

1. Cadmium Sulfide Quantum Dots, Synthesis, Characterization and Photoluminescence Quenching with Poly[3-hexylthiophene]

1.1 Quantum Dots Synthesis and Characterization

Cadmium sulfide quantum dots were synthesized from cadmium oxide, oleic acid and elemental sulfur in 1-octadecene at 250 °C following a procedure established by Peng *et al.* [REF: W. W. Yu and X. Peng; *Angew. Chem. Int. Ed.*, 2002, 41(13), 2368-2371]. The oleic acid coated nanocrystals were characterized by their UV-Vis and photoluminescence (PL) emission spectra. The size of the nanocrystals was determined using relationship described in the literature by Peng *et al.* between the first absorbance peak position and the size [REF: W. W. Yu, L. Qu, W. Guo and X. Peng; *Chem. Mater.*, 2003, 15(14), 2854-2860]. Four aliquots were taken from the reaction mixture at different time intervals and cooled down rapidly to quench the crystal growth resulting in a narrow particle size distribution.

These quantum dots represent a comparative example to the SILAR grown case. In the past we used transient absorbance spectroscopy and photoluminescence spectroscopy to show that the SILAR grown CdS does indeed transfer its excited state electron to the TiO₂. This electron transfer event is a fundamental step towards an efficient cell (via charge separation). In the near future we will investigate how the above prepared colloidal quantum dots behave on TiO₂. By comparing and contrasting the two quantum dot systems we will be able to draw conclusions as to how dot morphology and growth conditions affect the ability to effectively sensitize TiO₂ to the solar spectrum.

1.2 PL Quenching with Regioregular Poly[3-hexylthiophene]

Quenching of the quantum dots photoluminescence is indicative of charge transfer from the excited dot to the quenching media. We performed solution PL quenching of CdS dots with regioregular poly[3-hexylthiophene] (P3HT).

The experiment was performed at room temperature (about 25 °C) under ambient pressure in toluene or chloroform, the excitation wavelength is 290 nm and the emission spectrum is collected between 310 and 450 nm. Both the quantum dots and the polymer solutions were prepared in the same solvent, under ambient conditions (in air, at room temperature and at ambient pressure) and were not degassed or purged with inert gas.

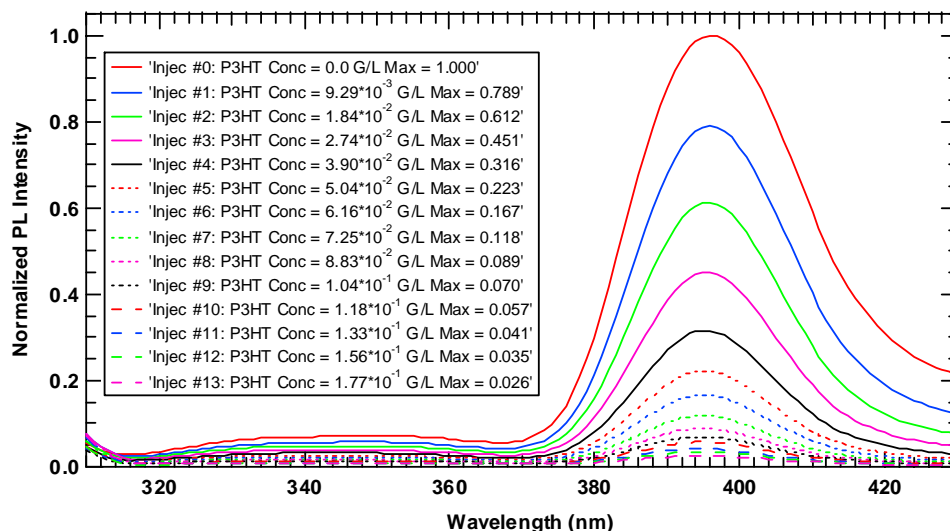


Figure 1: PL spectra of a CdS dots solution (size = 2.80 nm) in toluene after sequential additions of P3HT in toluene (excitation at 290 nm).

The titration is performed with the sequential addition of a 1 g/L solution of P3HT in toluene. Each addition is kept small (between 5 to 15 μ L) to minimize dilution effects. The mixture is thoroughly mixed and allowed to equilibrate for a 3 minutes period prior to recording the mixture PL spectrum. The each spectrum was corrected for dilution and normalized with respect to the original CdS concentration. A typical titration is shown in Figure 1 and Figure 2 shows the PL decay data for this titration. A series of four measurements have been completed to date and are summarized in Table 1. All four conditions yielded a similar quasi-exponential decay of the PL intensity with respect to the polymer concentration as seen in Figure 2.

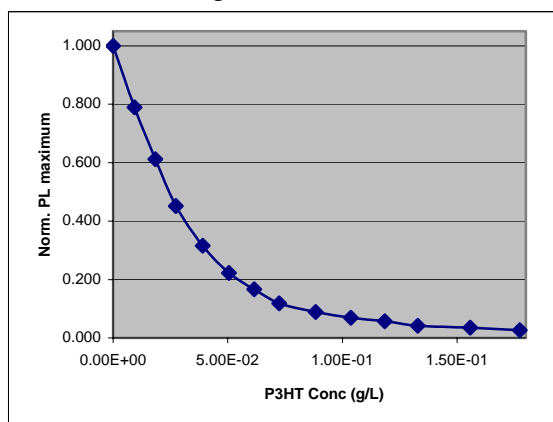


Figure 2: CdS dots (2.80 nm in toluene) PL intensity vs. P3HT concentration.

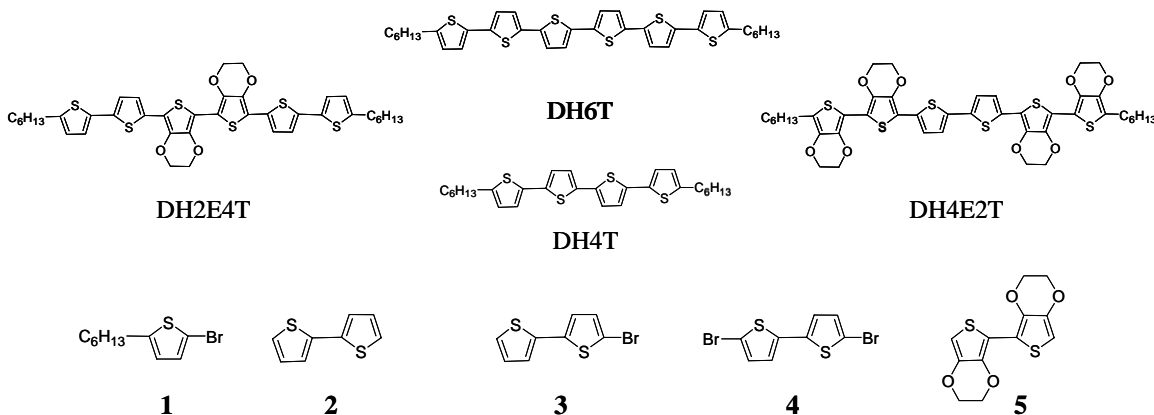
Table 1: Summary of the CdS quantum dots PL quenching experiments

Experiment	Surface Ligand	Dot Diameter	Solvent	Polymer
1	Oleic acid	2.80 nm	Toluene	P3HT
2	Oleic acid	2.38 nm	Toluene	P3HT
3	Oleic acid	2.80 nm	Chloroform	P3HT
4	Oleic acid	2.38 nm	Chloroform	P3HT

This PL quenching experiment provides us with good evidence that the quantum dots will be able to transfer their excited state hole to the solid-state hole conductor. This establishes that the proposed cell configuration is a viable candidate for solar energy conversion. The quantum dots absorb the solar photons (charge generation), the electron is transferred to the TiO₂ and the hole potentially can transfer to the polymer (charge separation). Although much work still needs to be done to fully realize a good cell, these initial results are quite promising.

2. Synthesis of Thiophene-Based Oligomers for Hole-Transport Material

Three six rings thiophene-based oligomers were selected as synthetic targets because of their electronic and physico-chemical properties. DH6T was chosen as it is a very well known conducting materials with high carrier mobilities as demonstrated in the literature. The two other oligomers were designed in order to investigate different band-gap organic electronic materials.



Oligomer DH6T has been prepared experiments with this compound have begun. The synthesis of compounds DH2E4T and DH4E2T is ongoing. Several necessary precursors have been prepared, including 2-bromo-5-hexylthiophene (**1**), bithiophene (**2**), 2-bromobithiophene (**3**), 2,5-dibromobithiophene (**4**), and bis(EDOT) (**5**). In addition, the four ring dihexylquaterthiophene (DH4T) as also been prepared as comparison with DH6T.