

The Roles of Crosslinking Ligands on Charge Carrier Transport in PbS Colloidal Quantum Dot Assemblies

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Colloidal quantum dot nanocrystals are attractive new class of materials for their potential applications in solution-processable electronic devices. The small size of the nanocrystals makes them exhibit quantum confinement effect that generate energy bandgap value variations by size and the formation of discrete energy levels.^[1] These properties make them colloidal quantum dots intriguing for the development of highly efficient solar cells, display/lightings, as well as thermoelectric devices. To stabilize the nanocrystals and to make them solution-processable, insulating long-chain organic molecular ligands (i.e. oleic acid) are used to cap the nanocrystal surface. However, these long ligands inhibit charge carrier transport in the fabricated electronic devices. To couple the nanocrystals to transport charge carrier, the long ligands are usually replaced by much shorter molecules (e.g. 1,2-ethanedithiol [EDT], 3-mercaptopropionic acid [MPA], oxalic acid, iodide, etc.).^[1] While these kinds of ligand exchange enhance the charge carrier transport significantly, the morphology of the formed films is largely disrupted due to the volume shrinkage of the nanocrystal assemblies, leaving cracks and disorders in large scale. Minimizing volume shrinkage by controlling the usage of proper molecular ligands to interconnect the nanocrystals in ordered large scale assemblies vital for many applications.

Here we show the selections of various ligand molecules that can crosslink PbS colloidal QDs to transport efficiently either holes or electrons; with reduced potential for volume shrinkage than the commonly used molecules. The design of the molecules are based on the understanding on how the of the end groups of the short bidentate molecular ligands (i.e. EDT, oxalic acid) influence the tendency of the transporting carrier in the PbS QD assemblies.^[2]

Subsequently, we designed molecules with various length and oligomer chains, and use them to fabricate PbS QD field-effect transistors. The ligand exchange process is performed in solid-state-film using the standard layer-by-layer spin coating deposition. In addition to the conventional SiO₂-gated FETs, we also employed ionic liquid gating^[3] to further characterize the electrical transport of the PbS QD films, crosslinked with the designed molecules. Despite some of the molecules are significantly longer than EDT, the corresponding FETs can demonstrate comparable conductivity and on/off ratio characteristics. Furthermore, we can select the types of molecular ligands to obtain enhanced hole transport or electron transport, depending on the requirements of different device applications.

Refs: [1] S.Z. Bisri, et al., *Adv. Mater.* 25, 4309 (2013); [2] L. Liu, et al. *ACS Appl. Nano Mater.*, 1, 5217 (2018); [3] S.Z. Bisri, et al. *Adv. Mater.* 29, 1607054 (2017)

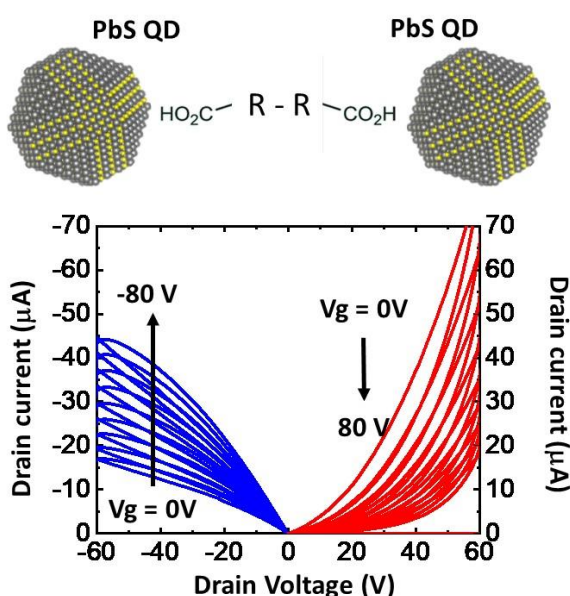


Figure 1 (top) Schematic diagram of PbS colloidal quantum dots crosslinked by bidentate organic ligand with variations of oligomers in the molecule. (bottom) I_D - V_D output characteristics of the FET using PbS QD crosslinked with one of the newly designed ligands that demonstrate high hole transport characteristics.