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Electron Transfer Dynamics from Single Near Infrared Emitting Lead Sulfide-Cadmium Sulfide Nanocrystals to Titanium Dioxide

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Abstract In this study we report the first successful demonstration of electron transfer between a single near infrared emitting PbS/CdS nanocrystals and an external acceptor, titanium dioxide (TiO₂). We demonstrate distance-dependent electron transfer from single nanocrystals to TiO₂ and explore the effect of this process on the photoluminescence dynamics of these nanocrystals. Isolated PbS/CdS QDs are found to exhibit blinking dynamics similar to other nanocrystals like CdSe/ZnS, however, their photoluminescence follow a quasi two-state pattern with heterogeneous photoluminescence lifetimes which may be the result of their emission originating from different energy states. Electron transfer of these nanocrystals with external acceptor inhibits their photoluminescence lifetime heterogeneity and biases their blinking dynamics in a similar manner as observed for visible emitting CdSe/ZnS nanocrystals undergoing electron transfer with external acceptors. While the present study reconfirms the universality of quantum dot blinking among various types of nanocrystals, it also demonstrates that universality is also valid for the communication of various types of nanocrystals with the exterior world, here pictured as electron transfer with external acceptors.

Introduction

Continuous photoexcitation of colloidal quantum dots (QDs) leads to photoluminescence (PL) blinking, or random switching between bright (on-) and dark (off-) states¹⁻⁷. PL blinking has been observed in a variety of molecular emitters including organic dyes⁸, fluorescent proteins⁹⁻¹⁰, light harvesting systems¹¹⁻¹², conjugated polymers¹³, and colloidal quantum dots^{1,4,6,14}. PL blinking of visible emitting, large bandgap QDs like CdSe/ZnS has been extensively investigated in the past two decades, and there exists hundreds, if not thousands experimental and theoretical reports on this topic. That cannot be said about near-infrared (NIR) emitting QDs like InP or PbS where single nanocrystal studies are scarce.^{6, 15-20} In particular, for the lower bandgap PbS QDs, there are currently only two reports on single nanocrystal emission studies.^{6, 20} Low bandgap QDs are technologically important as there are the visible emitting, wide bandgap QDs like CdS and CdSe. Meanwhile, the incentive for studying the dynamics of light emitted from PbS nanocrystals at a single-molecule level comes from a growing utilization of these materials in light harvesting, light emitting and bioimaging applications²¹⁻²⁵.

Herein, we report a time-resolved single nanocrystal electron transfer study involving NIR emitting core/shell PbS/CdS QDs. Because of their relatively small core size (≈ 3 nm), these QDs emit PL with a peak at around 935nm which is sufficiently strong to be detected at the single nanocrystal level with a commercial Si-based photodetector with a high signal-to-noise ratio. We were able to probe exciton recombination in isolated QDs, distance-dependent electron transfer (ET) from isolated QDs to TiO₂ film, and the effect of electron transfer on the blinking dynamics of isolated QDs. Based on these measurements, it was concluded that electron transfer can decrease the heterogeneity in PL lifetime of isolated QDs and increase PL blinking dynamics in a distance dependent manner.

Results and Discussion

PbS/CdS nanocrystals have a type I core/shell band structure which in combination with TiO_2 favors electron transfer (ET) from a photoexcited PbS core to TiO_2 (see band diagram in Fig.1a).²⁶⁻²⁷ PbS/CdS QDs used by us were monodisperse, with a core size of 3.0nm and a shell thickness of 0.7nm (Details on sample preparation and transmission electron microscopy are given in Supporting Information). These QDs feature a $1S_0$ absorption peak at 870 nm, a PL peak at 935nm (Fig.1b) a PL quantum yield of 70-80% and an average bulk PL lifetime of $2.55\mu\text{s}$ as measured by time-correlated single photon counting spectroscopy in toluene (Fig.S2, SI). Long lifetimes are common for IV-VI semiconductor nanocrystals and they are thought to originate from the screening of the radiative field inside the QD due to the large dielectric constant of these nanocrystals.²⁸ An Uv-vis absorption spectrum of TiO_2 is shown in Fig.1b to evidence the lack of spectral overlap between TiO_2 absorption and QD's PL emission spectrum, thus excluding energy transfer as a possible quenching process between PbS/CdS QDs and TiO_2 . Highly diluted PbS/CdS QDs in toluene were spin casted under argon atmosphere on three types of substrates: pre-cleaned glass coverslips, glass coverslips coated with TiO_2 thin film and glass coverslips coated with $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer thin film, with Al_2O_3 top layer.

Figure 1. a) Energy band diagram for core/shell PbS/CdS (3nm core size) and TiO_2 thin film with (red arrow indicates ET flow) with CB and VB values from²⁹⁻³¹ suggests the possibility of electron transfer from

photoexcited PbS core to TiO₂ via CdS tunneling. b) UV-vis absorption spectra of TiO₂ and of PbS/CdS QDs in toluene (left arrows) and PL spectrum of PbS/CdS QDs in toluene (right arrow).

These samples, having a QD density of $<0.25/\mu\text{m}^2$, were each transferred to a sealed, air free sample chamber and probed, while under nitrogen flow atmosphere, with a confocal fluorescence lifetime imaging microscope (FLIM) using 490 nm pulses of 400 kHz repetition rate with samples exposed to an average laser power of $2\mu\text{W}$. Details on the microscope setup are given in the Materials and Methods section. Figure 2 contains representative time trajectories of PL intensity and PL decays from single QDs on glass, TiO₂ thin film and Al₂O₃/TiO₂ bilayer thin film, with Al₂O₃ of 1 nm thickness deposited on top of TiO₂ by atomic layer deposition. PL signals from isolated QDs on glass coverslips were detected with a signal-to-noise ratio as high as 23 (Fig.2a) and they feature blinking with clear distinguishable on-states and off-states, as previously observed by others.^{6, 20} However, isolated PbS/CdS QDs on glass feature large variations in the amplitude of the “on-state” (Fig.2a) and we would like to call this behavior a “quasi-two state” blinking. The photon counting histogram from Fig.2b was built using the time trajectory of PL intensity from Figure 2a and it features clearly separated “Off-state” and a “Quasi on-state”, this later one with a large width. “On-states” observed in visible emitting QDs like CdSe/ZnS are usually of constant amplitude and they relate to radiative recombination of photogenerated excitons at the band edge^{1, 3-4, 7}. A quasi two-state blinking in the case of PbS/CdS QDs might indicate that emission results from different states in a single QD, as recently proposed in³², a band edge state and a thermally accessible pinned-energy defect state whose contributions depend on temperature and QD size. For individual PbS/CdS QDs deposited on glass, the PL lifetime is close to the bulk value measured in toluene (Fig.2b, single nanocrystal PL decay with an average lifetime of $\sim 2.4\mu\text{s}$ vs the bulk PL lifetime of $2.55\mu\text{s}$) (see SI for details on calculating PL lifetimes from isolated QDs). The PL lifetime of single PbS/CdS QDs deposited on TiO₂ decreases in value when compared to QDs

deposited on glass (Fig.2d, average PL lifetime of $1.0\mu\text{s}$ on TiO_2 vs $2.4\mu\text{s}$ on glass), presumably due to quenching by electron transfer on TiO_2 . For this same QD deposited on TiO_2 (Fig.2d-f), the PL intensity also decreases when compared to glass (Fig.2c vs Fig.2a). Furthermore, blinking for QDs on TiO_2 becomes multistate, without clear separation between off-state and on-state (Fig.2e). Changes in PL blinking dynamics of QDs undergoing electron transfer with external acceptors and leading to multistate blinking behavior have been reported previously for CdSe/ZnS QDs.^{3, 33-34} PL quenching following electron transfer is rather weak ($1.0\mu\text{s}$ on glass vs $2.4\mu\text{s}$ on TiO_2 , see Figs.2c vs 2f), thus providing the CdS shell surrounding the PbS core acts as a tunneling barrier for the electron transfer.^{33, 35-36} The TiO_2 film employed in the present study has a low roughness as measured by atomic force microscopy (0.4nm, see Fig.S3, SI) and this can lead to a poor interfacial contact between QDs and TiO_2 which can also contribute to the observed slow electron transfer. For QDs on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer, because the metal oxide is an insulator, it further spaces the QDs from TiO_2 , thus providing an additional tunneling barrier for ET. Indeed, from QDs deposited on TiO_2 film to QDs deposited on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer, we observed (i) a recovery (increase) in PL intensity (Fig.2g vs 2d), (ii) a recovery in PL lifetime ($1.4\mu\text{s}$ on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer vs $1.0\mu\text{s}$ TiO_2 , i.e. Fig.2i vs 2f) and (iii) the reappearance of the quasi two- state blinking (see Figs.2g and 2h) which might suggests the presence of an intermittent electron transfer from QDs to $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer.³⁷ The above experimental observations also confirmed the distance-dependency of the electron transfer from QD to TiO_2 .

Figure 2. (a)-(i) PL intensity trajectories, PL photon counting histograms and normalized PL decays from single PbS/CdS QDs (a-c) and QDs in contact with a TiO₂ thin film (d-f) and an Al₂O₃/TiO₂ thin film layered structure (g-i) with the Al₂O₃ layer of 1 nm thickness. PL intensity trajectories and photon counting histograms are represented using 100ms dwell times. Details on the analysis of the PL decays in panels c, f and i are given in the main text and in the supplementary information (SI).

In our single nanocrystal experiments, the PL emission from QDs was recorded over a dedicated period of time (300 seconds) as a time-tagged time-resolved (TTTR) photon stream.^{3,38} A TTTR photon stream provides, for each recorded photon, the arrival time from the starting of the experiment (macrotime) and the laser pulse-photon time interval (microtime). The macrotime builds up the time trajectory of the PL intensity (photon count rate vs time), while the microtime builds up the PL decay histogram. Using TTTR photon streams from isolated QDs, we constructed fluorescence lifetime–intensity distribution (FLID) maps²⁻³ for QDs on glass, on TiO₂ thin film and on Al₂O₃/TiO₂ bilayer (Figures 3a, 3b, 3c, respectively). FLIDs are correlative maps of PL (photon)

count rate and PL lifetimes generated for the same dwell time (here 1 s) along the TTTR photon stream of an isolated QD. The photon count rate is a sum of all photons in the dwell time, while the PL lifetime is the result of a single exponential fit of the PL decay constructed with the photons in the dwell time, all histogrammed in 64 channels covering a time window of 2.1 μs . To obtain a high trust in the value of the PL lifetime, especially for decays with poor statistics, fit minimization is done using a maximum likelihood estimation (MLE) approach.³⁸ The FLID for the QD on glass exhibits scattered data which is indicative of large heterogeneity. Visual inspection of the FLIDs corresponding to QDs undergoing electron transfer with $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer (Fig.3c) and TiO_2 (Fig.3b) suggest a decrease in PL count rate vs PL lifetime heterogeneity, with the observation of decreased heterogeneity (data scattering) with increase in charge transfer strength (TiO_2 film vs $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer or Fig.3c vs Fig.3b)

Figure 3. Fluorescence lifetime-intensity distributions of isolated PbS/CdS QDs on glass (a) on TiO_2 film (b) and on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer (c). Details on generation of FLIDs are given in the main text and in the SI.

To better quantify the heterogeneity observed in the FLIDs shown in Fig.3, we performed time-resolved single nanocrystal investigations for three populations of QDs, e.g. QDs deposited on glass, on TiO_2 thin film and on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer (Figs.4a, 4b, 4c, respectively). Each of the three distributions in Fig.4 were built from as many as 30 individual QDs per substrate. For each QD, the corresponding TTTR photon stream (300s) was divided in sets of 5000 consecutive

photons, with each set of photons building a PL decay histogram of 128 channels covering a $2.1\mu\text{s}$ time window. Each PL decay was then fit with a single exponential model and MLE minimization.³⁸ Following this approach we obtained similar statistical errors among the population of fitted PL lifetimes within each of the distributions shown in Fig.4. We then fitted these distributions with a Gauss model (OriginPro 8.5 software) and the resulting values for mean PL lifetime and full width at half maximum (FWHM) for each distribution are given in Table 1, and together with the calculated expected standard deviation error for each distribution.

Figure 4. PL lifetime histograms for isolated PbS/CdS QDs on (a) glass coverslip, (b) TiO_2 thin film and (c) $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer, with the intercalated Al_2O_3 layer of 1 nm thick. Blue curves are Gauss fits with peak (mean PL lifetimes) and FWHM values of (a) $2.24\mu\text{s}$ and $2.4\mu\text{s}$; (b) $1.06\mu\text{s}$ and $1.05\mu\text{s}$; (c): $1.5\mu\text{s}$ and $1.34\mu\text{s}$, respectively. Expected statistical errors for these distributions are provided in Table 1 and details on PL lifetime estimation and calculation of statistical errors are given in the main text and in SI, respectively.

Using the mean PL lifetime values from Table 1, we calculated electron transfer rates

$$k_{ET} = \tau_{QD-A}^{-1} - \tau_{QD}^{-1} \quad (1)$$

with τ_{QD} , PL lifetime of isolated QDs on glass (Fig.4a) and τ_{QD-A} , PL lifetimes of QDs on acceptor substrates (Figs.4b-c) and obtained $k_{ET} = 4.97 \times 10^5 \text{ s}^{-1}$ for QDs on TiO_2 and $k_{ET} = 2.21 \times 10^5 \text{ s}^{-1}$ for QDs on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer. These rates demonstrate again the donor-acceptor distance dependency of the electron transfer between QDs and TiO_2 .

The PL lifetime distribution for QDs on glass coverslip shown in Fig.4a exhibits a large breath defined here by the value of the full width at the half maximum (FWHM) which is $2.37 \mu s$. The expected statistical error (standard deviation) for PL lifetime is given by³⁸

$$\sigma^2 = \frac{\tau^4 k^2}{NT^2} \left(1 - e^{-\frac{T}{\tau}}\right) \left(\frac{e^{T/k\tau}(1 - e^{-T/\tau})}{(e^{T/k\tau} - 1)^2} - \frac{k^2}{(e^{T/\tau} - 1)} \right)^{-1} \quad (2)$$

Here k , T and N are the number of channels, the time window and the total number of photons of the PL decay, respectively. For a PL lifetime of $2.21 \mu s$ estimated from a decay of 5000 total photons spread over 128 channels totaling a time window of $2.1 \mu s$, the standard deviation is $\sigma = 0.23 \mu s$ which is one order of magnitude smaller than the observed PL lifetime distribution breath (Gauss FWHM, Table 1). We can define a measure for heterogeneity in PL lifetime³⁹

$$H(\tau_i) = FWHM(\tau_i) - \sigma(\tau_i) \quad (3)$$

For QDs on glass (Fig.4a) we obtained $H(\tau_i) = 2.17 \mu s$, a value which seconds the observation of heterogeneous FLID map for isolated QD (Fig.3a). Such large lifetime heterogeneity reflects the complex emission of isolated PbS/CdS QDs when deposited on neutral substrates like glass. Reasons behind such large heterogeneity could result from emission happening not only from the radiative exciton recombination state but also from defect states as recently proposed³² or it could be a result of electron and hole having similar effective masses in PbS (see below). When QDs undergo electron transfer with TiO_2 , the heterogeneity in PL lifetime $H(\tau_i)$ decreases (Fig.4b,4c and Table 1) and $H(\tau_i)$ becomes smaller with increased electron transfer strength (increased ET rate, see Table 1, PbS/CdS on Al_2O_3/TiO_2 vs PbS/CdS on TiO_2)

Table 1. PL lifetimes (mean values) and FWHM resulting from Gauss fits of the distributions shown in Fig.4, expected statistical errors estimated according to eq.(2) and PL lifetime heterogeneities (eq.(3)).

	mean PL lifetime $\tau(\mu\text{s})$	Gauss FWHM (μs)	Expected Statistical Error $\sigma(\mu\text{s})$	PL lifetime Heterogeneity $H(\tau)(\mu\text{s})$
PbS/CDS	2.21 ± 0.06	2.4 ± 0.22	0.23	2.17 ± 0.22
PbS/CdS on TiO_2	1.06 ± 0.03	1.05 ± 0.09	0.06	0.99 ± 0.09
PbS/CdS on $\text{Al}_2\text{O}_3/\text{TiO}_2$	1.5 ± 0.06	1.34 ± 0.14	0.11	1.23 ± 0.14

We also investigated how electron transfer with TiO_2 affects PL blinking of PbS/CdS QDs. We constructed probability distributions for the time a QD resides in the on-state, $P(t_{\text{on}})$ (Fig.5a) and in the off-state, $P(t_{\text{off}})$ (Fig.5b) by using a threshold method^{3, 7, 34, 40-41}. This method separates on- and off-states from traces like those shown in Figure 2 (binned at 10 ms) and it counts associated on/off times. Each probability distribution from Fig.5a-b (see SI for details on constructing these distributions) incorporates data from as many as 30 isolated PbS/CdS QDs, each QD probed for 300 seconds. Each distribution contains at least 1300 events in the first bin in order to provide confident fitting.⁴¹ Fits to these distributions were done according to power law (QDs on glass) and modified power law (QDs on TiO_2 and $\text{Al}_2\text{O}_3/\text{TiO}_2$) models^{35, 37-38}

$$P(t) = b \times t^{-m}, P(t) = b \times t^{-m} \exp(-t/T) \quad (4)$$

with m a power law exponent and T a cross-over time from power law to exponential dependency (see Fig.5). Fit values and errors for power law exponents and fall off times were estimated with OriginPro 8.5 software and they are given in Table 2. For PbS/CdS QDs on glass support we obtained power law exponents $m_{\text{on}} \sim 1.54$ and $m_{\text{off}} \sim 1.60$, similar to the reports of^{6, 20} and to isolated CdSe/ZnS QDs on similar substrates^{3, 7, 33}. For QDs deposited on TiO_2 film and undergoing electron transfer, we noticed an increase in the power law exponent to $m_{\text{on}} \sim 1.66$ (steeper dependency) (Fig.5a and Table 2), i.e., decrease in the on-time of blinking. This increase was

somewhat smaller for QDs deposited on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer (Table 2, $m_{\text{on}} \sim 1.57$), reflecting again the distance dependency of the electron transfer previously seen in PL intensity and PL lifetime (Fig2 and fig.4). Off-time distributions were also affected by electron transfer (Fig.5b and Table 2). Here we observed a decrease in power law exponent m_{off} from QDs on glass to QDs undergoing electron transfer on TiO_2 ($m_{\text{off}}=1.60$ on glass vs $m_{\text{off}}=1.54$ on TiO_2), which accounts for the observation of longer off-times for QDs undergoing electron transfer. However, we could not see a clear trend in m_{off} values with increased electron transfer strength as we observed for m_{on} values (Fig.5a, 5b and Table 2, TiO_2 vs $\text{Al}_2\text{O}_3/\text{TiO}_2$).

Figure 5. Probability distributions $P(t_{\text{on}})$ (a), and $P(t_{\text{off}})$ (b) for PbS/CdS QDs deposited on: glass (black squares), on TiO_2 thin film (blue squares), and on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer (green squares). Data are offset. Solid red lines are fits according to models described by eq.4.

Table 2. PL blinking parameters for PbS/CdS QDs on glass support and for PbS/CdS QDs undergoing electron transfer with TiO_2 and $\text{Al}_2\text{O}_3/\text{TiO}_2$ acceptor substrates. Details on data analysis are given in the main text and SI

Sample	m_{on}	$T_{\text{on}}/\text{msec}$	m_{off}	$T_{\text{off}}/\text{msec}$
<i>PbS/CdS QDs on glass support</i>	1.54 ± 0.01	-	1.60 ± 0.01	-
<i>PbS/CdS on TiO_2 thin film</i>	1.66 ± 0.01	359 ± 20	1.54 ± 0.01	1428 ± 54
<i>PbS/CdS on $\text{Al}_2\text{O}_3/\text{TiO}_2$ bilayer</i>	1.57 ± 0.01	1034 ± 42	1.56 ± 0.01	1078 ± 42

PL blinking of near infrared emitting PbS/CdS QDs deposited on glass substrate can be modeled by a power law function with an exponent of similar value as observed for visible emitting CdSe/ZnS QDs deposited on glass substrates or other insulating supports. This observation reconfirms the universality of the blinking process among various types of nanocrystals. However, for PbS/CdS QDs and under the experimental conditions used here we observed a quasi two-state blinking rather than a well-defined two-state blinking usually reported for CdSe/ZnS QDs. We associate this quasi 2-state behavior with emission from band edge and defect states. Emission from multiple states could also explain the high heterogeneity we observed in single nanocrystal PL lifetimes on glass (Fig.3a) From glass to TiO₂, PbS/CdS QDs undergoing electron transfer exhibit a decrease in on-time and an increase in off-time (Fig.5 and Table 2), similar to CdSe/ZnS QDs undergoing electron transfer with external acceptors^{3,33}. For both PbS/CdS and CdSe/ZnS QDs coupled to external electron acceptors it is observed that the on-time decreases more significantly with stronger electron transfer. Below we try to explain these changes that we observed in the PL blinking dynamics of PbS/CdS QDs undergoing electron transfer with external acceptors.

In the original model proposed by Nirmal for CdSe nanocrystals¹, PL blinking was associated with photocharging/neutralization of QD's core following optical excitation (Fig.6a). An on-state (on-time) is supposedly dominated by radiative recombination of the neutral exciton while an off-state is the result of trapping of either photoexcited electron or hole outside the core followed by trion formation in the core, with the trion undergoing efficient non-radiative Auger recombination (Fig.6a, bottom). A positive trion formed following electron trapping will produce a dark state (Fig.6a, bottom), while a negative trion following hole trapping will emit highly

quenched, producing a so called “grey-state”^{1-2, 42-44}. Charge recombination between the remaining charge in the core and the opposite charge trapped outside the core will eventually restore the nanocrystal neutral, so that the on-state can occur again (Fig.6a, bottom). To understand the similarities in emission between PbS/CdS and CdSe/ZnS nanocrystals in the presence of external electron transfer, we have computed the radial probability density for electron ($1S_e$) and hole ($1S_h$) for PbS/CdS and CdSe/ZnS QDs of similar dimensions (see Fig.S4b-e and Table S1, SI). PbS and CdSe are both II-VI semiconductors with similar effective mass and carrier mobility for electron, $m_e^* \sim 0.085m_0$ for PbS and $m_e^* \sim 0.13m_0$ for CdSe⁴⁵⁻⁴⁶, but rather different effective masses for holes, $m_h^* \sim 0.085m_0$ for PbS and $m_h^* \sim 0.45m_0$ for CdSe. Thus, a heavier hole exists for CdSe QDs. PbS/CdS and CdSe/ZnS have both type I band alignment, with shells of larger bandgap compared to cores and therefore acting as tunneling barriers for photogenerated charges created in the core. For both PbS/CdS and CdSe/ZnS, the electron wave-function extends outside the core (Fig.S4) and this reflects the probability of a photogenerated electron to tunnel through the shell in the case of both types of QDs. The hole wave functions are rather different, for PbS it extends outside the core, similar to that for the electron, for CdSe the hole wave function is highly confined in the core. Following these observations, a photogenerated electron in the QD core increases its chance to be expelled outside the core when external electron transfer is present (Fig.6b). This is because the external electron transfer becomes a non-radiative channel competing with radiative recombination and charge (electron) trapping. Therefore, external electron transfer will decrease the QD’s PL intensity, PL lifetime and the on-time associated with blinking when compared to the isolated QD (on glass). Because of the similarity in electron wave function between PbS/CdS and CdSe/ZnS, we now understand why external electron transfer biases blinking in similar way in both types of QDs.^{3, 33, 36} Charge recombination in the presence of external electron transfer will

now involve an additional path, via back electron transfer (Fig.6b) and this process might produce an increase in the off-time associated with blinking.

Figure 6. The effect of external electron transfer on the PL blinking of a PbS/CdS nanocrystal. a) QD only; b) QD undergoing electron transfer with TiO_2 ; X^0 , exciton, ET, electron transfer, BET, back electron transfer. In panel (a), top depicts the QD's on-state (neutral) evolving to an off-state by charge (electron) trapping, while bottom depicts the QD's off-state (trion) evolving to an on-state by charge (electron) de-trapping. In panel (b) top depicts the QD's on-state (neutral) evolving to an off-state either by charge (electron) trapping or by external electron transfer to TiO_2 while bottom depicts the QD in the off-state evolving to an on-state either by charge (electron) de-trapping or by back electron transfer. Simulated time trajectories of PL intensity indicate decreased on-time, increased off-time and decreased PL intensity for a QD undergoing electron transfer with TiO_2 (panel b) compared to a QD only (panel a), showing

decreased intensity and on-time and increased off-time in the former case (panel b vs panel a).

Conclusions

In short, we demonstrated the effect of external electron transfer on the near infrared photoluminescence emitted by isolated low bandgap PbS/CdSe nanocrystals. We found that an external electron transfer has a similar effect on PbS/CdS QD's blinking as observed previously for visible emitting CdSe/ZnS QDs, decreasing the on-time and an increase the off-time associated with blinking. We linked this similarity to electrons having similar effective masses and wave

functions extending outside the core onto the shell for both types of QDs. We also found that QDs on glass exhibit quasi two-state emitting behavior and heterogeneous PL lifetime distributions which might be the effect of PbS/CdS emission originating from multiple states³². Coupling PbS/CdS QDs via electron transfer with external acceptors inhibits such heterogeneity in PL lifetime. The present study reconfirms the universality of quantum dot blinking among various types of nanocrystals and extends this universality in terms of communication of various types of nanocrystals with the exterior world, here pictured as electron transfer with external acceptors.

Materials and Methods.

Details on PbS/CdS QDs are given in SI. Titanium (IV) butoxide was purchased from Sigma Aldrich Inc. Samples were prepared in a Mbraun Labmaster 130 glovebox under Argon atmosphere with O₂ and H₂O level less than 0.1ppm on precleaned coverglasses, then transferred to a home built sample holder inside the glove box, air-tight sealed, then transfer to the confocal FLIM microscope. Time resolved confocal FLIM was performed with a home-built confocal scanning stage microscope based on an inverted microscope (Olympus IX71, 1.45 NA 60× oil objective) equipped with a piezo scanning stage (Physik Instruments, Germany) and a frequency doubled (490 nm) pulsed picked laser (system based on Maitai BB, Spectra Physics Inc.) operated @400 KHz repetition rate. Fluorescence emitted by the sample was collected by the same objective lens, filtered from laser excitation by the dichroic mirror (Semrock, DiO-805) and a combination of band-pass filters (1010 short pass with 935/130, Semrock), spatially filtered by a pinhole (75 μm) and detected by a single photon counting avalanche photodiode (τ-SPAD, PicoQuant). The signal generated onto the τ-SPAD was fed into a time analyzer (PicoHarp 300, PicoQuant) and detected in time-tag time-resolved (TTTR) mode. FLIM images, local probing of isolated QDs, data analysis, all was performed with the Symphotime 5.32 software (Picoquant) and BIFL-DA

(Scientific Software Technology Center). Details of PL lifetime and blinking analysis are given in supplementary information.

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