**Supporting Information: Reversible Surface Electronic Traps in PbS Quantum Dot Solids Induced by an Order-Disorder Phase Transition in Capping Molecules**

Cory A. Nelson, X.-Y. Zhu*

## Quantum Dot Synthesis

We synthesized PbS colloidal QDs using the technique of Hines et al.[1] Lead oxide (0.3 g), oleic acid (3.58 g) and 1-octadecene (3.15 g) were combined in a three neck flask. The solution was heated to 110 °C under vacuum (<25 mtorr) until it was optically clear. Before injection the 3-neck flask was backfilled with $N_2$, the temperature was raised to 115 °C and a solution of Bis(trimethylsilyl) sulfide (167 µL) in 1-octadecene (6.312 mL) (prepared in a $N_2$ filled glove box) was injected into the three neck flask. The resulting solution was immediately cooled and transferred to a precipitation solution of methanol:butanol:ethanol (1:1:2). QDs were precipitated twice more and stored in a $N_2$ glove box in hexane in the dark until use. Particle size and concentration were determined using Moreels et al.[2] Size distribution was calculated using the HWHM of the absorption spectrum.

## Sample Preparation

*Solution samples*

For solution fluorescence ligands were exchanged in solution by adding 500 µL of 30 mM monothiol in chloroform to 50 uL of quantum dots in hexane. Treated CQDs (100 µL ) were placed into a quartz cuvette, dried under vacuum, and resuspended in 2 mL tetrachloroethylene. Cuvettes were sealed in a $N_2$ glove box before removal for fluorescence measurements.

*Film Samples*

Film samples were prepared by dip coating a 1x1 cm single crystal of alumina (MTI) in a solution of 143 µM PbS QDs in hexane. The withdrawal speed was set to 5 mm/s which produced a film of roughly 30 nm (approximately 6 layers) of QDs. These films were treated in 100 mM solutions of thiol, dithiol or amine in acetonitrile for 1 min to completely remove oleic

* To whom correspondence should be addressed. E-mail: zhu@cm.utexas.edu

acid (OA) from QD surfaces, as verified in FTIR spectroscopy.[3] Treated QD thin film samples were subsequently immersed in pure ACN for 1 min to remove any unbound ligands from the film. Samples were transferred without exposure to air to a sealed cryostat. All measurements were carried out under vacuum (approx. $10^{-4}$ torr).

**Fluorescence Measurements**

*Solution Fluorescence*

Solution fluorescence was taken on a Fluorolog -3 (Horiba) equipped with a NIR-PMT (Hamamatsu). Excitation wavelength was 482 nm using a mercury arc lamp.

*Film Fluorescence*

The response of the PMT detector on the Fluorolog cuts off near the wavelength range of interest. In order to get a full spectrum of our films we built a fluorimeter equipped with a thermoelectrically cooled PbS detector (Electro-Optical Systems). Samples were excited with a green HeNe (excitation wavelength of 543 nm) at a laser intensity of roughly 13 mW $cm^{-2}$. Fluorescence was collected and passed through an 800nm long wave pass filter to remove residual 543 nm light and dispersed in a monochromator (Acton sp-2300i).

**Absorption Measurements**

Near infrared measurements were taken on a modified FTIR (Thermo Fisher) equipped with a liquid nitrogen mercury cadmium telluride detector. All measurements were taken in a nitrogen filled glovebox. Samples were prepared by dip coating as described above on a single crystal $TiO_2$ substrate. The ends of the TiO2 were polished at a 45 degree angle and served as the waveguide for the film absorption experiments.

In films of QDs ligand exchanges cause the thin films to contract, shortening the inter QD distance. This increases the local dielectric environment experienced by a QD which is observed experimentally as a redshift in the absorbance spectra. Ligand exchanges on lead sulfide QD films are shown in figure S1 and display this behavior. Ligand exchanges with alkanethiols and

dithiols show -50±10 meV red-shifts. Given the quality of data, we are not able to unambiguously resolve the small differences in the red-shifts for different thiol molecules.

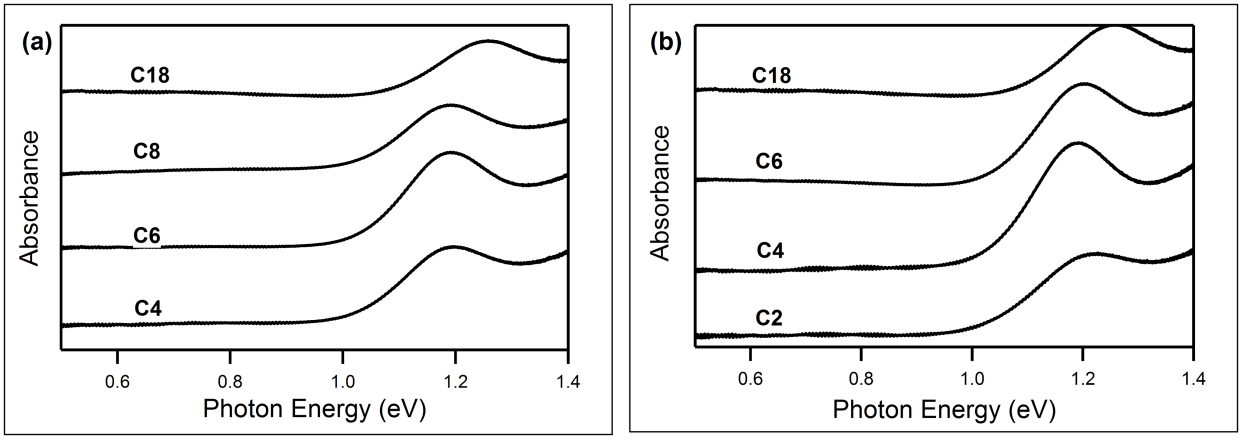


**Figure S1** Absorbance of thin films of PbS treated with monothiols (a) and dithiols (b).

## Fluorescence Redshift

Fluorescence spectra at 77K for oleic acid (OA) capped and various thiol and dithiol capped PbS QD thin films. The shift is near 40 meV for monothiols and varies between 30 and 50 meV for dithiols.

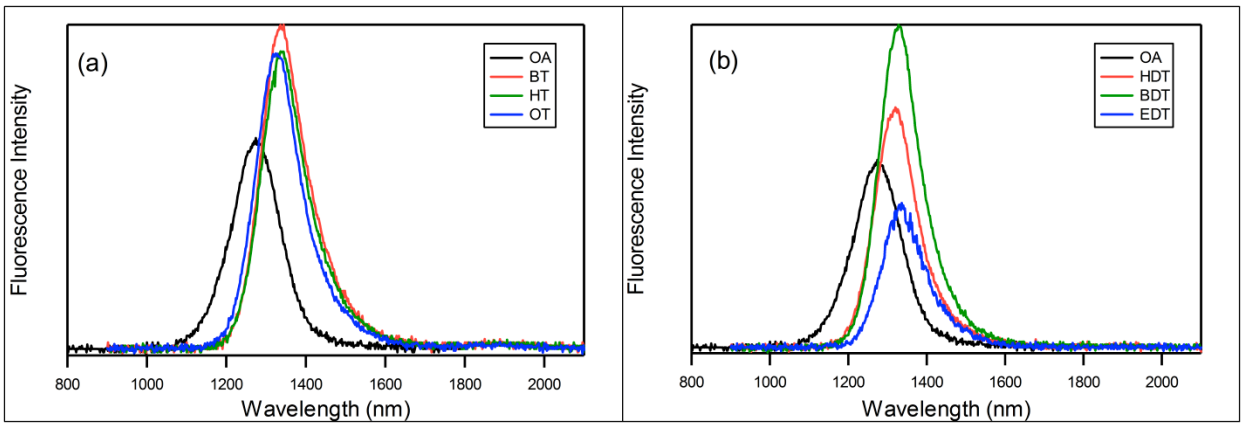


**Figure S2** Fluorescence of alkanethiol (a) and dithiol (b) treatments as compared with oleic acid capped QDs.

## *References*

(1) Hines, M.; Scholes, G. *Advanced Materials* **2003**, *15*, 1844–1849.
(2) Moreels, I.; Lambert, K.; Smeets, D.; De Muynck, D.; Nollet, T.; Martins, J. C.; Vanhaecke, F.; Vantomme, A.; Delerue, C.; Allan, G.; Hens, Z. ACS Nano 2009, 3, 3023–3030.
(3) Wolcott, A.; Doyeux, V.; Nelson, C. A.; Gearba, R. I.; Lei, K. W.; Yager, K. G.; Dolocan, A. D.; Williams, K.; Nguyen, D.; Zhu, X.-Y. *J. Phys. Chem. Lett.* **2011**, *2*, 795-800.