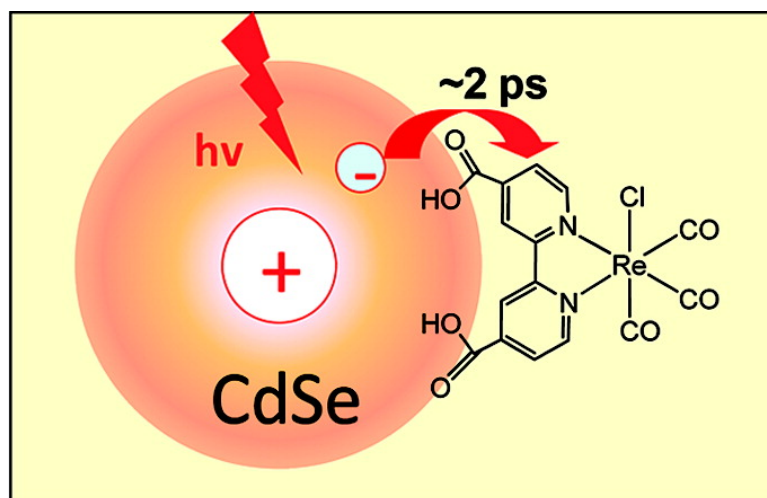


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## Photoinduced Ultrafast Electron Transfer from CdSe Quantum Dots to Re-bipyridyl Complexes

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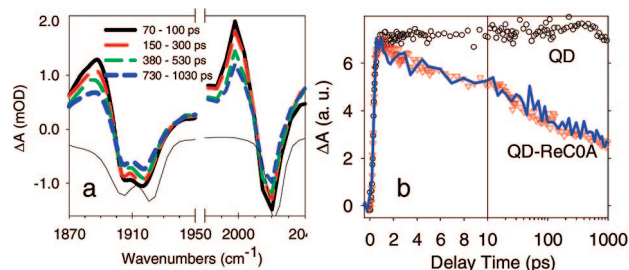
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Charge transfer to and from quantum dots (QDs) is of intense interest because of its important roles in QD-based devices, such as solar cells and light emitting diodes.<sup>1</sup> Recent reports of multiple exciton generation (MEG) by one absorbed photon in some QDs<sup>2</sup> offer an exciting possibility to improve the efficiency of QD-based solar cells dramatically.<sup>3</sup> However, the application of the MEG process requires ultrafast exciton dissociation by charge transfer to electron donors and acceptors before the exciton–exciton annihilation process, which occurs on the 10s to 100s ps time scale.<sup>4</sup> While there have been a few reports of ultrafast exciton (bound electron–hole pair) dissociation in QDs by electron transfer (ET) or by hole transfer to adsorbed acceptors, the factors that control the pathways and rates of charge transfer remain poorly understood.<sup>5–8</sup> Here, we report the exciton dissociation dynamics of CdSe QDs adsorbed with Re(CO)<sub>3</sub>Cl(dcbpy) (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) (ReC0A). We showed that the excitons in CdSe dissociated by ET to ReC0A complex. Furthermore, ET rate could be controlled by varying the size of QDs, and an exciton dissociation half-time of ~2.3 ps has been achieved, suggesting the possibility of separating multiple electron–hole pairs generated by the MEG process using QD-based donor–acceptor complexes.

The absorption spectra of CdSe QDs in heptane prepared by established literature procedure are shown in Figure S1a.<sup>9</sup> For convenience, we label these QDs by their first exciton peak positions, and CdSe(435nm), CdSe(477nm), and CdSe(505nm) have estimated diameters of 1.8, 2.2, and 2.4 nm, respectively.<sup>9</sup> The fluorescence quantum yields of these QDs are ~8–12%. ReC0A was synthesized by previously reported procedures.<sup>10</sup> QD–ReC0A assemblies were prepared by adding ReC0A to QD heptane solution followed by sonication and filtration to remove undissolved ReC0A. The number of adsorbed ReC0A per QD was controlled by varying the amount of added ReC0A and was determined by the measured absorbance and extinction coefficients of the first exciton band of CdSe (Figure S1a) and CO stretching band of ReC0A at 2020 cm<sup>-1</sup> (Figure S1b).<sup>9</sup> All dissolved ReC0A molecules are believed to be bound with CdSe because they are not soluble in heptane, and a controlled sample without QDs showed no measurable peaks in the CO stretching band region.

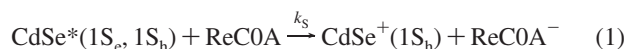
The fluorescence decay of CdSe (505nm) (recorded at 510 nm after 400 nm excitation) with different numbers of adsorbed ReC0A are shown in Figure S1c. The presence of ReC0A reduced the exciton lifetime in QD, and the quenching rate increased with the number of adsorbed molecules. Exciton quenching could occur by energy, electron, or hole transfer to the adsorbate. Energy transfer is unlikely in this system because



**Figure 1.** (a) Transient IR spectra of CdSe (435nm)–ReC0A assemblies in the CO stretching mode region at indicated delay times after 400 nm excitation. Also shown is the FTIR spectrum of the adsorbed ReC0A (thin solid line, inverted for better comparison). (b) Comparison of 1S electron decay kinetics probed by intraband transition at 2070 cm<sup>-1</sup> for CdSe (505nm) with (triangles) and without (circles) adsorbed ReC0A after 500 nm excitation. The bleach recovery kinetics (inverted and scaled for comparison) of exciton interband transition of the same CdSe–ReC0A sample after 400 nm excitation is shown as a solid line.

of the lack of spectral overlap of QD emission with the absorption of ReC0A. ET and hole transfer processes lead to different products that can be distinguished by transient absorption spectroscopy.

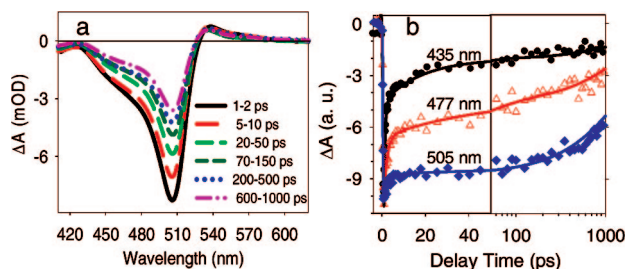
Figure 1a shows the transient IR spectra of CdSe (435nm)–ReC0A assemblies measured with a probe centered at 1900 and 2010 cm<sup>-1</sup>. The spectra show a decrease (bleach) of ReC0A ground state CO bands (at 1904, 1918, and 2020 cm<sup>-1</sup>) and formation of two new positive features (at ~1886 and 1998 cm<sup>-1</sup>). These features are red-shifted by ~20 cm<sup>-1</sup> from the CO stretching bands of the ground state and have been assigned to the reduced form (anion) of ReC0A molecules.<sup>11</sup> They cannot be attributed to excited or oxidized ReC0A, whose CO stretch bands are blue-shifted from the neutral ground state by ~40 and ~80 cm<sup>-1</sup>, respectively.<sup>10</sup> Similar transient IR features were observed in QD–ReC0A complexes of CdSe (477nm) and CdSe (505nm). These results suggest that excitons in CdSe dissociate by ET to ReC0A:



The ET process can also be measured by spectral changes in the QDs. The presence of 1S electrons in QDs results in a strong 1S(e)→1P(e) intraband transition in the mid-IR region, whose energy decreases with increasing size of QDs due to the quantum confinement effect.<sup>12</sup> For this measurement, we used CdSe (505nm), whose intraband absorption falls in the 2000 cm<sup>-1</sup> region. As shown in Figure 1b, optical excitation of QDs (without ReC0A) led to instantaneous formation of electron intraband absorption at 2070 cm<sup>-1</sup> that remained constant in the 1 ns delay time window due to the long-lived (>>1 ns) exciton state. In CdSe–ReC0A, the electron absorption signal

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**Figure 2.** (a) Transient spectra of CdSe (505nm)–ReCOA at indicated delay times after 400 nm excitation. (b) Comparison of the exciton bleach recovery kinetics of CdSe–ReCOA for three QD sizes.

at this wavelength decayed by  $\sim 60\%$  at 1 ns, consistent with the dissociation of QD excitons by ET to the adsorbates.

The transient visible spectra of CdSe (505nm)–ReCOA complexes measured at indicated delay times after 400 nm excitation are shown in Figure 2a. The transient spectra of CdSe (without ReCOA) measured under the same conditions are shown in Figure S2. These spectra show bleaches of  $1S_{3/2}(h)–1S_{1/2}(e)$  (at 505nm) and  $2S_{3/2}(h)–1S_{1/2}(e)$  (at 450nm) exciton interband transitions, which have been attributed to the filling of the  $1S(e)$  level by the photogenerated exciton.<sup>4</sup> In the absence of adsorbates (Figure S2), these exciton interband bleaches remain constant on the  $<1$  ns time window, indicating long-lived exciton and negligible exciton–exciton annihilation. In contrast, as shown in Figure 2a, in QD–ReCOA complexes, the bleach of exciton bands recovers by  $\sim 60\%$  at 1 ns, also consistent with the ET process shown in eq 1. Furthermore, because both the intraband decay and interband bleach recovery result from the ET process, their kinetics traces should agree with each other. This agreement, shown in Figure 1b, confirms that the exciton bleach recovery can be used to measure the ET kinetics in these QD–ReCOA complexes.

One of the most interesting properties of QDs is their size-dependent confinement energy. We have shown previously that ET rate from CdS QDs to adsorbed rhodamine increases with the number of adsorbates.<sup>6</sup> To investigate the size dependence of ET rate, we compared three CdSe samples of different particle sizes but with the same number of adsorbed ReCOA per QD (shown in Figure S1a,b). ET rate was measured by following the exciton bleach recovery kinetics after 400 nm excitation. As shown in Figure 2b, with the decrease of CdSe size (shorter exciton peak wavelength), the bleach recovery is accelerated, indicating an increase of ET rate from CdSe to ReCOA. The half-recovery time,  $\tau_{1/2}$ , the time when the bleach recovers to 50%, for CdSe (435 nm), CdSe (477 nm), and CdSe (505 nm) are 2.3 ps, 55.5 ps, and  $\sim 1$  ns, respectively.

Nonadiabatic ET rate is given by<sup>13</sup>

$$k = \frac{2\pi}{h} \frac{|H|^2}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(\lambda + \Delta G)^2}{4\lambda k_B T}\right] \quad (2)$$

where  $\Delta G$  is the driving force,  $H$  the electronic coupling strength, and  $\lambda$  the total reorganization energy for ET. For the ET process described in eq 1,  $\Delta G = -e[E^0(QD^+/QD^*) - E^0(A/A^-)]$ , where  $E^0(QD^+/QD^*)$  is the oxidation potential of the exciton in QD and  $E^0(A/A^-)$  is the reduction potential of ReCOA ( $-0.96$  V vs SCE).<sup>14</sup>

The oxidation potentials of excitons in CdSe QDs (CdSe\*) can be estimated according to the model of Brus,<sup>15</sup> in which the QDs are treated as spherical particles with infinite potential barrier. Assuming a flat band potential of valence band at  $+1.0$  V vs SCE and conduction band at  $-0.7$  V vs SCE for bulk

CdSe crystals and electron and hole effective mass of 0.13 and  $0.45 m_0$  ( $m_0$  is the mass of free electron),<sup>16</sup> the estimated exciton oxidation potentials for CdSe QDs with the first exciton bands at 435, 477, and 505 nm are  $-1.55$ ,  $-1.37$ , and  $-1.26$  V (SCE), respectively. The  $\Delta G$  values for ET from these particles are  $-0.59$ ,  $-0.41$ , and  $-0.3$  V, increasing at smaller particle sizes. The observed ET rate increases with the driving force, suggesting that the reaction is in the Marcus normal regime.<sup>13</sup> It is unclear whether the coupling strength is also size-dependent and how it contributes to the observed size-dependent ET rate. The result demonstrates that exciton dissociation rate in QD–acceptor complexes can be changed by orders of magnitude by varying the size of QDs, consistent with previous reports.<sup>6,7c</sup>

It is interesting to compare this finding with a recent report of hole transfer from excited CdSe to Ru-trisbipyridyl complexes.<sup>8</sup> Those Ru complexes have bipyridyl ligands and redox potentials that are similar to ReCOA. The factors that lead to completely different exciton dissociation pathways in these systems remain unclear.

In conclusion, we have shown that, for CdSe QDs with adsorbed ReCOA molecules, the excitons in the QDs dissociate by electron transfer to the adsorbed molecule. The dissociation rate increases with the decreasing sizes of QDs. The exciton dissociation half-time is about 2.3 ps in CdSe QDs with first exciton band at 435 nm. This time is shorter than the exciton–exciton quenching time reported in CdSe QDs, suggesting the possibility of separating multiple excitons before their annihilation process.

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**Supporting Information Available:** Experimental methods and spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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