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# Supporting Information

## Eliminating Fermi-Level Pinning in PbS Quantum Dots using Alumina Interfacial Layer

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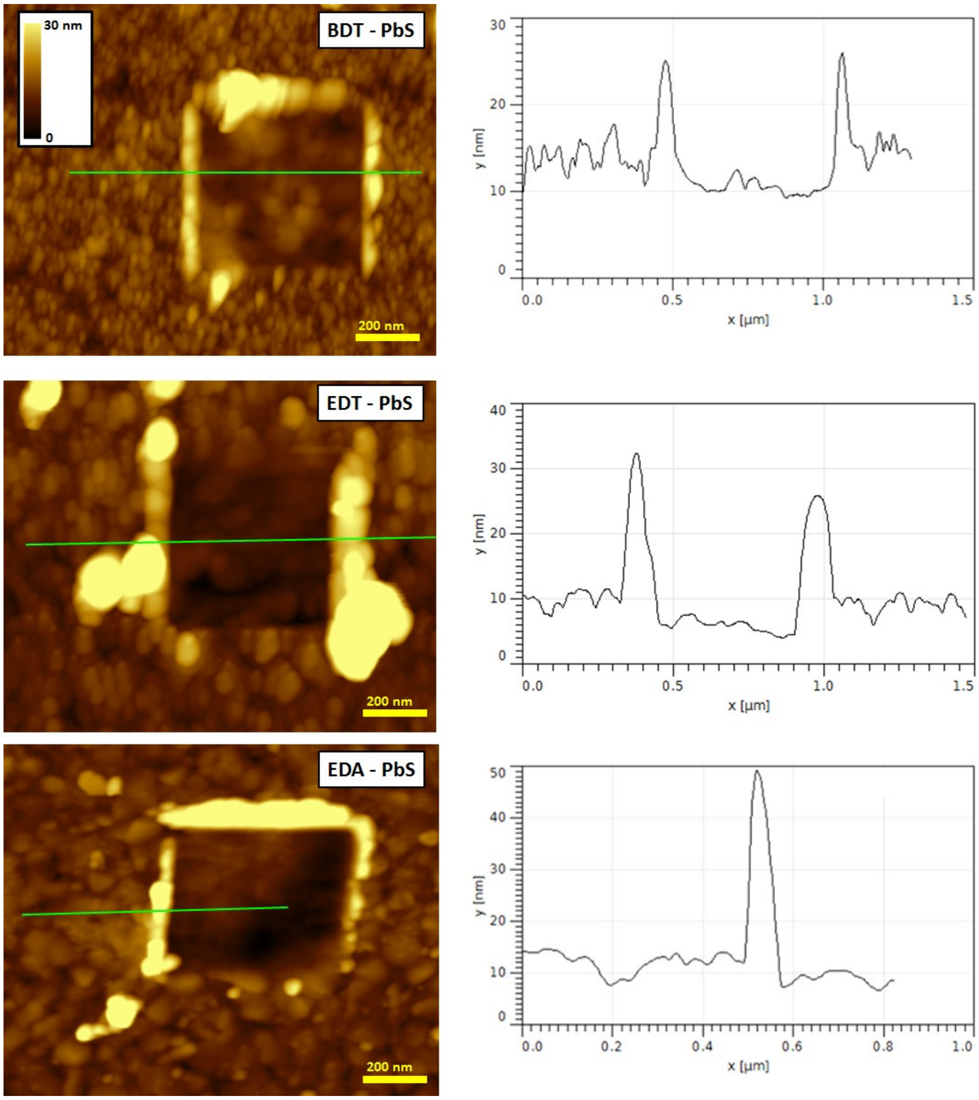

Figure S1. Shows representative AFM images of BDT, EDT, and EDA cross-linked 3.0 nm PbS and their respective thickness profiles. BDT, EDT and EDA had an average thickness of 4.0 nm, 3.9 nm, and 4.24 nm respectively.

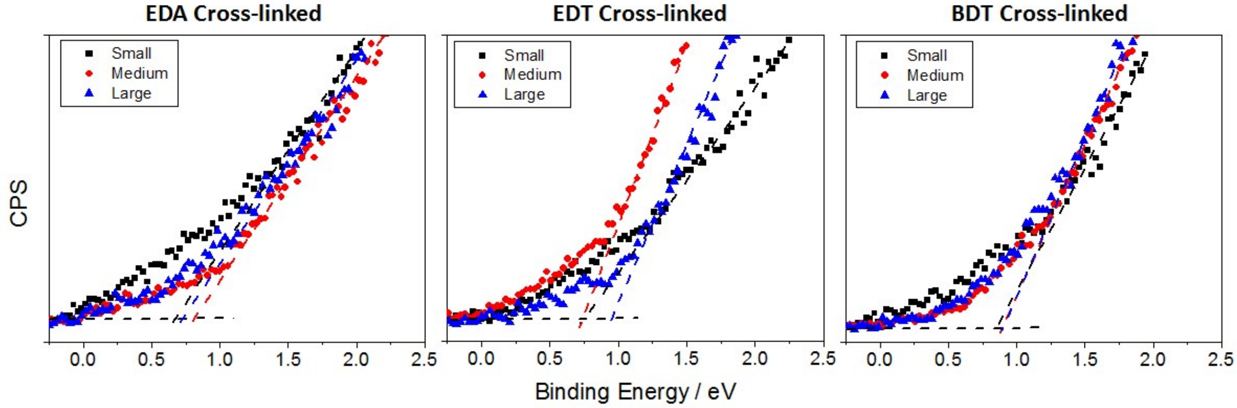

Figure S2. Shows representative UPS spectra for 2.5 nm (black), 3.0 nm (red), and 3.4 nm (blue) PbS QDs cross-linked with EDA (left), EDT (middle), and BDT ligands. The onset energy derived from these spectra, along with those determined from three additional sets of spectra for each ligand and size, were averaged to form the data points in Figure1.

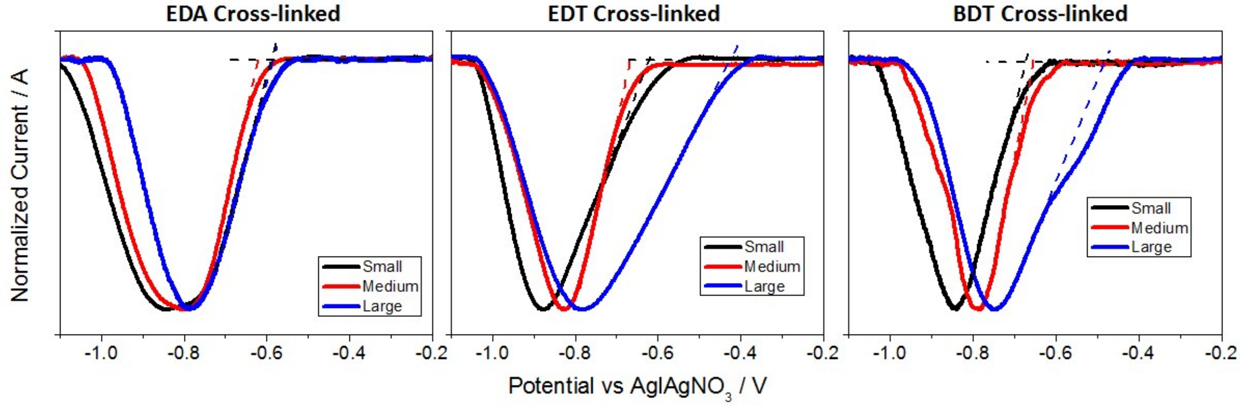

Figure S3. Shows representative background subtracted voltammograms for 2.5 nm (black), 3.0 nm (red), and 3.4 nm (blue) PbS QDs cross-linked with EDA (left), EDT (middle), and BDT ligands. The onset energy derived from these voltammograms, along with those determined from three additional sets of spectra for each ligand and size, were averaged to form the data points in Figure 3.

Table S1**.** Average electronic state energies in electron volts of the 2.5, 3.0, and 3.4 nm PbS QDs cross-linked with EDA, EDT, and BDT ligands. The CBMs were determined experimentally in the electrochemistry studies and the optical bandgap and exciton binding energy were used to calculate the VBMs. The VBMs were determined experimentally in the UPS studies and the optical band gap and exciton binding energy were used to calculate the CBMs. These values correspond to the data points in Figure 3.

| Electronic States of PbS NPs of with Different Sizes and Ligands on Au | | | | | | |
|---|---|---|---|---|---|---|
| Electrochemistry Data | | | | | | |
| | EDA VBM | EDA CBM | EDT VBM | EDT CBM | BDT VBM | BDT CBM |
| **2.5 nm** | 5.51 | 3.95 | 5.45 | 3.89 | 5.51 | 3.97 |
| **3.0 nm** | 5.23 | 3.92 | 5.31 | 4.00 | 5.28 | 3.97 |
| **3.4 nm** | 5.30 | 4.09 | 5.37 | 4.16 | 5.35 | 4.14 |
| | | | | | | |
| Ultraviolet Photoelectron Spectroscopy Data | | | | | | |
| | EDA VBM | EDA CBM | EDT VBM | EDT CBM | BDT VBM | BDT CBM |
| **2.5 nm** | 5.48 | 3.93 | 5.50 | 3.95 | 5.65 | 4.10 |
| **3.0 nm** | 5.67 | 4.36 | 5.57 | 4.26 | 5.70 | 4.39 |
| **3.4 nm** | 5.55 | 4.34 | 5.69 | 4.48 | 5.70 | 4.49 |

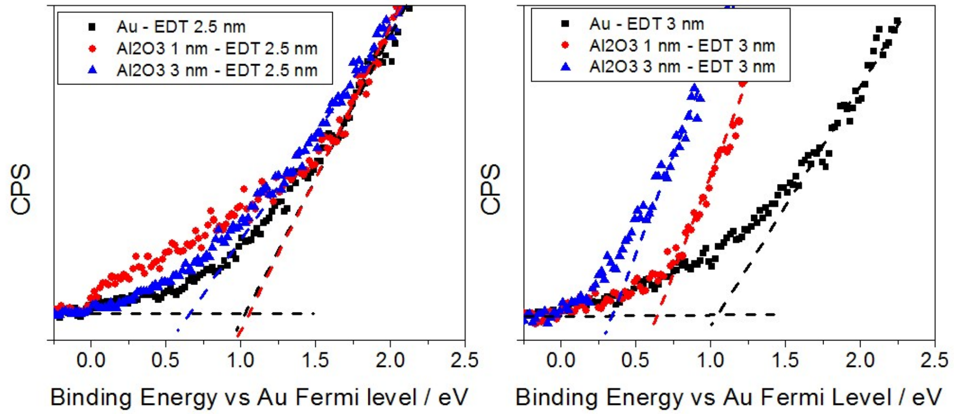

Figure S4. Shows the UPS spectra used for determining the VBM of EDT cross-linked 2.5 nm (left) and 3.0 nm (right) PbS QDs deposited on Au (black), 1.0 nm alumina (red), and 3.0 nm of alumina (blue). The shift in the onset energy as a function of alumina thickness is plotted in Figure 4.

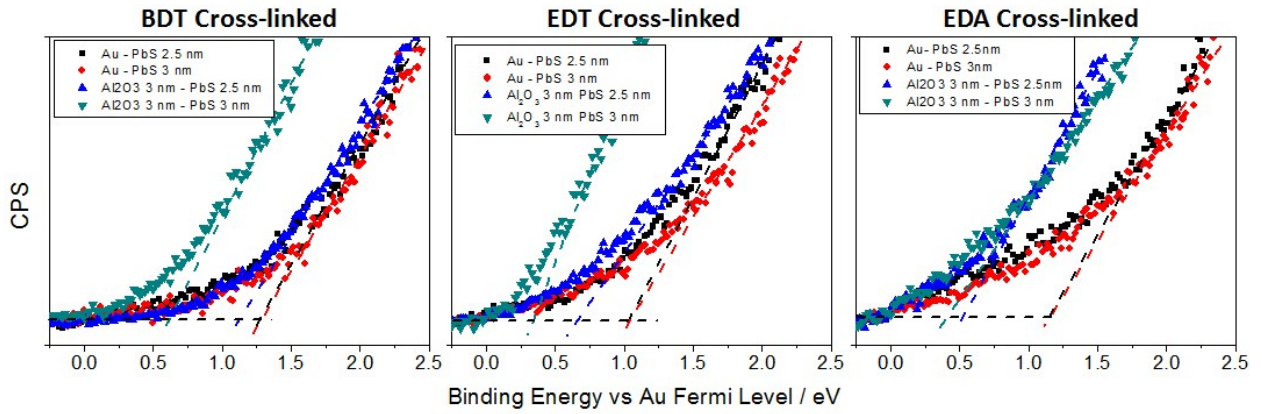

Figure S5. Shows UPS spectra of 2.5 nm (black) and 3.0 nm (red) PbS on Au substrates and 2.5 nm PbS (blue) and 3.0 nm PbS (teal) on 3.0 nm thick alumina substrates. The cross-linkers used in the experiments were BDT (left), EDT (middle), and EDA (right). These data correspond to the data points of Figure 5.

Table S2. Average electronic state energies in electron volts of 2.5 and 3.0 nm PbS QDs cross-linked with EDA, EDT, and BDT ligands reported against the Fermi edge of Au. The VBM were determined by UPS and the CBM was found by adding the optical band gap and exciton binding energy. These values correspond to the data points in Figure 5.

| **Comparison of Electronic States of PbS on Au and Alumina** | | | | | | |
|---|---|---|---|---|---|---|
| **Measured on Gold** | | | | | | |
| | EDA VBM | EDA CBM | EDT VBM | EDT CBM | BDT VBM | BDT CBM |
| **2.5 nm** | 1.21 | -0.46 | 1.01 | -0.657 | 1.21 | -0.43 |
| **3.0 nm** | 1.20 | -0.21 | 1.02 | -0.387 | 1.27 | -0.14 |
| | | | | | | |
| **Measured on 3.0 nm of Alumina** | | | | | | |
| | EDA VBM | EDA CBM | EDT VBM | EDT CBM | BDT VBM | BDT CBM |
| **2.5 nm** | 0.52 | -1.15 | 0.63 | -1.04 | 1.1 | -0.57 |
| **3.0 nm** | 0.42 | -0.99 | 0.32 | -1.09 | 0.55 | -0.86 |