

Microsecond Charge Recombination Lifetimes in Complexes of CdS Quantum Dots and Organic Hole Acceptors Enabled by Hole-Hopping within the Ligand Shell

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Abstract: Transient absorption (TA) and NMR measurements were used to demonstrate that carrier mobility within the ligand shell contributes to photoinduced charge transfer dynamics between a bis(diarylamino)biphenyl (TPD)-based thiol and cadmium sulfide quantum dots.

This paper describes the observation of a long-lived charge-separated state formed by photoexcitation of N-[4-(12-Mercaptobutyloxy)phenyl]-N'-phenyl-N,N'-di(m-tolyl)-biphenyl-4,4'-diamine (hereafter referred to as "TPD-C4-SH") and subsequent electron transfer to a CdS quantum dot (QD) to which the molecule is adsorbed through a thiolate linkage. TPD is a widely used hole-transport material within organic electronic devices, and is therefore an ideal model system for studying carrier motion within the ligand adlayer [1]. The lifetime of the charge separated state of this system increases as the density of TPD-C4-thiolate molecules on the surface of the QD decreases within mixed monolayers of TPD-C4-thiolate and electrically insulating oleate ligands.

In order to quantify the relationship between surface coverage of TPD-C4-SH on the QDs and the rate of charge recombination in CdS QD-TPD donor-acceptor systems, we determined the number of TPD-C4-SH and oleate bound within the mixed monolayers on the QDs within each sample. We prepared samples of oleate-capped CdS (D = 1.8 nm) treated with 3 eq, 8, eq and 13 eq TPD-C4-SH, and compared ¹H-NMR signal intensity per proton of the downfield-most aromatic peak (~7.3 ppm) to the vinyl region of free oleic acid. For each sample, the measured number of bound TPD-C4-SH and the measured number of displaced oleic acid were within ~10% of one another; this result suggests that each TPD-C4-SH displaces a single oleate and the total ligand count (~30) is conserved during the ligand exchange. The ¹H-NMR spectrum of each mixed monolayer also indicates that 5 - 6% of TPD-C4-SH present in each sample is free (unbound) [2].

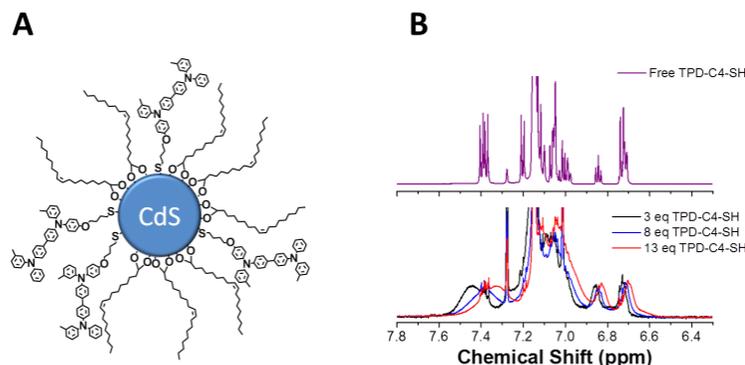


Figure 1. **A)** TPD-C4-SH molecules conjugated to CdS QDs. Samples were prepared by treating QDs capped with oleate ligands with a solution of TPD-C4-SH. **B)** Comparison of the aromatic region of ¹H-NMR spectrum of free TPD-C4-SH in d₆-benzene (purple, top) with ¹H-NMR of CdS QDs treated with 3 eq (black), 8 eq (blue), and 13 eq (red) of TPD-C4-thiol (bottom). Broadened peaks at ~7.4 ppm, 7.1 ppm, 6.85 ppm and 6.7 ppm correspond to surface-bound TPD-C4-thiolate. The sharp signals at 7.11 ppm, 7.3 ppm, and 7.05 ppm correspond to d₆-benzene. The remaining sharp peaks (for example, ~7.4 ppm) correspond to free TPD-C4-SH (~5-6% total population).

We measured the transient absorption (TA) spectrum of CdS QDs treated with 3, 8, and 13 TPD-C4-SH ligands per QD in d₆-benzene. We prepared the TA samples by simply diluting the NMR samples. Selective excitation of the QD-TPD complexes at 388 nm results in the transfer of an electron from TPD to the QD to form the radical cation of TPD (TPD^{•+}), which has a prominent absorption feature centered at ~1450 nm that is narrower than the absorption of ^{1*}TPD [3]. **Figure 2A** shows the growth of the TPD^{•+} feature following photoexcitation of the sample of CdS QDs coated with eight TPD-C4-SH molecules per QD; this growth is concurrent with the decay of the ^{1*}TPD excited state absorption at ~1050 nm. The radical cation feature persists on the microsecond timescale. In order to

obtain the charge separation time constant, τ_{CS} , and the charge recombination time constant, τ_{CR} , we fit the transient kinetics at 1450 nm for the 3, 8, and 13 TPD-C4-SH samples to a sum of two simple exponential functions convoluted with an instrument response function. Charge separation occurs in ~ 150 ps for all three samples. This consistency is unsurprising given that for each sample, we adjusted the pump fluence so that, on average, ~ 0.1 TPD dye was excited per QD. **Figure 2C** shows the recombination dynamics for each TPD-coated CdS QD sample. These dynamics were only adequately fit – that is, the residuals of the fit were symmetric around a center line – with a sum of four exponential components. The fitting parameters for these data sets are summarized in **Table 1**.

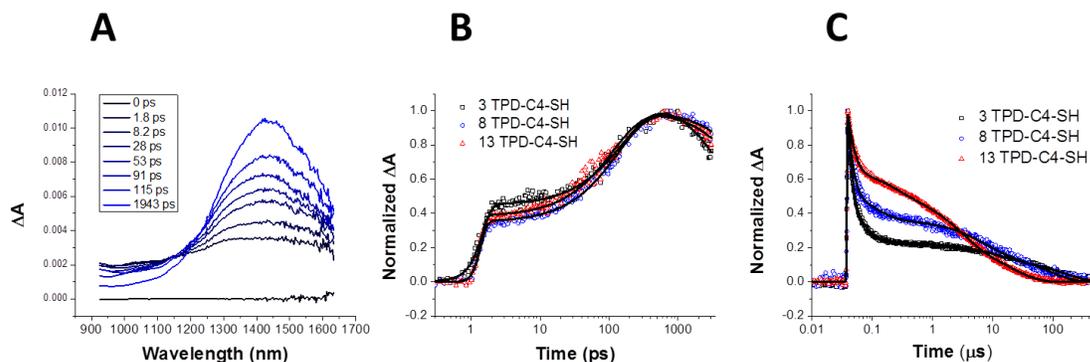


Figure 2. **A**) Near-infrared (NIR) transient absorption spectra of a sample of CdS QDs coated with 8 eq TPD-C4-thiol, in d6-benzene, following 388 nm excitation taken on the picosecond-nanosecond timescale. The sharp feature at 1450 nm corresponds to TPD⁺. **B**) Kinetic traces extracted from picosecond-nanosecond timescale TA experiment for samples of CdS treated with 3 eq TPD-C4-SH (black), 8 eq TPD-C4-SH (red), and 13 eq TPD-C4-SH (blue). Thin black lines correspond to fits of the data. **C**) Kinetic traces on the nanosecond-microsecond timescales probed at 1450 nm for samples described in **B**), where black lines correspond to fits of data to four exponential decays, with fit parameters summarized in Table 1.

Table 1. Fitting Parameters from Fits of Kinetic Traces at 1450 nm, for Samples of CdS QDs Treated with Various Equivalents of TPD-C4-SH.

Sample	A_1	τ_1 (μ s)	A_2	τ_2 (μ s)	A_3	τ_3 (μ s)	A_4	τ_4 (μ s)
3 eq TPD-C4-SH	0.63	0.0076	0.24	0.044	0.09	11.7	0.13	156
8 eq TPD-C4-SH	0.50	0.0093	0.16	0.0905	0.19	6.7	0.17	84
13 eq TPD-C4-SH	0.38	0.011	0.13	0.21	0.30	2.8	0.21	21.6

For each sample, we observe “fast” recombination times on the order of 10-100 ns (τ_1 and τ_2) whose contribution decreases with respect to increasing TPD surface coverage. We attribute these recombination dynamics to TPD⁺ recombining with an electron which is delocalized within the CdS QD. We also observe recombination times on the order of 10-50 microseconds (τ_3 and τ_4). These decay lifetimes shorten with respect to increasing TPD surface coverage while simultaneously increasing in their contribution to the total transient signal (see Table 1, A_3 and A_4). We propose that in some fraction of the nanocrystal-ligand population, the electron transferred from TPD to the CdS QD becomes localized at a trap site. Previous reports have demonstrated that trapped electrons can in some cases persist for hours following charge injection [4]. These trapped electrons recombine with TPD⁺ on the microsecond timescale due to poor wavefunction overlap between the electron and hole, and the observed dependence of this behavior on surface coverage is explained by hole mobility within the ligand shell. As the number of TPD on the surface increases, hole mobility within the ligand adlayer improves, and there is an increased probability of the hole encountering and recombining with the localized electron following charge separation and trapping.

This study lays the groundwork for a quantitative understanding of the relationship between the composition of the ligand shell and the rate of back electron transfer following photoinduced charge separation.

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