exchange, indicating FcC\(_6\)SH readily displaced the more labile chloride ligands from the surface of chloride-treated
CdTe QDs. The increased coverage of FeC₆SH resulted in more efficient hole transfer. Therefore, chloride treatment of CdTe QDs not only improved surface passivation, as indicated by the high QY and nearly monoexponential excited-state decay, but also provided a significantly higher loading of hole-accepting ligands, which in turn resulted in highly efficient hole transfer.

The Absence of Emission Quenching by the Thiolate Anchoring Group.

Thiolates at the surface of cadmium chalcogenide QDs are known to quench emission of cadmium via hole trapping. To investigate this possibility, emission-quenching experiments were carried out on mixed dispersions containing chloride-treated CdTe QDs and hexanethiol. The addition of hexanethiol to chloride-treated CdTe QDs resulted in red shifts of the first excitonic absorption maximum nm and the band-edge emission maximum by 3 nm (Figure 3.6) Normalized emission intensities at the band-edge maximum are plotted as a function of time after mixing in Figure S3.2. The addition of hexanethiol to chloride-treated CdTe QDs resulted in the enhancement of emission rather than quenching (Figure 3.6b). The steady-state emission was enhanced by more than 1.5-fold as the concentration of hexanethiol was increased from 0 to 170 μM. Steady-state emission spectra of the samples were monitored for 2 h before time-resolved emission data were acquired. Emission decay traces and corresponding triexponential reconvolution fits for all mixed dispersions at band-edge emission maxima are shown in Figure 6c. Average lifetimes increased from (18.4 ± 0.5) ns to (24.6 ± 1.4) ns as the concentration of hexanethiol increased from 0 to 170 μM (Table S3.2 in Supporting Information). The absence of quenching upon addition of hexanethiol indicates that the transfer of holes from CdTe QDs to adsorbed thiolates was negligible. This lack of hole transfer can be explained by the more positive oxidation potential of adsorbed thiolates relative to the valence band-edge potential of chloride-treated CdTe QDs. The enhancement of emission can be explained either by the increased
absorbance by chloride-treated CdTe QDs at the excitation wavelength of 450 nm, due to the red-shift of the first excitonic absorption band (Figure 3.6a), or by improved passivation of surface of CdTe QDs. Importantly, the lack of quenching of emission from CdTe QDs by hexanethiol suggests that the surface-anchoring thiolate groups did not contribute to the quenching of emission of chloride-treated CdTe QDs by FcC₆SH.
Figure 3.6. (a) UV-Vis spectra, (b) steady state emission spectra and (c) time-resolved emission spectra with tri-exponential fits of mixed dispersions containing as-synthesized untreated CdTe QDs and hexanethiol (HT).
Conclusions

Our steady-state and time-resolved emission quenching, together with $^1$H NMR measurements, have revealed new insights into the ligand-exchange and charge-transfer reactivity of cadmium chalcogenide QDs. A post-synthetic chloride treatment of as-synthesized CdTe QDs increased the fluorescence QY by approximately 6-18 fold and rendered emission decay profiles nearly monoexponential, indicating effective passivation of the QDs’ surface. Chloride treatment also facilitated ligand exchange involving the displacement of QD-adsorbed chlorides by FcC$_6$SH. The surface coverage of FcC$_6$SH per chloride-treated CdTe QD was nearly ten-fold higher than on untreated QDs. The higher loading of FcC$_6$SH on the surface of chloride-treated CdTe QDs provided additional hole-transfer pathways, which in turn increased the hole-transfer efficiency to nearly 99%. The overall rate constant of hole transfer initially increased linearly with the number of bound acceptors per QD, which we attribute to the additive nature of hole-transfer pathways provided by increased number of acceptors at the surface of chloride treated CdTe QDs. The overall rate constant of hole transfer then levelled off at higher hole acceptor coverages, possibly due to increased adsorption of FcC$_6$SH in configurations that were not active in hole transfer. However, the limitation of our TCSPC instrument in resolving lifetimes on the picosecond time scale may also have contributed to the nonlinearity at high loadings of FcC$_6$SH. In summary, chloride treatment of CdTe QDs suppressed deleterious charge-trapping at the surface of QDs and facilitated a much higher loading of the molecular hole acceptor FcC$_6$SH, which in turn accelerated and increased the quantum yield of excited-state hole transfer. Chloride treatment and surface passivation can apparently greatly influence ligand-exchange and charge-transfer processes of QDs and warrant further exploration.
Supporting Information

Highly Efficient Hole Transfer from Chloride Treated CdTe Quantum Dots to Covalently Tethered Molecular Acceptors

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Appendix S3.1. Calculations for addition of CdCl$_2$ used for chloride treatment.

Appendix S3.2. Calculations of quantum yield of emission (PLQY) for untreated and chloride treated CdTe QDs.

Appendix S3.3. Detailed description of preparation of samples for spectroscopic measurements.

Appendix S3.4. Detailed description of preparation of samples for $^1$H NMR measurements.

Appendix S3.5. Calculations for determining average number of bound FcC$_6$SH or oleylamine on the surface of chloride treated/untreated CdTe QDs.

Figure S3.1. UV-Vis and steady state emission spectra of as-synthesized (untreated) and treated CdTe QDs with photographs of QDs dispersions taken under room light.

Figure S3.2. Photoluminescence intensities at emission maximum as a function of time after preparation of samples for mixed dispersions containing untreated/chloride treated CdTe QDs and FcC$_6$SH/hexanethiol.

Figure S3.3. TRPL decay traces, instrument response function, multiexponential reconvolution fits, and corresponding residuals from representative measurements for each type of QD-containing dispersions at various wavelengths.

Figure S3.4. $^1$H NMR spectrum for mixed dispersion containing untreated CdTe QDs and FcC$_6$SH (170 µM).

Table S3.1. Values of average lifetimes ($\tau$), rate constant of hole transfer ($k_{HT}$) and efficiencies of hole transfer ($\eta_{HT}$) for mixed dispersions containing as-synthesized (untreated) CdTe QDs and FcC$_6$SH.
Table S3.2. Values of average lifetimes $\langle \tau \rangle$ for mixed dispersions containing chloride treated CdTe QDs and hexanethiol.
**Appendix S3.1.** Calculations for addition of CdCl₂ used for chloride treatment.²¹

Diameter (D) of as-synthesized CdTe QDs was calculated as follows⁴:

\[ D(\text{nm}) = (9.8127 \times 10^{-7}) \lambda^3 - (1.7147 \times 10^{-3}) \lambda^2 + 1.0064 \lambda - 194.84 \]  
(S3.1)

Where \( \lambda \) is the wavelength of first excitonic absorption peak of dispersion of as synthesized CdTe QDs in chloroform. The concentration of stock CdTe QDs dispersion was calculated as:

\[ C = \frac{A}{\varepsilon \times L} \times M \]  
(S3.2)

Where \( A \) and \( \varepsilon \) are the absorbance and molar absorptivity coefficient of stock dispersion of CdTe QDs at \( \lambda \), and \( L \) is the path length. \( \varepsilon \) was calculated as follows⁴:

\[ \varepsilon = 10043 \times D^{2.12} \text{ } M^{-1} \text{ } cm^{-1} \]  
(S3.3)

The total surface area of CdTe QDs in stock dispersion was calculated assuming spherical shaper of CdTe QDs as:

\[ SA = (\pi \times D^2) \times (C \times V) \text{ } nm^2 \text{ } mol \]  
(S3.4)

Where \( V \) is the volume of stock dispersion of CdTe QDs in chloroform. The volume of 0.33 M CdCl₂ stock solution (\( V_{CdCl2} \)) corresponding to 96 Cl⁻ per nm² surface area of CdTe QDs was calculated as:

\[ (0.33 \times 2)M \times V_{CdCl2}(lt) = (96 \times SA) \text{ } mol \]  
(S3.5)

Or,

\[ V_{CdCl2}(lt) = \frac{(96 \times SA)}{0.66} \text{ } lt \]  
(S3.6)
Appendix S3.2. Calculations of quantum yield of emission (PLQY) for untreated and chloride treated CdTe QDs.

PLQY for a dispersion of chloride treated/untreated CdTe QDs ($\phi_{QD}$) was calculated as follows:

$$\phi_{QD} = \phi_{ref} \times \frac{PLI_{QD}}{PLI_{ref}} \times \left(\frac{\eta_{QD}}{\eta_{ref}}\right)^2 \times \frac{OD_{ref}}{OD_{QD}}$$  \hfill (S3.7)

where $\phi_{ref}$ is PLQY for the reference, $\eta$ is the refractive index of the solvent used, PLI is integrated photoluminescence intensity under the emission spectrum and OD is the optical density of QD/reference at the excitation wavelength used to acquire the emission spectra.

Rhodamine dye 101 ($\phi_{Rhodamine\, 101} = 1$) solution in ethanol (200 proof) was used as a reference\textsuperscript{59}. 

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Appendix S3.3. Detailed description of preparation of samples for spectroscopic measurements.

The stock solution of chloride treated/untreated CdTe QDs was prepared by dissolving a definite amount of dried CdTe powder in 20 mL chloroform to give an absorbance value of approximately 0.45 at the first excitonic absorption peak. This stock solution was further diluted to 60 mL by addition of chloroform. The concentration of QDs in all mixed dispersions containing QDs and/or FcC6SH/HT was kept same. 500 μM stock solution of FcC6SH was prepared by diluting 910 μL of 16.5 mM FcC6SH stock solution to 30 mL CHCl₃. Similarly, 500 μM stock solution of HT was prepared by diluting 2.8 μL of HT (as purchased) solution to 40 mL CHCl₃. The mixed dispersions were prepared as follows.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume of stock QD (chloride treated/untreated) dispersion (mL)</th>
<th>Volume of stock FcC₆SH/HT solution (mL)</th>
<th>Volume of CHCl₃ (mL)</th>
<th>Total volume (mL)</th>
<th>Concentration of FcC₆SH/HT in dispersion (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD alone</td>
<td>10.0</td>
<td>0.0</td>
<td>5.0</td>
<td>15.0</td>
<td>0</td>
</tr>
<tr>
<td>QD+Fc/HT 0.5</td>
<td>10.0</td>
<td>0.5</td>
<td>4.5</td>
<td>15.0</td>
<td>17</td>
</tr>
<tr>
<td>QD+Fc/HT 1</td>
<td>10.0</td>
<td>1.0</td>
<td>4.0</td>
<td>15.0</td>
<td>34</td>
</tr>
<tr>
<td>QD+Fc/HT 2</td>
<td>10.0</td>
<td>2.0</td>
<td>3.0</td>
<td>15.0</td>
<td>68</td>
</tr>
<tr>
<td>QD+Fc/HT 3</td>
<td>10.0</td>
<td>3.0</td>
<td>2.0</td>
<td>15.0</td>
<td>102</td>
</tr>
<tr>
<td>QD+Fc/HT 5</td>
<td>10.0</td>
<td>5.0</td>
<td>0.0</td>
<td>15.0</td>
<td>170</td>
</tr>
</tbody>
</table>
Appendix S3.4. Detailed description of preparation of samples for $^1$H NMR measurements.

Samples containing chloride treated CdTe QDs and FcC6SH. Mixed dispersions containing chloride treated CdTe QDs and/or FcC6SH prepared for spectroscopic measurements were flocculated by addition of acetonitrile to each dispersion. After centrifugation, supernatant was stored for other measurements. The powders were dried under glovebox overnight under vacuum. The powders were dispersed in 1 mL of CDCl$_3$ and 600 μL of dispersion was transferred in an NMR tube. 100 μL of 10 mM benzene solution in CDCl$_3$ was added to each tube. The tubes were shaken gently to get a homogenous dispersion and $^1$H NMR measurements were taken.

Samples containing untreated CdTe QDs and FcC6SH. Mixed dispersions containing untreated CdTe QDs and/or FcC6SH prepared for spectroscopic measurements didn’t flocculate on addition of acetonitrile. Therefore, the mixed dispersions were evaporated under vacuum and were washed with 10 mL of acetonitrile thrice to separate free and bound FcC$_6$SH. The powders were dried under vacuum overnight. The powders were dispersed in 1 mL of CDCl$_3$ and 600 μL of dispersion was transferred in an NMR tube. 100 μL of 10 mM benzene solution in CDCl$_3$ was added to each tube. The tubes were shaken gently to get a homogenous dispersion and $^1$H NMR measurements were taken.
Appendix S3.5. Calculations for determining average number of bound FcC₆SH or oleylamine on the surface of chloride treated/untreated CdTe QDs.

Benzene was used as an external reference to calculate the number of moles of other species in the mixed dispersions containing chloride treated/untreated CdTe QDs and FcC₆SH.

\[
\frac{n_{\text{FcC}_6\text{SH}}}{n_{\text{C}_6\text{H}_6}} = \frac{A_{\text{FcC}_6\text{SH}}/\#_{\text{FcC}_6\text{SH}}}{A_{\text{C}_6\text{H}_6}/\#_{\text{C}_6\text{H}_6}} = \frac{A_{\text{FcC}_6\text{SH}}/9}{A_{\text{C}_6\text{H}_6}/6}
\]

(S3.8)

Where \( n_{\text{FcC}_6\text{SH}} \) and \( n_{\text{C}_6\text{H}_6} \) are the number of moles of bound FcC₆SH and C₆H₆ in the mixed dispersion respectively. \( A_{\text{FcC}_6\text{SH}} \) is the area under the peak (3.9-4.1 ppm) corresponding to 9 protons on the cyclopentadiene ring in FcC₆SH and \( A_{\text{C}_6\text{H}_6} \) is the area under the peak (7.36 ppm) corresponding to the protons on the benzene ring (Figure 3a). “\#” indicates the number of protons giving rise to a particular peak in 1H NMR spectrum.

Number of moles of chloride treated/untreated CdTe QDs were calculated from the absorption spectra of the mixed dispersions acquired after the NMR measurement as followed:

\[
A = \varepsilon C l
\]

(S3.9)

Where A is the absorbance of the mixed dispersion containing chloride treated/untreated CdTe QDs at the first excitonic peak. The extinction coefficient of QDs “\( \varepsilon \)” was calculated according to Yu et. al.⁴ \( C \) is the concentration of the mixed dispersion and \( l \) is the path length (0.2 cm). So, concentration of QDs in mixed dispersion,

\[
C = \frac{A}{\varepsilon l}
\]

(S3.10)

Then, number of moles of QDs,

\[
n_{\text{QD}} = C \cdot V
\]

(S3.11)

where V is the volume of the mixed dispersion used for the 1H NMR measurements.
Number of FcC6SH per QD ($N_{FcC6SH}$) were calculated as:

$$N_{FcC6SH} = \frac{n_{FcC6SH}}{n_{QD}} \quad (S3.12)$$

Similarly, number of oleylamine per QD was calculated by calculating the number of moles of bound oleylamine by integrating under the oleylamine peak (5.3-5.4 ppm).
Figure S3.1. UV-Vis and steady state emission spectra of various batches of untreated/chloride treated CdTe QDs with photographs of QDs dispersions (left: untreated, right: chloride treated) taken under room light.
Figure S3.2. Photoluminescence intensities at emission maximum as a function of time after preparation of samples for mixed dispersions containing: (a) chloride treated CdTe QDs and FeC₆SH, (b) untreated CdTe QDs and FeC₆SH and (c) chloride treated CdTe QDs and hexanethiol.
Figure S3.3. Top graphs: TRPL decay traces (blue), IRF (red), multiexponential reconvolution fits from eq. 1 (black) from representative measurements for each type of QD-containing dispersions at various wavelengths. Bottom graphs: corresponding residuals (data minus fit). Each set of graphs shows fits to monoexponential (left), biexponential (middle), and triexponential (right) functions. Corresponding chi-square values are in the insets.

**Chloride treated CdTe QDs alone (λ<sub>em</sub> = 590 nm):**

**Chloride treated CdTe QDs + FeC<sub>6</sub>SH 0.5 (λ<sub>em</sub> = 590 nm):**
Chloride treated CdTe QDs +FcC₆SH 1 ($\lambda_{em} = 590$ nm):

Chloride treated CdTe QDs +FcC₆SH 2 ($\lambda_{em} = 590$ nm)

Chloride treated CdTe QDs +FcC₆SH 3 ($\lambda_{em} = 590$ nm)
Chloride treated CdTe QDs +FcC₆SH 5 ($\lambda_{em} = 590$ nm)

Untreated CdTe QDs alone ($\lambda_{em} = 590$ nm)

Untreated CdTe QDs +FcC₆SH 1 ($\lambda_{em} = 590$ nm)
Untreated CdTe QDs + FeC₆SH 2 ($\lambda_{em} = 590$ nm)

Untreated CdTe QDs + FeC₆SH 3 ($\lambda_{em} = 590$ nm)

Untreated CdTe QDs + FeC₆SH 5 ($\lambda_{em} = 590$ nm)
Figure S3.4. $^1$H NMR spectrum for mixed dispersion containing untreated CdTe QDs (black) and untreated CdTe QDs and FcC$_6$SH (170 µM) (red). $^1$H NMR spectrum for mixed dispersion containing untreated CdTe QDs and FcC$_6$SH (170 µM) shows predominantly unbound FcC$_6$SH (sharp peaks at 4.05 ppm, m and 4.1 ppm, s). However, some broadening (shaded region) under the peaks can be resolved and used to estimate the number of bound FcC$_6$SH per QD.
Table S3.1. Values of average lifetimes $\langle \tau \rangle$, rate constant of hole transfer ($k_{HT}$) and efficiencies of hole transfer ($\eta_{HT}$) for mixed dispersions containing untreated CdTe QDs and FcC₆SH.

<table>
<thead>
<tr>
<th>[FcC₆SH] (in µM)</th>
<th>$\langle \tau \rangle$ (in ns)</th>
<th>$k_{HT}$ (s⁻¹)</th>
<th>$\eta_{HT}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.3±0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>34</td>
<td>14.0±0.2</td>
<td>(2.2±0.1)x10⁷</td>
<td>30.9±1.5</td>
</tr>
<tr>
<td>68</td>
<td>11.5±0.2</td>
<td>(3.8±0.2)x10⁷</td>
<td>43.3±1.2</td>
</tr>
<tr>
<td>102</td>
<td>10.4±0.2</td>
<td>(4.6±0.2)x10⁷</td>
<td>48.5±1.2</td>
</tr>
<tr>
<td>170</td>
<td>8.7±0.2</td>
<td>(6.5±0.2)x10⁷</td>
<td>57.0±1.0</td>
</tr>
</tbody>
</table>

Table S3.2. Values of average lifetimes $\langle \tau \rangle$ for mixed dispersions containing chloride treated CdTe QDs and hexanethiol.

<table>
<thead>
<tr>
<th>[Hexanethiol] (in µM)</th>
<th>$\langle \tau \rangle$ (in ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18.4±0.2</td>
</tr>
<tr>
<td>34</td>
<td>21.5±0.4</td>
</tr>
<tr>
<td>68</td>
<td>22.0±0.4</td>
</tr>
<tr>
<td>102</td>
<td>23.2±0.5</td>
</tr>
<tr>
<td>170</td>
<td>24.6±0.7</td>
</tr>
</tbody>
</table>
References


48. Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S., Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-


Chapter IV

Exploring the Role of Driving Force and Surface Coverage in Hole Transfer Dynamics from Cadmium Chalcogenide Quantum Dots to Covalently Tethered Molecular Acceptors
**Introduction**

Semiconductor nanocrystals or quantum dots (QDs) are intriguing materials for solar energy conversion and photocatalysis because they exhibit size-dependent optical and electronic properties,\(^1\) high oscillator strength,\(^4^5\) hot electron extraction\(^6^8\) and multi-exciton generation.\(^9^\) As-synthesized QDs are often surrounded by long aliphatic ligands which provide effective surface passivation and dispersibility in non-polar solvents. Due to the high surface-to-volume ratio of QDs, the surface constitutes a significant fraction of QDs and therefore can significantly affect their optical and electronic properties. Incomplete passivation results in under-coordinated surface atoms, also known as dangling bonds, which contribute to electronic states with energies lying between the valence band (VB) and conduction band (CB) of QDs.\(^1\) These mid-gap states (also known as trap states or surface states) can act as charge traps for photo-excited charge carriers which results in loss of potential energy of charge carriers, low photoluminescence quantum yields (PLQYs) and poor performance of QD based electronic devices.

The surfaces of QDs can be modified for various applications, in which the native ligands on the surface of QDs undergo ligand exchange with a desired ligand. For example, insulating and bulky aliphatic ligands can be displaced with smaller ligands to improve charge separation\(^14^\)\(^16\) and carrier mobilities within thin films to improve device performance.\(^13\)\(^17^\)\(^19\) Similarly, thick inorganic shells of wide-bandgap semiconductors can be grown over core QDs to efficiently passivate their surface.\(^20^\)\(^22\) More recently, atomic-ligand passivation with, for example, halides, sulfides, thio cyanates, or amines, has been used effectively to passivate the surface of QDs.\(^23^3\) Owen and coworkers adapted Green’s covalent bond classification method to establish ligand-exchange reactions to modify the surfaces of QDs. In this formalism, ligands can be broadly categorized into
X-type (1-electron donating anionic), L-type (2-electron donating neutral) and Z-type (Lewis-acidic electron-accepting).\textsuperscript{28, 32}

Surface states within the electronic structure of QDs are often visualized by the deep trap state model in which unpassivated surface atoms contribute to a distribution of electron- and hole-surface states within the electronic bandgap.\textsuperscript{33-34} In this model, undercoordinated cadmium and chalcogen atoms form the basis of electron and hole surface states, respectively, in cadmium chalcogenide (CdE, where E= S, Se, Te) QDs. Recent efforts, involving both experimental and computational studies, have shown that cadmium chalcogenide QDs are rich in hole surface states due to undercoordinated chalcogen atoms or removal of Z-type ligands from the surface of CdE QDs.\textsuperscript{33, 35-36} However, recently the deep trap state model view has been challenged by a quantized surface-state model derived from temperature-dependent photoluminescence (PL) measurements on a myriad of QD systems.\textsuperscript{36-38} This model treats the surface states as charge-transfer states coupled to the core excitonic state with strong electron-phonon coupling. Interestingly, the authors were able to fit the temperature-dependent PL data of QDs with only one quantized surface state.\textsuperscript{37}

Efficient charge separation from photoexcited QDs dictates the overall power conversion efficiencies of QD-based solar cells or performances of QD-derived photocatalysts. Numerous studies have been conducted on QD-metal oxide interfaces and QD-molecule complexes to study the factors affecting charge transfer under the context of Marcus theory of electron transfer.\textsuperscript{3, 39} However, the role of surface states of QDs in charge transfer is relatively unexplored relative to the role of excitonic states.

In this study, we explored the role of excitonic and surface states of CdE QDs in the transfer of photogenerated holes to covalently-bound molecular hole acceptors (6-(ferrocenyl)hexanethiol (FcC\textsubscript{6}SH) or hexanethiol) to gain deeper understanding of the electronic landscape of QDs. We
found that thiolates adsorbed to CdS and CdSe QDs can accept photogenerated holes. In contrast, for CdTe QDs, hole transfer to surface-bound thiolates is thermodynamically unfavorable, as the VB of CdTe QDs lies at higher energy than the oxidation potential of thiolates. Additionally, hole transfer to ferrocene was found to be much more efficient than hole transfer to thiolates in all three cases of CdE QDs. Holes were transferred from both band edge and surface states of CdE QDs to molecular ferrocene with a range of measured rate constants, consistent with driving force-dependent hole transfer in normal Marcus region. Faster hole transfer to surface-bound FcC₆SH than to hexanethiolates precludes the possibility of sequential, stepwise hole transfer from QDs to thiolates to ferrocene. More importantly, our hole-transfer data are consistent with the existence of a distribution of surface states rather than a single quantized surface state.

**Experimental**

**Materials**

Cadmium oxide (CdO), sulfur powder, technical grade 90% oleic acid (OA) and tri-n-octylphosphine (TOP, 98%) were purchased from Alfa Aesar. Silica LUDOX dispersion, selenium powder, tellurium powder (200 mesh, 99.8%), 1-octadecene, 1-hexanethiol (HT, 95%) and FcC₆SH were purchased from Sigma Aldrich. HPLC grade solvents such as toluene, hexane, chloroform, methanol, acetonitrile and acetone were purchased from Fisher Scientific. Deuterated chloroform (CDCl₃) for NMR measurements was purchased from Cambridge Isotope Laboratories, Inc. All reagents were used as received.

**Synthesis of OA-CdS QDs**

OA-capped CdS (OA-CdS) QDs were prepared following the procedure reported by Harris et al.¹⁴ Briefly, cadmium precursor was prepared by adding CdO (360 mg, 2.8 mmol) with 4.4 mL OA
(14 mmol) and 14 mL octadecene in a three-neck flask. The cadmium precursor was heated to 260 °C under Ar environment with constant stirring until the solution became clear and colorless. In a separate flask, elemental sulfur (64 mg, 2 mmol) was added to 4 mL of octadecene, and the solution was heated to 60 °C under Ar environment with constant stirring. The cadmium precursor was cooled to 250 °C, and then the sulfur precursor was swiftly injected to the cadmium precursor. QDs were allowed to grow for approximately 5 min until the solution turned slightly yellow. Heat was removed to quench the growth of QDs, and the reaction was allowed to cool to room temperature. A CHCl₃/CH₃OH solution (40 mL of 1:1 v/v) was added to the dispersions of QDs in octadecene to separate the unreacted precursors from QDs. The octadecene layer was separated by centrifugation, and acetone was added to flocculate the QDs. QDs were then separated by centrifugation and redispersed into CHCl₃. One more cycle of flocculation/redispersion was performed. Finally, the CHCl₃ dispersion of OA-CdS QDs was stored under dark until further use.

**Synthesis of OA-CdSe QDs**

OA-capped CdSe (OA-CdSe) QDs were prepared following the method reported by Chen et al.⁴⁰ Briefly, CdO (0.50 g, 3.9 mmol) was added to OA (5.54 g, 20.0 mmol) and 70 mL octadecene in a 3 neck flask. The cadmium precursor was heated with vigorous stirring to 270 °C under Ar environment until the solution turned clear and colorless. In a separate flask, Se (0.10 g, 1.3 mmol) powder and TOP (0.50 g, 1.3 mmol) were dissolved in 10 mL octadecene with constant stirring under Ar atmosphere. The cadmium-containing mixture was allowed to cool to 250 °C, at which point the Se precursor was swiftly injected to the cadmium precursor and QDs were allowed to grow. The growth of QDs was evidenced by the change of color of the reaction mixture from yellow to orange to red. Once the desired size was reached, the reaction was quenched by removing heat, and the QD-containing mixture was allowed to cool to room temperature. The resulting
dispersion of QDs in octadecene was divided equally among several centrifuge tubes, and acetone was added to flocculate the QDs to separate the unreacted precursors. The flocculated QDs were redispersed into CHCl₃ and stored under dark until further usage.

**Synthesis of OA-CdTe QDs**

OA-capped CdTe (OA-CdTe) QDs were prepared following the method by Haram et al.⁴¹ Briefly, Te powder (80 mg, 0.6 mmol) was added to 5 mL TOP under Ar environment, and the mixture was heated gently to 210 °C until the solution turned pale greenish yellow in color. The reaction mixture was then diluted to 20 mL by addition of octadecene. In a separate three-neck flask, CdO (320 mg, 2.5 mmol) was mixed with 5 mL OA (16 mmol) and 12.5 mL octadecene, and the resulting mixture was heated to 300 °C at which point the solution turned clear and colorless. The cadmium precursor was allowed to cool down to 270 °C, at which point the Te precursor was swiftly injected to the cadmium precursor. The growth of QDs was monitored by the change in color of the reaction mixture from yellow to red. Once the desired size was reached, heat was removed to quench the reaction and the mixture was allowed to cool to room temperature. A hexane/CH₃OH mixture (40 mL of 1:1 v/v) was added to the stock dispersion of QDs to separate the QDs from unreacted precursors. The hexane layer containing QDs was extracted and divided into 5 centrifuge tubes. QDs were flocculated by addition of 15 mL of 2:1 v/v acetone/acetonitrile solution to each tube. The flocculated QDs were dried under Ar environment inside a glovebox and stored in the dark until further use. The major difference between CdTe QDs used in studies reported in chapter III and chapter IV is the capping group.

**Ligand Exchange with FcC₆SH or Hexanethiol**

Mixed dispersions containing OA-CdE (E = S, Se, Te) QDs and hexanethiol or FcC₆SH were prepared as explained in the Supporting Information (Appendix S1). Briefly, the concentration of
QDs was kept the same while the concentration of hexanethiol or FcC₆SH was varied systematically (from 0 to 1.7 mM for hexanethiol and from 0 to 17 µM for FcC₆SH). Mixed dispersions were allowed to equilibrate for 2 h in the dark before any spectroscopic measurements. The extent of ligand exchange was monitored by acquiring ¹H NMR spectra of mixed dispersions.

Methods

UV/Vis absorption spectra for mixed dispersions were acquired with an Agilent 8453 spectrophotometer. Steady-state emission spectra were collected with a Varian Cary Eclipse fluorimeter. Steady-state emission spectra of dispersions containing CdS, CdSe, and CdTe QDs were acquired by exciting at 360 nm, 450 nm and 450 nm, respectively. Time-resolved photoluminescence (TRPL) decay profiles were acquired using a Becker and Hickl Tau 130 time-correlated single photon counting (TCSPC) setup, the details of which were reported previously. Briefly, the repetition rate of the diode laser (445 nm) was set to 1 MHz to allow samples to decay to baseline before re-excitation. The time-to-amplitude converter (TAC) was set to 50 ns, and delay cables were employed in the sync channel to achieve high time resolution (12.2 ps per time bin). Decay profiles were collected for 600 s for band edge emission and 2500 s for surface state emission. Silica LUDOX solution was used to acquire the instrument response function (IRF). At a laser gain of 20% and detector gain of 90%, the full width at half maximum (FWHM) of the IRF was found to be approximately 250 ps. All decay profiles were fitted with Fluofit software by Picoquant to extract average lifetimes.

¹H NMR spectra for dispersions of CdE QDs with micromolar concentrations were acquired with Inova 400 MHz instrument. The samples for NMR measurements were prepared by concentrating the mixed dispersions by evaporating the solvent under vacuum and then redispersing the QDs
into deuterated CDCl$_3$. All spectra were integrated for 256 scans. $^1$H NMR spectra were processed by ACD Spectrus software by ACD/Labs.

**Results and Discussion**

**Strategy to Characterize Hole-Transfer Dynamics from QDs to Covalently-Bound Hole Acceptors**

Thiols are known to undergo X-type ligand exchange with bound oleates at the surface of cadmium chalcogenide QDs.$^{43}$ Depending upon the oxidation potential of the adsorbed thiolates, they can accept photogenerated holes from QDs.$^{44-45}$ We modified the surfaces of oleate-capped CdE QDs by preparing mixed dispersions containing OA-CdE QDs and hexanethiol or FcC$_6$SH. Scheme 1 shows estimated relative energetics of reduction potentials of hexanethiolates and FcC$_6$SH vs the valence band edge energy (E$_v$) of CdE QDs. E$_v$s of QDs are often estimated by photoelectron spectroscopy,$^{3, 46-48}$ cyclic voltammetry,$^{3, 41, 49-50}$ or molecular simulations. However, there is hardly any consensus among the numerous studies. E$_v$s for CdSe and CdTe QDs were estimated from an empirical relationship established by Jasieniek et al. for various sizes of TOPO-capped CdSe and CdTe QDs calculated by photoelectron spectroscopy in air (PESA)$^{46}$. Changing the capping group on the surface of QDs can also affect the values of E$_v$ and the conduction band edge energy (E$_c$).$^3$ However, a quantitative study of the effect of various capping groups on E$_v$s of CdE QDs is unknown to the best of our knowledge. In Scheme 1, the E$_v$ of CdS QDs was estimated by considering the reported E$_v$ of bulk CdS and quantum confinement effects according to Grandhi et al.$^{51-52}$ The HOMO, or equivalently the $E_{1/2}$(Fe$_{III/II}$) potential for FcC$_6$SH, was estimated on the basis of a cyclic voltammetry study conducted by Alivisatos et al.$^{50}$ Thiols are known to be shallow hole traps for photoexcited QDs;$^{42, 44, 53}$ however, the reduction potential of hexanethiolates
(E_{1/2}(RS/RS^-) adsorbed to CdE QDs is unknown to the best of our knowledge. The HOMO of hexanethiol was placed at an energy closer to the E_v of CdSe QDs based on our experimental results. E_c of CdE QDs shown in Scheme 1 were estimated by adding the optical bandgap (calculated based on the absorption onset in absorption spectra of as-synthesized OA-CdE QDs shown in Figure 4.1) to the E_v.s.
Scheme 4.1: Energy level diagram of VBs of CdE QDs relative to oxidation potential of FeC₆SH and hexaenthiolates. Dashed lines above the VB of CdS QDs (blue) and CdSe QDs (green) represent unknown random distributions of hole surface states. Solid straight arrows represent electron-hole recombination and curved arrows represent hole transfer from photoexcited QDs to molecular acceptors. Assumptions underlying the energies in this diagram, and related references, are in the text.

According to the energy-level diagram in Scheme 4.1, for all CdE QDs, the transfer of photogenerated holes from OA-CdE QDs to FeC₆SH is facilitated by a positive driving force.
However, in case of hexanethiol, hole transfer is feasible only from CdS and CdSe QDs but not from CdTe QDs. The dotted lines above VBs of the CdS and CdSe QDs represent random and unknown distributions of hole surface states. Such surface states in CdE QDs have often been attributed to unpassivated chalcogens on the surfaces of QDs.\textsuperscript{13,35} Difference in energies between the holes lying in VB or a hole surface state in photoexcited CdE QDs and the oxidation potential of surface bound hole acceptors (hexanethiolates or FcC\textsubscript{6}SH) constitute the driving force of hole transfer. Transfer of holes from photoexcited CdE QDs to hole acceptors would result in competition between hole transfer and electron-hole recombination processes within QDs (Scheme 4.1) and in turn would result in dynamic quenching of emission. Thus, time-resolved emission measurements provide an indirect method to quantify the rate of excited-state hole transfer in these QD-acceptor systems. Importantly, several other phenomena could also result in emission quenching, such as (a) Forster resonance energy transfer (FRET) from QDs to molecular acceptors and (b) electron transfer from QDs to molecular acceptors. Special caution was taken while preparing OA-CdE QDs to minimize the overlap between the emission spectra of QDs and the absorption spectrum of FcC\textsubscript{6}SH to exclude the possibility of FRET; however, in case of OA-CdS QDs, the possibility of FRET cannot be ignored because of the difficulty in growing CdS QDs and the limitation of our laser (excitation wavelength of 445 nm). The bandgap of FcC\textsubscript{6}SH is approximately 2.7 eV\textsuperscript{50,53} which would put the LUMO of FcC\textsubscript{6}SH at higher potential energy than the CBs of CdE QDs used in this study (Scheme 4.1). Therefore, the possibility of electron transfer from photoexcited CdE QDs to FcC\textsubscript{6}SH or hexanethiol can be excluded.

**Electronic Spectra of OA-CdE QDs**

Absorption and normalized steady-state emission spectra of OA-CdE QDs are shown in Figure 4.1. OA-CdS QDs exhibited a first excitonic absorption band with wavelength of maximum
absorbance ($\lambda_{\text{max}}$) of 430 nm (Figure 4.1). The emission spectrum of OA-CdS QDs showed a narrow band-edge emission centered at 450 nm and a broad, red-shifted surface-state emission centered at 640 nm. For OA-CdSe QDs, $\lambda_{\text{max}}$ was 550 nm. The emission spectrum of OA-CdSe QDs exhibited a narrow band-edge emission band centered at 570 nm and a weak and broad surface-state emission band at lower energies. For OA-CdTe QDs, $\lambda_{\text{max}}$ was 625 nm. OA-CdTe QDs exhibited only band-edge emission with a maximum at 663 nm. On the basis of the empirical size equation reported by Yu et al., we estimated the average diameters of OA-capped CdS, CdSe, and CdTe QDs to be 4.4 nm, 3.0, and 3.9 nm, respectively.\textsuperscript{4}

\textbf{Figure. 4.1.} Absorption (solid lines) and normalized steady state emission spectra (dashed lines) of OA-CdS (blue), OA-CdSe (green) and OA-CdTe QDs (red).

\textbf{Ligand Exchange of Oleates with FcC\textsubscript{6}SH or Hexanethiol}

The displacement of native oleate ligands on the surface of CdE QDs with the desired ligand (FcC\textsubscript{6}SH or hexanethiol), via X-type ligand exchange, was carried out by mixing dispersions of CdE QDs with stock solutions of FcC\textsubscript{6}SH or hexanethiol of varying concentrations in CHCl\textsubscript{3}. 

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Ligand exchange was monitored by acquiring $^1$H NMR spectra of concentrated mixed dispersions containing CdE QDs and FeC$_6$SH or hexanethiol. The $^1$H NMR spectrum of OA-CdE QDs exhibited broad peaks corresponding to bound oleates ($\delta = 5.3$-$5.4$ ppm, $\delta = 2.3$-$2.4$ ppm and $\delta = 1.9$-$2.1$ ppm) at the surface of CdE QDs. The addition of hexanethiol to OA-CdE QDs resulted in sharpening of peaks corresponding to bound oleates at the surface of CdE QDs (Figures S4.2a, S4.3a in Supporting Information), consistent with X-type ligand exchange of thiolates for oleates. However, broad resonances corresponding to bound hexanethiolates were not discernible. Similarly, addition of FeC$_6$SH to OA-CdE QDs resulted in sharpening of bound oleate peaks along with broadening of peaks corresponding to bound FeC$_6$SH ($\delta = 4.0$-$4.1$ ppm) indicating X-type ligand exchange between FeC$_6$SH and oleates (Figures S4.2b, S4.3b, S4.4 in Supporting Information).

**Dynamics of Hole Transfer from OA-CdS QDs to Hexanethiol or FeC$_6$SH**

**Emission Quenching of OA-CdS QDs by Hexanethiol**

UV-Vis spectra of mixed dispersions containing OA-CdS QDs and hexanethiol are shown in Figure 4.2. Surface modification of OA-CdS QDs upon addition of hexanethiol resulted in increased absorbance within the first and higher excitonic features along with a red-shift of approximately 4 nm (Figure S4.5 in Supporting Information). Changes in the absorption spectra of hexanethiolate-capped CdS QDs can be explained by the relaxation of quantum confinement of charge carriers as well as changes in oscillator strengths due to changes in chemical environment of QDs surface.$^{13, 54}$
Figure 4.2. Absorption (a) and steady-state emission spectra (b and c) of mixed dispersions containing OA-CdS QDs and hexanethiol within the band-edge (b) and surface-state (c) emission regions; normalized emission spectra (d) with respect to the surface-state emission maxima; and (e) % quenching of emission as a function of wavelength. In graph e, the error bars represent plus-or-minus one standard deviation relative to the average value from steady-state emission measurements for 3 different samples. The red dotted line in e represents the lower energy end of band-edge emission of OA-CdS QDs.

Addition of hexanethiol to OA-CdS QDs resulted in quenching of both band-edge and surface-state emission (Figure 4.2b and 4.2c). The extent of quenching of steady-state emission was quantified as the percentage of quenching:

$$\% Q (\lambda) = \frac{(I_{0,\lambda} - I_{\lambda})}{I_{0,\lambda}} \times 100$$  \hspace{1cm} (4.1)

where $I_{0,\lambda}$ is the emission intensity of a mixed dispersion containing OA-CdS QDs only, and $I_{\lambda}$ is the emission intensity of a mixed dispersion containing OA-CdS QDs and hexanethiol, at emission wavelength $\lambda$. Values of $\% Q$ were calculated for all concentrations of hexanethiol used and are plotted in Figure 4.2e as a function of emission energy (eV). Band-edge emission was quenched
to a much greater extent than surface-state emission. The extent to which surface-state emission was quenched varied with energy. Emission from shallow surface states (shorter-wavelength emission) was quenched more strongly as compared to deeper surface states (longer-wavelength emission). However, as the concentration of hexanethiol increased in the mixed dispersion, % Q increased throughout the emission spectrum along with a decreased slope of the gradient quenching of surface-state emission (Figure 4.2e). Preferential quenching of band-edge emission as compared to surface-state emission is highlighted by normalizing the emission spectra of mixed dispersions containing OA-CdS QDs and hexanethiol at the surface-state emission maxima (Figure 4.2d). The intensity of band-edge emission relative to surface state emission decreased with an increase in concentration of hexanethiol in mixed dispersions. Also, the surface-state emission maximum in such spectra shifted to longer wavelengths as the concentration of hexanethiol was increased, indicating wavelength-dependent gradient quenching within the surface state emission band.

The wavelength dependence of emission quenching is consistent with driving force-dependent hole-transfer kinetics. Assuming that surface-state emission arises predominantly from the recombination of electrons at the conduction band edge with trapped holes, in unpassivated S²⁻ sites,⁵⁵-⁵⁶ then the wavelength-dependence of % Q can be explained by driving force-dependent hole transfer. The driving force for hole transfer from CdS QDs to adsorbed thiolates is greatest from Eᵥ of CdS QDs and decreases as holes are trapped more deeply (i.e. at energies higher into the band gap). Therefore, assuming Marcus normal region behavior, holes at the Eᵥ would be expected to transfer more rapidly than holes localized in surface states. Similarly, the rate of hole transfer would be expected to decrease as holes are trapped more deeply. Hole transfer competes with electron-hole recombination; therefore, an increase of the rate of hole transfer should lead to
an increase of % \( Q \). Finally, the surface coverage of hexanethiolates should also influence % \( Q \). The surface coverage of bound hexanethiolates increases with the concentration of hexanethiol in mixed dispersions (Figure S4.2a). Increased surface coverage of hexanethiolates on the surface of CdS QDs should provide multiple additive pathways for hole transfer, increasing the rate of hole transfer, which in turn is expected to result in increased quenching of both band-edge and surface-state emission.

In order to gain insight into the hole-transfer dynamics from CdS QDs to adsorbed hexanethiolates, time-resolved emission decay profiles were acquired throughout the emission bands for all mixed dispersions containing OA-CdS QDs and hexanethiol. Decay profiles were fitted using multi-exponential reconvolution (equation 4.2):

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

where, \( t \) is time, \( I(t) \) is intensity, \( A_i \) is amplitude of the \( i^{th} \) component, \( \tau_i \) is lifetime of the \( i^{th} \) component and \( IRF(t') \) is the instrument response function. Goodness of fit was evaluated by residual plots and chi-square values. Fits resulting in chi-square values between 0.9-1.4 were regarded as acceptable. An additional exponential component was added to a given fit if it resulted in significant improvement in reduced chi-square and the flatness of a plot of residual as a function of wavelength. Intensity-weighted average lifetime values \( \langle \tau \rangle \) were calculated from the extracted fitting parameters according to equation 4.3:

\[
\langle \tau \rangle = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}
\]

Representative decay traces and corresponding fits for band-edge and surface-state emission of mixed dispersions containing OA-CdS QDs and hexanethiol are shown in Figure 4.3a and 4.3b.
Interestingly, for free OA-CdS QDs, average lifetimes corresponding to electron-hole recombination from surface states were significantly higher than those from band-edge states. For example, \((\tau)\) increased from \((23.2 \pm 0.5)\) ns for band-edge emission \((\lambda = 460\) nm\) to \((74 \pm 13)\) ns for trap state emission \((\lambda = 635\) nm\). Poor overlap between the wavefunctions of the electron and the localized, trapped hole can result in longer recombination lifetimes as compared to band-edge recombination of delocalized electrons and holes.\(^{55}\) The average lifetime for band-edge emission \((\lambda = 460\) nm\) decreased from \((23.2 \pm 0.5)\) ns to \((4.1 \pm 1.1)\) ns as the concentration of hexanethiol was increased from 0 to 1.7 mM in mixed dispersions. Similarly, for surface state emission \((\lambda = 610\) nm\), the average excitonic lifetime decreased from \((66 \pm 8)\) ns to \((26 \pm 4)\) ns. This dynamic quenching of emission throughout the emission spectrum of OA-CdS QDs indicates the presence of an additional deactivation pathway, which we attribute to hole transfer from photoexcited CdS QDs to the thiolate group of adsorbed hexanethiolates.
Figure 4.3. (a,b) Time-resolved emission decay profiles and respective multi-exponential reconvolution fits for mixed dispersions containing OA-CdS QDs and hexanethiol (0-17 mM) at emission wavelengths of 460 nm (a) and 610 nm (b). Also plotted is the IRF. (c) Rate constants of hole transfer ($k_{HT}$) as a function of emission energy for mixed dispersions containing OA-CdS QDs and hexanethiol. The red dotted line in e represents the lower energy end of band edge emission of OA-CdS QDs.
Assuming that the hole transfer is the only additional deactivation process, and that the rate constants for radiative and non-radiative processes within CdS QDs do not change when native capping groups are displaced with hexanethiolates, the rate constants for hole transfer ($k_{HT}$) can then be calculated according to equation 4.4:\textsuperscript{15,42,59-61}

$$k_{HT} = \frac{1}{\langle \tau \rangle_{QD\text{--alone}}} - \frac{1}{\langle \tau \rangle_{QD\text{--hexanethiol}}}$$

Values of $k_{HT}$ extracted from time-resolved emission data are summarized in Table S1 in Supporting Information. For hole transfer from band-edge states ($\lambda = 460$ nm), $k_{HT}$ increased from $(2.3 \pm 0.3) \times 10^7$ s$^{-1}$ to $(20.0 \pm 6.5) \times 10^7$ s$^{-1}$ as the concentration of hexanethiol increased from 0.17 mM to 1.7 mM in mixed dispersions. Similarly, for hole transfer from surface states ($\lambda = 610$ nm), $k_{HT}$ increased from $(0.5 \pm 0.3) \times 10^7$ s$^{-1}$ to $(2.4 \pm 0.6) \times 10^7$ s$^{-1}$ as the concentration of hexanethiol increased from 0.17 mM to 1.7 mM in mixed dispersions. Values of $k_{HT}$ for all mixed dispersions are plotted as a function of energy, throughout the band-edge and surface-state emission, in Figure 4.3c. The dotted line in Figure 4.3c indicates the low-energy threshold of band-edge emission; therefore, the values of $k_{HT}$ extracted from wavelengths the left (higher energy) of the dotted line can be assigned to hole transfer from band-edge states of CdS QDs to hexanethiolates. Similarly, the values of $k_{HT}$ extracted from wavelengths the right (lower energy) of the dotted line can be assigned to hole transfer from surface states of CdS QDs to hexanethiolates. The higher values of $k_{HT}$ extracted from band-edge states, relative to surface states, indicate that holes are transferred more rapidly an efficiently from band-edge states than from surface states. The values of $k_{HT}$ for hole transfer from the VB of CdS QDs to thiolates, at relatively higher concentrations of hexanethiol (0.7 mM and 1.7 mM) lie within the error of each
other, possibly because of imprecise fitting of the corresponding decay profiles given the substantial quenching of emission and scattering of incident light. Notably, $k_{HT}$ decreases significantly with increasing wavelength (decreasing energy) within the surface emission, indicating that holes were transferred more rapidly and efficiently from shallow surface states than from deeper surface states. All of these observations are consistent with driving force-dependent hole transfer, as outlined above. As the driving force for hole transfer decreases, measured values of $k_{HT}$ decrease, consistent with Marcus normal region behavior.$^{62-64}$
(b)

(c)
Figure 4.4. Steady-state emission spectra (a and b) of mixed dispersions containing OA-CdS QDs and FcC₆SH within the band-edge (a) and trap-state (b) regions; normalized emission spectra (c) with respect to the trap-state emission maxima; and (d) %Q of emission as a function of wavelength. In graph d, the error bars represent plus-or-minus one standard deviation relative to the average value from steady-state emission measurements for 3 different samples. The red dotted line in e represents the lower energy end of band edge emission of OA-CdS QDs.

**Emission Quenching of OA-CdS QDs by FcC₆SH**

The addition of FcC₆SH to OA-CdS QDs resulted in quenching of emission throughout the emission spectrum of OA-CdS QDs (Figure 4.4a and 4.4b). Values of %Q were calculated for all mixed dispersions (equation 4.1) and are plotted as a function of energy in Figure 4.4d. Band edge emission was quenched to a greater extent than surface-state emission for all mixed dispersions. Notably, the gradient quenching within the surface state emission was minimal or negligible, and was much less pronounced for quenching by FcC₆SH (Figure 4.4c) than for quenching by hexanethiol (Figure 4.2c). Preferential quenching of band-edge emission relative to surface emission is highlighted by steady-state emission spectra of mixed dispersions containing OA-CdS QDs and FcC₆SH normalized to the respective band-edge emission maxima (Figure 4.4c). As the
concentration of FcC₆SH increases, the relative intensity of surface-state emission initially increases; however, at relatively higher concentrations of FcC₆SH (6.8 µM and 17 µM), the intensity of surface-state emission relative to band edge emission decreases, indicating more efficient quenching of surface-state emission. This change in trend can be explained by the increase in loading of FcC₆SH on CdS QDs and relatively long lifetimes of trapped holes in surface states. An increase in surface coverage of FcC₆SH would result in increased rate of hole transfer, which can outcompete the slower electron-hole recombination from surface states more effectively and, therefore, would result in more efficient quenching of surface state emission.
Figure 4.5. (a,b) Time-resolved emission decay profiles and respective multi-exponential reconvolution fits for mixed dispersions containing OA-CdS QDs and FcC₆SH (0-17 µM) at emission wavelengths of 460 nm (a) and 610 nm (b). Also plotted is the IRF. (c) Rate constants of hole transfer ($k_{HT}$) as a function of energy for mixed dispersions containing OA-CdS QDs and FcC₆SH. (d) Effective intrinsic rate constant of hole transfer ($k_{HT, eff}$) as a function of energy for mixed dispersions containing OA-CdS QDs and FcC₆SH. The red dotted lines in c, d represent the low-energy threshold of band-edge emission of OA-CdS QDs.

Time-resolved emission decay profiles were collected throughout the emission spectrum for mixed dispersions containing OA-CdS QDs and FcC₆SH. Emission decay profiles and corresponding multi-exponential reconvolution fits for band-edge emission ($\lambda = 460$ nm) and surface-state emission ($\lambda = 610$ nm) are shown in Figures 4.5a and 4.5b. The addition of FcC₆SH to OA-CdS QDs resulted in a decrease of the average lifetime from $(23.2 \pm 0.5)$ ns to $(4.1 \pm 0.3)$ ns as the concentration of FcC₆SH was increased from 0 to 17 µM in mixed dispersions. Over the same range of concentrations, the average lifetime of surface-state emission ($\lambda = 610$ nm) decreased from $(66 \pm 8)$ ns to $(23 \pm 5)$ ns. The dynamic quenching of emission confirms the presence of an additional deactivation pathway, which can be logically assigned to hole transfer from OA-CdS QDs.
QDs to FcC₆SH as outlined in Scheme 4.1. The value of $k_{HT}$, as calculated using equation 4.4, increased from $(1.3 \pm 0.2) \times 10^7$ s⁻¹ to $(20 \pm 2) \times 10^7$ s⁻¹ for band-edge emission and from $(0.4 \pm 0.3) \times 10^7$ s⁻¹ to $(2.8 \pm 0.9) \times 10^7$ s⁻¹ for surface-state emission as the concentration of FcC₆SH in mixed dispersions was increased from 0.17 µM to 17 µM. Values of $\langle \tau \rangle$ and $k_{HT}$ are summarized in Table S2 in Supporting Information, and $k_{HT}$ is plotted as a function of energy in Figure 4.5c. The dotted line indicates the low-energy threshold of band-edge emission of OA-CdS QDs. Holes were transferred more rapidly and efficiently from band-edge states than from surface states, presumably due to the higher driving force (Scheme 4.1). Similarly, the significant decrease in $k_{HT}$ with increasing wavelength within the surface emission indicates that holes were transferred more rapidly and efficiently from relatively shallow surface states than from deeper surface states, consistent with the decrease of hole-transfer driving force as holes are trapped more deeply within the distribution of hole trap states.

The surface coverage of FcC₆SH also influenced the dynamics of hole transfer. As the average number of bound FcC₆SH increased on the surface of CdS QDs, the rate constant of hole transfer increased due to multiple additive hole-transfer pathways (equation 4.5):$^{50, 53, 62-63, 65}$

$$k_{HT} = N \times k_{HT,\text{int}}$$ (4.5)

where $N$ is the average number of hole acceptors (FcC₆SH) on the surface of CdE QDs and $k_{HT,\text{int}}$ is the intrinsic rate constant of hole transfer, defined as the average rate constant of hole transfer for hole transfer from CdE QDs bound to a single acceptor molecule (FcC₆SH).

Assuming a linear relationship between number of bound FcC₆SH and the concentration of FcC₆SH (equation 4.6),

$$N = \alpha \times [\text{FcC₆SH}]$$ (4.6)
where, $\alpha$ is a proportionality constant and $[\text{FcC}_6\text{SH}]$ is concentration of FcC$_6$SH in mixed dispersions containing OA-CdE QDs and FcC$_6$SH, an effective intrinsic rate constant of hole transfer ($k_{HT,eff}$) can be calculated as (equation 4.7),

$$k_{HT,eff} = \frac{k_{HT}}{[\text{FcC}_6\text{SH}]} \tag{4.7}$$

where $k_{HT,eff} = \alpha \cdot k_{HT,int}$. The assumption inherent in equation 4.6 is reasonable at relatively low fractional surface coverages of FcC$_6$SH. Values of $k_{HT,eff}$ were extracted from plots of $k_{HT}$ and $[\text{FcC}_6\text{SH}]$ at various emission energies within the emission spectrum of OA-CdS QDs, as shown in Figure 4.5d.

Values of $k_{HT,eff}$ are plotted as a function of energy in Figure 4.5d and are consistent with driving force dependent hole transfer in normal Marcus region. Notably, the values of $k_{HT,eff}$ corresponding to hole transfer from band-edge states are within the error of each other and decrease with emission energy within the surface-state emission due to decreased driving force of hole transfer (Scheme 4.1).

It should be noted that the concentration of FcC$_6$SH used in this experiment is much lower than the concentration of hexanethiol used. FcC$_6$SH quenched the emission of OA-CdS QDs much more effectively than did hexanethiol. For example, $k_{HT}$ from band-edge states of CdS QDs to adsorbed hexanethiolates, for the mixed dispersion containing the maximum concentration of hexanethiol (1.7 mM), was calculated as $(20.0 \pm 6.5) \times 10^7 \text{ s}^{-1}$. In contrast, $k_{HT}$ from band-edge states of CdS QDs to adsorbed FcC$_6$SH, corresponding to the mixed dispersion containing the maximum concentration of FcC$_6$SH (17 µM) was calculated as $(20.3 \pm 1.6) \times 10^7 \text{ s}^{-1}$ at 100 times lesser concentration than hexanethiol. Molecular ferrocene is attached to the surface of CdS QDs via the thiolate anchoring group, which itself can accept photogenerated holes, albeit with smaller
driving forces (Scheme 4.1). Additionally, ferrocene is 6 alkyl chains away spatially from CdS QDs as compared to thiolates, which are directly coordinated to the surface of CdS QDs. Numerous studies have explored distance-dependent charge transfer in QDs donor-acceptor systems.\textsuperscript{14, 53, 66-68} Notably, Alivisatos et al. studied distance-dependent hole transfer from core/shell CdSe/CdS QDs to covalently linked ferrocenylalkanethiols and reported an exponential decrease in rate constant of hole transfer with damping coefficient of ($\beta = 0.85 \pm 0.1$) $\text{Å}^{-1}$ for alkyl chain as distance between the donor-acceptor increased (equation 4.8):\textsuperscript{53}

$$k_{CT} = k_0 e^{-\beta d} \quad (4.8)$$

where, $k_{CT}$ is rate constant of charge transfer where donor and acceptor are separated by a distance $d$, $k_0$ is the rate constant of charge transfer where donor and acceptor are in close contact with each other and $\beta$ is the damping coefficient. Therefore, $k_{HT}$ is expected to fall off exponentially considering 6 carbon alkyl chains between CdS QDs and ferrocene in FcC$_6$SH as compared to hole transfer from CdS QDs to hexanethiolates.

Despite being 6 alkyl chains further from the surface of CdS QDs, and despite the fact that the concentration of FcC$_6$SH in mixed dispersions was 100-fold lower than that of hexanethiolates, holes were still transferred with similar $k_{HT}$ from CdS QDs to adsorbed FcC$_6$SH and hexanethiolates. Highly-efficient hole transfer from CdS QDs to FcC$_6$SH can be attributed to the higher driving force for hole transfer as compared to hexanethiolates (Scheme 4.1) along with possible differences in reorganization energies of hole transfer from CdS QDs to FcC$_6$SH or hexanethiolates. Additionally, the higher value of $k_{HT}$ for CdS-FcC$_6$SH, at 100-fold lower concentration in dispersions than hexanethiol, and despite being 6 alkyl chains further from the surface of CdS QDs, suggests that hole transfer from CdS QDs to FcC$_6$SH did not proceed via sequential hole transfer from CdS QDs to surface bound thiolates to ferrocene.
Figure 4.6. Steady-state emission spectra (a and b) of mixed dispersions containing OA-CdSe QDs and hexanethiol within the band-edge (a) and surface-state (b) regions; normalized emission spectra (c) with respect to the surface emission maxima; and (d) %Q as a function of emission wavelength. In graph e, the error bars represent plus-or-minus one standard deviation relative to the average value from steady-state emission measurements for 3 different samples. The red dotted line in d represents the low-energy end of band-edge emission of OA-CdSe QDs.
Dynamics of Hole Transfer from CdSe QDs to Hexanethiol or FeC₆SH

Similar experiments were conducted to study the hole-transfer dynamics in OA-CdSe/OA-CdTe QDs bound to hexanethiol or FeC₆SH. The displacement of native of oleate by hexanethiolate on CdSe QDs did not result in any significant changes in excitonic absorption features of CdSe QDs, as observed also for CdS QDs (Figure S4.5 in SI). Addition of hexanethiol to OA-CdSe dispersions resulted in preferential quenching of band-edge emission as compared to surface-state emission for all concentrations of hexanethiol used. The data for OA-CdSe QDs were similar to those for OA-CdS QDs, albeit with some key differences (Figure 4.6). First, plots of % Q as a function of wavelength contain a derivative-like feature around the lower-energy (longer-wavelength) tail of band edge emission (λ = 600 nm), providing evidence for stronger quenching than in the higher-energy (shorter-wavelength) region of band-edge emission. This feature may have arisen due to the blue-shift of band edge emission maxima as a result of surface functionalization of OA-CdSe QDs with hexanethiolate (Figure 4.6c). Second, the gradient quenching of surface-state emission is not as pronounced as in case of OA-CdS QDs (Figure 4.6d). This difference is attributed in part to the inability of our instrument to probe deeper in the surface-state emission. Assuming that the surface emission corresponding to the values of energies lying on the right side of the dotted red line in Figure 4.6d arises from the recombination of delocalized electrons with holes trapped in a distribution of surface states above the VB of OA-CdSe QDs (Scheme 4.1), our instrument allows us to probe only approximately 0.4 eV into the surface state distribution, as compared to approximately 0.9 eV in case of OA-CdS QDs. Regardless, band-edge emission was quenched more strongly than surface-state emission (Figure 4.6d), which is also highlighted in steady-state emission spectra of mixed dispersions containing OA-CdSe QDs and hexanethiols, normalized to respective band-edge emission maxima (Figure 4.6c).
As the concentration of hexanethiol increased in mixed dispersions, \( \% Q \) increased for both band-edge and surface-state emission, presumably due to the increased surface coverage of hexanethiolate on CdSe QDs. Also, the slope of the gradient quenching of surface-state emission became smaller, resulting in uniform quenching of surface-state emission (Figure 4.6d). With an increase in surface coverage of hexanethiolates, the rate of hole transfer is expected to increase and outcompete surface-related electron-hole recombination more effectively.
Figure 4.7. (a,b) Time-resolved emission decay profiles and respective multi-exponential reconvolution fits for mixed dispersions containing OA-CdSe QDs and hexanethiol (0-17 mM) at emission wavelengths of 560 nm (a) and 710 nm (b). Also plotted is the IRF. (c) Rate constants of hole transfer ($k_{HT}$) as a function of energy for mixed dispersions containing OA-CdS QDs and hexanethiol. The vertical red dotted line in c represents the lower energy end of band edge emission of OA-CdSe QDs. The horizontal red dotted line in c represent the value of $k_{HT} = 0$. 
Average lifetimes were extracted from time-resolved emission decay traces collected throughout the emission spectrum of CdSe QDs for all mixed dispersions containing OA-CdSe QDs and hexanethiol. Representative decay traces and corresponding multiexponential fits for band-edge emission ($\lambda = 560$ nm) and surface-state emission ($\lambda = 710$ nm), for different concentrations of hexanethiol, are shown in Figures 4.7a and 4.7b. The average lifetimes for OA-CdSe QDs showed a strong dependence on emission wavelength, similar to case of OA-CdS QDs. For example, $\langle \tau \rangle$ increased from $(25.5 \pm 0.8)$ ns for band-edge emission ($\lambda = 535$ nm) to $(51 \pm 7)$ ns for surface-state emission ($\lambda = 725$ nm). Addition of hexanethiol resulted in dynamic quenching of emission throughout the emission spectrum of CdSe QDs, although with some peculiarities. The value of $\langle \tau \rangle$ for band-edge emission decreased from $(24.8 \pm 0.7)$ ns to $(15.6 \pm 1.1)$ ns as the concentration of hexanethiol increased from 0.17 mM to 1.7 mM in mixed dispersions. Similarly, $\langle \tau \rangle$ decreased from $(56 \pm 8)$ ns to $(36 \pm 7)$ ns for surface-state emission with the increase in concentration of hexanethiol. Corresponding values of $k_{HT}$ are tabulated in Table S3 in Supporting Information and are plotted in Figure 4.7c as a function of emission energy for all concentrations of hexanethiol. Interestingly, a strong dependence of $k_{HT}$ on emission energy was observed within the band-edge emission. The value of $k_{HT}$ decreased from $(5.1 \pm 0.7) \times 10^7 \text{ s}^{-1}$ at $\lambda = 535$ nm to $(1.3 \pm 0.6) \times 10^7 \text{ s}^{-1}$ at $\lambda = 575$ nm as the concentration of hexanethiol increased from 0 to 1.7 mM. This decrease in $k_{HT}$ can be attributed to hole transfer from the VBs of a distribution of different-sized QDs to surface-bound hexanethiolate. As the size of the QDs decreases, the energy of VB becomes lower due to quantum confinement. The effect decreases the driving force of hole transfer and, assuming Marcus normal-region behavior, should increase $k_{HT}$ for hole transfer from relatively small QDs to surface-bound hexanethiolate as compared to relatively large QDs. Surprisingly, the addition of hexanethiol resulted in increased lifetime for a few emission wavelengths near the red
end of the band-edge emission ($\lambda = 600$-630 nm). We speculate that near the $E_v$ of OA-CdSe QDs, the driving force for hole transfer is almost zero (Scheme 4.1), which would result in hexanethiolate passivating the QD surface without effectively acting as a hole acceptor. However, at longer emission wavelengths throughout the surface-state emission, hole transfer becomes activated despite having negative driving forces of hole transfer. This effect can be explained by considering the emission wavelength-dependent electron-hole recombination lifetimes in OA-CdSe QDs. At longer emission wavelengths within surface-state emission, hole transfer can compete more effectively with electron-hole recombination due to long-lived nature of photoexcited hole in deeper surface states. As the concentration of hexanethiol increases, the surface coverage of hexanethiolate on CdSe QDs increases resulting in additional hole transfer pathways, which in turn increases $k_{HT}$ (Figure 4.7c).
(b) 

Intensity (a.u.) vs. Wavelength (nm) for different concentrations of [FcC₆SH] (µM).

(c) 

Normalized Intensity vs. Wavelength (nm) for different concentrations of [FcC₆SH] (µM).
Figure 4.8. Steady-state emission spectra (a and b) of mixed dispersions containing OA-CdSe QDs and FcC₆SH within the band-edge (a) and trap-state (b) regions; normalized emission spectra (c) with respect to the trap-state emission maxima; and (d) %Q of emission as a function of wavelength. In graph d, the error bars represent plus-or-minus one standard deviation relative to the average value from steady-state emission measurements for 3 different samples. The red dotted line in d represents the low-energy threshold of band-edge emission of OA-CdSe QDs.

**Emission Quenching of OA-CdSe QDs by FcC₆SH**

The addition of FcC₆SH to dispersions of OA-CdSe QDs resulted in quenching of emission throughout the emission spectrum of CdSe QDs (Figure 4.8). Plots of %Q as a function of wavelength for mixed dispersions containing OA-CdSe QDs and different concentrations of FcC₆SH are plotted in Figure 4.8d. Again, band-edge emission was quenched to a greater extent than surface-state emission. Plots of %Q as a function of wavelength reveal gradient quenching of the surface-state band; however, the slope of these plots is minimal or negligible as compared to the quenching of surface-state emission by hexanethiol (Figure 4.6d). As the concentration of FcC₆SH was increased in mixed dispersions, %Q increased throughout the emission spectrum. Time-resolved emission decay traces were acquired for all mixed dispersions containing OA-CdSe...
QDs and FcC₆SH at wavelengths throughout the emission spectrum of CdSe QDs. Corresponding values of $\langle \tau \rangle$ were extracted and are tabulated in Table S4 in Supporting Information. Addition of FcC₆SH to OA-CdSe QDs resulted in dynamic quenching of emission, as $\langle \tau \rangle$ decreased from (24.8 ± 0.7) ns to (1.8 ± 0.1) ns for band-edge emission ($\lambda = 560$ nm) and from (56 ± 8) ns to (6.6 ± 4.1) ns for surface-state emission ($\lambda = 710$ nm) as the concentration of FcC₆SH was increased from 0 to 17 µM (Figures 4.9a and 9b). Values of $k_{HT}$ were calculated throughout the emission spectrum of OA-CdSe QDs for all concentrations of FcC₆SH used and are plotted in Figure 4.9c as a function of emission energy. The dotted line represents the low-energy threshold of band-edge emission of OA-CdSe QDs.

On the basis of the assumptions that $k_{HT}$ varies linearly with surface coverage of FcC₆SH (equation 4.5) and that surface coverage of FcC₆SH on CdSe QDs varies linearly with increase in concentration of FcC₆SH in mixed dispersions (equation 4.6), values of $k_{HT,eff}$ were calculated as a function of emission energy and are plotted in Figure 4.9d. The value of $k_{HT,eff}$ was found to decrease with a decrease in emission energy. Assuming that surface-state emission in OA-CdSe QDs arises from the recombination of delocalized electrons and trapped holes, in a distribution of surface states, the variation of $k_{HT}$ with emission energy can be explained by driving force-dependent hole transfer. As emission energy decreases, holes are trapped more deeply into the distribution of hole-trap states, thereby decreasing the driving force of hole transfer (Scheme 4.1).

Assuming normal-region behavior, this effect should, in turn, decrease $k_{HT,eff}$. Notably, the concentrations of FcC₆SH used are ~100 times lower than for hexanethiol; however, these concentrations of FcC₆SH still resulted in more efficient quenching of emission due to the higher driving force and possible differences in electronic coupling and reorganization energies for hole transfer in the case of FcC₆SH as compared to hexanethiolate. For example, $k_{HT}$ was calculated to
be \((2.4 \pm 0.5) \times 10^7 \text{ s}^{-1}\) at \(\lambda = 560\) nm for mixed dispersion containing OA-CdSe QDs and hexanethiol (1.7 mM) as compared to \((5.1 \pm 0.4) \times 10^8 \text{ s}^{-1}\) at \(\lambda = 560\) nm for mixed dispersion containing OA-CdSe QDs and FcC\(_6\)SH (17 \(\mu\)M). The 20-fold higher \(k_{HT}\) at 100-fold lower concentration of FcC\(_6\)SH, despite the iron center being 6 alkyl chains further from the surface of CdSe QDs than the thiolate group, precludes the possibility of sequential hole transfer from CdSe QDs to surface-bound thiolates to ferrocene.
Figure 4.9. (a,b) Time-resolved emission decay profiles and respective multi-exponential reconvolution fits for mixed dispersions containing OA-CdSe QDs and FcC₆SH (0-17 µM) at emission wavelengths of 560 nm (a) and 710 nm (b). Also plotted is the IRF. (c) Rate constants of hole transfer ($k_{HT}$) as a function of energy for mixed dispersions containing OA-CdSe QDs and FcC₆SH. (d) Effective intrinsic rate constant of hole transfer ($k_{HT, eff}$) as a function of energy for mixed dispersions containing OA-CdS QDs and FcC₆SH. The red dotted lines in c, d represent the low-energy threshold of band-edge emission of OA-CdSe QDs.

Dynamics of Hole Transfer from CdTe QDs to Hexanethiol or FcC₆SH

Ligand exchange of oleates with hexanethiolates on CdTe QDs did not result in any significant changes in excitonic absorption features of CdTe QDs as observed in case of CdS QDs (Figure S4.6 in SI). Addition of hexanethiol to OA-CdTe QDs initially resulted in increased emission as compared to OA-CdTe QDs (Figure S4.8a in Supporting Information). However, further increase in concentration of hexanethiol caused a decrease in emission, although the intensity was still higher than for OA-CdTe QDs alone. Normalized emission spectra of mixed dispersions containing OA-CdTe QDs and hexanethiol reveal a red shift of emission maxima as the concentration of hexanethiol increased (Figure S4.8b in Supporting Information). This red shift may have arisen from changes in the chemical environment of the surface of QDs upon
displacement of oleate with hexanethiolate. Interestingly, average excitonic lifetimes within the band-edge emission band of OA-CdTe QDs varied more widely, from \((8.2 \pm 0.4)\) ns for \(\lambda = 610\) nm to \((18.4 \pm 0.6)\) ns for \(\lambda = 690\) nm, than for OA-CdS QDs or OA-CdSe QDs. This distribution of lifetimes suggests that the size distribution of OA-CdTe QDs was relatively broad. Emission-frequency dependent lifetimes have been observed previously by various groups, where an increase in emission frequency resulted in an increase of rates of spontaneous emission.\(^{69-71}\)

Assuming that the breadth of the steady-state emission spectrum of OA-CdTe QDs is primarily due to a broad size distribution within the ensemble of QDs, the emission wavelength-dependent lifetimes observed for OA-CdTe QDs can be attributed to electron-hole recombination in different sized QDs within the ensemble of CdTe QDs. Excited states in smaller QDs decayed more rapidly than those in larger QDs, presumably due to the differences in electron-hole overlap within the QD volume.

Time-resolved emission data revealed that the addition of hexanethiol resulted in increase in average excitonic lifetime throughout the emission band (Figure S4.8c and Table S4.6 in SI). This increase in emission intensity and lifetime is consistent with the passivation of surface states of OA-CdTe QDs upon surface functionalization with hexanethiolate. Since the oxidation potential of hexanethiol is more positive than the \(E_v\) of CdTe QDs (Scheme 4.1), the transfer of holes from photoexcited CdTe QDs to surface-bound hexanethiol is thermodynamically unfavorable.
Figure 4.10. (a) Steady-state emission spectra of mixed dispersions containing OA-CdTe QDs and FcC₆SH (0-17 µM), (b) %Q of emission as a function of wavelength. (c) Time-resolved emission decay profiles and respective multi-exponential reconvolution fits for mixed dispersions containing OA-CdTe QDs and FcC₆SH (0-17 µM) at emission wavelengths of 660 nm. Also plotted is the IRF. (d) Rate constants of hole transfer ($k_{HT}$) as a function of energy for mixed dispersions containing OA-CdTe QDs and FcC₆SH. In graph b, the error bars represent plus-or-minus one standard deviation relative to the average value from steady-state emission measurements for 2 different samples.
In contrast, the addition of FcC₆SH to dispersions of OA-CdTe QDs resulted in quenching of emission. Normalized emission spectra of mixed dispersions containing OA-CdTe QDs and FcC₆SH exhibited a blue shift of emission maxima as the concentration of FcC₆SH was increased from 1.7 µM to 17 µM (Figure S4.9 in Supporting Information). This blue shift indicates preferential quenching of lower-energy emission within the band-edge emission. % Q plots for mixed dispersions containing OA-CdTe QDs and FcC₆SH reveal relatively higher quenching of emission of the lower-energy end than higher-energy end of band-edge emission of CdTe QDs (Figure 4.10b). Assuming that the differences in band-edge emission quenching arise from the difference in sizes of QDs, the preferential quenching of lower-energy regions of the band edge emission may have arisen from the higher loading of FcC₆SH on the larger QDs due to their higher surface area.

Time-resolved emission data (Figures 4.10c and 4.10d) for mixed dispersions containing OA-CdTe QDs and FcC₆SH revealed dynamic quenching of emission throughout the band-edge emission band, as ⟨τ⟩ decreased from (10.3 ± 0.2) ns for QD alone to (0.8 ± 0.1) ns for mixed dispersions containing the highest concentration of FcC₆SH (17µM) at λ = 660 nm. This dynamic quenching can logically be attributed to hole transfer from photoexcited CdTe QDs to surface-bound FcC₆SH (Scheme 4.1). Values of $k_{HT}$ were calculated for all concentrations of FcC₆SH (Table S4.5 in Supporting Information) and are plotted as a function of emission energy in Figure 4.10d. The values of $k_{HT}$ depend strongly on emission energy for all concentrations. Qualitatively, at lower concentrations of FcC₆SH, smaller sized QDs exhibit both faster hole transfer and faster electron-hole recombination. As the size of the QDs decreases, $E_V$ of QDs decreases due to quantum confinement effects, which would result in increased driving force of hole transfer and therefore faster hole transfer from smaller QDs than larger QDs to FcC₆SH within the distribution
of different sized CdTe QDs. However, at higher concentrations of FcC₆SH (17 µM), the trend in $k_{HT}$ changed (Figure 4.10d), wherein medium-sized QDs transferred holes more rapidly than smallest QDs. This change in trends of $k_{HT}$ may have arisen from changes in the surface coverage of FcC₆SH on CdTe QDs of varying size. Larger QDs can potentially accommodate more FcC₆SH molecules per QDs than smaller QDs, which would result in higher overall $k_{HT}$ due to additive nature of hole transfer pathways provided by multiple hole acceptors adsorbed on a single QD (equation 4.5). Steady-state emission quenching trends can then be explained by the relative competition between the rates of electron-hole recombination and hole transfer, where $k_{HT}$ is influenced by surface coverage of FcC₆SH. Even though hole transfer is expected to be faster from smaller CdTe QDs to FcC₆SH, longer electron-hole recombination lifetimes in larger QDs along with the possibility that larger size QDs can potentially accommodate higher loading FcC₆SH, can potentially render hole transfer more efficient from larger QDs despite having lower driving forces of hole transfer.

These results signify the complex nature of charge transfer in QD-molecular donor-acceptor assemblies, particularly when both band-edge and surface states can participate in charge transfer. Hole transfer from surface states was found to be much slower than from band-edge states, consistent with driving force-dependent charge transfer in normal Marcus region. One caveat is that reorganization energies should be very different for hole transfer taking place from delocalized band-edge states versus the localized surface states. Scholes et al. used molecular simulation to estimate reorganization energies required for charge transfer from band-edge states and surface states and found much higher reorganization energies for charge transfer from band-edge states than surface states, due to the strong polarization of the surfaces of QDs and surrounding solvent upon localization of charges on the surface of QDs.³³ Plots of % $Q$ as a function of wavelength
(Figure 4.10b) revealed more efficient quenching of band-edge emission as compared to surface state emission, consistent with the time-resolved emission quenching data, where higher driving force of hole transfer from band edge states of QDs to molecular acceptors resulted in faster hole transfer from band edge states than surface states.

Overall, % quenching trends can be qualitatively understood by the competition between electron-hole recombination and hole transfer, where hole transfer is also affected by the surface coverage of molecular acceptors on QDs. Even though values of $k_{HT}$ were much lower for hole transfer from surface states than from band-edge states, the quenching of surface-state emission band was still efficient due to the long lifetime of surface states and therefore the better competition between electron-hole recombination and hole transfer processes. Higher loading of molecular acceptors on the surface of QDs provided additional hole transfer pathways, resulting in more efficient quenching of both band-edge and surface-state emission at higher concentration of molecular acceptors in mixed dispersions.

Notably, our results are consistent with the presence of a distribution of hole surface states which participate in hole transfer, rather than a narrow or single surface state. If a single quantized state was the origin of the broad surface-state emission, we would have expected a uniform quenching of surface state emission as a function of wavelength, rather than the observed wavelength-dependent gradient emission quenching of surface-state emission upon hole transfer from surface states of CdE QDs to molecular acceptors. Our results, therefore, have significant implications with respect to the nature of surface-localized charge-trap states in QDs.
Conclusions

Excited-state hole transfer was studied by a combination of steady-state and time-resolved emission spectroscopy in a myriad of CdE QD-molecule donor-acceptor systems prepared via X-type ligand exchange of surface bound oleates with thiolates. In case of OA-CdS QDs, holes were transferred from both band-edge states and a distribution of surface hole-trap states to surface-bound hexanethiolate and FcC₆SH, due to positive driving force for hole transfer. Values of $k_{HT}$ were much greater for hole transfer from band-edge states than surface states. Also, as the concentration of a given molecular acceptor increased, hole transfer became more efficient due to the higher loading of molecular acceptors on the surfaces of CdS QDs. The transfer of holes to FcC₆SH was much more efficient than to hexanethiolate, precluding the possibility of sequential hole transfer from QDs to surface bound thiolates to ferrocene. The wavelength dependence of $k_{HT,\text{eff}}$ was consistent with driving force-dependent hole transfer, with Marcus normal-region behavior, from photoexcited CdS QDs to surface bound FcC₆SH.

For OA-CdSe QDs, hole transfer to hexanethiolate from band-edge states was much more efficient than from surface states, due to close energetic match between the oxidation potential of hexanethiolate and $E_v$ of CdSe QDs. The rate of hole transfer from CdSe QDs to hexanethiolate decreased with size of QDs. Despite of almost 100-fold lower concentration of FcC₆SH relative to hexanethiol, and despite the redox-active iron center of FcC₆SH being six sp3 carbons away from the surface of CdSe QDs, hole transfer from band-edge state and surface states of CdSe QDs to FcC₆SH was much more rapid and efficient than to hexanethiolates. Increasing the concentration of FcC₆SH in mixed dispersions resulted in increased surface coverage of FcC₆SH, which resulted in multiple additive hole transfer pathways, such that hole transfer outcompeted
electron-hole recombination. The value of $k_{HT,\text{eff}}$ decreased with driving force for hole transfer from band-edge states and from the distribution of hole-surface states to FcC$_6$SH.

OA-CdTe QDs presented an interesting case, in which the addition of hexanethiol apparently passivated the surface of QDs and increased the excitonic lifetime, consistent with thermodynamically unfavorable hole transfer from CdTe QDs to surface bound hexanethiolates. On the other hand, FcC$_6$SH efficiently quenched the emission of CdTe QDs, consistent with hole transfer from photoexcited CdTe QDs to surface bound FcC$_6$SH. The values of $k_{HT}$ decreased significantly within the band edge emission, consistent with faster hole transfer from smaller-sized QDs within the distribution of CdTe QDs due to higher driving force, with the additional complexity that relatively large QDs can accommodate higher loadings of FcC$_6$SH, which increases the overall rate of hole transfer.

Our studies highlight the mechanistic complexity of excited-state charge-transfer between QDs and adsorbed molecular charge acceptors. Both band-edge states and surface states can participate in charge transfer, and driving force can strongly influence charge-transfer dynamics. Additionally, the increasing the surface coverage of molecular acceptors can increase the number of additive charge-transfer pathways, accelerating the overall rate of charge transfer. Thiolates have often been regarded as effective hole traps in photoexcited QDs; however, our studies revealed that molecular ferrocene with increased driving force can effectively outcompete charge transfer to surface bound thiolates despite being separated from the surface of the QDs by a six-carbon alkyl chain.

Surface states, often termed as trap states, are traditionally regarded as deleterious for charge transfer due to trapping-induced decrease of the driving force of charge transfer and the corresponding decrease of charge-transfer rate constants and yields. However, our studies reveal
that electron-hole recombination from surface states is much slower than from delocalized band-edge states and, therefore, charge carriers can still be extracted efficiently from surface states. The surface coverage of charge acceptors provides another avenue to tune the efficiency of charge transfer. Finally, our results support the existence of a distribution of surface states rather than a single quantized surface state, which can actively participate in charge transfer despite having lower driving forces.

**Acknowledgements**

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Supporting Information

Exploring the Role of Driving Force and Surface Coverage in Hole Transfer Dynamics from Cadmium Chalcogenide Quantum Dots to Covalently Tethered Molecular Acceptors

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Appendix S4.1. Detailed description of preparation of samples for spectroscopic measurements.

Appendix S4.2. Calculation of effective intrinsic rate constant of hole transfer ($k_{HT, eff}$) for hole transfer from CdE QDs to surface bound FcC$_6$SH.

Figure S4.2. 1-H NMR spectra of mixed dispersions containing OA-CdS QDs and (a) hexanethiol, (b) FcC$_6$SH.

Figure S4.3. 1-H NMR spectra of mixed dispersions containing OA-CdSe QDs and (a) hexanethiol, (b) FcC$_6$SH.

Figure S4.4. 1-H NMR spectra of mixed dispersions containing OA-CdTe QDs and FcC$_6$SH.

Figure S4.5. Normalized UV-Vis spectra of mixed dispersions containing hexanethiol and OA-CdS QDs.

Figure S4.6. Normalized UV-Vis spectra of mixed dispersions containing OA-CdSe QDs and hexanethiol.

Figure S4.7. Normalized UV-Vis spectra of mixed dispersions containing OA-CdTe QDs and hexanethiol.

Figure S4.8. (a) Steady state emission spectra, (b) normalized steady state emission spectra and, (c) time-resolved emission spectra ($\lambda = 660$ nm) of mixed dispersions containing OA-CdTe QDs and hexanethiol.

Figure S4.9. Normalized steady state emission spectra of mixed dispersions containing OA-CdTe QDs and FcC$_6$SH.

Table S4.1. Values of average lifetimes ($\tau$), rate constant of hole transfer ($k_{HT}$) for mixed dispersions containing OA-CdS QDs and hexanethiol.

Table S4.2. Values of average lifetimes ($\tau$), rate constant of hole transfer ($k_{HT}$) for mixed dispersions containing OA-CdS QDs and FcC$_6$SH.
Table S4.3. Values of average lifetimes $\langle \tau \rangle$, rate constant of hole transfer ($k_{HT}$) for mixed dispersions containing OA-CdSe QDs and hexanethiol.

Table S4.4. Values of average lifetimes $\langle \tau \rangle$, rate constant of hole transfer ($k_{HT}$) for mixed dispersions containing OA-CdSe QDs and FcC₆SH.

Table S4.5: Values of average lifetimes $\langle \tau \rangle$, and average rate constants of hole transfer ($k_{HT}$) for all mixed dispersions containing OA-CdTe QDs and FcC₆SH for band edge emission.

Table S4.6: Values of Average lifetimes $\langle \tau \rangle$, for all mixed dispersions containing OA-CdTe QDs and hexanethiol for band edge emission.
Appendix S4.1. Detailed description of preparation of samples for spectroscopic measurements.

Stock dispersions of 60 mL, 0.5 µM CdE QDs in CHCl₃ were prepared by monitoring the absorbance of CdE dispersions at respective first excitonic peaks of CdE QDs. Size dependent extinction coefficients of CdE QDs at the respective first excitonic peaks were estimated according to Yu et al.⁴ The concentration of QDs in all mixed dispersions containing QDs and/or FcC₆SH/hexanethiol was kept same. A stock solution of 5 mM hexanethiol in CHCl₃ was prepared by diluting 14.2 µL of hexanethiol to 20 mL with CHCl₃. Mixed dispersions containing CdE QDs and hexanethiol were prepared as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume of stock CdE QDs dispersions (mL)</th>
<th>Volume of stock hexanethiol solution (mL)</th>
<th>Volume of CHCl₃ (mL)</th>
<th>Total volume (mL)</th>
<th>[Hexanethiol] in dispersion (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD alone</td>
<td>10.0</td>
<td>0.0</td>
<td>5.0</td>
<td>15.0</td>
<td>0</td>
</tr>
<tr>
<td>QD+HT 0.5</td>
<td>10.0</td>
<td>0.5</td>
<td>4.5</td>
<td>15.0</td>
<td>0.17</td>
</tr>
<tr>
<td>QD+HT 2</td>
<td>10.0</td>
<td>2</td>
<td>3.0</td>
<td>15.0</td>
<td>0.68</td>
</tr>
<tr>
<td>QD+HT 5</td>
<td>10.0</td>
<td>5</td>
<td>0.0</td>
<td>15.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Serial dilution was used to prepare 50 µM stock solution of FcC₆SH in CHCl₃. A 16.5 mM stock solution of FcC₆SH was prepared first by adding 250 mg of FcC₆SH to 50 mL CHCl₃. A 16.5 mM stock solution of FcC₆SH was kept under Ar environment in dark atmosphere. A fresh stock solution of 50 µM FcC₆SH was prepared by diluting the 16.5 mM stock solution of FcC₆SH before preparing each mixed dispersion containing CdE QDs and FcC₆SH.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume of stock CdE QDs dispersions (mL)</th>
<th>Volume of 50 µM FcC₆SH solution (mL)</th>
<th>Volume of CHCl₃ (mL)</th>
<th>Total volume (mL)</th>
<th>[Hexanethiol] in dispersion (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD alone</td>
<td>10.0</td>
<td>0.0</td>
<td>5.0</td>
<td>15.0</td>
<td>0</td>
</tr>
<tr>
<td>QD+Fc 0.5</td>
<td>10.0</td>
<td>0.5</td>
<td>4.5</td>
<td>15.0</td>
<td>1.7</td>
</tr>
<tr>
<td>QD+Fc 1</td>
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<td>1.0</td>
<td>4.0</td>
<td>15.0</td>
<td>3.4</td>
</tr>
<tr>
<td>QD+Fc 2</td>
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<td>2.0</td>
<td>3.0</td>
<td>15.0</td>
<td>6.8</td>
</tr>
<tr>
<td>QD+Fc 5</td>
<td>10.0</td>
<td>5.0</td>
<td>0.0</td>
<td>15.0</td>
<td>17</td>
</tr>
</tbody>
</table>

All mixed dispersions were purged with Ar for 5 min before spectroscopic measurements.
Appendix S4.2. Calculation of effective intrinsic rate constant of hole transfer ($k_{HT,eff}$) for hole transfer from CdE QDs to surface bound FcC₆SH.

Assumption 1. Overall rate constant of hole transfer ($k_{HT}$) varies linearly with surface coverage of bound FcC₆SH. Therefore,

$$k_{HT} = N \cdot k_{HT,int}$$

Where $N$ is the average number of hole acceptor (FcC₆SH) on the surface of CdE QDs and $k_{HT,int}$ is the intrinsic rate constant of hole transfer, defined as the rate constant of hole transfer for hole transfer from CdE QDs bound to a single acceptor molecule (FcC₆SH) on average.

Assumption 2. Surface coverage of FcC₆SH on CdE QDs varies linearly with increase in concentration of FcC₆SH in mixed dispersion. Therefore,

$$N = \alpha \cdot [FcC₆SH]$$

Where $\alpha$ is a proportionality constant and $[FcC₆SH]$ is concentration of FcC₆SH in mixed dispersions containing OA-CdE QDs and FcC₆SH.

Therefore,

$$k_{HT} = \alpha \cdot [FcC₆SH] \cdot k_{HT,int}$$

Thus, the effective intrinsic rate constant of hole transfer ($\alpha \cdot k_{HT,int}$) can be calculated as the slope of the linear fit from the plot between $k_{HT}$ (from time resolved emission) and [FcC₆SH] (known) as shown in Figure S1.
Figure S4.1. Rate constant of hole transfer ($k_{HT}$) as a function of concentration of FcC$_6$SH in mixed dispersions containing OA-CdTe QDs and FcC$_6$SH. Also, shown is a linear fit between $k_{HT}$ and [FcC$_6$SH] at emission wavelength of 637 nm.
Figure S4.2: 1-H NMR of mixed dispersions containing (a) OA-CdS QDs and hexanethiol (0-17 mM), (b) OA-CdS QDs and FcC₆SH (0-68 µM).
Figure S4.3: 1-H NMR of mixed dispersions containing (a) OA-CdSe QDs and hexanethiol (0-17 mM), (b) OA-CdSe QDs and FcC$_6$SH (0-68 µM).
Figure S4.4: 1-H NMR of mixed dispersions containing OA-CdTe QDs FcC₆SH (0-68 μM).
Figure S4.5: Normalized absorption spectra of mixed dispersions containing OA-CdS QDs and hexanethiol.

Figure S4.6: Normalized absorption spectra of mixed dispersions containing OA-CdS QDs and hexanethiol.
Figure S4.7: Normalized absorption spectra of mixed dispersions containing OA-CdTe QDs and hexanethiol.
Figure S4.8. (a) Steady state emission spectra, (b) normalized steady state emission spectra and, (c) time-resolved emission spectra ($\lambda = 660$ nm) of mixed dispersions containing OA-CdTe QDs and hexanethiol.

Figure S4.9. Normalized steady state emission spectra of mixed dispersions containing OA-CdTe QDs and FcC$_6$SH.
Table S4.1: Average lifetimes and average rate constants of hole transfer ($k_{HT}$) for all mixed dispersions containing OA-CdS QDs and hexanethiol for band edge and trap state emission.

<table>
<thead>
<tr>
<th>Emission Band</th>
<th>λ (nm)</th>
<th>QD alone</th>
<th>QD+HT (0.17 mM)</th>
<th>QD+HT (0.70 mM)</th>
<th>QD+HT (1.7 mM)</th>
<th>QD+HT (17 mM)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>〈τ〉 (ns)</td>
<td>〈τ〉 (ns) $k_{HT}$ (x10^7 s⁻¹)</td>
<td>〈τ〉 (ns) $k_{HT}$ (x10^7 s⁻¹)</td>
<td>〈τ〉 (ns) $k_{HT}$ (x10^7 s⁻¹)</td>
<td>〈τ〉 (ns) $k_{HT}$ (x10^7 s⁻¹)</td>
</tr>
<tr>
<td>BE</td>
<td>460</td>
<td>(23.2±0.5)</td>
<td>(15.1±0.6) (2.3±0.3)</td>
<td>(4.5±1.2)</td>
<td>(17.8±6.0)</td>
<td>(4.1±1.1)</td>
</tr>
<tr>
<td></td>
<td>472.5</td>
<td>(28.1±2.7)</td>
<td>(15.0±1.1) (2.5±0.5)</td>
<td>(3.2±0.5)</td>
<td>(27.3±4.9)</td>
<td>(3.3±0.6)</td>
</tr>
<tr>
<td>BE</td>
<td>485</td>
<td>(28.1±2.7)</td>
<td>(15.0±1.1) (2.5±0.5)</td>
<td>(3.2±0.5)</td>
<td>(27.3±4.9)</td>
<td>(3.3±0.6)</td>
</tr>
<tr>
<td>TS</td>
<td>501</td>
<td>(33.3±3.2)</td>
<td>(20.9±2.4) (1.8±0.6)</td>
<td>(9.1±2.0)</td>
<td>(8.0±2.4)</td>
<td>(6.0±1.3)</td>
</tr>
<tr>
<td>TS</td>
<td>522.5</td>
<td>(33.5±3.0)</td>
<td>(22.8±2.4) (1.4±0.5)</td>
<td>(9.7±1.7)</td>
<td>(7.3±1.8)</td>
<td>(6.9±1.5)</td>
</tr>
<tr>
<td>TS</td>
<td>535</td>
<td>(39.2±3.5)</td>
<td>(26.8±2.5) (1.2±0.4)</td>
<td>(13.5±2.2)</td>
<td>(4.8±1.2)</td>
<td>(7.8±1.4)</td>
</tr>
<tr>
<td>TS</td>
<td>547.5</td>
<td>(44.6±4.1)</td>
<td>(30.9±2.9) (1.0±0.4)</td>
<td>(17.5±2.6)</td>
<td>(3.5±0.9)</td>
<td>(10.6±1.9)</td>
</tr>
<tr>
<td>TS</td>
<td>560</td>
<td>(48.1±4.3)</td>
<td>(35.0±3.0) (0.8±0.3)</td>
<td>(21.0±2.9)</td>
<td>(2.7±0.7)</td>
<td>(14.5±2.4)</td>
</tr>
<tr>
<td>TS</td>
<td>572.5</td>
<td>(52.3±5.0)</td>
<td>(37.8±3.3) (0.7±0.3)</td>
<td>(24.5±3.4)</td>
<td>(2.2±0.6)</td>
<td>(16.7±2.8)</td>
</tr>
<tr>
<td>TS</td>
<td>585</td>
<td>(56.3±5.4)</td>
<td>(44.0±4.1) (0.5±0.3)</td>
<td>(29.3±3.9)</td>
<td>(1.6±0.5)</td>
<td>(20.1±3.3)</td>
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<tr>
<td>TS</td>
<td>597.5</td>
<td>(63.5±7.3)</td>
<td>(44.5±4.0) (0.7±0.3)</td>
<td>(32.5±4.5)</td>
<td>(1.5±0.5)</td>
<td>(23.9±3.8)</td>
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<tr>
<td>TS</td>
<td>610</td>
<td>(66.4±7.8)</td>
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<td>(35.0±4.7)</td>
<td>(1.4±0.4)</td>
<td>(25.5±3.9)</td>
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<tr>
<td>TS</td>
<td>622.5</td>
<td>(63.2±8.7)</td>
<td>(59.8±8.6) (0.1±0.3)</td>
<td>(37.4±6.3)</td>
<td>(1.1±0.5)</td>
<td>(29.8±5.9)</td>
</tr>
<tr>
<td>TS</td>
<td>635</td>
<td>(73.6±13.2)</td>
<td>(54.0±7.2) (0.5±0.3)</td>
<td>(39.6±7.0)</td>
<td>(1.2±0.5)</td>
<td>(29.8±6.0)</td>
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Uncertainties in 〈τ〉 and $k_{HT}$ are calculated from measurements on three different samples along with uncertainties from fitting of time-resolved emission decay profiles with multi-exponential reconvolution.
Table S4.2: Average lifetimes and average rate constants of hole transfer ($k_{HT}$) for all mixed dispersions containing OA-CdS QDs and FcC$_6$SH for band edge and trap state emission.

<table>
<thead>
<tr>
<th>Emission Band</th>
<th>λ (nm)</th>
<th>QD alone $\langle \tau \rangle$ (ns)</th>
<th>QD+FcC$_6$SH (1.7 µM) $\langle \tau \rangle$ (ns)</th>
<th>QD+ FcC$_6$SH (3.4 µM) $\langle \tau \rangle$ (ns)</th>
<th>QD+ FcC$_6$SH (6.8 µM) $\langle \tau \rangle$ (ns)</th>
<th>QD+ FcC$_6$SH (17 µM) $\langle \tau \rangle$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_{HT}$ (x10$^6$/s$^{-1}$)</td>
<td>$k_{HT}$ (x10$^6$/s$^{-1}$)</td>
<td>$k_{HT}$ (x10$^6$/s$^{-1}$)</td>
<td>$k_{HT}$ (x10$^6$/s$^{-1}$)</td>
<td>$k_{HT}$ (x10$^6$/s$^{-1}$)</td>
</tr>
<tr>
<td>BE</td>
<td>460</td>
<td>(23.2±0.5)</td>
<td>(18.0±0.4)</td>
<td>(12.6±1.6)</td>
<td>(14.4±0.4)</td>
<td>(26.1±2.2)</td>
</tr>
<tr>
<td>BE</td>
<td>472.5</td>
<td>(24.1±0.9)</td>
<td>(18.9±0.7)</td>
<td>(11.5±2.5)</td>
<td>(15.0±0.7)</td>
<td>(25.2±3.4)</td>
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<tr>
<td>BE</td>
<td>485</td>
<td>(25.8±2.0)</td>
<td>(19.7±1.6)</td>
<td>(11.9±5.0)</td>
<td>(17.0±1.8)</td>
<td>(19.9±7.0)</td>
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<tr>
<td>BE</td>
<td>497.5</td>
<td>(28.1±2.7)</td>
<td>(24.6±2.9)</td>
<td>(5.1±5.6)</td>
<td>(20.1±2.7)</td>
<td>(14.1±7.5)</td>
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<tr>
<td>TS</td>
<td>510</td>
<td>(33.3±3.2)</td>
<td>(27.6±3.0)</td>
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<td>(23.9±3.2)</td>
<td>(11.9±6.3)</td>
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<tr>
<td>TS</td>
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<td>(35.5±3.0)</td>
<td>(27.5±2.8)</td>
<td>(6.5±4.6)</td>
<td>(23.7±2.7)</td>
<td>(12.4±5.5)</td>
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<tr>
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<td>535</td>
<td>(39.2±3.5)</td>
<td>(31.6±3.0)</td>
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<td>(35.8±3.6)</td>
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<td>(10.4±4.0)</td>
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<tr>
<td>TS</td>
<td>560</td>
<td>(48.1±4.3)</td>
<td>(39.5±3.9)</td>
<td>(4.6±3.1)</td>
<td>(33.8±3.4)</td>
<td>(8.8±3.5)</td>
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<tr>
<td>TS</td>
<td>572.5</td>
<td>(52.3±5.0)</td>
<td>(44.3±4.8)</td>
<td>(3.4±3.1)</td>
<td>(37.2±4.0)</td>
<td>(7.7±3.4)</td>
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<tr>
<td>TS</td>
<td>585</td>
<td>(56.3±5.4)</td>
<td>(49.8±5.5)</td>
<td>(2.3±2.8)</td>
<td>(40.2±4.4)</td>
<td>(7.1±3.2)</td>
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<tr>
<td>TS</td>
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<td>(63.5±7.3)</td>
<td>(48.6±5.4)</td>
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<td>(41.5±4.7)</td>
<td>(8.4±3.3)</td>
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<tr>
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<td>610</td>
<td>(66.4±7.8)</td>
<td>(52.7±6.2)</td>
<td>(3.9±2.8)</td>
<td>(43.3±5.0)</td>
<td>(8.0±3.2)</td>
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<tr>
<td>TS</td>
<td>622.5</td>
<td>(63.2±8.7)</td>
<td>(57.4±9.1)</td>
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<td>(52.0±8.7)</td>
<td>(3.4±3.9)</td>
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<tr>
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<td>(58.0±12.4)</td>
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</table>

 uncertainties in $\langle \tau \rangle$ and $k_{HT}$ are calculated from measurements on three different samples along with uncertainties from fitting of time-resolved emission decay profiles with multi-exponential reconvolution.
Table S4.3: Average lifetimes and average rate constants of hole transfer ($k_{HT}$) for all mixed dispersions containing OA-CdSe QDs and hexanethiol for band edge and trap state emission.

<table>
<thead>
<tr>
<th>Emission Band</th>
<th>$\lambda$ (nm)</th>
<th>QD alone</th>
<th>QD+HT (0.17 mM)</th>
<th>QD+HT (0.70 mM)</th>
<th>QD+HT (1.7 mM)</th>
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<td>$(\tau)$ (ns)</td>
<td>$(\tau)$ (ns)</td>
<td>$k_{HT}$ ($x10^6$ s$^{-1}$)</td>
<td>$(\tau)$ (ns)</td>
<td>$k_{HT}$ ($x10^6$ s$^{-1}$)</td>
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<tr>
<td>BE</td>
<td>535</td>
<td>(25.5±0.8)</td>
<td>(20.5±0.9)</td>
<td>(9.5±2.5)</td>
<td>(13.4±0.5)</td>
</tr>
<tr>
<td>BE</td>
<td>548</td>
<td>(25.4±0.7)</td>
<td>(22.2±0.8)</td>
<td>(5.7±1.9)</td>
<td>(15.5±0.5)</td>
</tr>
<tr>
<td>BE</td>
<td>560</td>
<td>(24.8±0.7)</td>
<td>(24.2±0.9)</td>
<td>(1.0±1.9)</td>
<td>(18.3±0.6)</td>
</tr>
<tr>
<td>BE</td>
<td>573</td>
<td>(23.7±0.8)</td>
<td>(24.8±1.3)</td>
<td>-</td>
<td>(20.2±1.1)</td>
</tr>
<tr>
<td>TS</td>
<td>585</td>
<td>(23.2±1.3)</td>
<td>(25.4±2.1)</td>
<td>-</td>
<td>(22.3±1.9)</td>
</tr>
<tr>
<td>TS</td>
<td>598</td>
<td>(26.3±0.6)</td>
<td>(29.1±1.1)</td>
<td>-</td>
<td>(29.3±2.0)</td>
</tr>
<tr>
<td>TS</td>
<td>610</td>
<td>(30.9±1.1)</td>
<td>(34.2±2.0)</td>
<td>-</td>
<td>(35.7±3.3)</td>
</tr>
<tr>
<td>TS</td>
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<td>(34.4±1.8)</td>
<td>(35.6±2.5)</td>
<td>-</td>
<td>(32.6±3.4)</td>
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<tr>
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<td>(36.6±3.0)</td>
<td>(1.4±2.9)</td>
<td>(35.3±4.1)</td>
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<tr>
<td>TS</td>
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<td>(38.0±3.2)</td>
<td>(2.4±2.9)</td>
<td>(35.0±3.9)</td>
</tr>
<tr>
<td>TS</td>
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<td>(43.5±3.6)</td>
<td>(39.8±3.7)</td>
<td>(2.1±3.0)</td>
<td>(38.6±4.8)</td>
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<td>TS</td>
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<td>(45.3±3.7)</td>
<td>(41.2±3.9)</td>
<td>(2.2±2.9)</td>
<td>(38.1±4.4)</td>
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<tr>
<td>TS</td>
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<td>(41.4±4.3)</td>
<td>(2.8±3.3)</td>
<td>(37.4±4.7)</td>
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<tr>
<td>TS</td>
<td>698</td>
<td>(50.1±5.4)</td>
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<td>(39.4±5.0)</td>
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<td>(44.5±5.6)</td>
<td>(4.7±3.8)</td>
<td>(39.8±5.8)</td>
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<tr>
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<td>(43.9±5.5)</td>
<td>(3.1±3.9)</td>
<td>(39.2±5.7)</td>
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</table>

Uncertainties in $\langle \tau \rangle$ and $k_{HT}$ are calculated from measurements on three different samples along with uncertainties from fitting of time-resolved emission decay profiles with multi-exponential reconvolution.
Table S4.4: Average lifetimes and average rate constants of hole transfer ($k_{HT}$) for all mixed dispersions containing OA-CdSe QDs and FeCl₆SH for band edge and trap state emission.

<table>
<thead>
<tr>
<th>Emission Band</th>
<th>λ (nm)</th>
<th>QD alone</th>
<th>QD+FcC₆SH (1.7 µM)</th>
<th>QD+ FeCl₆SH (3.4 µM)</th>
<th>QD+ FeCl₆SH (6.8 µM)</th>
<th>QD+ FeCl₆SH (17 µM)</th>
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<td>(τ) (ns)</td>
<td>(τ) (ns)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(k&lt;sub&gt;HT&lt;/sub&gt; (x10&lt;sup&gt;5&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>(k&lt;sub&gt;HT&lt;/sub&gt; (x10&lt;sup&gt;5&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>(k&lt;sub&gt;HT&lt;/sub&gt; (x10&lt;sup&gt;5&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>(k&lt;sub&gt;HT&lt;/sub&gt; (x10&lt;sup&gt;5&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>BE</td>
<td>535</td>
<td>(25.5±0.8)</td>
<td>(13.5±0.4)</td>
<td>(3.5±0.3)</td>
<td>(7.7±0.3)</td>
<td>(9.0±0.5)</td>
</tr>
<tr>
<td>BE</td>
<td>548</td>
<td>(25.4±0.7)</td>
<td>(13.5±0.3)</td>
<td>(3.5±0.2)</td>
<td>(7.7±0.2)</td>
<td>(9.1±0.4)</td>
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<tr>
<td>BE</td>
<td>560</td>
<td>(24.8±0.7)</td>
<td>(13.1±0.3)</td>
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<td>(7.4±0.2)</td>
<td>(9.4±0.4)</td>
</tr>
<tr>
<td>BE</td>
<td>573</td>
<td>(23.7±0.8)</td>
<td>(13.0±0.3)</td>
<td>(3.5±0.2)</td>
<td>(7.8±0.2)</td>
<td>(8.7±0.4)</td>
</tr>
<tr>
<td>TS</td>
<td>585</td>
<td>(23.2±1.3)</td>
<td>(13.5±0.4)</td>
<td>(3.1±0.3)</td>
<td>(8.2±0.3)</td>
<td>(7.8±0.5)</td>
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<tr>
<td>TS</td>
<td>598</td>
<td>(26.3±0.6)</td>
<td>(14.4±0.5)</td>
<td>(3.1±0.3)</td>
<td>(8.7±0.4)</td>
<td>(7.7±0.6)</td>
</tr>
<tr>
<td>TS</td>
<td>610</td>
<td>(30.9±1.1)</td>
<td>(17.4±0.9)</td>
<td>(2.5±0.3)</td>
<td>(10.6±0.8)</td>
<td>(6.2±0.7)</td>
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<tr>
<td>TS</td>
<td>623</td>
<td>(34.4±1.8)</td>
<td>(21.6±1.5)</td>
<td>(1.7±0.4)</td>
<td>(14.7±1.4)</td>
<td>(3.9±0.7)</td>
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<tr>
<td>TS</td>
<td>635</td>
<td>(38.5±2.7)</td>
<td>(26.6±2.5)</td>
<td>(1.2±0.4)</td>
<td>(18.7±2.6)</td>
<td>(2.8±0.8)</td>
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<tr>
<td>TS</td>
<td>648</td>
<td>(41.8±3.1)</td>
<td>(29.4±3.3)</td>
<td>(1.0±0.4)</td>
<td>(20.0±2.7)</td>
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<tr>
<td>TS</td>
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<td>(43.5±3.6)</td>
<td>(32.4±3.9)</td>
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<td>(2.0±0.8)</td>
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<tr>
<td>TS</td>
<td>673</td>
<td>(45.3±3.7)</td>
<td>(33.7±4.0)</td>
<td>(0.8±0.4)</td>
<td>(24.5±4.0)</td>
<td>(1.9±0.7)</td>
</tr>
<tr>
<td>TS</td>
<td>685</td>
<td>(46.9±4.7)</td>
<td>(33.3±4.3)</td>
<td>(0.9±0.4)</td>
<td>(23.8±4.0)</td>
<td>(2.0±0.7)</td>
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<tr>
<td>TS</td>
<td>698</td>
<td>(50.1±5.4)</td>
<td>(36.4±5.1)</td>
<td>(0.8±0.5)</td>
<td>(26.0±4.8)</td>
<td>(1.8±0.7)</td>
</tr>
<tr>
<td>TS</td>
<td>710</td>
<td>(56.2±7.8)</td>
<td>(35.4±5.8)</td>
<td>(1.0±0.4)</td>
<td>(26.9±5.0)</td>
<td>(1.9±0.7)</td>
</tr>
<tr>
<td>TS</td>
<td>723</td>
<td>(50.8±6.7)</td>
<td>(35.4±4.7)</td>
<td>(0.9±0.5)</td>
<td>(32.2±8.3)</td>
<td>(1.1±0.8)</td>
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</tbody>
</table>

Uncertainties in $\langle \tau \rangle$ and $k_{HT}$ are calculated from measurements on three different samples along with uncertainties from fitting of time-resolved emission decay profiles with multi-exponential reconvolution.
Table S4.5: Average lifetimes and average rate constants of hole transfer ($k_{HT}$) for all mixed dispersions containing OA-CdTe QDs and FcC₆SH for band edge emission.

<table>
<thead>
<tr>
<th>Emission Band</th>
<th>λ (nm)</th>
<th>QD alone</th>
<th>QD+FcC₆SH (1.7 µM)</th>
<th>QD+ FcC₆SH (3.4 µM)</th>
<th>QD+ FcC₆SH (6.8 µM)</th>
<th>QD+ FcC₆SH (17 µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\langle \tau \rangle$ (ns)</td>
<td>$\langle \tau \rangle$ (ns)</td>
<td>$\langle \tau \rangle$ (ns)</td>
<td>$\langle \tau \rangle$ (ns)</td>
<td>$\langle \tau \rangle$ (ns)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{HT}$ ($x10^8 s^{-1}$)</td>
<td>$k_{HT}$ ($x10^8 s^{-1}$)</td>
<td>$k_{HT}$ ($x10^8 s^{-1}$)</td>
<td>$k_{HT}$ ($x10^8 s^{-1}$)</td>
<td>$k_{HT}$ ($x10^8 s^{-1}$)</td>
</tr>
<tr>
<td>BE 612</td>
<td>(8.2±0.4)</td>
<td>(3.0±0.6)</td>
<td>(2.1±0.2)</td>
<td>(2.0±0.2)</td>
<td>(3.8±0.4)</td>
<td>(1.7±0.2)</td>
</tr>
<tr>
<td>BE 624.5</td>
<td>(9.0±0.2)</td>
<td>(3.5±1.1)</td>
<td>(1.8±0.1)</td>
<td>(2.2±0.1)</td>
<td>(3.5±0.3)</td>
<td>(1.7±0.1)</td>
</tr>
<tr>
<td>BE 637</td>
<td>(10.3±0.2)</td>
<td>(4.9±1.8)</td>
<td>(1.1±0.1)</td>
<td>(2.9±0.1)</td>
<td>(2.5±0.1)</td>
<td>(2.2±0.2)</td>
</tr>
<tr>
<td>BE 649.5</td>
<td>(12.2±0.2)</td>
<td>(6.4±2.4)</td>
<td>(0.7±0.1)</td>
<td>(3.9±0.1)</td>
<td>(1.8±0.1)</td>
<td>(3.0±0.1)</td>
</tr>
<tr>
<td>BE 662</td>
<td>(14.2±0.5)</td>
<td>(7.9±2.4)</td>
<td>(0.6±0.1)</td>
<td>(4.8±0.2)</td>
<td>(1.4±0.1)</td>
<td>(3.9±0.2)</td>
</tr>
<tr>
<td>BE 674.5</td>
<td>(16.3±0.4)</td>
<td>(9.9±2.4)</td>
<td>(0.4±0.1)</td>
<td>(6.1±0.3)</td>
<td>(1.0±0.1)</td>
<td>(4.9±0.3)</td>
</tr>
<tr>
<td>BE 687</td>
<td>(18.4±0.6)</td>
<td>(10.6±2.5)</td>
<td>(0.4±0.1)</td>
<td>(6.3±0.5)</td>
<td>(1.1±0.1)</td>
<td>(5.0±0.4)</td>
</tr>
</tbody>
</table>

Uncertainties in $\langle \tau \rangle$ and $k_{HT}$ are calculated from measurements on three different samples along with uncertainties from fitting of time-resolved emission decay profiles with multi-exponential reconvolution.
Table S4.6: Average lifetimes for all mixed dispersions containing OA-CdTe QDs and hexanethiol for band edge emission.

<table>
<thead>
<tr>
<th>Emission Band</th>
<th>λ (nm)</th>
<th>QD alone</th>
<th>QD+HT (0.17 mM)</th>
<th>QD+HT (0.70 mM)</th>
<th>QD+HT (1.7 mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(τ) (ns)</td>
<td>(τ) (ns)</td>
<td>(τ) (ns)</td>
<td>(τ) (ns)</td>
</tr>
<tr>
<td>BE</td>
<td>612</td>
<td>(8.2±0.4)</td>
<td>(11.6±0.4)</td>
<td>(15.4±0.7)</td>
<td>(13.5±0.7)</td>
</tr>
<tr>
<td>BE</td>
<td>624.5</td>
<td>(9.0±0.2)</td>
<td>(13.2±0.3)</td>
<td>(16.4±0.4)</td>
<td>(15.4±0.5)</td>
</tr>
<tr>
<td>BE</td>
<td>637</td>
<td>(10.3±0.2)</td>
<td>(14.6±0.2)</td>
<td>(18.3±0.3)</td>
<td>(17.2±0.3)</td>
</tr>
<tr>
<td>BE</td>
<td>649.5</td>
<td>(12.2±0.2)</td>
<td>(16.1±0.2)</td>
<td>(20.4±0.3)</td>
<td>(19.2±0.3)</td>
</tr>
<tr>
<td>BE</td>
<td>662</td>
<td>(14.2±0.5)</td>
<td>(17.6±0.3)</td>
<td>(21.5±0.3)</td>
<td>(21.2±0.4)</td>
</tr>
<tr>
<td>BE</td>
<td>674.5</td>
<td>(16.3±0.4)</td>
<td>(20.4±0.4)</td>
<td>(25.4±0.5)</td>
<td>(24.2±0.6)</td>
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<tr>
<td>BE</td>
<td>687</td>
<td>(18.4±0.6)</td>
<td>(21.8±0.6)</td>
<td>(26.5±0.8)</td>
<td>(27.3±0.9)</td>
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</table>

Uncertainties in $\langle \tau \rangle$ are calculated from measurements on three different samples along with uncertainties from fitting of time-resolved emission decay profiles with multi-exponential reconvolution.
References


Chapter V

Ultrafast Exciton Dissociation and Long-lived Charge Separation in Novel Type II Cadmium Chalcogenide Quantum Dots / $\alpha$-Vanadium Pentoxide Nanowires Heterostructures

This work was conducted in collaboration with Dr. Sarbajit Banerjee’s group at Texas A&M University. Aaron Sheng (Watson’s Group) and Junsang Cho (Banerjee’s group) synthesized various heterostructures used in this study and acquired transient absorption data at Brookhaven National Lab. Saurabh Chauhan, Aaron Sheng, Junsang Cho, Dr. David Watson, Dr. Sarbajit Banerjee analyzed data.
Introduction

Fast directional excited-state charge transfer across interfaces to yield long-lived charge-separated states is the key to efficient solar energy harvesting. Staggered band alignment in type II heterostructures can facilitate such charge separation. Following photoexcitation of either component of a type II interface, rapid interfacial charge separation results in the formation of a charge-separated state in which electrons and holes are located in different components of heterostructures. Charge transfer must occur more rapidly than electron-hole recombination to separate charges efficiently. In this study, we interfaced cadmium chalcogenide (CdE where E= S, Se, Te) quantum dots (QDs) with vanadium pentoxide (V$_2$O$_5$) nanowires (NWs) by two different approaches, namely linker assisted assembly (LAA) and successive ionic layer adsorption and reaction (SILAR), and studied charge-transfer dynamics in these novel type II heterostructures.

The high molar absorptivities$^{2-4}$ and size-dependent optoelectronic properties$^{5-7}$ of QDs render them intriguing materials for solar energy harvesting and photocatalysis. Wide-bandgap metal oxides such as TiO$_2$, SnO$_2$ and ZnO are often interfaced with QDs for electron extraction from photoexcited QDs.$^{8-15}$ However, in this regard, V$_2$O$_5$ has been relatively unexplored to the best of our knowledge. V$_2$O$_5$ and its doped derivatives have been studied extensively for their unusual temperature-dependent metal-to-insulator transitions.$^{16}$ We hypothesized that V$_2$O$_5$/CdE heterostructures should form type II energetic interfaces that should facilitate both electron transfer from QDs to NWs and hole transfer from NWs to QDs. Thus, following the absorption of light by either component, interfacial charge transfer to yield a charge-separated state with electrons localized in NWs and holes in QDs, should be thermodynamically favorable. Moreover, the high surface area of V$_2$O$_5$ NWs should allow for easy incorporation and high loading of QDs onto the
Finally, the smaller bandgap (approximately 2.7 eV) of V$_2$O$_5$, relative to the aforementioned previously-explored metal oxides, should promote the absorption of UV and visible light.$^{1,17}$

Both SILAR and LAA have been used extensively to interface QDs and metal-oxide substrates, and each approach has distinct advantages and disadvantages.$^{9,18}$ SILAR involves the successive deposition of cationic and anionic precursors of QDs onto substrates, thereby resulting in the growth of a given material onto the substrate surface.$^{19-21}$ Although SILAR provides high loading of QDs on to substrates, it often results in very broad size distributions of QDs.$^{22}$ In LAA, pre-synthesized QDs are tethered to the surface of a substrate via molecular linkers.$^{9,15,18,22}$ The linker is chosen such that one terminal functional group can selectively adsorb to QDs while another can selectively adsorb to the substrate.$^{9,18}$ LAA allows for better control over size, and thus energetics, but often results in poorer loading of QDs onto substrates relative to SILAR.$^9$

We have used LAA and SILAR to synthesize type II V$_2$O$_5$/CdE heterostructures, and we have studied their photoinduced charge-transfer reactivity using transient absorption spectroscopy. Our results are reported in this chapter. Our experiments revealed that, regardless of the method used to synthesize heterostructures, excited-state charge separation occurs on time scales from sub-picosecond to tens of picoseconds, yielding a charge-separated state that persists for microseconds. Thus, the V$_2$O$_5$/CdE heterostructures are intriguing candidates for harvesting solar energy harvesting and separating photogenerated charges for redox photocatalysis.

**Experimental**

**Materials**

Cadmium sulfate octahydrate (3CdSO$_4$·8H$_2$O), cadmium chloride hemipentahydrate (CdCl$_2$·5/2H$_2$O), sodium telluride (Na$_2$Te) and sodium borohydride (NaBH$_4$) were obtained from
Alfa Aesar. Selenium powder, tellurium powder, vanadium pentoxide (V₂O₅) and l-cysteine (cys) were obtained from Sigma Aldrich. Sodium sulfite (Na₂SO₃) anhydrous, sodium thiosulfate (Na₂S₂O₃), sodium hydroxide, methanol, and hydrochloric acid were obtained from Fisher Scientific. Ethanol was obtained from Decon. Oxalic acid was obtained from J.T. Baker. All reagents were used without further purification.

**Synthesis of cys- CdSe quantum dots**

Cysteinate-capped CdSe (cys-CdSe) QDs were synthesized following the procedure reported by Nevins et al.²³ Briefly, a selenide precursor solution was prepared by dissolving selenium powder (0.17 g, 2.2 mmol) and Na₂SO₃ (0.80 g, 6.4 mmol) in deionized (DI) water (42 mL) in a round-bottom flask. The flask was heated to reflux and stirred until selenium was dissolved. The cadmium precursor was prepared by dissolving 3CdSO₄.8H₂O (0.57 g, 0.74 mmol) and l-cysteine (1.03 g, 8.48 mmol) in DI water (53 mL). The pH of the solution containing cadmium precursor was adjusted to ~12 by adding NaOH pellets. The cadmium precursor solution was heated to 80°C, and then 23 mL of the selenide precursor solution was added via hot injection. The resulting mixture was stirred at 80°C for approximately 2 h and then cooled to room temperature and stored until further use.

**Synthesis of cys-CdS quantum dots**

Cysteinate-capped CdS (cys-CdS) QDs were synthesized by modification of the synthesis of cys-CdSe.²³⁻²⁴ The sulfide precursor solution was prepared by dissolving Na₂S₂O₃ (1.17 g, 7.41 mmol) in DI water (25 mL). The mixture was heated to reflux and stirred to dissolve the solid. The cadmium precursor solution was prepared by dissolving 3CdSO₄.8H₂O (0.87 g, 3.4 mmol) and l-cysteine (2.05 g, 16.9 mol) in DI water (42 mL). The pH of the solution containing cadmium precursor solution was adjusted to ~12 by addition of NaOH pellets. The cadmium precursor was
heated to 80° C, and then 9 mL of sulfide precursor solution was added via hot injection. The resulting mixture was stirred and kept at 80° C for approximately 3 h and then cooled to room temperature and stored until further use.

**Synthesis of cys-CdTe quantum dots**

Cysteinate-capped CdTe (cys-CdTe) QDs were synthesized by modification of the procedure reported by Li et al.\textsuperscript{25} The telluride precursor solution was prepared by dissolving tellurium (0.076 g, 0.60 mmol) and NaBH\textsubscript{4} (0.128 g, 3.40 mmol) in DI water (10 mL) in a small Erlenmeyer flask. The flask was sealed with a septum and a needle to allow for the evolution of produced gas. The solution was stirred at room temperature for approximately 4 h to yield a clear purple solution. The cadmium precursor solution was prepared by adding CdCl\textsubscript{2}·5/2H\textsubscript{2}O (0.29 g, 1.3 mmol) and L-cysteine (0.61 g, 5.0 mmol) in DI water (100 mL). The pH of the solution containing cadmium precursor was adjusted to ~11 by addition of NaOH pellets. The cadmium precursor solution was then purged with Ar gas for 30 min. The telluride precursor solution was then injected into cadmium precursor solution, immediately turning the reaction mixture orange. The reaction mixture was then heated to reflux under inert atmosphere for 2 h and then cooled to room temperature and stored until further use.

**Synthesis of α-V\textsubscript{2}O\textsubscript{5} nanowires**

α-V\textsubscript{2}O\textsubscript{5} NWs were synthesized via hydrothermal reduction of V\textsubscript{2}O\textsubscript{5} as reported previously.\textsuperscript{26} Hydrothermal reaction of bulk V\textsubscript{2}O\textsubscript{5} and oxalic acid yielded V\textsubscript{3}O\textsubscript{7} NWs, which were then oxidized in air at 300° C in a muffle furnace to yield V\textsubscript{2}O\textsubscript{5} NWs.
Assembly of QD/V$_2$O$_5$ Heterostructures

SILAR method

SILAR-derived $\alpha$-V$_2$O$_5$/CdE (E=S, Se, Te) heterostructures were assembled following the procedure reported by Pelcher et al. with slight modifications when necessary.$^1$ Precursor solutions were prepared as follows. A 100-mM cadmium precursor solution was prepared by dissolving Cd(NO$_3$)$_2$·4H$_2$O in ethanol. A 50-mM selenide precursor was prepared by dissolving SeO$_2$ in ethanol and purging with Ar. NaBH$_4$ was then added, and the solution was stirred for 2 h. A 50-mM sulfide precursor solution was prepared by dissolving Na$_2$S·9H$_2$O in ethanol. A 50-mM telluride precursor was prepared by dissolving Na$_2$Te in ethanol. In SILAR deposition, $\alpha$-V$_2$O$_5$ NWs were first dispersed in ethanol. The dispersed NWs were then combined with the cadmium precursor solution in a 1:1 ratio by volume, decreasing the concentration of Cd$^{2+}$ to 50 mM. This mixture was stirred for 30 s. The NWs were removed via centrifugation and washed with ethanol. The solid NWs were then dispersed into a given chalcogenide precursor solution. The resulting mixture solution was stirred, centrifuged, and washed with ethanol. This series of steps represents one SILAR cycle. NW/QD heterostructures were prepared via variable numbers of SILAR deposition cycles.

LAA method

LAA-derived $\alpha$-V$_2$O$_5$/CdE heterostructures were assembled following the procedure reported by Pelcher et al.$^1$ Stock dispersions of CdE QDs in water were washed to remove unreacted precursors. CdS QDs were diluted to twice the stock volume with DI water and then washed three times; CdSe QDs were washed twice; and CdTe QDs were washed once. One washing step consisted of flocculating QDs by addition of a MeOH to the QD dispersion in a 3:1 ratio by volume, collecting the QDs by centrifugation, discarding the supernatant, and redispersing the
QDs into DI water to the original volume. Stock dispersions of V$_2$O$_5$ NWs were prepared by adding 10 mg of NWs to 1 mL of DI water while sonicating. Aqueous dispersions of CdE QDs (0.8 mL for CdS, 0.4 mL for CdSe, and 7.5 mL for CdTe) were added to dispersions of NWs (2 mL per sample) with constant stirring. The pH of the final mixture was adjusted to ~5 by addition of dilute HCl solution. The mixed dispersion was allowed to stir for 1 h, and then the heterostructures were collected via centrifugation. The supernatant was discarded, and the heterostructures were washed once with DI water to remove unattached QDs. The resulting V$_2$O$_5$/CdE heterostructures were then dried and stored as a solid until further use.

**Materials Characterization**

UV/vis absorbance spectra were obtained with an Agilent 8453 diode array spectrophotometer. UV/vis diffuse reflectance spectra were obtained with an Agilent 8453 diode array spectrophotometer with a Labsphere RSA-HP-53 reflectance accessory attachment. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) spectra were acquired with a Hitachi SU-70 instrument equipped with an X-ray detector. Transmission electron microscopy (TEM) images were obtained using a JEOL-2010 instrument operated at 200 kV. Raman spectra of α-phase V$_2$O$_5$/CdE heterostructures were acquired using a Jobin-Yvon Horiba Labram HR instrument coupled to an Olympus BX41 microscope. Samples were excited at 514.5 nm with an Ar-ion laser. The hole and slit widths were 500 μm and 150 μm, respectively. Raman spectra were acquired with spectral resolution of 3 cm$^{-1}$ using a grating with 1800 lines per mm. The samples for Raman measurements were prepared by placing solid powders onto micro slide glasses.

Transient absorption experiments were performed at the Center for Functional Nanomaterials at Brookhaven National Laboratory. Measurements were obtained using a Ti:sapphire amplified
laser system (SpectraPhysics Splitfire pro, 800 nm, 1 kHz repetition rate), the details of which were described previously.\textsuperscript{27} Briefly, the wavelength-tunable pump pulse (100 fs, 1 kHz, 1.2 mJ/s) was generated with an optical parametric amplifier from LightConversion. The femtosecond white-light probe pulse was obtained via supercontinuum generation with a sapphire disk and was delayed mechanically. The nanosecond probe pulse was created by a second supercontinuum laser and was delayed electronically. The probe light was split into signal and reference beams, which were detected with fiber-coupled silicon (visible) diode arrays on a shot-by-shot basis.
Scheme 5.1. Interfacial energetics of V$_2$O$_5$/CdE heterostructures. All energy values are reported relative to the Fermi level of V$_2$O$_5$ NWs. Details about estimation of E$_v$s and E$_c$s of all components of various V$_2$O$_5$/CdE heterostructures are mentioned in the text.
Results and Discussion

Interfacial Energetics in V$_2$O$_5$/CdE Heterostructures

The estimated energies of conduction band edges (E$_c$) and valence band edges (E$_v$) of CdE QDs relative to the band edges of α-V$_2$O$_5$ NWs are shown in Scheme 5.1. The E$_v$s of V$_2$O$_5$ NWs, cys-CdS QDs and cys-CdSe QDs were determined from XPS measurements conducted on V$_2$O$_5$ NWs and SILAR-derived Pb$_{0.33}$V$_2$O$_5$/CdSe and Pb$_{0.33}$V$_2$O$_5$/CdS heterostructures.$^{1,28}$ The E$_v$ of CdTe QDs was estimated by comparing the E$_v$s of bulk CdSe and bulk CdTe semiconductors.$^{29}$ We note that SILAR deposition usually results in a broad size distribution of QDs onto substrates, and quantum confinement effects can significantly affect the energies of E$_c$s and E$_v$s of QDs.$^{5,7,30}$ However, the variation of the bandgaps of QDs with size arises primarily from shifts of E$_c$, due to the lower effective masses of electrons compared to holes.$^{30}$ Therefore, we make the simplifying assumption that E$_v$s of QDs used in this study are invariant with size. Optical bandgaps of these materials were estimated from the diffuse reflectance spectrum of V$_2$O$_5$ NWs (Figure 5.1a) and the transmission-based absorption spectra of cys-CdE QDs dispersions in water (Figure S5.1 in Supporting Information). The E$_v$s of all components (V$_2$O$_5$ NWs and CdE QDs) were then estimated by adding the optical bandgaps to the respective E$_v$s. Interestingly, all V$_2$O$_5$/CdE heterostructures are predicted to form type II energetic interfaces, favoring interfacial charge separation in which photogenerated electrons can transfer from the CdE QDs to V$_2$O$_5$ NWs and, similarly, holes can transfer from V$_2$O$_5$ NWs to CdE QDs. A representative excited-state charge-separation process is depicted in Scheme 5.1.
Figure 5. 1. (a) TEM images of V$_2$O$_5$/CdSe heterostructures prepared by LAA and SILAR. (b) Raman spectra of V$_2$O$_5$ NWs (black), LAA-derived V$_2$O$_5$/CdSe heterostructures (red) and SILAR-derived V$_2$O$_5$/CdSe heterostructures (blue). The solid black lines indicate the position of characteristic LO and 2LO phonon modes of bulk wurtzite CdSe semiconductors. (c) EDS spectra of V$_2$O$_5$/CdSe heterostructures prepared by LAA (top) and SILAR (bottom).
Assembly and Structural Characterization of V$_2$O$_5$/CdE Heterostructures

CdE QDs were interfaced with V$_2$O$_5$ NWs using SILAR and LAA methods. In LAA, aqueous dispersions of presynthesized cys-CdE QDs were combined with aqueous dispersions of V$_2$O$_5$ NWs, and the resultant heterostructures were collected by centrifugation. Protonated amines are known to adsorb to the negatively-charged, hydroxylated surface of V$_2$O$_5$ through electrostatic interactions.$^{1,31-32}$ Cysteinates are known to bind to CdE QDs through thiolates due to the strong affinity of thiols (soft base) for surface-localized Cd$^{2+}$ ions (soft acids).$^{33}$ Under acidic conditions, amine functional groups in cysteinates on the surfaces of CdE QDs would be protonated and, therefore, should adsorb to the surface of V$_2$O$_5$ NWs, resulting in the attachment of CdE QDs to the NWs.$^1$ In SILAR, ethanol dispersions of V$_2$O$_5$ NWs were reacted sequentially with cadmium and chalcogenide precursors to deposit layers of CdE onto the NWs.

We characterized the products of LAA and SILAR by TEM, EDS, and Raman spectroscopy. TEM images of LAA- and SILAR-derived V$_2$O$_5$/CdSe, V$_2$O$_5$/CdS, and V$_2$O$_5$/CdTe heterostructures are shown in Figure 5.1a and in Figure S5.2a in Supporting Information. Dark black regions of CdSe QDs on pristine V$_2$O$_5$ NWs are clearly discernible in TEM images of LAA- and SILAR-derived V$_2$O$_5$/CdSe heterostructures (Figure 5.1a), consistent with the attachment of CdSe QDs to V$_2$O$_5$ NWs. Similar-looking TEM images (Figure S5.2a in Supporting Information) were obtained for LAA- and SILAR-derived V$_2$O$_5$/CdS and SILAR-derived V$_2$O$_5$/CdTe heterostructures; however, TEM images of LAA-derived V$_2$O$_5$/CdTe samples did not reveal a significant amount of QDs on V$_2$O$_5$ NWs. Qualitatively, SILAR-derived heterostructures exhibited much rougher surfaces and relatively higher loadings of CdE QDs onto V$_2$O$_5$ NWs as compared to LAA-derived heterostructures.
EDS data (Figure 5.1c and Figure S5.2c in Supporting Information) for V$_2$O$_5$/CdE heterostructures confirm the presence of Cd and E (S, Se, and Te) on V$_2$O$_5$ NWs. Average amounts of Cd and E, relative to the V$_2$O$_5$ formula unit, were calculated from five measurements on each sample, yielding apparent molecular formulas of V$_2$O$_5$/Cd$_{(0.09±0.04)}$Se$_{(0.08±0.06)}$, V$_2$O$_5$/Cd$_{(0.06±0.07)}$S$_{(0.07±0.08)}$, and V$_2$O$_5$/Cd$_{(0.03±0.03)}$Te$_{(0.03±0.04)}$ for LAA-derived heterostructures and V$_2$O$_5$/Cd$_{(0.41±0.25)}$Se$_{(0.42±0.25)}$, V$_2$O$_5$/Cd$_{(0.48±0.10)}$S$_{(0.72±0.14)}$, and V$_2$O$_5$/Cd$_{(0.35±0.14)}$Te$_{(1.57±0.83)}$ for SILAR-derived V$_2$O$_5$/CdE heterostructures. The higher loading of QDs onto V$_2$O$_5$ NWs in SILAR-derived heterostructures relative to LAA-derived heterostructures is consistent with TEM analysis.

V$_2$O$_5$/CdE heterostructures were further characterized by Raman spectroscopy. Raman spectra of V$_2$O$_5$ NWs and LAA- and SILAR-derived V$_2$O$_5$/CdE heterostructures are shown in Figure 5.1b and in Figure S5.2b in Supporting Information. The Raman spectrum of bare NWs exhibited unique phonon modes of $\alpha$-V$_2$O$_5$ including the displacement of [VO$_5$] units below 200 cm$^{-1}$, bond-rocking and bending at 200-500 cm$^{-1}$, and vibrational stretching of V-O bonds above 500 cm$^{-1}$, consistent with previous measurements.\textsuperscript{26} Integration of CdE QDs onto V$_2$O$_5$ NWs gave rise to distinct Raman bands corresponding to CdE, along with characteristic Raman bands of bare V$_2$O$_5$ NWs. Raman spectra of LAA- and SILAR-derived V$_2$O$_5$/CdSe heterostructures contain prominent Raman bands at 205 cm$^{-1}$ and 409 cm$^{-1}$, corresponding to the longitudinal optical (LO) mode and second-order LO (2LO) mode of bulk wurtzite CdSe, respectively (Figure 5.1b).\textsuperscript{34-35} The 2LO mode of CdSe overlaps substantially with a Raman band of bare V$_2$O$_5$ at 404 cm$^{-1}$. V$_2$O$_5$/CdS heterostructures exhibited intense, sharp Raman bands at 300 cm$^{-1}$ and 600 cm$^{-1}$ corresponding to the LO and 2LO modes of bulk wurtzite CdS, respectively (Figure S5.2b in Supporting Information).\textsuperscript{36-37} Similarly, Raman spectra of V$_2$O$_5$/CdTe heterostructures exhibited strong bands at 163 cm$^{-1}$ and 327 cm$^{-1}$, corresponding to the LO and 2LO modes of bulk wurtzite CdTe.
respectively (Figure S5.2b in Supporting Information). LAA-derived $V_2O_5$/CdTe heterostructures yielded very weak Raman signals due to poor loading of QDs onto $V_2O_5$ NWs.

In summary, TEM, EDS, and Raman spectral measurements on LAA- and SILAR-derived $V_2O_5$/CdE heterostructures confirmed the attachment of CdE QDs onto $V_2O_5$ NWs, except for LAA-derived $V_2O_5$/CdTe heterostructures, for which the loading of CdTe QDs was minimal or negligible. Therefore, the spectroscopic characterization of LAA-derived $V_2O_5$/CdTe heterostructures will not be discussed further.

**Photophysical Characterization**

LAA- and SILAR-derived $V_2O_5$/CdE heterostructures were further characterized with diffuse reflectance and transient absorption spectroscopy to study charge-transfer dynamics in these novel type II heterostructures. In the remainder of this chapter, the discussion of the spectroscopic characterization of these heterostructures focuses first on $V_2O_5$/CdSe heterostructures, in detail, and then focuses on the other $V_2O_5$/CdE heterostructures.

**Diffuse reflectance**

Diffuse reflectance spectra of $V_2O_5$ NWs and LAA- and SILAR-derived $V_2O_5$/CdSe heterostructures are presented in Figure 5.2A. $V_2O_5$ NWs exhibit a bandgap absorption onset at approximately 580 nm with a steep rise at shorter wavelengths, consistent with previously-reported measurements. LAA- and SILAR-derived $V_2O_5$/CdSe heterostructures exhibit increased absorption at longer wavelengths than bare $V_2O_5$ NWs, consistent with the functionalization of the NWs with QDs. The absorption spectrum of LAA-derived $V_2O_5$/CdSe heterostructures is only minimally perturbed compared to bare NWs, whereas SILAR-derived $V_2O_5$/CdSe heterostructures exhibit a much broader and more intense absorption band at substantially longer wavelengths than the absorption onset of bare NWs. These differences can be attributed to differences in the size
distribution and relative loading of CdSe QDs when deposited onto NWs via LAA vs SILAR. LAA-derived V₂O₅/CdSe heterostructures are prepared by attaching presynthesized CdSe QDs, which have relatively narrow and well-defined excitonic absorption bands (Figure S5.1 in Supporting Information) and, therefore, narrow size distributions. Additionally, the lower loading of CdSe QDs onto V₂O₅ NWs, as evidenced by TEM and EDS, results in minimal changes in the absorption features of the bare V₂O₅ NWs following the attachment of CdSe QDs via LAA. On the other hand, SILAR-derived V₂O₅/CdSe heterostructures are expected to have broader size distributions and relatively higher loadings of CdSe, resulting in a much broader and more intense absorption band extending to longer wavelengths. Overall, the absorption spectra of LAA- and SILAR-derived V₂O₅/CdSe heterostructures can be understood as a linear combination of absorption spectra of bare V₂O₅ NWs and a distribution of different sized CdSe QDs.

Nanosecond Transient Absorption

Cys capped CdSe QDs

The ground-state absorption spectrum of cys-CdSe QDs exhibited a first excitonic absorption band with wavelength of maximum absorbance at ~500 nm. The TA spectrum of CdSe QDs, acquired on the nanosecond timescale (Figure S5.3 in Supporting Information), exhibited two important features: (a) a first excitonic bleach at 500 nm consistent with filling of the 1S(e) state in CdSe QDs and (b) a broad induced absorption band from ~550 to 900 nm attributed to the intraband excitation of holes trapped at the surface of CdSe QDs.⁴⁰⁻⁴¹ Decay curves were obtained for these bleach and induced absorption features, and average lifetimes (⟨τ⟩) were obtained by fitting decay profiles with multiexponential decay kinetics using equations 5.1 and 5.2.

\[ \Delta A = y_0 + \sum_l A_l \exp\left(-\frac{t}{\tau_l}\right) \]  

(5.1)
\[ \langle \tau \rangle = \frac{\sum A_i \tau_i}{\sum A_i} \]  

(5.2)

Where \( \Delta A \) is the difference in absorption between ground state and excited state absorption, \( A_i \) is the amplitude of population of excited state decaying with lifetime \( \tau_i \) and \( y_0 \) is the background noise. Goodness of fit was evaluated by plots of residual (data minus fit) as a function of wavelength and by chi-square values. An additional exponential component was added to a given fit if it resulted in discernible improvement of the flatness of plots of residual vs wavelength and a lowering of the chi-square value. The bleach at 500 nm and the induced absorption feature at 650 nm decayed with bi-exponential kinetics with values of \( \langle \tau \rangle \) of \((163 \pm 9) \) ns and \((149 \pm 18) \) ns, respectively.

**V_2O_5 NWs**

The TA spectrum of V_2O_5 NWs, obtained as the average of spectra acquired at delay times of 1 to 10 ns, (Figure 5.2b) exhibits an excitonic bleach at \(~430\) nm, a low intensity bleach at \(~500\) nm, and a broad induced absorption from \(~510\) to \(900\) nm with maximum at \(~550\) nm. The spectral evolution of TA spectrum of V_2O_5 NWs is shown in Figure S5.5a in Supporting Information. The 500-nm bleach may be due to the filling of the lower-energy split-off CB of V_2O_5 NWs.\(^{42-43}\) The broad induced absorption feature is similar to the steady-state absorption of oxidized V_2O_5 NWs and has been previously assigned to the excitation of holes in V_2O_5 NWs to states deeper within the VB.\(^{27}\) Decay traces corresponding to the bleach at 430 nm (Figure 5.2c) and the induced absorption at 550 nm (Figure S5.6 in Supporting Information) were fitted to biexponential kinetics to extract average lifetimes using equation 5.2. The bleach and induced absorption features decayed with values of \( \langle \tau \rangle \) of \((263 \pm 37) \) ns and \((244 \pm 33) \) ns, respectively. The multiexponential decay kinetics of TA features of V_2O_5 NWs have been previously observed and assigned to the presence of distributions of electron and hole trap states in V_2O_5 NWs.\(^{27,44}\)
The TA spectrum of V₂O₅ NWs at delay times of 1 to 100 ps (Figure 5.3a) is strikingly different than the nanosecond time scale spectrum. The 3-D color maps of spectral evolution of TA spectra of V₂O₅ NWs is included in Figure S5.4 in Supporting Information. First, the 430-nm excitonic bleach of V₂O₅ NWs is poorly resolved in picosecond timescale spectra. Second, spectra acquired at delay times of several picoseconds contain an intense, broad bleach, which decays within several nanoseconds to the long-lived TA spectrum of photoexcited V₂O₅ NWs. After ~500 ps, the bleach at ~500 nm and the broad induced absorption feature around 550 to 800 nm do not evolve further, as is expected given that the excited state of V₂O₅ NWs decays on the microsecond timescale. To deconvolute the broad bleach at early timescales from the picosecond-timescale spectra of V₂O₅ NWs, the TA spectrum acquired at a delay time of 2.5 ns was subtracted from all other TA spectra at earlier delay times. The subtracted TA spectra (hereafter referred to as ΔΔA spectra) of V₂O₅ NWs are shown in Figure 5.3b. Interestingly, the profile of the ΔΔA spectrum of V₂O₅ NWs corresponds closely to the steady-state emission spectrum of V₂O₅ NWs (Figure S5.7 in Supporting Information), suggesting that the broad and short-lived apparent bleach in the TA spectrum arose from stimulated emission. Decay profiles were obtained at various probe wavelengths within the ΔΔA spectrum of V₂O₅ NWs and are shown with corresponding fits in Figure S5.8a in Supporting Information. The broad bleach in the ΔΔA spectrum of V₂O₅ NWs decayed with ⟨τ⟩ of 10-50 ps. Therefore, at early timescales, the TA spectrum of V₂O₅ NWs can be regarded as a linear combination of the TA spectrum of excited NWs and a contribution from stimulated emission.
Figure 5.2. Diffuse reflectance spectra (a) and TA spectra averaged from delay times of 1-10 ns (b) for V$_2$O$_5$ NWs and LAA- and SILAR-derived V$_2$O$_5$/CdSe heterostructures, and corresponding decay traces and multiexponential fits (c) for the bleach of V$_2$O$_5$ NWs ($\lambda = 430$ nm, black) and the absorption corresponding to the charge-separated state of V$_2$O$_5$/CdSe heterostructures ($\lambda = 850$ nm, red and blue).
**V₂O₅/CdSe Heterostructures**

TA spectra for V₂O₅/CdSe heterostructures prepared by SILAR and LAA, obtained by averaging spectra acquired at delay times of 1-10 ns, are shown in Figure 5.2b. The spectral evolution of TA spectra are included in Figures S5.4 and S5.5b, S5.5c respectively, in Supporting Information, respectively. There are striking differences between the TA spectra of SILAR- and LAA-derived heterostructures. The TA spectrum of SILAR-derived V₂O₅/CdSe heterostructures does not exhibit any features related to the TA spectrum of bare V₂O₅ NWs or CdSe QDs. The TA spectrum of SILAR-derived CdSe QDs and as-synthesized cys-CdSe QDs may be considerably different considering the differences in steady-state absorption features of LAA- and SILAR-derived V₂O₅/CdSe heterostructures; however, the TA spectrum of the excited state of SILAR-deposited CdSe QDs would still be expected to contain a similar bleach corresponding to 1S(e) state filling and an induced absorption corresponding to the trapped hole and intraband hole excitation. Instead, the spectrum of SILAR-derived V₂O₅/CdSe heterostructures contains a broad induced absorption band throughout the visible region along with a weak bleach at wavelengths below 470 nm (Figure 5.2b). The interfacial energetics of CdSe QDs and V₂O₅ NWs (Scheme 5.1) promotes charge separation wherein electrons can transfer from CdSe QDs to V₂O₅ NWs and holes from V₂O₅ NWs to CdSe QDs, resulting in the localization of electrons in the CB of V₂O₅ NWs and holes in the VB of CdSe QDs irrespective of which component of the heterostructures was initially excited. The spectral signature of such a charge-separated state should then resemble a combination of the spectral features of reduced V₂O₅ NWs and oxidized QDs. Our group has previously reported the ΔA spectrum of electrochemically reduced V₂O₅ NWs, exhibiting a well resolved bleach feature centered at ~420 nm.²⁷ The TA spectrum of oxidized CdSe QDs has been reported previously to exhibit a broad induced absorption feature extending from the visible into the near-IR. This feature

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has been assigned to trapped holes and intraband hole excitation.\textsuperscript{41-48} Therefore, the measured TA spectrum of SILAR-derived V\textsubscript{2}O\textsubscript{5}/CdSe heterostructures (Figure 5.2b) indeed exhibits features associated with electrons localized in V\textsubscript{2}O\textsubscript{5} NWs and holes localized in CdSe QDs. That the spectrum exhibits these features, but not features attributable to excited states of V\textsubscript{2}O\textsubscript{5} NWs or CdSe QDs, provides compelling evidence for rapid and efficient interfacial charge transfer to yield a charge-separated state in which electrons and holes are localized in V\textsubscript{2}O\textsubscript{5} NWs and CdSe QDs, respectively.

TA decay traces were obtained at various wavelengths throughout the TA spectrum of SILAR-derived V\textsubscript{2}O\textsubscript{5}/CdSe QDs heterostructures (Figure S5.5d in Supporting Information). Decay traces were fitted at 550 nm, 650 nm, 750 nm and 850 nm, yielding values of $\langle \tau \rangle$ of (0.4 ± 0.1) µs, (0.5 ± 0.1) µs, (1.0 ± 0.7) µs and (2.9 ± 0.8) µs, respectively. The wavelength dependence of $\langle \tau \rangle$ suggests that electrons and holes may have decayed on different time scales or that distinct populations of charge-separated states, for example such as electrons in NWs and holes in a distribution of trap states of CdSe QDs, may have decayed on different time scales.

The TA spectrum of LAA-derived V\textsubscript{2}O\textsubscript{5}/CdSe heterostructures contains similar spectral features as the TA spectra of both V\textsubscript{2}O\textsubscript{5} NWs alone and SILAR-derived V\textsubscript{2}O\textsubscript{5}/CdSe heterostructures, albeit with subtle differences. First, the excitonic bleach of V\textsubscript{2}O\textsubscript{5} NWs was redshifted by ~10 nm, possibly due to the change in environment of V\textsubscript{2}O\textsubscript{5} NWs upon functionalization with cys-capped CdSe QDs. Second, the TA spectrum contained a much broader induced absorption band extending from ~520 nm to 900 nm. This broad induced absorption feature is similar to the absorption assigned to the presence of holes in CdSe QDs in the TA spectrum of SILAR-derived V\textsubscript{2}O\textsubscript{5}/CdSe heterostructures. Type–II energetic offsets at the interface between the NWs and cys-CdSe QDs (Scheme 5.1) would result in presence of electrons in NWs and holes in QDs regardless of which
component gets excited. The TA spectra shown in Figure 5.2b were acquired by exciting the heterostructures at 360 nm, where both components, QDs and NWs, absorb light. Since LAA-derived V$_2$O$_5$/CdSe heterostructures have lower loadings of CdSe QDs compared to SILAR-derived V$_2$O$_5$/CdSe heterostructures, it is not surprising that some features corresponding to bare V$_2$O$_5$ NWs are present in the TA spectrum of LAA derived V$_2$O$_5$/CdSe heterostructures. Therefore, the TA spectrum of LAA derived V$_2$O$_5$/CdSe heterostructures can be treated as a linear combination of the TA spectra of the charge-separated state (electrons in NWs and holes in QDs) and the excited state of V$_2$O$_5$ NWs that did not participate in charge transfer.

TA decay traces were obtained at various wavelengths throughout the TA spectrum of LAA-derived V$_2$O$_5$/CdSe QDs heterostructures. Decay traces were fitted at 440 nm, 550 nm, 700 nm and 850 nm (Figure S5.5e in Supporting Information), yielding values of $\langle \tau \rangle$ of ($1.7 \pm 0.7$) µs, ($2.2 \pm 0.6$) µs, ($4.0 \pm 0.4$) µs and ($5.0 \pm 0.5$) µs, respectively. Interestingly, the bleach at 440 nm and the induced absorption at 550 nm for LAA-derived V$_2$O$_5$/CdSe heterostructures decay much slowly than those of bare V$_2$O$_5$ NWs ($\langle \tau \rangle$ of ($0.26 \pm 0.04$) µs for bleach at 430 nm and ($0.24 \pm 0.03$) µs for induced absorption at 550 nm). Longer recombination lifetimes in LAA-derived V$_2$O$_5$/CdSe heterostructures is consistent with the formation of a long-lived charge separated state in which electrons and holes are separated spatially in different components of V$_2$O$_5$/CdSe heterostructures (electrons in V$_2$O$_5$ NWs and holes in CdSe QDs). However, the bleach and induced absorption features in TA spectrum of LAA-derived V$_2$O$_5$/CdSe heterostructures have some contributions from residual V$_2$O$_5$ NWs, unlike for SILAR-derived V$_2$O$_5$/CdSe heterostructures, where the TA spectrum was assigned to charge separated state exclusively. In order to compare the longevity of charge-separated state in LAA- and SILAR-derived V$_2$O$_5$/CdSe heterostructures, we fitted decay profiles at 850 nm, within the induced absorption band and where
residual V₂O₅ NWs do not contribute to the measured ΔA. Therefore, the induced absorption at 850 nm can be assigned solely to the charge-separated state (Figures 5.2b and 5.2c). Values of (τ) were (4.4 ± 0.7) µs for LAA- and (2.9 ± 0.8) µs for SILAR-derived V₂O₅/CdSe heterostructures. The slightly faster decay of the charge-separated state in SILAR-derived V₂O₅/CdSe heterostructures can be attributed to the intimate contact between CdSe QDs and V₂O₅ NWs, whereas, in LAA-derived heterostructures, the presence of cysteinate between CdSe QDs and V₂O₅ NWs creates a spatial barrier for charge recombination, which results in a longer-lived charge-separated state.

To gain insight into the dynamics of charge transfer, picosecond-timescale TA spectra were obtained for both LAA- and SILAR-derived heterostructures. The corresponding color maps are included (Figure S5.4 in Supporting Information). Picosecond-timescale spectra of SILAR derived V₂O₅/CdSe heterostructures (Figure 5.3a) differed significantly from those of V₂O₅ NWs. TA spectra acquired at delay times of several picoseconds contain a bleach from 450-550 nm and an induced absorption band from 550 nm to 800 nm. Both of these features decay within several nanoseconds to the long-lived TA spectrum of SILAR-derived V₂O₅/CdSe heterostructures, assigned previously to charge separated state. Notably, the TA spectra acquired at the earliest delay times (3 ps to 2.5 ns) contain a well-resolved isosbestic point at ~605 nm with ΔA ~1 mOD. The presence of an isosbestic point, ΔA value of 0, in TA spectra of colloidal QDs and other chromophores is common at wavelengths at which the excited and ground states have identical molar absorption coefficients. However, the positive (non-zero) value of ΔA at the isosbestic point in the TA spectra of SILAR-derived V₂O₅/CdSe heterostructures indicates that a third component, other than the ground and excited states, is present at the earliest timescales after pulsed excitation. This third component has a positive absorbance at the ground/excited-state isosbestic point, is
formed within 3 ps, and does not decay to any measurable extent within 2.5 ns. The ΔΔA spectra (Figure 5.3b), calculated by subtracting the TA spectrum acquired at 2.5 ns from the earlier-timescale spectra, consist of a well-resolved bleach from 450-605 nm, an absorption from 605-800 nm, and an isosbestic point at 605 nm with ΔA of 0. (The ΔΔA spectrum extracted at 1 ps differed and was red-shifted relative to the spectra at longer delay times). The ΔΔA spectra of SILAR-derived V$_2$O$_5$/CdSe heterostuctures are similar to the TA spectrum of dispersed cys-CdSe QDs (Figure S5.3a in Supporting Information), in which the bleach arises from filling of the 1S(e) state and the induced absorption is attributed to the trapped hole and intraband hole excitation. On the basis of its similarity to the spectrum of dispersed CdSe QDs, we assign the ΔΔA spectra of SILAR-derived V$_2$O$_5$/CdSe heterostuctures to the excited state of SILAR-deposited CdSe QDs. (Equivalently, the TA spectra of SILAR-derived V$_2$O$_5$/CdSe heterostuctures can be treated as the linear combination of the TA spectra of charge-separated state and residual excited CdSe QDs). Notably, the value of ΔA at the 605-nm isosbestic point is unchanged in the TA spectra, or equivalently the isosbestic point in the corresponding ΔΔA spectra remains at 0 on the y axis, as the bleach and absorption arising from the excited state of CdSe decay. Therefore, a population of CdSe QDs within the SILAR-derived V$_2$O$_5$/CdSe heterostructures decays to the ground state rather than through electron transfer to V$_2$O$_5$ NWs. Additionally, the formation of charge-separated state is complete within the first few picoseconds after pulsed excitation of the heterostructures.

We fitted decay profiles at 500 nm (within the bleach) and 700 nm (within the absorption), and extracted $⟨τ⟩$ of (16 ± 1) ps and (18 ± 1) ps, respectively (Figure S5.8c in Supporting Information). These values of $⟨τ⟩$ are much shorter than the characteristic $⟨τ⟩$ of as-synthesized dispersions of cys-CdSe QDs ((163 ± 9) ns for the bleach, Figure S5.3 in Supporting Information). The accelerated decay of the excited state of CdSe within the SILAR-derived heterostructures may be
attributable to the higher local concentration of QDs on the NWs, relative to QDs in dilute dispersions, giving rise to excited state-excited state annihilation.

**Figure 5.3.** Picosecond-timescale TA spectra and corresponding ΔΔA plots of V$_2$O$_5$ NWs (a,b), LAA-derived V$_2$O$_5$/CdSe heterostructures (c,d), and SILAR-derived V$_2$O$_5$/CdSe heterostructures (e,f). ΔΔA plots were obtained by subtracting the TA spectrum of a given heterostructure acquired at a delay time of 2.5 ns from spectra acquired at delay times less than 2.5 ns.
TA spectra of SILAR-derived \(V_2O_5/CdSe\) heterostructures, at timescales of 3 ps and longer, do not contain any spectral signature of stimulated emission from \(V_2O_5\) NWs, in contrast to the picosecond-timescale TA spectra of bare \(V_2O_5\) NWs (Figure 5.3b). The absence of stimulated emission suggests that holes were transferred from \(V_2O_5\) NWs to CdSe QDs within several picoseconds. The red shift of the 1-picosecond TA spectrum, relative to the longer-timescale spectra, of SILAR-derived \(V_2O_5/CdSe\) heterostructures (Figure 5.3b) may provide evidence for some residual stimulated emission from \(V_2O_5\) at the earliest measurable timescales. Indeed, the TA spectrum corresponding to delay time of 1 ps is modeled accurately as a linear combination of the TA spectra of stimulated emission from \(V_2O_5\) NWs (\(\Delta\Delta A\) spectrum of \(V_2O_5\) NWs), excited CdSe QDs (\(\Delta\Delta A\) spectrum of SILAR derived \(V_2O_5/CdSe\) heterostructures corresponding to delay times > 3 ps), and charge-separated state (TA spectrum of SILAR derived \(V_2O_5/CdSe\) heterostructures at delay times of 2.5 ns) (Figure S5.9d in Supporting Information). The close correspondence between the measured and fitted spectra suggests that stimulated emission indeed was present at a delay time of 1 ps but decayed within ~3 ps due to the transfer of holes from \(V_2O_5\) NWs to SILAR-deposited CdSe QDs. In summary, in SILAR-derived \(V_2O_5/CdSe\) heterostructures, charge separation occurs within ~3 ps to yield a charge-separated state that persists for several microseconds.

Figure 5.3c shows the picosecond TA spectra of LAA-derived \(V_2O_5/CdSe\) heterostructures at various delay times. Interestingly, the evolution of TA spectra of LAA derived heterostructures is similar to that of bare \(V_2O_5\) NWs (Figure 5.3a). Spectra acquired at early timescales (< 5 ps) contain a broad bleach, which decays to yield a spectrum similar to that measured on nanosecond timescales for LAA-derived \(V_2O_5/CdSe\) heterostructures, with the only difference that the bleach at 430 nm is poorly resolved in picosecond timescale spectra. Similar to the nanosecond-timescale
spectrum, the picosecond-timescale spectra of LAA-derived V$_2$O$_5$/CdSe heterostructures can be treated as a linear combination of the charge-separated state and residual V$_2$O$_5$ NWs. To deconvolve the effects of stimulated emission of V$_2$O$_5$ NWs, the TA spectrum acquired at 2.5 ns was subtracted from all other TA spectra at earlier delay times and are shown in Figure 5.3d. The resulting ΔΔA spectra of LAA-derived V$_2$O$_5$/CdSe heterostructures (Figure 5.3d) resemble the spectral features from stimulated emission of V$_2$O$_5$ NWs. We fitted the decay profiles at 500 nm, 575 nm, 650 nm and 725 nm within the ΔΔA spectrum of LAA-derived V$_2$O$_5$/CdSe heterostructures and extracted $\langle \tau \rangle$ of (6 ± 1) ps, (16 ± 1) ps, (24 ± 1) ps and (37 ± 1) ps, respectively (Figure S5.8b in Supporting Information). The corresponding values of $\langle \tau \rangle$ for decay of stimulated emission of bare V$_2$O$_5$ NWs are (18 ± 1) ps, (30 ± 1) ps, (33 ± 2) ps and (43 ± 6) ps, respectively (Figure S5.8a in Supporting Information). The accelerated decay of stimulated emission in the case of LAA-derived V$_2$O$_5$/CdSe heterostructures, relative to bare V$_2$O$_5$ NWs, is logically attributed to hole transfer from V$_2$O$_5$ NWs to CdSe QDs. Based on $\langle \tau \rangle$, we calculated rate constants of hole transfer ($k_{HT}$) from V$_2$O$_5$ NWs to LAA deposited CdSe QDs using equation 3.$^{1,11,14,15}$

$$k_{HT} = \frac{1}{\langle \tau \rangle_{V2O5}} - \frac{1}{\langle \tau \rangle_{V2O5/CdSe}}$$

(3)

where $\langle \tau \rangle_{V2O5}$ and $\langle \tau \rangle_{V2O5/CdSe}$ are average lifetimes for the decay of stimulated emission for bare V$_2$O$_5$ NWs and LAA-derived V$_2$O$_5$/CdSe heterostructures, respectively. The calculated values of $k_{HT}$ decreased with emission wavelength from $(1.1 \pm 0.3) \times 10^{11}$ s$^{-1}$ at 575 nm to $(3.8 \pm 3.3) \times 10^{9}$ s$^{-1}$ at 725 nm. The dependence of $k_{HT}$ on emission wavelength may have arisen from the transfer of holes from a distribution of hole surface states on V$_2$O$_5$ NWs with varying driving forces of hole transfer. As emission wavelength increases, holes are trapped more deeply within the distribution of surface states, giving rise to a decreased driving force for hole transfer, and are
indeed transferred much more slowly and less efficiently. The spectral signature of stimulated emission in ΔΔA spectrum of LAA derived V₂O₅/CdSe heterostructures persists until ~500 ps (Figure 5.2d), indicating holes are transferred much more slowly in LAA-derived heterostructures than in SILAR-derived heterostructures. This difference may have arisen from differences in electronic coupling between CdSe QDs and V₂O₅ NWs. SILAR-derived V₂O₅/CdSe heterostructures have QDs directly deposited onto NWs, whereas, in LAA-derived V₂O₅/CdSe heterostructures, QDs and NWs are separated by an insulating linker.

The ΔΔA spectra of LAA-derived heterostructures did not show any features related to the bleach of CdSe QDs (Figure 5.3d). Electron transfer from excited CdSe QDs competes with electron-hole recombination within QDs. It is well-established that the bleach in a TA spectrum for cadmium chalcogenide QDs is proportional to population of electrons in CB of excited QDs.⁴⁶,⁴⁹ Thus, the absence of the bleach in ΔΔA spectra of LAA-derived heterostructures suggests that electrons were transferred from CdSe QDs to V₂O₅ NWs within the instrument response.

Finally, to investigate further our interpretation of the picosecond timescale spectra of LAA and SILAR-derived V₂O₅/CdSe heterostructures, the spectrum acquired at 2.5 ns for LAA-derived V₂O₅/CdSe heterostructures was fitted to a linear combination of TA spectra corresponding to 2.5 ns delay time for SILAR-derived V₂O₅/CdSe heterostructures (as a signature of the charge-separated state) and V₂O₅ NWs, under the assumption that the spectral signature for charge-separated state for LAA-derived V₂O₅/CdSe heterostructures is identical to that of SILAR-derived heterostructures (Figure S5.10c in Supporting Information). The close fit between the two supports our interpretation of the TA spectra.

In summary, the V₂O₅/CdSe heterostructures prepared by SILAR and LAA undergo ultrafast charge transfer to yield long-lived charge-separated states. This separation of photogenerated
charges is potentially useful for light harvesting and photocatalysis. The close contact between the QDs and V$_2$O$_5$ NWs in SILAR heterostructures facilitates faster charge recombination as compared to LAA prepared heterostructures as described previously. The intimate contact between QDs and NWs in SILAR-derived heterostructures probably also facilitates faster charge separation; however, we were unable to resolve the dynamics of charge separation, which occurred within the instrument response.

**V$_2$O$_5$/CdS and V$_2$O$_5$/CdTe Heterostructures**

The size and composition-dependent energetics of QDs may enable programmable light-harvesting properties and dynamics and efficiency of charge separation. V$_2$O$_5$/CdS and V$_2$O$_5$/CdTe heterostructures were prepared by SILAR and LAA to investigate the effects of interfacial energetics on charge separation. All heterostructures containing V$_2$O$_5$ NWs/CdE (E = S, Se, Te) QDs are expected to exhibit type II band alignment, facilitating charge separation (Scheme 5.1). The nanosecond-timescale TA spectra of V$_2$O$_5$/CdS and V$_2$O$_5$/CdTe heterostructures were analyzed in a similar fashion as V$_2$O$_5$/CdSe heterostructures. LAA-derived V$_2$O$_5$/CdTe heterostructures are not discussed because of the low loading of CdTe QDs over V$_2$O$_5$ NWs as explained previously.
Figure 5.4. TA spectra averaged between 1-10 ns for (a) V₂O₅ NWs (black), LAA-derived V₂O₅/CdS (yellow) and V₂O₅/CdSe heterostructures (red) and (b) SILAR-derived V₂O₅/CdS (orange), V₂O₅/CdSe (blue), and V₂O₅/CdTe heterostructures (purple). Corresponding decay profiles with fits for (c) excitonic bleach of V₂O₅ NWs (λ = 430 nm), charge separated state in LAA derived V₂O₅/CdS, and V₂O₅/CdSe heterostructures (λ = 850 nm), and (d) charge-separated state in SILAR-derived V₂O₅/CdS, V₂O₅/CdSe and V₂O₅/CdTe heterostructures (λ

There are similarities between the nanosecond timescale spectra of heterostructures containing V₂O₅/CdS, V₂O₅/CdSe and V₂O₅/CdTe (Figure 5.4). All SILAR-derived heterostructures exhibit a weak bleach below ~500 nm, assigned previously to electrons in V₂O₅ NWs, and a broad absorption extending from 500 nm to 900 nm, assigned previously to trapped holes and intraband hole excitations in CdE QDs (Figure 5.4b). Therefore, nanosecond TA spectra of SILAR-derived V₂O₅/CdS and V₂O₅/CdTe heterostructures are assigned to charge-separated, as explained above for SILAR-derived V₂O₅/CdSe heterostructures. Decay profiles were fitted at various wavelengths throughout the TA spectra of SILAR-derived V₂O₅/CdS and V₂O₅/CdTe heterostructures (Figures
The values of $\langle \tau \rangle$ extracted from these fits are tabulated in Table S1 in Supporting Information. Charge separated states were long-lived in all SILAR derived $V_2O_5$/CdE heterostructures, as charge recombination occurred on $\mu$s timescales.

Nanosecond TA spectra of LAA-derived $V_2O_5$/CdS heterostructures contain features of both residual $V_2O_5$ NWs and the charge-separated state. The latter is indicated by an increased absorption at longer wavelengths (500 nm to 900 nm), similar to the TA spectrum of LAA-derived $V_2O_5$/CdSe heterostructures. The excitonic bleach of $V_2O_5$ NWs was redshifted by $\sim$10 nm in TA spectrum of LAA-derived $V_2O_5$/CdS heterostructures and decayed much slowly than the excitonic bleach of $V_2O_5$ NWs in the TA spectrum of $V_2O_5$ NWs. Decay profiles were obtained at various wavelengths (Figure S5.5g in Supporting Information) throughout the TA spectrum of LAA-derived $V_2O_5$/CdS heterostructures and extracted $\langle \tau \rangle$ are tabulated in Table S2 in Supporting Information. The longer-lived TA features in LAA-derived $V_2O_5$/CdS heterostructures compared to TA features of bare $V_2O_5$ NWs indicate that charge recombination is much slower in LAA-derived $V_2O_5$/CdS heterostructures, consistent with the increased spatial separation of electrons in NWs and holes in QDs. Charge recombination in LAA-derived $V_2O_5$/CdS heterostructures was approximately 3-fold slower than in SILAR derived $V_2O_5$/CdS heterostructures, due to the spatial barrier of cysteinate between QDs and NWs in case of LAA derived $V_2O_5$/CdS heterostructures.

Picosecond-timescale TA spectra for SILAR- and LAA-derived $V_2O_5$/CdS and $V_2O_5$/CdTe heterostructures were analyzed similarly to those of $V_2O_5$/CdSe heterostructures (Figure 5.5). We first consider SILAR-derived $V_2O_5$/CdTe heterostructures. Picosecond-timescale spectra of these heterostructures (Figure 5.5c) exhibit an isosbestic point at approximately 790 nm. The corresponding $\Delta\Delta A$ spectra of SILAR-derived $V_2O_5$/CdTe at delay times $> 3$ ps exhibit a broad excitonic bleach centered at 600 nm with an isosbestic point at 790 nm at which the value of $\Delta\Delta A$
equals 0 (Figure 5.5d). This broad bleach was assigned to residual excited states of CdTe QDs that decay independently and do not participate in charge separation. Therefore, the picosecond TA spectra of SILAR-derived V$_2$O$_5$/CdTe heterostructures can be treated as a linear combination of the TA spectra of charge-separated state and excited CdSe QDs decaying independently on V$_2$O$_5$ NWs. Interestingly, we were able to fit the TA spectrum of SILAR-derived V$_2$O$_5$/CdTe heterostructures corresponding to delay times of 1 ps as a linear combination of the stimulated-emission spectrum of V$_2$O$_5$ NWs (ΔΔA spectrum of V$_2$O$_5$ NWs), the TA spectrum of charge-separated state (TA spectrum of SILAR-derived V$_2$O$_5$/CdTe heterostructures at delay time of 2.5 ns), and the TA spectrum of residual CdTe QDs (ΔΔA spectrum of SILAR-derived V$_2$O$_5$/CdTe heterostructures at delay time of 3 ps) (Figure S5.11 in Supporting Information). The quality of this fit suggests that stimulated emission indeed contributed to the TA spectrum of SILAR-derived V$_2$O$_5$/CdTe heterostructures at the earliest measurable timescales, that charge separation in occurred within 3 ps, and that the charge-separated state decayed on timescales of several microseconds, similar to the case of SILAR-derived V$_2$O$_5$/CdSe heterostructures.
Figure 5.5. Picosecond timescale TA spectra of (a) LAA derived V\textsubscript{2}O\textsubscript{5}/CdS heterostructures, (b) SILAR derived V\textsubscript{2}O\textsubscript{5}/CdS heterostructures and, (c) SILAR derived V\textsubscript{2}O\textsubscript{5}/CdTe heterostructures at various delay times ranging from 1 ps to 2.5 ns. Corresponding ΔΔA spectra of SILAR derived V\textsubscript{2}O\textsubscript{5}/CdTe heterostructures. ΔΔA spectra were obtained by subtracting TA spectrum corresponding to 2.5 ns from all other TA spectra at delay times lesser than 2.5 ns. The picosecond spectra of LAA- and SILAR-derived V\textsubscript{2}Os/CdS heterostructures (Figures 5.5 a,b) present an interesting case, wherein both spectra contain (1) a narrow high-energy bleach (430 nm for LAA- and 500 nm for SILAR-derived V\textsubscript{2}Os/CdS heterostructures), similar to the characteristic excitonic bleach of CdS QDs, and (2) a broad, red-shifted bleach, previously assigned to the stimulated emission of V\textsubscript{2}O\textsubscript{5} NWs (Figure S5.7 in Supporting Information), which then evolved into an absorption. The excitonic bleach of CdS QDs was much narrower for LAA-derived heterostructures than for SILAR-derived heterostructures, consistent with the expected narrower
size distributions of the presynthesized QDs used in LAA. The picosecond-timescale TA spectra of SILAR-derived V₂O₅/CdS heterostructures differs significantly from TA spectra of SILAR-derived V₂O₅/CdSe and V₂O₅/CdTe heterostructures. First, stimulated emission from V₂O₅ NWs is clearly discernible and persists much longer (~100-500 ps) in case of V₂O₅/CdS heterostructures as compared to SILAR-derived V₂O₅/CdSe and V₂O₅/CdTe heterostructures, where stimulated emission from V₂O₅ NWs is only present at delay times of less than 3 ps, irrespective of similar loading of CdE QDs on V₂O₅ NWs. Second, there is no isosbestic point in the picosecond-timescale TA spectra of V₂O₅/CdS heterostructures, in contrast to the TA spectra of SILAR-derived V₂O₅/CdSe and V₂O₅/CdTe heterostructures. These differences can be explained by slower charge separation in V₂O₅/CdS heterostructures. The interfacial energetics of CdE QD and V₂O₅ NWs in Scheme 5.1 predict the lowest driving force of hole transfer from V₂O₅ NWs to CdS QDs, which should in turn result in the slowest hole transfer in V₂O₅/CdS heterostructures. Therefore, despite the intimate contact between CdS QDs and V₂O₅ NWs in SILAR-derived V₂O₅/CdS heterostructures, electron-hole recombination within V₂O₅ NWs can compete effectively with interfacial hole transfer. We fitted TA decay traces corresponding to the bleach of CdS QDs and extracted (τ) of (48 ± 3) ps (Figure S5.12 in Supporting Information), which is much lower than the characteristic excited-state lifetime of dispersed cys-CdS QDs. The accelerated bleach decay is consistent with electron transfer from photoexcited CdS QDs to V₂O₅ NWs. We note that both stimulated emission from V₂O₅ NWs and the charge-separated state in SILAR-derived V₂O₅/CdS heterostructures, give rise to broad spectral features; therefore, deconvolution of electron-transfer and hole-transfer kinetics from TA spectra of SILAR derived V₂O₅/CdS heterostructures is not trivial. However, considering that bleach associated with electrons in CdS QDs and stimulated emission associated with V₂O₅ NWs persists for ~100-500 ps, we can safely
conclude that charge separation is much slower in SILAR derived V$_2$O$_5$/CdS than other SILAR derived heterostructures, where charge separation occurs within ~3 ps.

We expect charge separation to be even slower in the case of LAA-derived V$_2$O$_5$/CdS heterostructures, due to the spatial separation between the NWs and QDs arising from the presence of the linker, cysteinate. However, due to the convolution of the bleach of CdS QDs, stimulated emission from V$_2$O$_5$ NWs and contributions from charge-separated state, we were unable to quantify charge-transfer dynamics from picosecond-timescale TA spectra of LAA-derived V$_2$O$_5$/CdS heterostructures.

**Conclusion**

A variety of V$_2$O$_5$/CdE (E= S, Se and Te) heterostructures were prepared by LAA and SILAR. Type II interfacial energetic offsets between the NWs and QDs facilitated excited-state charge transfer, in which electrons were transferred from QDs to NWs and holes from NWs to QDs. Charge-transfer dynamics in these heterostructures was monitored by picosecond and nanosecond timescale TA spectroscopy.

Charge-separated states formed on picosecond or sub-picosecond timescales and decayed on microsecond timescales. SILAR-derived heterostructures promoted faster charge separation but also resulted in faster decay of the charge-separated state, through interfacial electron-hole recombination, due to the intimate contact between NWs and QDs. Ultrafast charge separation and the long-lived nature of the charge-separated state renders these type II heterostructures intriguing and potentially useful for light harvesting and photocatalysis. Further studies on using these heterostructures for photocatalysis are underway.
Acknowledgements

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Supporting Information

Ultrafast Exciton Dissociation and Long-lived Charge Separation in Novel Type II Cadmium Chalcogenide Quantum Dots / α-Vanadium Pentoxide Nanowires Heterostructures

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Figure S5.1. UV-Vis spectra of aqueous dispersions of cys-CdS, cys-CdSe and cys-CdTe QDs.

Figure S5.2. (a) TEM images for bare V$_2$O$_5$ NWs (panels I and IV), V$_2$O$_5$/CdS (panels II and V) and V$_2$O$_5$/CdTe heterostructures (panels III and VI) prepared by successive ionic layer adsorption and reaction (SILAR) method. (b) Raman Spectra of bare V$_2$O$_5$ NWs and SILAR derived V$_2$O$_5$/CdS, V$_2$O$_5$/CdSe and V$_2$O$_5$/CdTe heterostructures (c) EDS spectra of V$_2$O$_5$/CdS heterostructures and V$_2$O$_5$/CdTe heterostructures prepared by LAA (top) and SILAR (bottom).

Figure S5.3. (a) Transient absorption (TA) spectra of colloidal cys-CdSe QDs (averaged at 1.5-10 ns delay times), (b) Decay kinetics of bleach ($\lambda = 510$ nm) and induced absorption feature ($\lambda = 650$ nm) of cys-CdSe QDs.

Figure S5.4. 3D color maps showing ps and ns timescale TA spectra of V$_2$O$_5$ NWs and various V$_2$O$_5$/CdE heterostructures prepared by linker assisted assembly (LAA) and successive ionic layer adsorption and reaction (SILAR) method.

Figure S5.5. Nanosecond timescale spectral evolution of V$_2$O$_5$ NWs (a), LAA (b) and SILAR derived V$_2$O$_5$/CdSe heterostructures (c) and, corresponding decay kinetics of charge separate state in SILAR and LAA derived V$_2$O$_5$/CdSe heterostructures (d,e), V$_2$O$_5$/CdS heterostructures (f,g) and SILAR derived V$_2$O$_5$/CdTe heterostructures (h).

Figure S5.6. TA spectrum of V$_2$O$_5$ NWs (Averaged between 1-10 ns) and corresponding decay kinetics of bleach ($\lambda = 430$ nm) and induced absorption ($\lambda = 550$ nm).

Figure S5.7. Steady state emission spectrum and normalized $\Delta \Delta A$ spectrum of V$_2$O$_5$ NWs.

Figure S5.8. Decay kinetics of $\Delta \Delta A$ spectra of V$_2$O$_5$ NWs (a), LAA (b) and SILAR derived V$_2$O$_5$/CdSe heterostructures (c) with corresponding fits and ($\langle \tau \rangle$).

Figure S5.9. (a) Spectral signature of stimulated emission of V$_2$O$_5$ NWs in TA spectrum of V$_2$O$_5$ NWs (extracted from $\Delta \Delta A$ spectrum of V$_2$O$_5$ NWs at 1 ps), (b) TA spectrum of charge separated state in SILAR derived V$_2$O$_5$/CdSe heterostructures (extracted from TA spectrum of SILAR
derived V₂O₅/CdSe heterostructures at delay time of 2.5 ns) (c) TA spectrum of excited SILAR deposited CdSe QDs (extracted from ∆ΔA spectrum of SILAR derived V₂O₅/CdSe heterostructures at delay time of 3 ps) and, (d) fit between TA spectrum of SILAR dervied V₂O₅/CdSe heterostructures at delay time of 1 ps and a linear combination of a,b and c.

**Figure S5.10.** (a) TA spectrum of V₂O₅ NWs at 2.5 ns delay time, (b) TA spectrum of SILAR derived V₂O₅/CdSe heterostructures at 2.5 ns and, (c) fit between TA spectrum of LAA derived V₂O₅/CdSe heterostructures and a linear combination of picosecond timescale TA spectrum of V₂O₅ NWs and SILAR derived V₂O₅/CdSe heterostructures at 2.5 ns timescale.

**Figure S5.11.** (a) Spectral signature of stimulated emission of V₂O₅ NWs in TA spectrum of V₂O₅ NWs (extracted from ∆ΔA spectrum of V₂O₅ NWs at 1 ps), (b) TA spectrum of charge separated state in SILAR derived V₂O₅/CdTe heterostructures (extracted from TA spectrum of SILAR derived V₂O₅/CdTe heterostructures at delay time of 2.5 ns) (c) TA spectrum of excited SILAR deposited CdTe QDs (extracted from ∆ΔA spectrum of SILAR derived V₂O₅/CdTe heterostructures at delay time of 3 ps) and, (d) fit between TA spectrum of SILAR dervied V₂O₅/CdTe heterostructures at delay time of 1 ps and a linear combination of a,b and c.

**Figure S5.12.** Decay traces, corresponding fits and extracted (τ) corresponding to bleach and induced absorption features of LAA (a) and SILAR (b) derived V₂O₅/CdS heterostructures.

**Table S5.1.** Average lifetimes (⟨τ⟩) extracted from nanosecond TA spectra of various SILAR derived V₂O₅/CdE heterostructures.

**Table S5.2.** Average lifetimes (⟨τ⟩) extracted from nanosecond TA spectra of various LAA derived V₂O₅/CdE heterostructures compared to bare V₂O₅ NWs.
Figure S5.1. UV-Vis spectra of aqueous dispersions of cys-CdS, cys-CdSe and cys-CdTe QDs.
Figure S5.2. (a) TEM images for bare $\text{V}_2\text{O}_5$ NWs (panels I and IV), $\text{V}_2\text{O}_5$/CdS (panels II and V) and $\text{V}_2\text{O}_5$/CdTe heterostructures (panels III and VI) prepared by successive ionic layer adsorption and reaction (SILAR). (b) Raman Spectra of bare $\text{V}_2\text{O}_5$ NWs and SILAR-derived $\text{V}_2\text{O}_5$/CdS, $\text{V}_2\text{O}_5$/CdSe, and $\text{V}_2\text{O}_5$/CdTe heterostructures. (c) EDS spectra of $\text{V}_2\text{O}_5$/CdS heterostructures and $\text{V}_2\text{O}_5$/CdTe heterostructures prepared by LAA (top) and SILAR (bottom).
Figure S5.3. (a) Transient absorption (TA) spectrum of colloidal cys-CdSe QDs (averaged at 1.5-10 ns delay times), (b) Decay kinetics of bleach ($\lambda = 510$ nm) and induced absorption feature ($\lambda = 650$ nm) of cys-CdSe QDs. Superimposed on the data is a biexponential fit (equation 5.1).
Figure S5.4. 3D color maps showing picosecond and ns timescale TA spectra of V$_2$O$_5$ NWs and various V$_2$O$_5$/CdE heterostructures prepared by linker assisted assembly (LAA) and successive ionic layer adsorption and reaction (SILAR) method.
Figure S5.5. TA spectrum of V$_2$O$_5$ NWs (Averaged between 1-10 ns) and corresponding decay kinetics of bleach ($\lambda = 430$ nm) and induced absorption ($\lambda = 550$ nm). Superimposed on the data are biexponential fits (equation 5.1).
\( \Delta A/10^{-3} \)

\[ \begin{align*}
\text{Wavelength (nm)} & \\
500 & 600 & 700 & 800 & 900
\end{align*} \]

\( <\tau>(\text{us}) \)

\[ \begin{align*}
0.44 \pm 0.08 \\
0.55 \pm 0.04 \\
1.02 \pm 0.73 \\
2.93 \pm 0.80
\end{align*} \]

\( <\tau>(\text{us}) \)

\[ \begin{align*}
0.44 \pm 0.08 \\
0.55 \pm 0.04 \\
1.02 \pm 0.73 \\
2.93 \pm 0.80
\end{align*} \]
\[ \langle \tau \rangle (\mu s) \]

- \( 1.72 \pm 0.71 \)
- \( 2.18 \pm 0.57 \)
- \( 3.98 \pm 0.43 \)
- \( 4.99 \pm 0.51 \)

\[ \langle \tau \rangle (\mu s) \]

- \( 0.31 \pm 0.04 \)
- \( 1.77 \pm 0.40 \)
- \( 1.93 \pm 0.14 \)
- \( 1.52 \pm 0.28 \)
Figure S5.6. Nanosecond timescale spectral evolution of V$_2$O$_5$ NWs (a), LAA (b) and SILAR derived V$_2$O$_5$/CdSe heterostructures (c) and, corresponding decay kinetics of charge separate state in SILAR and LAA derived V$_2$O$_5$/CdSe heterostructures (d,e), V$_2$O$_5$/CdS heterostructures (f,g) and SILAR derived V$_2$O$_5$/CdTe heterostructures (h). Superimposed on the data are biexponential fits (equation 5.1).
Figure S5.7. Steady state emission spectrum and normalized ΔΔA spectrum of V$_2$O$_5$ NWs
\begin{align*}
\langle \tau \rangle \text{ (ps)} &
\begin{cases}
18.3 \pm 1.0 \\
30.3 \pm 1.3 \\
32.5 \pm 2.3 \\
43.1 \pm 5.7
\end{cases} \\
\langle \tau \rangle \text{ (ps)} &
\begin{cases}
6.08 \pm 0.62 \\
16.2 \pm 0.77 \\
24.0 \pm 1.3 \\
36.8 \pm 4.0
\end{cases}
\end{align*}

(a) 
(b)
Figure S5.8. Decay kinetics of ΔΔA spectra of V$_2$O$_5$ NWs (a), LAA (b) and SILAR derived V$_2$O$_5$/CdSe heterostructures (c) with corresponding fits and $(\langle \tau \rangle)$. Superimposed on the data are biexponential fits (equation 5.1).
(a) Stimulated Emission of V$_2$O$_5$ NWs

(b) Excited CdSe QDs
Fig. S5.9. (a) Spectral signature of stimulated emission of V₂O₅ NWs in TA spectrum of V₂O₅ NWs (extracted from ∆∆A spectrum of V₂O₅ NWs at 1 ps), (b) TA spectrum of charge separated state in SILAR derived V₂O₅/CdSe heterostructures (extracted from TA spectrum of SILAR derived V₂O₅/CdSe heterostructures at delay time of 2.5 ns) (c) TA spectrum of excited SILAR deposited CdSe QDs (extracted from ∆∆A spectrum of SILAR derived V₂O₅/CdSe heterostructures at delay time of 5 ps) and, (d) fit of TA spectrum of SILAR derived V₂O₅/CdSe heterostructures at delay time of 1 ps to a linear combination of a,b and c. The fit was obtained by minimizing the sum of square of residuals (data-fit). A chi-square value of 4.69 × 10⁻⁵ was obtained.
(a) Excited V$_2$O$_5$ NWs 2.5 ns

(b) Charge Separated State 2.5 ns
**Fig. S5.10.** (a) TA spectrum of V$_2$O$_5$ NWs at 2.5 ns delay time, (b) TA spectrum of SILAR-derived V$_2$O$_5$/CdSe heterostructures at 2.5 ns, and (c) fit of TA spectrum of LAA derived V$_2$O$_5$/CdSe heterostructures to a linear combination of $a$ and $b$. The fit was obtained by minimizing the sum of square of residuals (data-fit). A chi-square value of $4.69 \times 10^{-5}$ was obtained.
Fig. S5.11. (a) Spectral signature of stimulated emission of V$_2$O$_5$ NWs in TA spectrum of V$_2$O$_5$ NWs (extracted from ΔΔA spectrum of V$_2$O$_5$ NWs at 1 ps), (b) TA spectrum of charge separated state in SILAR-derived V$_2$O$_5$/CdTe heterostructures (extracted from TA spectrum of SILAR-derived V$_2$O$_5$/CdTe heterostructures at delay time of 2.5 ns), (c) TA spectrum of excited SILAR-deposited CdTe QDs (extracted from ΔΔA spectrum of SILAR derived V$_2$O$_5$/CdTe heterostructures at delay time of 5 ps), and (d) fit between TA spectrum of SILAR dervied V$_2$O$_5$/CdTe heterostructures at delay time of 1 ps and a linear combination of a, b and c. The fit was obtained by minimizing the sum of square of residuals (data-fit). A chi-square value of 1.08 × 10$^{-5}$ was obtained.
Figure S5.12. Decay traces, corresponding fits and extracted $\langle \tau \rangle$ corresponding to bleach and induced absorption features of LAA (a) and SILAR (b) derived V$_2$O$_5$/CdS heterostructures. Superimposed on the data are biexponential fits (equation 5.1).
**Table S5.1.** Average lifetimes ($\langle \tau \rangle$) extracted from nanosecond TA spectra of various SILAR-derived V$_2$O$_5$/CdE heterostructures.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>SILAR V$_2$O$_5$/CdS $\langle \tau \rangle$ (µs)</th>
<th>SILAR V$_2$O$_5$/CdSe $\langle \tau \rangle$ (µs)</th>
<th>SILAR V$_2$O$_5$/CdTe $\langle \tau \rangle$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>(0.3 ± 0.1)</td>
<td>(0.5 ± 0.1)</td>
<td>(1.7 ± 0.2)</td>
</tr>
<tr>
<td>650</td>
<td>(1.8 ± 0.4)</td>
<td>(0.9 ± 0.1)</td>
<td>(1.6 ± 0.1)</td>
</tr>
<tr>
<td>750</td>
<td>(1.9 ± 0.1)</td>
<td>(1.4 ± 0.1)</td>
<td>(2.7 ± 0.8)</td>
</tr>
<tr>
<td>850</td>
<td>(1.5 ± 0.3)</td>
<td>(3.2 ± 0.3)</td>
<td>(2.9 ± 0.3)</td>
</tr>
</tbody>
</table>

**Table S5.2.** Average lifetimes ($\langle \tau \rangle$) extracted from nanosecond TA spectra of various LAA-derived V$_2$O$_5$/CdE heterostructures and bare V$_2$O$_5$ NWs.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>V$_2$O$_5$ NWs $\langle \tau \rangle$ (µs)</th>
<th>LAA V$_2$O$_5$/CdS $\langle \tau \rangle$ (µs)</th>
<th>LAA V$_2$O$_5$/CdSe $\langle \tau \rangle$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleach maximum</td>
<td>(0.3 ± 0.1)</td>
<td>(2.2 ± 0.7)</td>
<td>(1.7 ± 0.7)</td>
</tr>
<tr>
<td>550</td>
<td>(1.8 ± 0.4)</td>
<td>(1.6 ± 0.2)</td>
<td>(2.2 ± 0.6)</td>
</tr>
<tr>
<td>700</td>
<td>-</td>
<td>(4.6 ± 1.8)</td>
<td>(4.0 ± 0.4)</td>
</tr>
<tr>
<td>850</td>
<td>-</td>
<td>(4.4 ± 0.7)</td>
<td>(5.0 ± 0.5)</td>
</tr>
</tbody>
</table>
References


