Competition of Branch-to-core Exciton Localization and Interfacial Electron Transfer in CdSe Tetrapods

Ye Yang, Kaifeng Wu, Zheyuan Chen, Ban-Seok Jeong, and Tianquan Lian.*

Department of Chemistry, Emory University, 1515 Dickey Drive NE, Atlanta, GA, 30322, USA

KEYWORDS: quantum dots, quantum rods, tetrapod, exciton transport, exciton trapping, interfacial electron transfer

ABSTRACT: Quantum confined nanorod heterostructures offer the opportunity to control the energy of electrons and holes by rod diameters and the spatial location of carriers along the long axis through their length. We showed that CdSe tetrapods had a quasi-type II band alignment between the Zinc Blend CdSe quantum dot core and four Wurtzite CdSe nanorod branches and 88% of the excitons generated in the CdSe branches localized to the core with a time constant of 1.01 ± 0.06 ps, driven by the lower conduction band energy in the core. We demonstrated that electron transfer to methylene blue molecules (with an average time constant of 33 ± 8 ps) occurred after the exciton were localized to the core, while ultrafast electron transfer (0.31 ± 0.01 ps) to methyl viologen occurred prior to the localization of the exciton. Thus, the competition of exciton interfacial dissociation and transport along the rod enabled the control of the nature of charge separated states in nanorod-electron acceptor complexes.

Introduction

When the size of nanocrystals is smaller than the exciton Bohr's radius, the motion of electrons become quantum confined.^{1,2} Quantum confined spherical semiconductor nanocrystals, or quantum dots (QDs), are often referred to as artificial atoms because of their atomic-like discrete electronic states.^{3,4} Strong confinement endows these artificial atoms with many unique properties, including tunable absorption spectra,¹ fast interfacial charge transfer,⁵⁻⁸ charge carrier multiplication,⁹⁻¹¹ and hot carrier transfer.^{7,12,13} Although the energies of conduction and valence band edges can be tuned by the size of particles, the tuning range is limited by their bulk band edge position and electron and hole effective masses. Further opportunities for tailoring these properties are afforded by coupling two or more quantum confined materials to fabricate nano-hetero-structures, or artificial molecules.¹⁴⁻²³ For example, compared with single component (or core-only) QDs, the photo-induced electron transfer and back electron transfer rates for core/shell QDs can be more selectively controlled by independently tuning the electronic states of the core and shell.²⁴⁻²⁶ In addition to core/shell QDs, many other types of artificial molecules, such as dot-in-rod nanorods (with a QD seed inside a nanorod) and tetrapods (with a QD core surrounded by four nanorod branches), have been designed to more efficiently harvest sunlight and separate excitons for solar energy conversion.²⁷⁻³²

Due to the delocalized electron and hole wavefunctions and small exciton-exciton interaction energy ($\sim 10-35$ meV),^{33,34} the electronic structure of artificial molecules is not significantly altered in the presence of additional carriers, which enables the excited or charged artificial molecules to continue to function as excellent light absorbers. This property, differing significantly from conventional molecules, is particularly intriguing for applications in solar-to-fuel conversion because these reactions, such as water splitting or CO₂ reduction, require the

accumulation of multiple charges at the catalyst and can greatly benefit from light absorbers that can continue to absorb photons and transport charge carriers to reaction sites in the excited or charge states. Among artificial molecules, heterostructures with branched morphology, such as tetrapods, are of great interest for solar-to-fuel conversion.^{27,30,31} It can be envisioned that the four one dimensional (1D) branches can serve as efficient antenna for light harvesting due to their giant absorption coefficient;^{35,36} and the charge carriers generated in the branch can be transported to and accumulated at the tetrapod core. The latter can be functionalized to incorporate catalysts for multiple electron reduction or oxidation. The design and development of such integrated light harvesting antenna and charge separator complexes requires a fundamental understanding of many competing processes such as exciton/carrier localization and transport, exciton dissociation via interfacial charge transfer, exciton Auger recombination in charged or excited states and finally the effect of Pauli exclusion principle on the sequentially generated charges/excitons.

In this paper, we report a study of rod-to-seed single exciton transport and interfacial electron transfer in CdSe tetrapods (TP) comprised of a quantum dot core in the zinc blend (ZB) structure and four nanorod branches in the wurtzite (WZ) structure. Using pump/probe transient absorption measurement, we showed that 86% of excitons initially generated in the CdSe TP branch was transport to the core ($\tau \sim 1$ ps) and the remaining 14% had electrons in the core conduction band and holes trapped near the core. In the presence of electron acceptors (Methyl viologen, MV^{2+} , Methylene blue, MB^+), excitons can be dissociated efficiently by interfacial electron transfer. However, the nature of the charge-separated states (location of the electron and hole) can differ dramatically depending on the rate of interfacial electron transfer relative to that of exciton transport.

Experimental methods

Synthesis of CdSe tetrapod. The CdSe TP was synthesized following a published procedure with slight modification (see Supporting Information).³⁷⁻³⁹ The difference between conditions for tetrapods and quantum dots (QDs) formations lies in the concentration of precursors: higher monomer concentration favors branched structure (Tetrapods) formation instead of spherical QDs.⁴⁰ In a typical synthesis, 0.06 g Cadmium Oxide (CdO) and 0.5 mL Oleic acid (OA) and 4 mL 1-octadecene (ODE) were heated to 290 °C under argon atmosphere until complete dissolution of CdO. After the temperature was stabilized, a selenium stock solution, containing 0.05 g of Se powder, 1 mL of ODE and 0.2 mL of triobutylphosphine (TBP), were swiftly injected. The reaction was stopped after 4 min by injection of 5 mL ODE solution and removing the heating mantle. The CdSe tetrapods were precipitated out by addition of ethanol followed by centrifuge at 4000 rpm for 10 min. The precipitation processes were repeated for several times. The TEM image (Figure 1A) of the TPs showed that branches were 23.3 ± 2.4 nm in length and 2.4 ± 0.4 nm in diameter.

The as-synthesized TPs had oleate ligands on the surface and were dispersed in chloroform solution for all the spectroscopic studies to be described later. Methyl viologen dichloride (MV^{2+}) and methylene blue chloride (MB^+) were purchased from Sigma-Aldrich and used as received. TP-acceptor complexes were prepared by adding the compounds into TP chloroform solution following by sonication and filtration (to removed un-dissolved molecules).^{26,41,42} Free TP and TP-acceptor solutions were controlled to have the TP concentrations, and these samples were measured under the same conditions in TA studies.

Transient absorption spectroscopy. The transient absorption setup used in this study was based on a regeneratively amplified Ti:Sapphire laser system (Coherent Legend, 800 nm, 150 fs, 2.5 mJ/pulse, 1 KHz repetition rate).^{5,6} Briefly, 400 nm pump pulses were generated by second harmonic generation of the 800 nm fundamental output of the amplified system in a BBO crystal and sent through a synchronized chopper (New Focus 3500) at 500 Hz before focusing onto a 1mm thick cuvette containing the sample. The pump beam diameter at the sample was 250 μm . The visible probe was generated by attenuating and focusing ~ 10 μJ of the 800 nm fundamental pulse into a 2 mm thick sapphire window to produce a white light continuum from 430 to 780 nm. The probe was focused to the sample by an aluminum parabolic mirror. The diameter of the probe at the focal point was 150 μm . After the sample, the probe was detected by a CMOS sensor (1024 pixels) and absorbance changes as a function wavelength and pump/probe delay times were obtained to construct transient spectra and kinetics. All experiments were carried out at room temperature. During data collection, samples were constantly stirred to avoid photo-degradation.

Time resolved photoluminescence. Time resolved photoluminescence (TRPL) was measured *via* time correlated single photon counting (TCSPC). The 800nm pulse with a repetition rate of 80 MHz was generated by a mode-locked Ti:Sapphire laser (Tsunami oscillator pumped by a 10 W Millennia Pro, Spectra-Physics), and its frequency is then doubled by a BBO crystal to obtain 400 nm pump pulse. The emission light was focused into a monochromator (Acton SP2150i, Princeton Instrument) and the output with a selected narrow band of wavelength was detected by a micro-channel-PMT (Hamamatsu R3809U-51), the output of which was amplified and analyzed by a TCSPC board (Becker & Hickel SPC 600). To reach a good signal to noise, the spectral width of the output of the monochromator was chosen as ~ 10 nm.

Photoluminescence emission and excitation. PL and PLE spectra were collected on a FluoroMax 3 spectrofluorimeter. PL spectra were measured at an excitation wavelength of 400 nm. In the PLE measurement, the emission intensity at the peak of emission bands at 616 ± 2 nm were recorded as a function of excitation wavelength.

Figure 1. Morphology, band alignment and optical properties of CdSe Tetrapods (TP). (A) TEM image. (B) Absorption and emission spectra, showing two transitions (T1 and T2) near the band gap. (C) Schematic diagram of the lowest electronic energy levels and exciton transitions. Two lowest conduction band electron states, CB1 and CB2, are mainly localized in core and branch of the TP, respectively. The lowest valence band hole state, VB1, is isoenergetic in the entire nanostructure. Transitions from VB1 to CB1 and CB2 correspond to the two lowest energy transitions T1 and T2 in absorption and emission spectra. Grey dashed lines indicate the band alignment of the bulk ZB and WZ CdSe. (D) Comparison of the PLE (monitored at 616 ± 2 nm) and absorbance ($1-10^{-OD(\lambda)}$) spectra. The PLE spectrum is scaled to match the absorbance spectrum at T1 transition (600-630nm).

Results and discussions

Assignment of exciton transitions in CdSe tetrapod

The absorption spectrum of the sample (Figure 1B) showed two exciton bands (T1 and T2) near the band gap. Best fit by the sum of two Gaussian functions revealed the center positions and widths (full-width at half maxima, FWHM) to be (599 nm, 132 meV) and (571 nm, 82 meV) for T1 and T2 absorption transitions, respectively. The best fit of the emission spectrum gives the corresponding centers and widths of the T1 and T2 emission bands at (616 nm, 132 meV) and (582 nm, 82 meV), respectively. The fitted spectra (Figure S1) and fitting parameters are provided in Supporting Information. The origins of T1 and T2 transitions are discussed in the following paragraph. The broad emission extending from the red side of the T2 emission to the near-IR region is attributed to the radiative recombination between the CB1 electron and trapped hole states.^{43,44}

Previous studies have demonstrated that CdSe TP nanocrystals synthesized according to the procedure used in this work³⁷⁻³⁹ contain a ZB center and four WZ branches.⁴⁵⁻⁴⁷ The conduction band (CB) and valence band (VB) offsets between the bulk WZ and ZB CdSe are 94 and 35 meV, respectively, forming a type II bulk band alignment, as indicated by the dashed line in Figure 1C.⁴⁸ However, due to the stronger quantum confinement in the branches (smaller radius) than in the center, the CB offset is further enlarged, while the VB offset is reduced. According to the effective mass calculation (see Supporting Information), the VB offset of the reported sample is estimated to be ~6 meV. Therefore, at room temperature ($K_bT \sim 26$ meV), the lowest hole state (VB1) of the TP can be considered to be similar throughout the entire nanostructure (indicated

by the solid line in Figure 1C). The lowest electron state (CB1) of the TP is localized in the center due to the large offset (of 129 meV) between this state and the lowest electron state in the branches (CB2). Therefore, the tetrapod can be considered as a quasi-type II heterostructure. This estimated electronic structure is also consistent with theoretical calculation based on semiempirical pseudopotential method.⁴⁹ Thus, as shown in Figure 1c, T1 transition (between CB1 and VB1) is largely localized in the core and T2 transition (between CB2 and VB1) is localized in the branches. The measured Stokes shifts, from the difference of the peak positions of the absorption and emission bands, of T1 (57 meV) and T2 (41 meV) are similar to reported values for nanorods and QDs, respectively, consistent with this assignment.^{26,36,50,51} The difference in the Stokes shifts are believed to result from the details of the valence band level and exciton fine structures, which have been neglected in the simple energy level scheme in Figure 1C and is beyond the scope of this paper. The absorption at T2 transition is ~8 times stronger than that at T1 transition, which can be attributed in part to ~56 times larger volume of the four 1D branches than the core at the center.^{35,36} The difference in their emission intensity is much smaller due to rapid localization of the exciton from the branches (T2) to the core (T1) which is directly probed by the TA study to be discussed below. Comparison of the photoluminescence excitation (PLE) spectrum measured at T1 emission (616 ± 2 nm) and the absorbance spectrum (Figure 1D), indicated that T1 PL quantum yield at T2 excitation was ~ 87% of that at T1 excitation, suggesting that 13% of the excitons generated at the T2 state did not relax to the T1 state.

Single exciton dynamics in CdSe TPs

Figure 2. Single exciton dynamics in CdSe TPs measured with 400 nm excitation. TA spectra of CdSe TPs at (A) short (0-5 ps) and (B) long (10 ps to 1 μ s) delay times. (C) The kinetics of the T1 (dashed black line) and T2 (red solid line) bleach. (D) Photoluminescence (PL) decay kinetics at T1 (PL 630 nm, red solid line), T2 (PL 565 nm, black solid line), and trap state (PL 730 nm, green solid line). These kinetic traces are normalized to 1 at 0.2 ns. Also shown are the instrument response (IRF) (cyan line) and the scaled T1 bleach kinetics (blue circles).

Figure 2A and B show the TA spectra of the sample recorded at 0-5 ps and 10 ps -1 μ s after 400 nm excitation. In this experiment, the intensity of the pump was adjusted to as low as 1.0 nJ/pulse to ensure negligible multiple photon absorption by a single TP. The lack of noticeable contribution of biexciton Auger recombination is evident in the long-lived T1 exciton bleach kinetics shown in Figure 2C, which will be further discussed below. The TA spectra show

distinct transient bleach signals of T2 and T1 absorption bands centered at 569 nm and 599 nm, respectively. The TA spectra, difference absorption spectra between the pumped and un-pumped samples, can be well fit to a model in which the presence of an exciton in the TP (generated by the pump) leads to a peak shift and electron state filling induced amplitude decrease (i.e. bleach) of the exciton absorption bands, following previously described procedures (see Supporting Information, Figure S2).⁵² Similar to other quantum confined CdSe nanomaterials (dots and rods), the bleaches of exciton bands mainly arise from the state filling of CB electron levels with negligible hole contributions. At short delay times (0-5 ps), the recovery of T2 bleach leads to the formation of T1 bleach. This TA spectral evolution suggests that the electron initially populates CB2 level in the branches, consistent with the fact that the branch has much larger absorption coefficient at this excitation wavelength (400 nm), and is subsequently transported to the CB1 level at the TP center. As shown in panel B, TA spectra are dominated by the T1 bleaches after 30ps, indicating the electron has localized to the CB1 states. The derivative-like features at shorter wavelength (450-530nm) can be attributed to the shift of the higher energy transitions caused by the presence of the exciton in the excited TP.

The kinetics of T1 and T2 are shown in Figure 2C. The T1 kinetics was recorded at 610 nm to avoid the spectral overlap with T2 bleach and T2 kinetics was obtained by subtracting the overlapping T1 contribution from the total signal at 569 nm. We simulate the T1 contribution at 569 nm by linearly scaling the T1 kinetics at 610 nm with a scaling factor determined from the relative signal amplitude between 569 nm and 610 nm of pure T1 bleach at long delay (~10 ns). The decay of T2 bleach and the growth of T1 bleach can be well fit globally by a bi-exponential function (86.3% at 1.02 ± 0.08 ps and 13.7% at 11.1 ± 2.1 ps) with an amplitude-weighted average

time constant of 2.4 ± 0.4 ps, which confirms that the formation of T1 bleach is caused the electron relaxation from CB2 states in the branches to the CB1 level in the core.

The PLE result (Figure 1D) suggests that 87% of excitons move from the branch to core. Comparison of the PLE and transient kinetics suggests that the fast component of T2 bleach recovery and T1 formation (with a time constant of ~ 1.0 ps and $\sim 86\%$ of the amplitude) can be assigned to the exciton localization process. Although we don't have direct spectroscopic evidence to discern whether the electron and hole move together as an exciton or independently as free carriers, previous studies of the exciton dynamics in 1D nanostructures have demonstrated that electron-hole pairs are strongly bound due to the 1D dielectric confinement effect^{50,53,54} and they transported as excitons in similar quantum confined structures.⁵⁵ In CdSe TPs, because of the large 1D exciton binding energy in the branch (~ 350 mV, see the Supporting Information) and the small CB offset (~ 129 meV), it is most likely that the e-h pair move together as an exciton and the measured electron localization rate reflects the exciton localization from the branch to the core and the localization rate is limited by the motion of the hole due to its much heavier mass. The slower component (with a time constant of ~ 11 ps and $\sim 14\%$ of the amplitude) was observed in TA and did not lead to PL, suggesting that only the electron was transferred from the rod to the core while the hole remained in the rod and/or in some trapped states. Although the nature of the hole trap is not clear, it likely located at the core or core/rod interface to provide strong electron-hole binding energy. These branch-to-core exciton and electron localization processes are depicted in Figure 3. Similar exciton localization dynamics have been observed in 1D dot-in-rod nanorods, such as CdSe/CdS^{50,56,57} and ZnSe/CdS⁵⁸.

Figure 3. Schematic illustration of the branch-to-core exciton and electron transport/localization in CdSe TPs.

The lifetime of the electrons at the CdSe core can be followed by the kinetics of T1 bleach recovery. The recovery kinetics can be fit to three-exponential decay function, from which the amplitude-weighted average decay time was determined to be 62.3 ± 8.1 ns (Table S2). The TA signal is only sensitive to the dynamics of the CB electrons. We also measured the time-resolved photoluminescence (PL) decay, which depends on both the electron and hole dynamics in the CdSe TPs. The PL kinetics of T1 (PL 565nm), T2 (PL 630 nm) and trap state (PL 730 nm) emissions are normalized and compared in Figure 2D. Also plotted are the scaled T1 bleach kinetics (from 0.1 to 10 ns) and the instrument response function (IRF) for the PL decay measurement. The amplitude of the T1 bleach at 0.1 ns was normalized to 1 for easier comparison. As indicated by the comparison with IRF, the fast decay component of the T2 PL cannot be well resolved due to the limited time resolution, which is consistent with the fast (~ 2.4 ps) electron transport from CB2 to CB1. The slow tail of the T2 PL kinetics agrees well with the

T1 PL decay and can be attributed to the T1 PL due to the overlap of these two PL emissions. Despite the short (2.4 ps) T2 lifetime, T2 emission can still be observed (Figure 1C), which is consistent with the fast radiative decay rate of 1-D excitons in the branch, similar to those reported in nanorods.^{53,59,60} The T1 PL decays much faster than the T1 bleach recovery kinetics. Because T1 exciton bleach recovery reflects the decay of CB electron and T1 PL decay is affected by both electron and hole decay, this result suggests that T1 PL decay is dominated by hole trapping, presumably to the trap states at/near the center. Multiple exponential fits of the T1 PL decay kinetics revealed an amplitude-weighted average hole trapping time at the center of 825 ± 52 ps (Table S2). The hole trapping time determined in current work is consistent with that in large sized core-only CdSe QDs,⁶¹ although the reported hole trapping times range from 0.1 ps to 10 ns.⁶¹⁻⁶⁵ T1 bleach recovery time appears to be on similar time scale as the PL decay of the trap state emission (Figure 2d), suggesting that the lifetime of the electron in CB1 states is primarily determined by its recombination with the trapped hole. Unfortunately, a more quantitative comparison of these kinetics was not possible because trap PL decay was not accurately measured due to a limited delay time window (only to 12 ns).

Competition of electron transfer and exciton localization in CdSe-MB⁺ and in CdSe-MV²⁺

Figure 4. (A) Transient absorption spectra CdSe TP-MB⁺ complexes at indicated delay times measured with 400 nm excitation. (B) Comparison of TA spectra between CdSe TP-MB⁺ and CdSe TP at the same delay time. (C). Comparison of T1 and T2 bleach kinetics in CdSe TP-MB⁺ and CdSe TP. (D) The kinetics of MB⁺ ground state bleach.

Previous studies showed that ET from CdSe QDs to MB⁺ complexes occurs on the a few ps time scale, while ET to MV²⁺ can occur on the 100 fs time scale.^{26,37} Thus these systems offer an opportunity to examine the effect of the rod-to-seed exciton transport dynamics on interfacial charge transfer in CdSe TPs. Figure 4A shows the TA spectra of TP-MB⁺ at indicated delay times after 400 nm excitation. Similar to the spectral evolution for free TPs, at early delay times (< 5ps), the formation of T1 bleach was accompanied by the recovery of the T2 bleach. In

addition to T1 and T2 bleaches, MB^+ ground state bleach (GSB) was also formed at 667 nm, which is more clearly shown in Figure 3B. This feature provides direct evidence of the photoreduction of MB^+ . Comparison of CdSe TP- MB^+ and CdSe TP (Figure 4B) showed the same T2 bleach recovery kinetics, indicating that the branch to core charge localization is not affected by the electron acceptor. The T1 kinetics of the complex and free TPs were consistent at the formation phase ($< 2\text{ps}$), but differed at later delay times. In contrast to the long-lived T1 bleach for free TPs, the T1 bleach in the TP- MB^+ complexes decayed by over 50% within 1 ns. The T1 bleach recovery led to a corresponding growth of the MB^+ GSB, indicating the interfacial electron transfer from CB1 state to MB^+ . The MB^+ GSB kinetics (Figure 3D) was well fit by a bi-exponential function to reveal an electron transfer time constant of $33 \pm 8\text{ ps}$. In TP- MB^+ complexes, the electron localization rate was over 10 times faster than interfacial electron transfer, suggesting that majority of excitons created in the branches localized to core before exciton dissociation. Dissociation of core-localized excitons generated charge-separated states with holes in the core and electrons transferred to MB^+ adsorbed at or near the core (Figure 5a).

Figure 5. Competition of exciton branch-to-core localization and interfacial dissociation in CdSe tetrapod– electron acceptor complexes with a) MB^+ and b) MV^{2+} .

Figure 6. (A) Transient absorption spectra of CdSe TP-MV²⁺ complexes at indicated delays measured with 400 nm excitation. (B) Comparison of TA spectra between CdSe TP-MV²⁺ and CdSe TP at the same delay time (3 ps). The CdSe TP spectrum is linearly scaled ($\times 0.075$) for better comparison. (C) Kinetics of the T2 and MV radical absorption. The x-axis is in linear scale before 10 ps and in logarithm scale after 10 ps. The black lines are the fit.

The TA spectra of TP-MV²⁺ complexes at indicated delay times after 400 nm excitation are shown in Figure 6A and 6B. The TP-MV²⁺ TA spectra do not show the formation of T₁ bleach that was observed in free TPs. Instead, the TA spectra at 3 ps show derivative like features near T₁ and T₂ exciton bands (with the negative features blue shifted from exciton transitions) and a broad absorption band of the reduced MV²⁺ (i.e. MV^{•+}). The derivative-like features have been

attributed to shift of exaction bands caused by holes (produced by electron transfer to MV^{2+}).²⁶ These features are consistent with a ultrafast charge transfer from the TP to MV^{2+} prior to the rod-to-core exciton localization process with $MV^{+·}$ radical formed on the rod and hole remains in rod. The latter explain the much larger derivative feature of the T2 transition than T1 transition. The kinetics of the bleach signal at 559 nm and the $MV^{+·}$ absorption kinetics are shown in Figure 6C. The recovery of bleach was well fit by a tri-exponential function, and the best fit suggested a charge transfer time constant of 0.31 ± 0.01 ps (decay of electron state filling signal) and an averaged charge recombination time constant of 2.3 ± 0.1 ns (decay of Stark effect signal). The $MV^{+·}$ absorption kinetics was also fit by a tri-exponential function and revealed similar radical growth (or charge separation) time constant of 0.25 ± 0.02 ps and decay (recombination) time constant of 1.9 ± 0.1 ns. The charge separation time was faster than the exciton localization process, suggesting electron transfer from TP branches to adsorbed MV^{2+} prior to exciton localization to the core (Figure 5b). This process generated charge separated states with holes remained on the branch as indicated by the larger Stark effect signal in the T1 exciton band.

Summary

The dynamics of exciton transport and dissociation in CdSe TPs with quasi-type II core/branch band alignment have been investigated. In free TPs, excitons generated in the CdSe branches was shown to transport efficiently to the core, driven by the offset of their conduction positions. 86% of the excitons moved to core with a time constant of 1.02 ± 0.08 ps, while remaining 14% of the electrons moved to the core conduction band with holes likely trapped near the core. In the presence of electron acceptors, excitons can be efficiently dissociated,

however, the nature of charge separated state was affected by the competition of exciton dissociation with transport. With MB^+ electron acceptors, the electron transfer (with time constant of 33 ± 8 ps) occurred after the excitons were localized to the core, generating charge separated states with holes in the core and electrons on MB^+ molecules (presumably adsorbed on the core). With MV^{2+} electron acceptors, ultrafast electron transfer (0.31 ± 0.01 ps) occurred prior to the localization of the exciton, producing charge separated states with electrons transferred to acceptor molecules adsorbed on the rod and holes on the rod. Thus, the mobility of excitons and carriers along the branch in tetrapods offers the opportunity to control the location of electrons and holes in charge-separated states.

ACKNOWLEDGMENT

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Solar Photochemistry Program under Award Number (DE-FG02-12ER16347)

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