The Optical Properties of CdSe Quantum Dot-Bithiophene Complexes
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We studied the optical and electrochemical properties of four model oligomers M3, M5, M9 and M17, Fig. 1. We have performed extensive experimental and theoretical analyses of the M series oligomers in order to determine the oligomers that would be the best charge transfer partners for CdSe quantum dots with respect to spectral overlap and band level alignment. The steady-state absorption and fluorescence spectra are shown in Fig. 2 for the M3, M5, M9, and M17 molecules in toluene solutions. Two main peaks observed in the absorption spectra are assigned to S1 and S2, which correspond to the S1 ← S0 and S2 ← S0 transitions, respectively. Both the large Stokes shift and the vibrational broadening of the fluorescence spectra have contributions from conformational changes between the excited and ground states. The optical bandgap of the materials were determined using the tangential extrapolation through the turning point of the low energy side of the absorption spectrum. Cyclic voltammetry on the M3 and M9 oligomers yielded redox potentials that formed the desired type-II junction with the valence and conduction band of CdSe QDs. M3 provides a bigger driving force for CT, and a more complementary absorption spectrum for CdSe than does M9. We therefore initially chose M3 as a starting point studying the QD-oligomer interaction.

Fig. 1. M(2n+1). For M3, n = 1, for M5, n = 2, etc.

Fig. 2 Absorption (solid line) and emission spectra (dashed line) of the M3-M17 oligomers.

Fig. 2 shows the absorption (top) and emission (bottom) spectra of several solutions of 4.1 nm CdSe quantum dots and M3 in DCM. It is assumed that M3 is physisorbed to CdSe (if interacting at all) because M3 has no metal-coordinating site. A roughly 10 percent decrease in the emission of the CdSe quantum dots is observed. To better define the system, acid-terminated M oligomers are desirable. Since this is a complicated synthesis, we first synthesized the hexylthiophene monomer and dimer with a phosphonic acid linker to perform initial thiophene/CdSe binding studies. The absorption of the phosphonic acid terminated monomer (1PA) is red-shifted from the spectrum of the unsubstituted thiophene monomer, indicating some conjugation through the linker.

Fig. 4 shows PL spectra of QD-1PA mixtures. As 1PA is added to a constant concentration of QDs, the emission of the QDs decreases, but the mechanism of this quenching is unclear. Similar results were obtained for the bithiophene moiety, and several redshifted peaks were also observed, which indicates the quantum dots are being etched by the

Fig. 3 Absorption and emission spectra of M3, CdSe, and a mixed solution in dichloroethane.
phosponic acid group. We therefore studied the binding of QDs with the 3-thiophene acetic acid (3-TAA) monomer. As the concentration of TAA increases, the QD emission first increases as a result of enhanced surface passivation, and then decreases as the surface becomes etched. Our preliminary studies determined that the phosphonic acids are too strong of binders (they tear Cd ions from the surface), so we are synthesizing the carboxylic acid derivatives of the model compounds and M oligomers.

We have also measured the excited state lifetimes of the M oligomers using fluorescence upconversion, and calculated the effects of acid substituents on the orbital energies of the oligomers using AM1 semi-empirical methods. We will continue to optimize the binding chemistry between the model compounds and CdSe, and then synthesize the M series with that binding chemistry. Transient absorption experiments will then yield the rates of charge separation and recombination for the QD-oligomer complexes.