Supporting Information: Passivating Ligand and Solvent Contributions to the Electronic Properties of Semiconductor Nanocrystals

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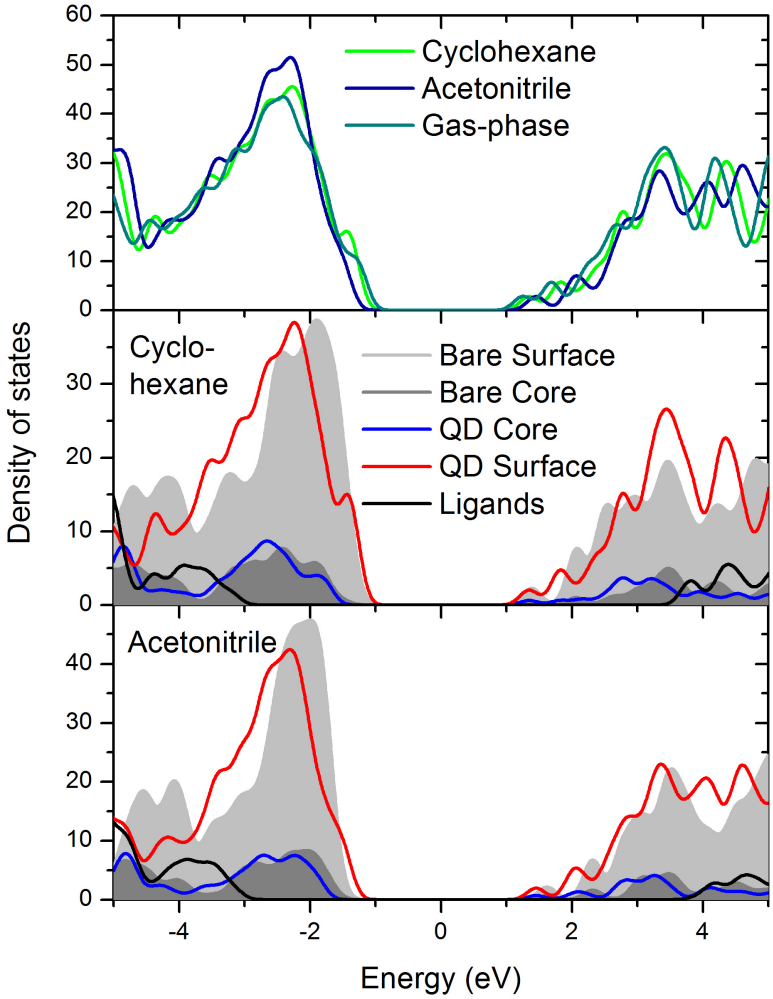

Figure 1: **S1**: Total density of states (DOS) for the methylamine (NH_2Me) capped QD in the gas phase and two solvents with different polarity (top panel) and fragment DOS for the methylamine capped QD in cyclohexane (middle panel) and in acetonitrile (bottom panel). The band gap of the system increases with increasing polarity of the surrounding medium, as seen in the top panel.

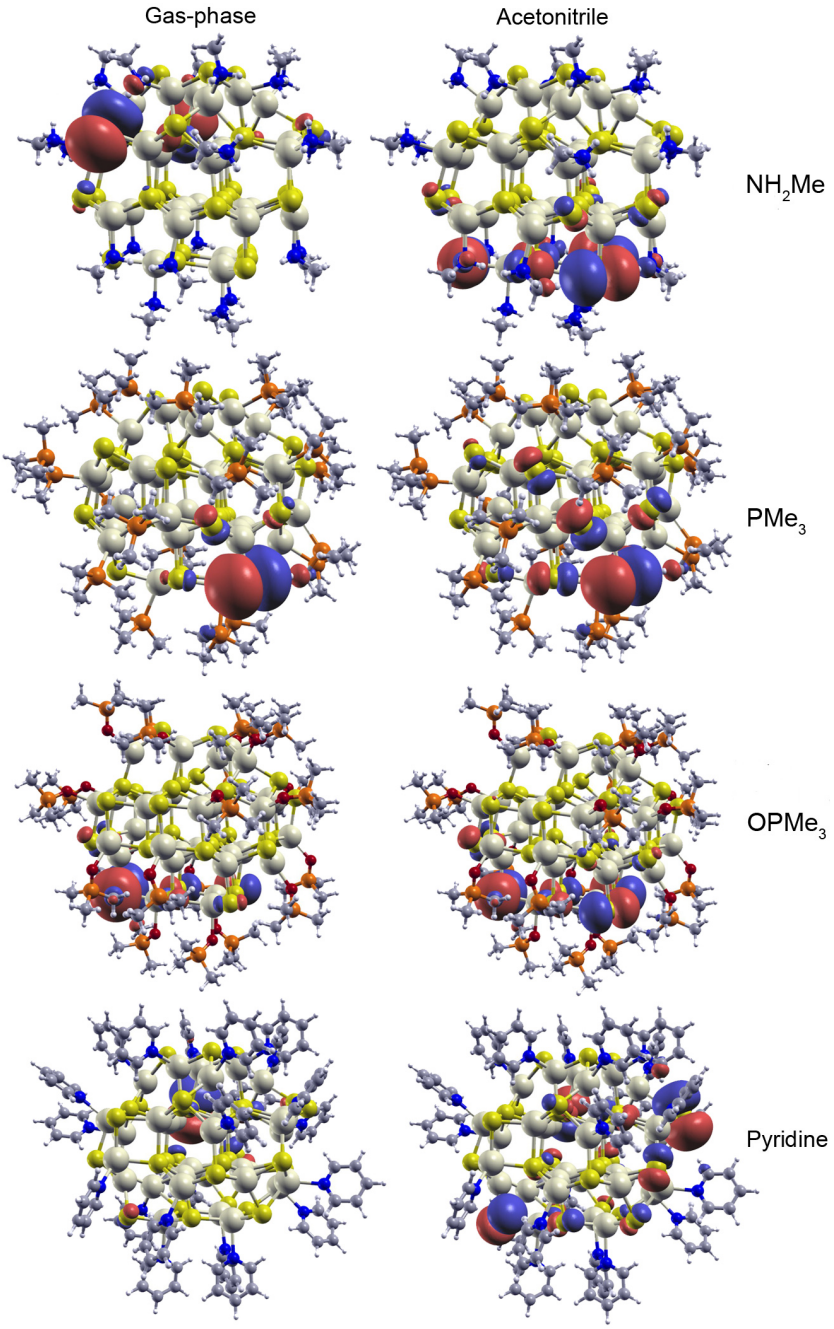

Figure 2: **S2**: The highest occupied molecular orbitals (HOMOs) of ligated $Cd_{33}Se_{33}$ clusters. Orbitals in the left and right columns are calculated in the gas-phase and acetonitrile solvent, respectively. For all passivating ligands, HOMO shows the p-character of Se atoms with the strongest localization (a trap character) for phosphine and pyridine capped QDs. Solvent environment noticeably increases delocalization of the orbital, although this delocalization is less pronounced compared to the unoccupied states. The phosphine and pyridine passivated QDs shows a high level of localization of HOMO even in solvent.

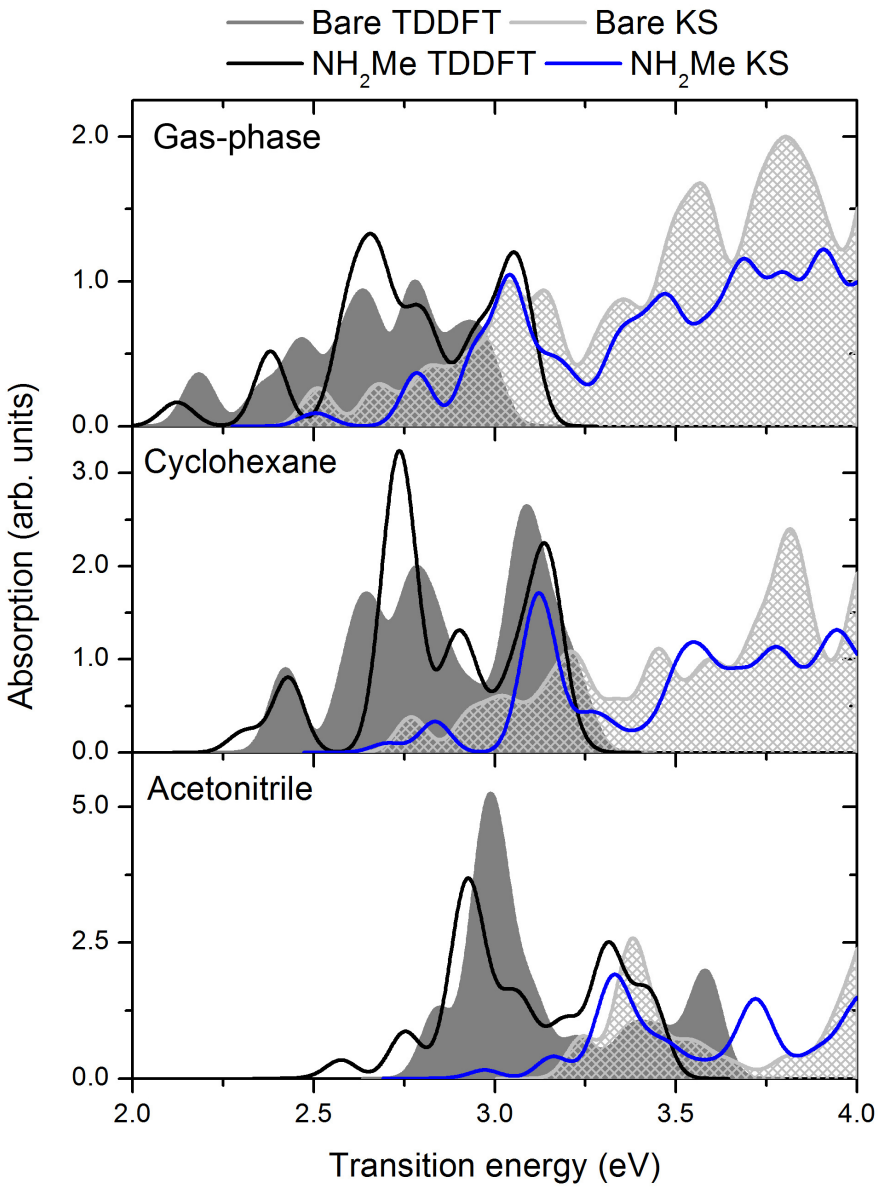

Figure 3: **S3**: Optical absorption spectra calculated for the methylamine (NH_2Me) capped QD in the gas-phase (top panel), cyclohexane (middle panel), and acetonitrile (bottom panel) with TDDFT and Kohn-Sham approaches. The corresponding spectra of the uncapped QD are plotted for the reference. Cyclohexane results are intermediate between the gas-phase and acetonitrile data.

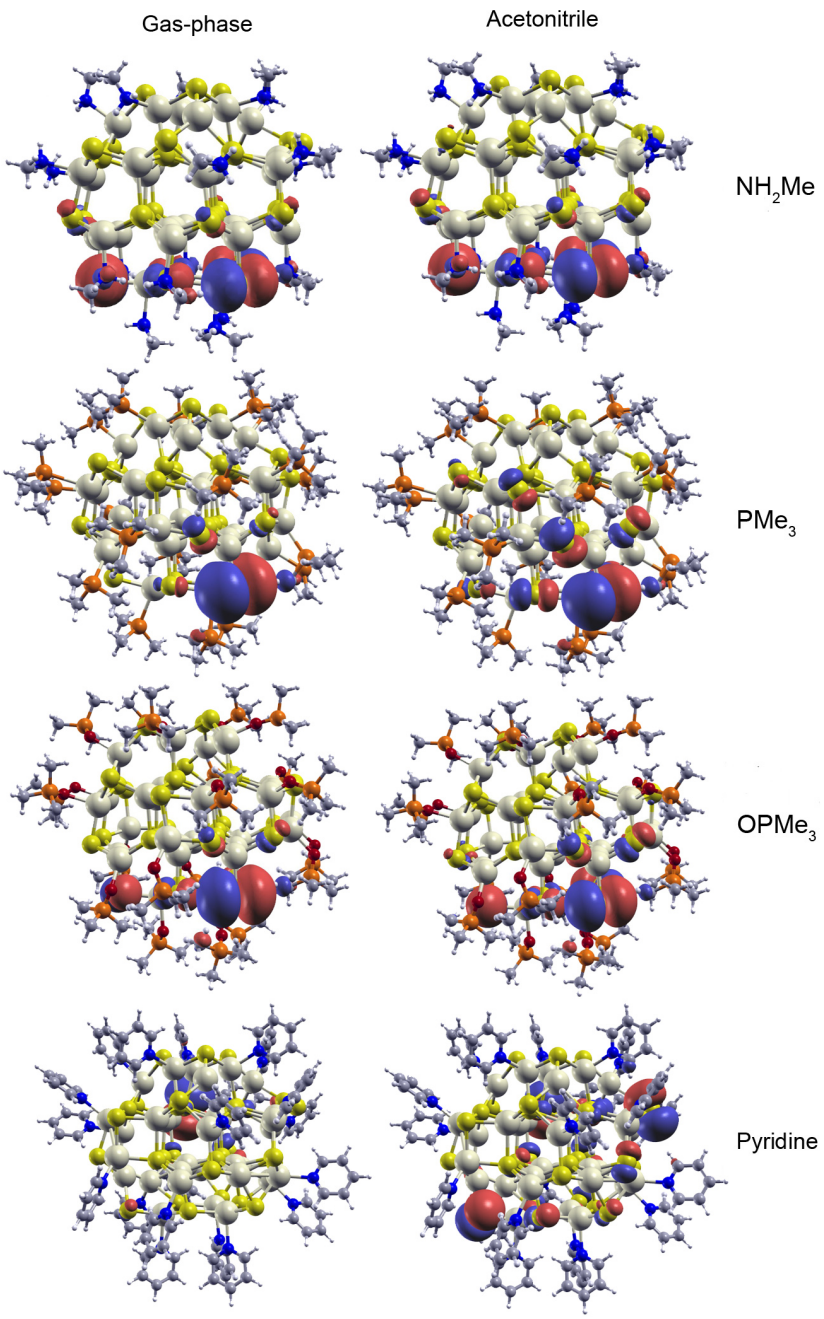

Figure 4: **S4**: The highest occupied molecular orbitals (HOMOs) ligated $Cd_{33}Se_{33}$ clusters after removal of a single ligand molecule calculated in the gas-phase (left column) and in acetonitrile (right column). Inclusion of solvent helps to delocalize the orbitals, though the effect is not as dramatic as is seen with the unoccupied orbitals.