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Charge Transfer from Single Semiconductor Nanocrystal to Single Molecules

author | **James Loy**

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Dr. Matthew Pelton

BIOGRAPHY

James Loy dual-majored in physics and mathematics at UMBC. He graduated *summa cum laude* in May 2016, and began pursuing a Ph.D. degree in physics at Princeton University, focusing on quantum information. He enjoys teaching physics to students and loves working on his family's farm. James would like to thank his research mentor, Dr. Matthew Pelton, for his guidance and wisdom throughout his research experience. He would also like to thank Mr. Haixu Leng for the help and teachings offered during the research project. Finally, he would like to thank his family for supporting him throughout his undergraduate career, and Ms. Allison Osborne for motivation to work beyond his limits.

DEMYSTIFICATION

I entered research in the Department of Physics on the recommendation of my first laboratory class teacher, Dr. Laszlo Takacs, because of my devotion to lab work. He directed me to Dr. Pelton, whose research was in nanophotonics. After our first meeting, I was intrigued by the types of research occurring in the lab, but lacked the background for contributing. Therefore, my first project in the lab was to produce a computer interface for a new microscopy unit being set up in the lab, which seemed like an excellent way to contribute my skills at the time while learning the background necessary to later pursue a research project. I learned of the Undergraduate Research Award (URA) program through the Honors College and decided to apply in 2014 with Dr. Pelton's approval. Being awarded the URA supported the development of the interface on a devoted computer system and construction of the microscopy unit. After completing the interface, allowing full control of and data-collection from the microscopy unit, I began one of the first projects to use the new instrument. This separate project was awarded a second URA, and led to a manuscript on which I was co-author. This was my favorite accomplishment of my undergraduate career, and I strongly encourage every student to perform a research project at UMBC.

ABSTRACT

A candidate material for next-generation photovoltaics is a lattice of nanometer-scale semiconductor crystals (quantum dots, or QDs).[1] To efficiently convert light into current, electrons must be photoexcited out of the QD at a fast rate to avoid being trapped in defects on the QD surface.[2] We created a model system to quantify the rate at which excited electrons are transferred out of the QD following photoexcitation. Our model used organic molecules adsorbed to the surface of the QDs to accept excited electrons that leave the crystal. The number of surface molecules, which can be as few as one, shortens the excited-state lifetime by offering electrons more pathways out of the excited state, increasing the excited-state decay rate. We examined QD structures individually to resolve integer numbers of surface molecules on the crystals, allowing us to determine the effect a single acceptor had on the rate. By measuring the excited-state decay rate (the inverse of the characteristic time that electrons remain in an excited state), we found a discrete change in the rate corresponding to the number of surface molecules.

INTRODUCTION

A potential material for converting light to electrical energy includes lattices of semiconductor nanocrystals called quantum dots (QDs).[1] A key current issue for this type of renewable energy conversion is the cost of materials. QDs may be produced in bulk at low cost using colloidal chemistry techniques, and thus may offer a higher ratio of efficiency to cost-of-production than current silicon-based photocells.[3] Consisting of distinct core and shell materials, the QDs confine the electrons in three dimensions, which quantizes the energy allowed to electron states within the structure. Thus, the QDs only emit and absorb certain frequencies of light, depending on their physical size. A lattice formed by using QDs of varying sizes could potentially harvest energy from different regions of the solar spectrum for optimal efficiency.

Once excited, the electrons remain trapped in the structure and cannot escape to perform work unless they transfer to available states outside of the QD. Figure 1 demonstrates this process in a simple manner. An electron is excited to a higher energy in the structure, perhaps due to absorption of a photon. The electron can then either relax back to its original state, emitting a photon to conserve energy, or it can transfer out of the QD. Figure 1 shows an acceptor molecule on the QD surface, which accepts the electron and keeps it physically separated from the QD. This separation prevents the electron from returning to the QD after transfer. Since the acceptor molecule gives the electron a place to go, it facilitates the electron transfer process, increasing the rate at which it occurs.

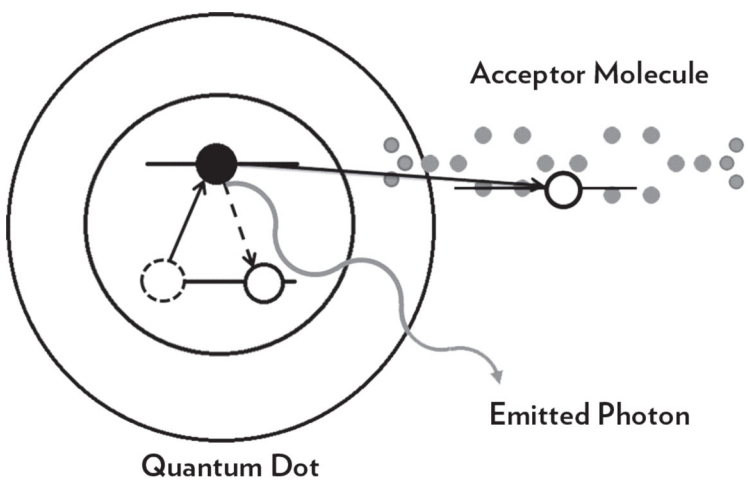


Fig. 1. **The electron transfer process from a quantum dot. An electron (solid black circle), is excited from a lower energy state (dashed circle) in the QD. The electron has two paths: relax to its original state (dashed arrow) and emit a photon, or transfer out of the QD to a surface acceptor molecule (solid arrow). This molecule accepts the electron and physically separates it from the QD.**

The transfer process competes with other pathways the electron may follow, which lowers the efficiency of the light-to-electrical-energy transfer. For example, crystal defects on the QD surface such as missing atoms, extra atoms, and impurities can create states that trap electrons, preventing them from exiting the QD.[2] It is ideal to increase the rate at which the transfer occurs so that it dominates these other processes. Any molecules that offer states which accept excited electrons facilitate electron transfer and thus increase the efficiency of the QDs for photovoltaics. In this project, we quantified the effect that individual acceptor molecules have on the transfer rate, using acceptor molecules as a model for future transfer sites. We produced a model system that allows investigation of the various features of the QD-acceptor molecule complexes.

This measurement has been performed previously using ensemble measurements, which involve exciting many QDs with a distribution of different acceptor molecule quantities all at once. In such measurements, the collected optical signal is analyzed using various assumptions about the QD emission distribution and the distribution of surface molecule quantity to obtain an average transfer rate per individual acceptor molecule.[4] Ensemble measurements are efficient due to the size of the structures, but suffer from complicated data analyses and the small differences between each QD complicate the signal obtained. In our research project, we observed individual QDs to resolve exact integer numbers of acceptor molecules. With this method, we were able to verify or refute the results of previous ensemble measurements directly.

SAMPLES

As shown in Figure 2, we used cadmium selenide core, cadmium sulfide shell (CdSe/CdS) QDs supplied by collaborators at Northwestern University. The benefit of using these QDs lies in their documented use as model systems for charge transfer.[5] Furthermore, these QDs emit light in the visible spectrum, which helps in qualitatively monitoring the QD density when preparing samples. This property also enables our optical analysis, as our camera and Time-Correlated Single Photon Counting (TCSPC) equipment are sensitive to visible light.

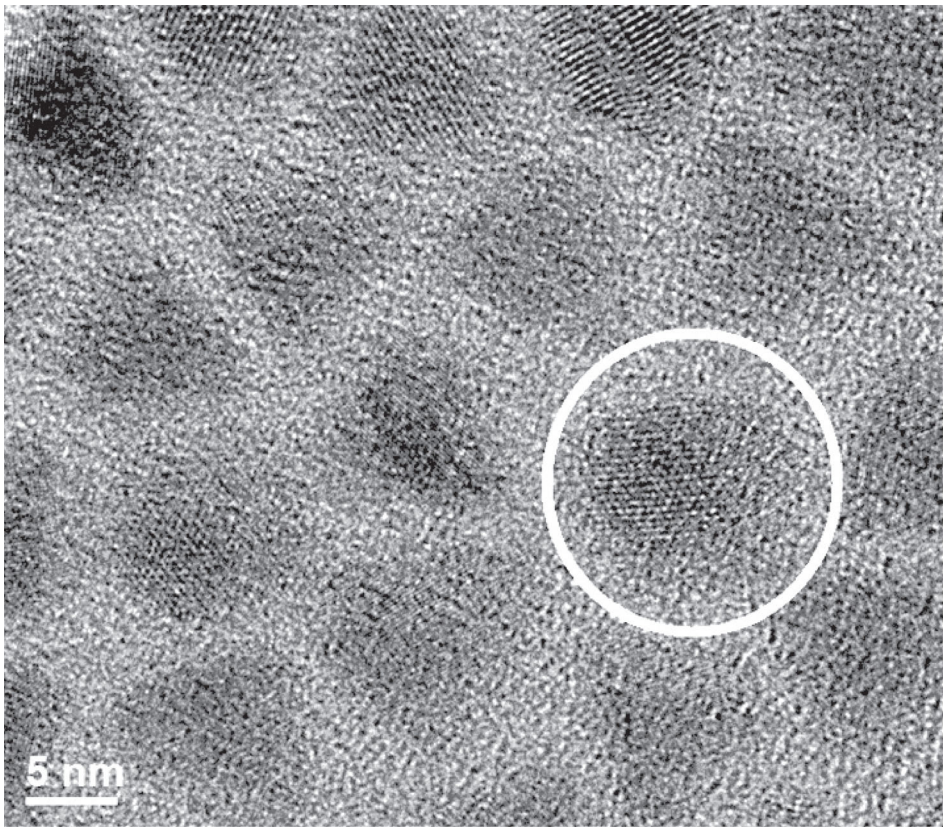


Fig. 2. **A transmission electron micrograph image of our QDs. The white outline encloses a single QD. Due to their crystalline structure, the QD edges terminate along crystal planes, preventing them from being exactly spherical.**

For our acceptors, we used an organic molecule called viologen, again due to its documented success with facilitating electron transfer. Using materials known to induce electron transfer will help us determine if our single particle analysis is reliable and a viable method of analysis.

Since the acceptor-molecule quantity is a variable we want to control, we produce the QD-viologen complexes in our lab. This involves suspending a dilute sample of QDs and viologen in chloroform. In chloroform, neither substance dissolves, so they are kept separate in the liquid. Physical contact between the QDs and molecules is facilitated by use of a sonicator that vibrates the sample for a variable period of time. When viologen encounters a QD, it adsorbs to the shell surface. The stochastic method results in a distribution of acceptor-molecule quantities; some QDs have none, some one, some two, etc. molecules adsorbed to their surface. We controlled the distribution by varying the mixing time and dilution of the substances, and found that a qualitatively optimal distribution is obtained after 30 seconds of adsorption time. Shorter times than this lead to too few QDs with any viologen adsorbed, while longer times lead to saturation of the QDs with viologen, which prevents them from emitting a detectable signal.

INSTRUMENT

To analyze our complexes, we relied on an optical microscope built specifically to control and analyze nanoparticles individually. Figure 3 shows an overview of the system.

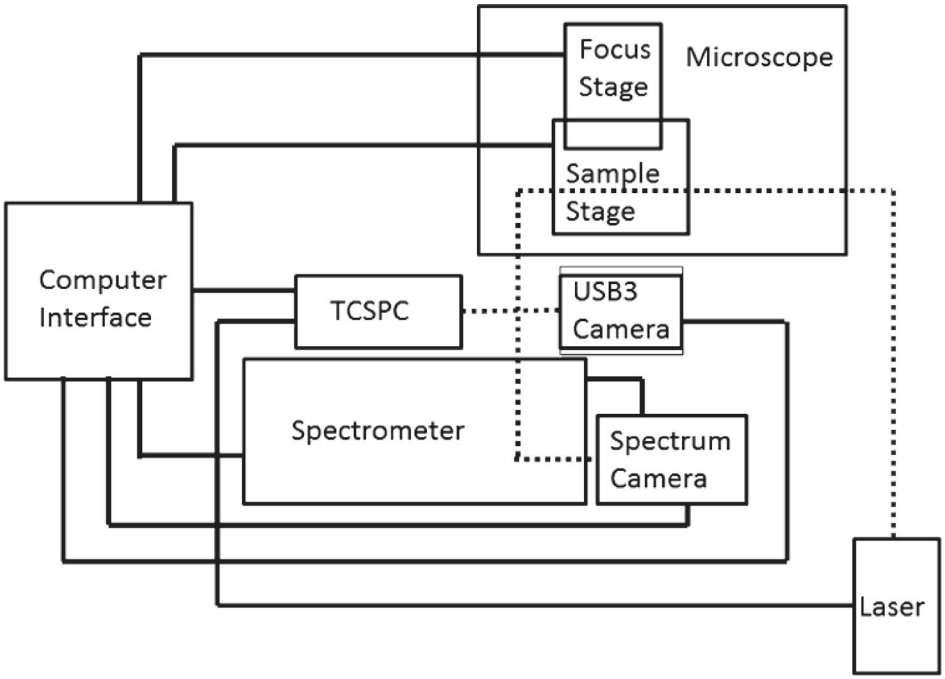


Fig. 3. **Schematic showing instruments of the microscopy unit in their rough relative positions. Connections between instruments are depicted; solid lines depict data communication paths and dashed lines depict laser light propagation paths.**

A dilute drop of the QD-viologen complex suspension (approximately 20 μL) was spread over a glass coverslip (Fisherfinest Premium Superslip) and allowed to dry. The QDs separated during this process, allowing us to then magnify and excite the structures individually. Pulsed laser light (diode laser PicoQuant PDL-800D) photoexcites the samples in 1 MHz pulses. We used a wavelength of 510 nm so that only electrons in the QD cores are excited, as the shell electrons absorb light of higher energy and thus cannot interfere with our signal. Pulses were focused through an objective lens (Nikon, Plan Apo 100X / N.A. = 1.40) to a minimally-focused point on the slide. Light emitted from the sample was reflected back through the lens and could then be intercepted by three different instruments for analysis. Note that this setup only collected light back-emitted from the sample and does not collect the stimulating laser pulse.

The microscopy unit was controlled by a specially-built computer interface that controlled the stages, spectrometer (Acton SpectraPro 500i), camera (Princeton Instruments Pixis 400), and the Time-Correlated

Single-Photon Counter (TCSPC) (PicoQuant model PicoHarp 300) instruments. The final device measures the arrival times of individual photons from the observed sample relative to the time of laser pulse emission, and collects the main data for this experiment.

DATA COLLECTION

During data collection, QDs were located and centered on the laser focus. It was important that we isolated individual QDs rather than excite clusters of multiple QDs. To verify this, we used three parameters. First, abnormally bright samples, relative to surrounding QDs, were ignored, as the higher intensity was likely a combination of multiple QDs fluorescing. Second, we used a property of QDs called "fluorescence intermittency," which appeared as an apparent blinking off and on during continuous excitation.[6] A cluster of QDs would contain overlapping QDs of different states, and the blinking would be less pronounced. This is because when some QDs blink off, others of the cluster will be in an "on" state, preventing the cluster from completely extinguishing. Therefore, a sample that blinked was more likely to be a single QD. Finally, we used spectral analysis of the QDs as sufficient proof of QD quantity. A single QD has a narrow spectral peak (roughly a 12-18 nm peak width at half the peak's height). For a cluster of QDs, small inhomogeneities between the QDs shifts their peak wavelengths slightly, widening the observed peak (greater than 20 nm width).

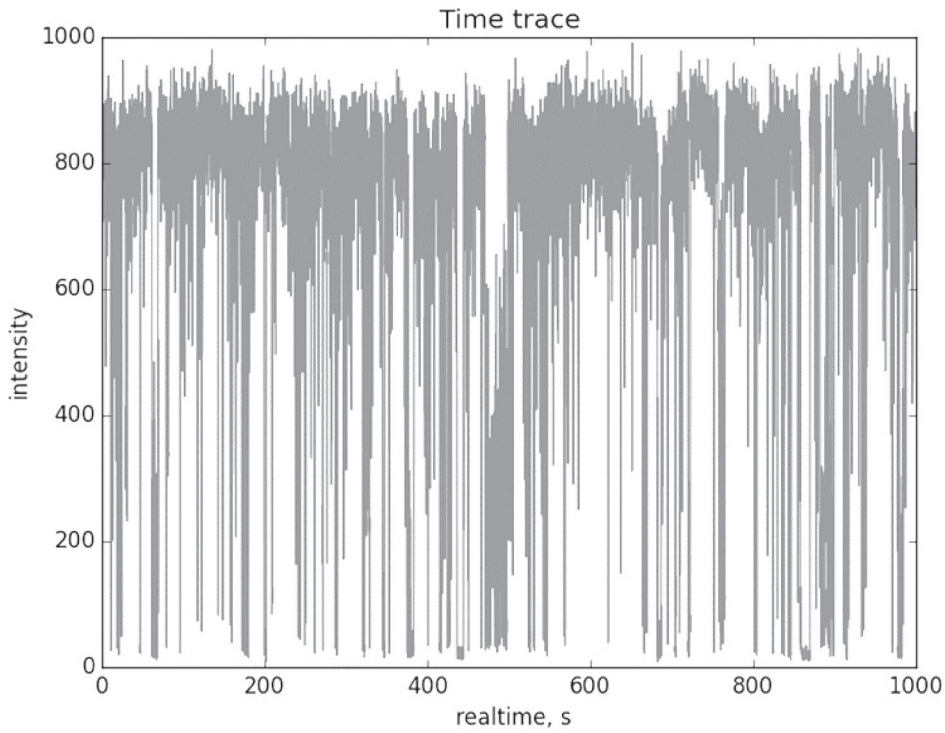
After verifying that a sample was an individual QD, we switched to data recording with the TCSPC. Samples were monitored for five to sixteen minutes, during which the intensity of the QD (in photon counts) was recorded against the time of arrival since the laser pulse.

DATA ANALYSIS

Our collected data could not be used directly without processing to address certain factors in our system. To process, we plotted the intensity of the QD over time for the experiment. Figure 4 shows various types of intensity plots. Figure 4(a) is an ideal data set, as the maximum intensity stays roughly constant over the data collection. The rapid change in intensity observed is due to the blinking phenomenon of the QDs themselves. Figure 4(b) shows a less ideal data set, where the blinking is more pronounced and eliminates the optical signal for significant periods of time. The loss of signal due to blinking is distinguished by how abrupt the change in intensity is. Another source of signal damage comes from instability in our microscope system. Figure 4(c) shows the effect that instability has on the intensity plot. The steady decrease in intensity over time is indicative of

drifting in our system, perhaps of the QD itself, the focus of the objective, or both. As the QDs are on the order of 10 nm in scale, the alignment of the sample must be very precise, and over a ten-minute interval the sample can drift out of focus. Temperature shifts and tension stored in the microscope from securing the system are likely to blame for much of the instability we observe. For some QDs, the drift in intensity is sinusoidal, perhaps corresponding to small variations in optimal focus due to sinusoidal interference like temperature shifts.

Since we collected an optical signal, the times during which the QD blinked off or drifted out of focus offered no valid data for analysis. To discern which states were usable, we used a variable threshold. The top and bottom half of the data (determined via the mean of the minimum and maximum of the data) were fitted separately to sinusoidal functions. The average between these two oscillating thresholds allowed us to track which states were "on" (above the averaged threshold), and were thus valid for our data.



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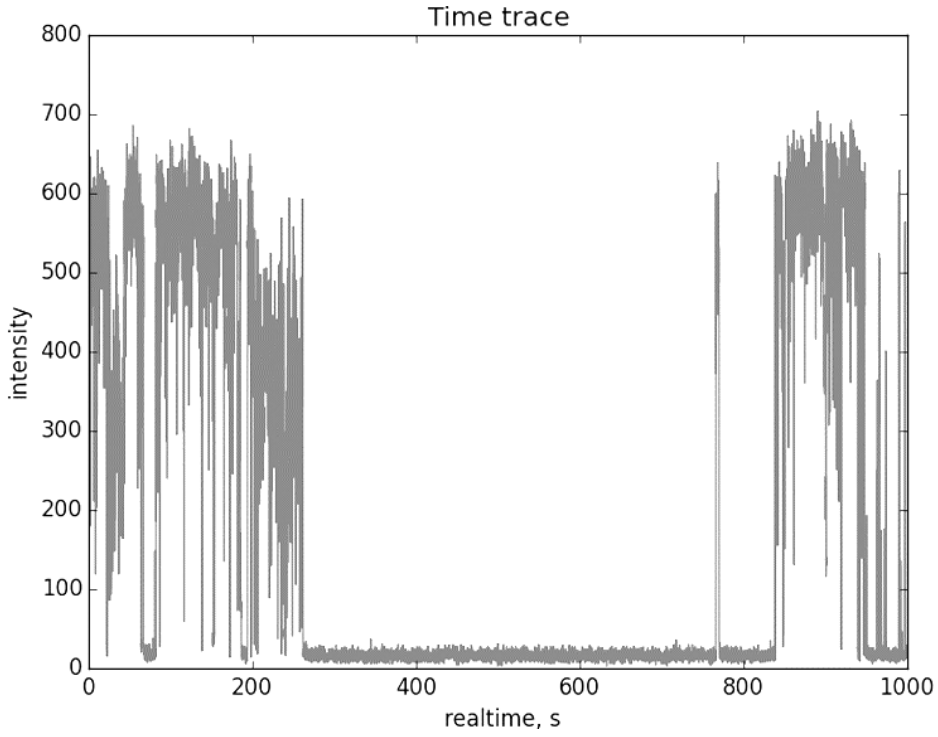
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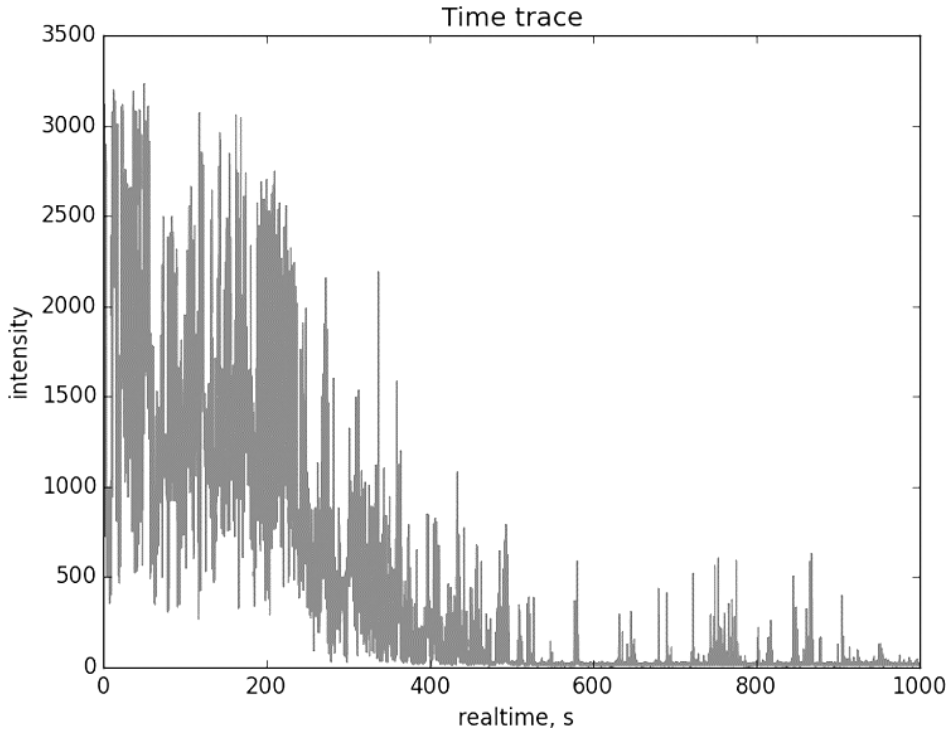
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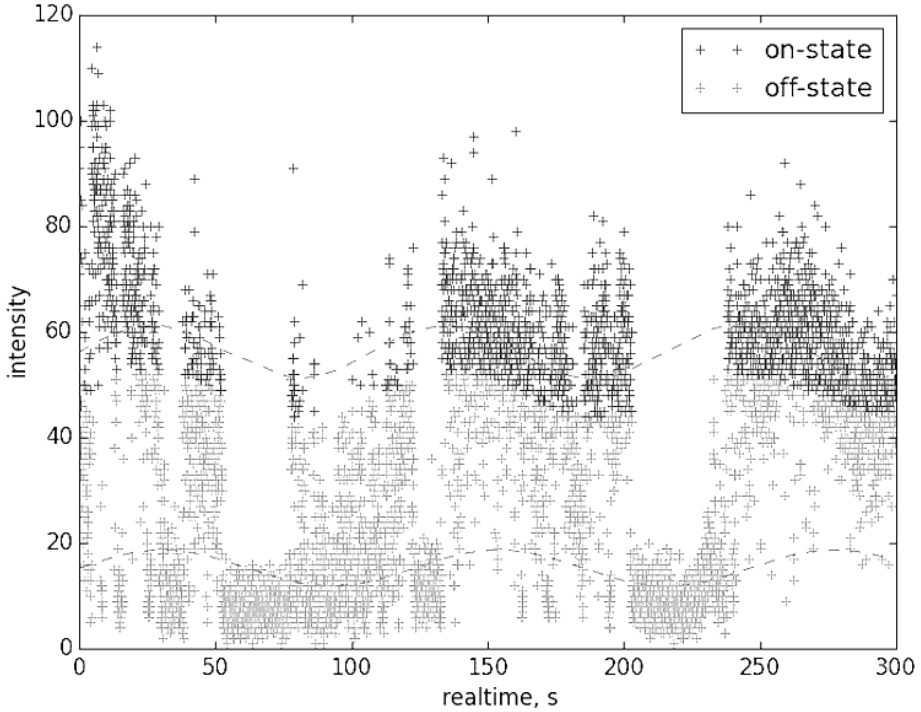

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Fig. 4. **Examples of the most common types of intensity plots. Each graph plots intensity of light (photon counts per second) against time in the experiment (seconds). (a) An ideal data set, with the maximum intensity roughly constant across the experiment, indicating a stable QD. (b) A data set featuring very pronounced blinking. The immediate loss of signal with the eventual return shows that the QD went into an "off" state for almost ten minutes of a 16-minute experiment. The signal's return cannot be explained by drift. (c) A data set featuring drift, perhaps of the focus, the QD itself, or both. Characterized by a gradual loss of signal over the experimental run, this data set is essentially useless as we cannot compare maximum intensities of the QD at different times during the experiment. (d) A data set where blinking is dealt with via a fitting function. Above-mean points (dark gray) are fitted separately from below-mean points (light gray) to separate sinusoidal functions that fit the intensity over time. These fittings develop a threshold that decides which QDs are in the "on" state, and therefore offer valid data.**

From the data corresponding to "on" states, we produced a lifetime plot. The data consisted of arrival times of individual photons relative to the most recent excitation of the sample via laser pulse. Over the course of the experiment (ranging from 5 to 16 minutes), we excited the same QD repeatedly, essentially resetting the initial time to zero after each excitation by a laser pulse. During the nanoseconds after the laser pulse, the QD decayed back to its ground state energy, emitting photons. Because the probability of relaxation is identical for every excitation, we expected an exponential decay curve to describe the number of QDs that remain in the excited state. If we defined a quantity Q(t) to be the ratio of QDs that remain excited after a time t, and we defined a natural rate of decay k for our QDs, then we expect the form:

$$Q(t) = e^{-kt}$$

However, of the remaining QDs that have not relaxed back to ground state, it is possible for the electrons to transfer to surface acceptor molecules. We expected another exponential rate of transfer, characterized by rate L. Then, the total equation governing Q(t) has the form

$$Q(t) = e^{-kt} e^{-Lt} = e^{-(k+L)t}$$

Therefore, we expected the natural decay rate and the rate of transfer to sum for a QD-viologen complex. From the "on" states for the QD, we plotted the arrival times of photons over the entire experiment, obtaining the exponential curve. Fitting the curve to an exponential function determined the rate of decay for that QD, as shown in Figure 5. The analysis process was performed for every QD collected in a single sample, for which we collected 30-60 QDs. Our QD quantity was limited by the time each data collection takes and the stability of our samples, which we found did not reliably exceed one day. Therefore, each set of 30-60 QDs refers to a single day of measurements.

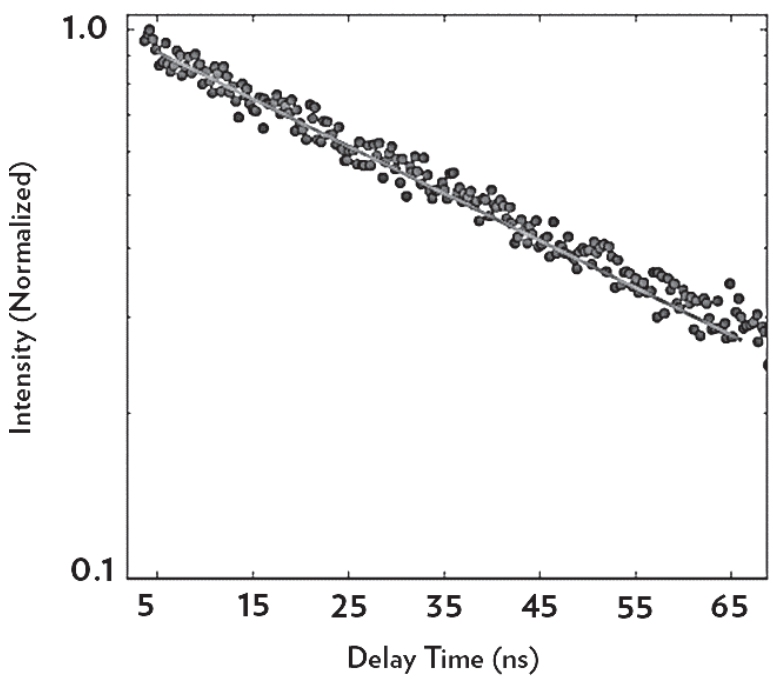


Fig. 5. **Fitting an exponential to the photon delay, which signals the time the electrons of the QD were in the excited state. Plot is of normalized intensity (photon counts per second) against time since the most recent laser excitation (nanoseconds).**

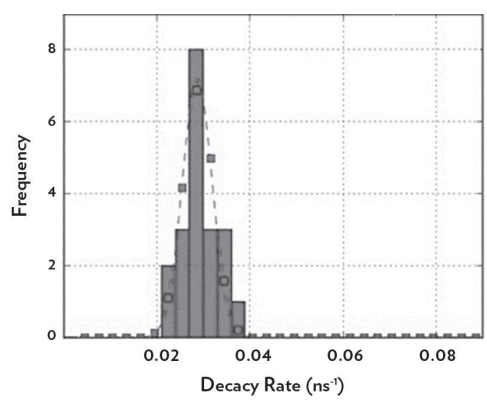
A histogram was produced, binning QDs with similar excitation decay rates together (bin size was 0.003 ns^{-1}). The results in Figure 6 show the formations of peaks of QDs with similar rates rather than collections of QDs with randomly larger rates. Each peak corresponds to a different integer number of acceptor molecules on the QD surfaces. The first peaks, which agree with our results from analyzing bare QDs with no acceptor molecules, correspond to QDs with no viologen adsorbed, the next highest peak corresponds to one molecule of viologen adsorbed, and so on. The fact that the peak maxima are equally spaced in our data indicates that each additional molecule increases the transfer rate individually, as if it were the only molecule on the QD surface. Therefore, the acceptor molecules are not interacting on the QD surface, and the rates change linearly. This result is especially helpful, since it allows us to predict the transfer rate for any given number of acceptor molecules.

Note that our increased rates must be due to the acceptor molecules, as the spread of natural decay rates for bare QDs is too small to explain the larger rates we observe for samples with acceptor molecules.

For our CdSe/CdS QD and viologen acceptor complexes, the rate change per molecule is L = (0.009 ± 0.003) ns^{-1}. Then our equation for Q(t) follows the form

$$Q(t) = e^{-(k+n\times L)t}$$

where n is the integer number of acceptor molecules on the QD.



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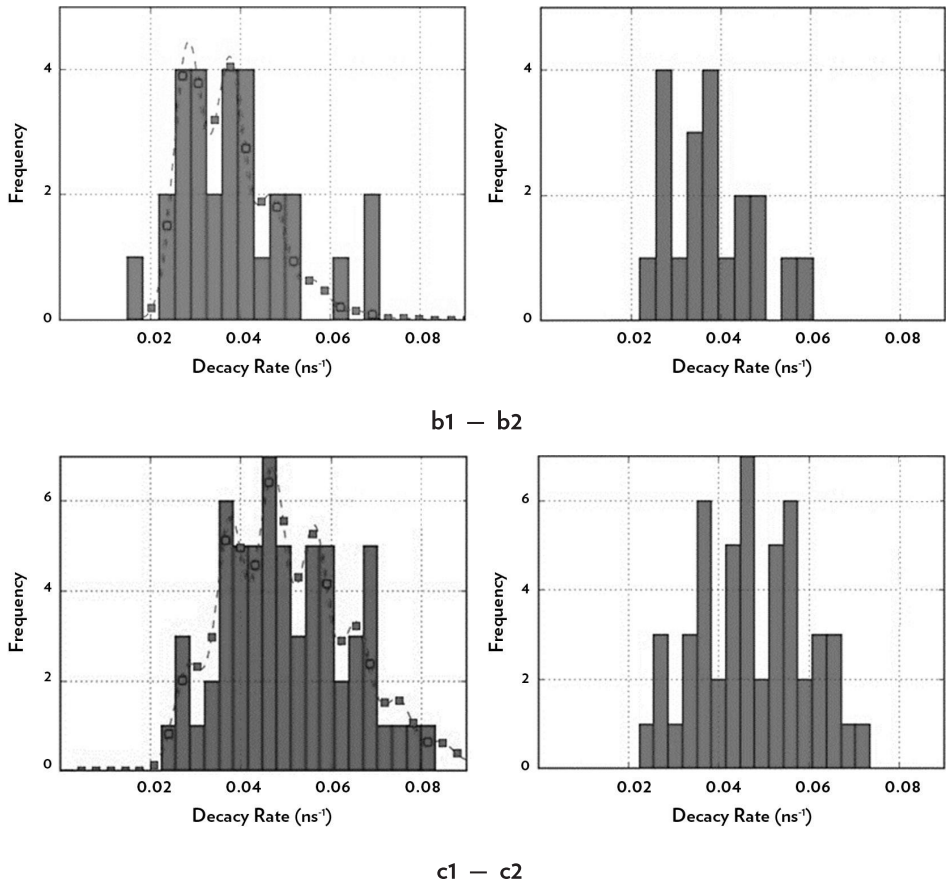

Fig. 6. **Histograms plotting excitation decay rates against quantity of QDs showing a rate in that bin. Bin size is 0.003 ns^{-1}. (a) A control group of bare QDs, showing the spread of lifetime rates for QDs with no acceptor molecules on the surface. (b1) and (c1) Different samples of QD-acceptor molecule complexes, both showing an increase in the rates obtained. The increased rate of transfer appears quantized because of the equidistant peaks. The presence of peaks is explained by QDs of different integer quantities of acceptor molecules on the surface. (b2) and (c2) Theoretical plots produced based on measurements made of our QDs, showing predicted peaks in close agreement with our data peaks. Note that both samples support the existence of discrete peaks, and that the increased rates cannot be explained by the spread of rates from individual QDs.**

CONCLUSIONS

From our results, we concluded that acceptor molecules increase the charge transfer rate in a predictable, linear manner. The use of surface acceptor molecules may improve the efficiency of QD materials for use as photovoltaic materials. The predictable, linear improvement to the transfer rate improves the practicality of producing QD arrays.

We have verified that individual QD analysis is a valid method for quantifying the effects that acceptor molecules have on the charge trans-

fer rate. This is evidenced by the fact that we were able to resolve individual peaks that were reasonably attributed to different, integer quantities of acceptor molecules on the QD surface, and that the change in rate was clearly discernable from the typical distribution of rates exhibited by QDs of a single sample. Now that it has been verified, our model system can be used in further applications of the field. For instance, new acceptor molecules or combinations of acceptor molecules can be studied, as well as adjustments to the QD properties, such as the QDs shell thickness.

In this project, we relied on the spherical symmetry of the QDs to remove any spatial dependency on where the molecules adsorbed to the QD. A possible advancement can be made where we use asymmetrical particles to determine what spatial dependencies might exist for the charge transfer rate. For instance, semiconductor nanorods offer a break in symmetry along one axis, such that acceptor molecules adsorbed on the ends of the rods may lead to a transfer rate distinct from that of those adsorbed on the rod centers. Ensemble measurements would be incapable of resolving where on a collection of nanorods the acceptors were adsorbed, further justifying our development of individual nanoparticle analysis.

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