

Photoconductivity of PbSe Quantum- Dot Solids: Dependence on Ligand Anchor Group and Length

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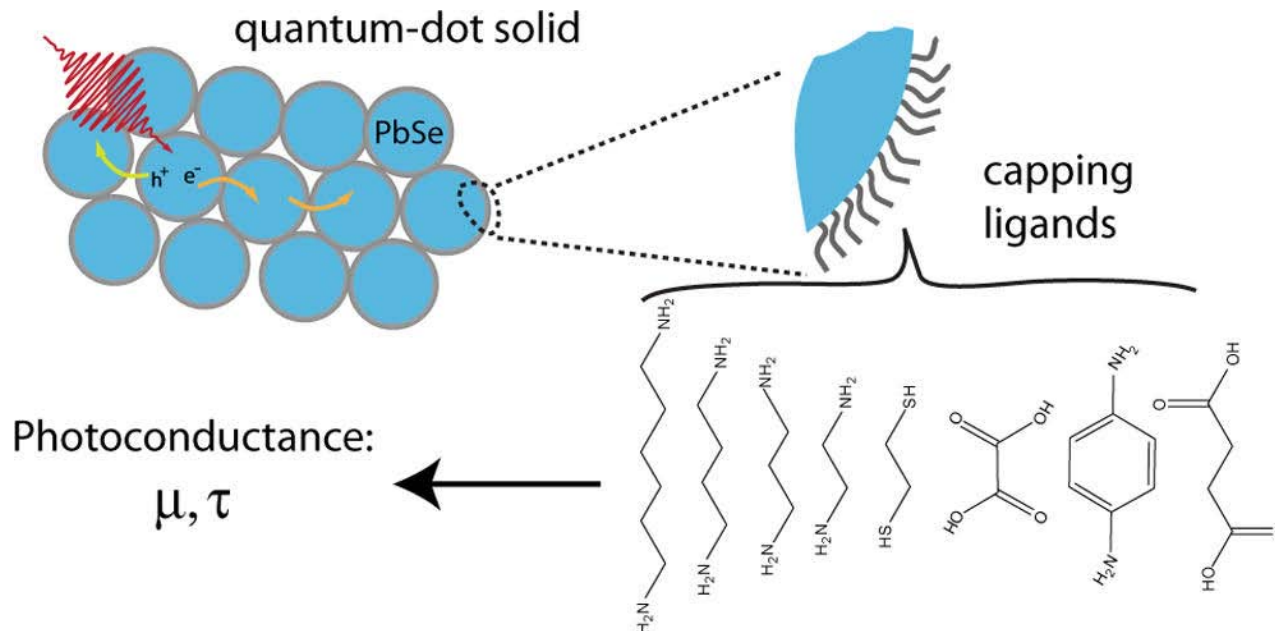
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Introduction

- Research on thin films of quantum dots (QD), so-called QD solids, has recently achieved great progress toward many applications, such as photodetectors, field-effect transistors and solar cells.
- These applications require conductive QD solids, in which QDs are electronically coupled and charge carriers can efficiently move to electrodes.
- QDs generally have long and insulating native capping ligands that should be replaced by short ligands to get a conductive film to obtain enhanced performance from a QD device.
- Various organic molecules with different anchor groups, such as amine, thiol or carboxylic acid and with different lengths have been used as replacing ligands.
- A variety of preparation methods have been used to fabricate QD solids, and the charge carrier mobilities were determined by different methods.
- However, in contrast to the large number of studies on charge carrier mobility, only a few studies on carrier kinetics exist.

In this paper.....



A systematic study on the influence of the replacing ligands on charge carrier mobility and carrier lifetime in PbSe QD solids, using the time-resolved microwave conductivity technique (TRMC) is reported.

Small organic replacing ligands have been used in this study as they have been, so far, most used in the fabrication of QD solar cells and photodetectors.

Methods

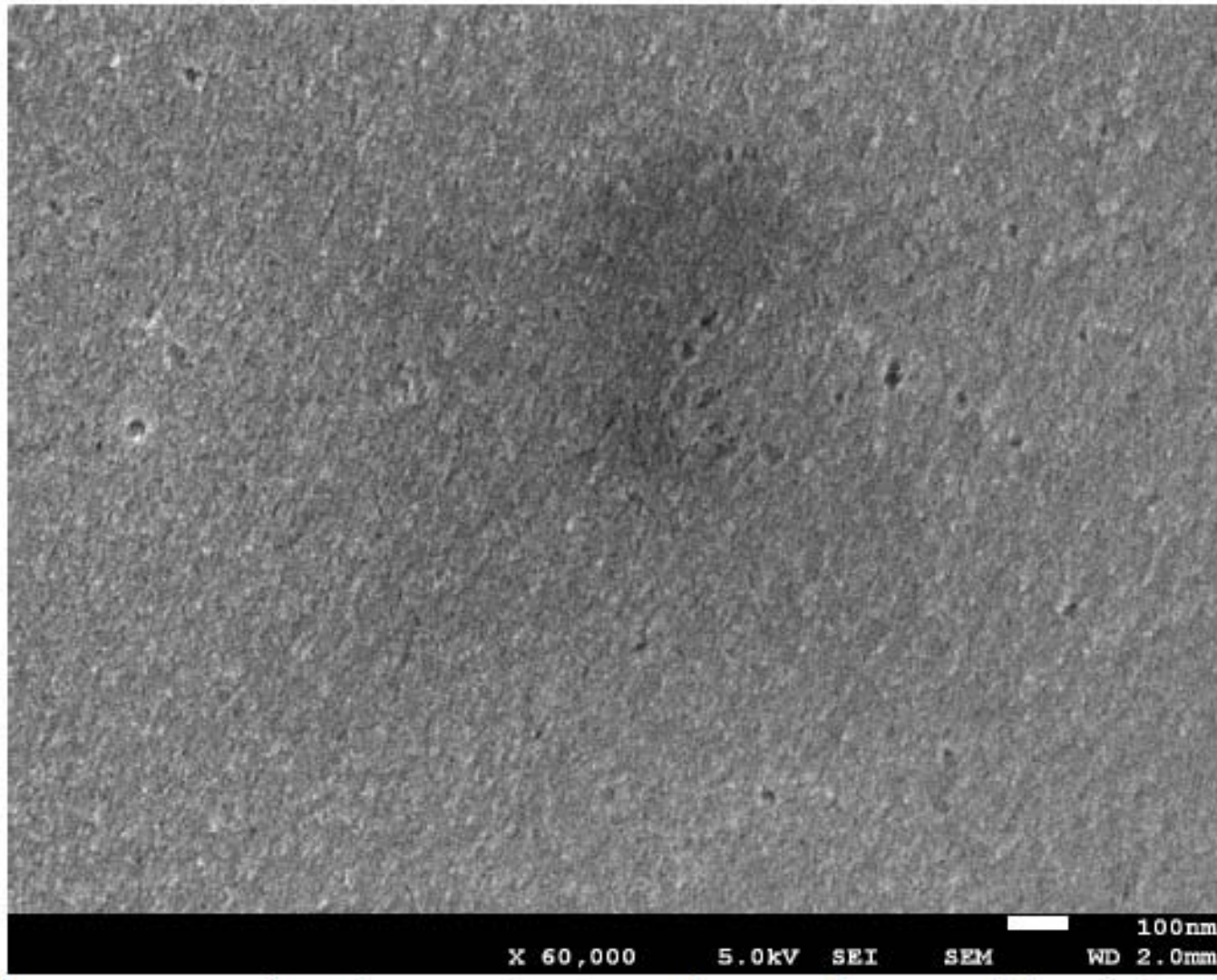
Layer-by-layer dip coating method

The QD solids are fabricated using the LbL dip-coating method.

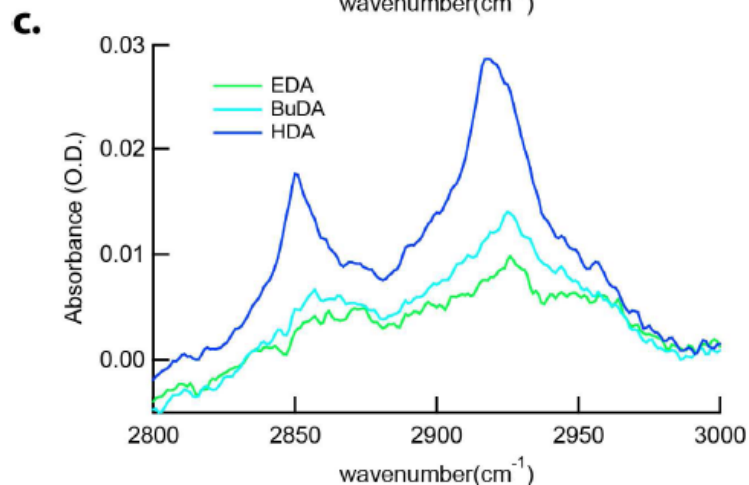
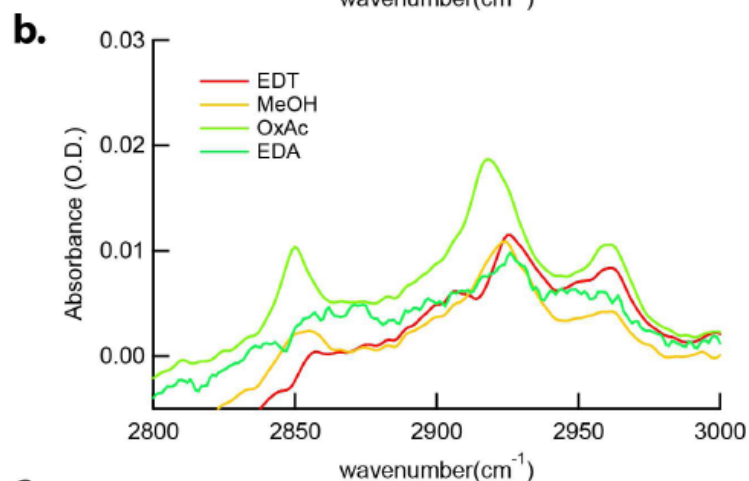
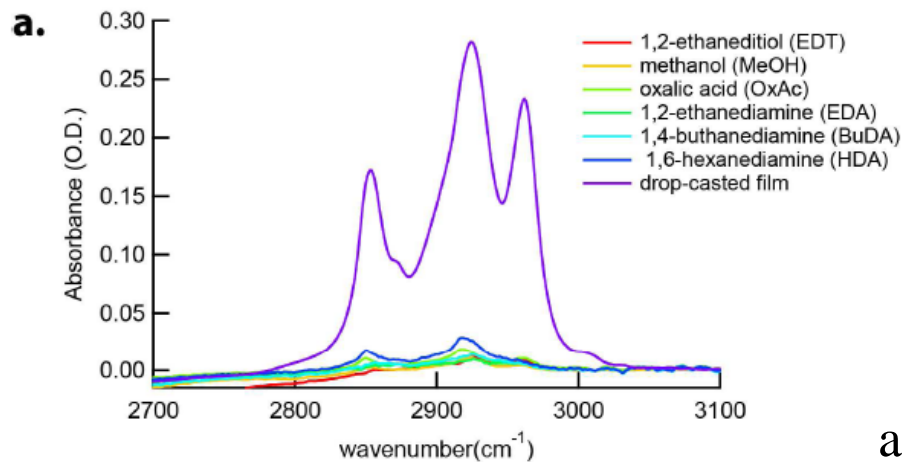
microwave conductivity technique (TRMC)

TRMC determines the local ac photoconductivity. The sample is excited with a tunable nanosecond laser pulse, resulting in the generation of charge carriers. The accompanying increase in conductivity is determined by measuring the increase of the absorption of microwave radiation. The conductivity is probed in a film domain with a typical size of ~ 30 nm. Therefore TRMC measures the intrinsic charge transport properties and is not sensitive to global film properties such as cracks.

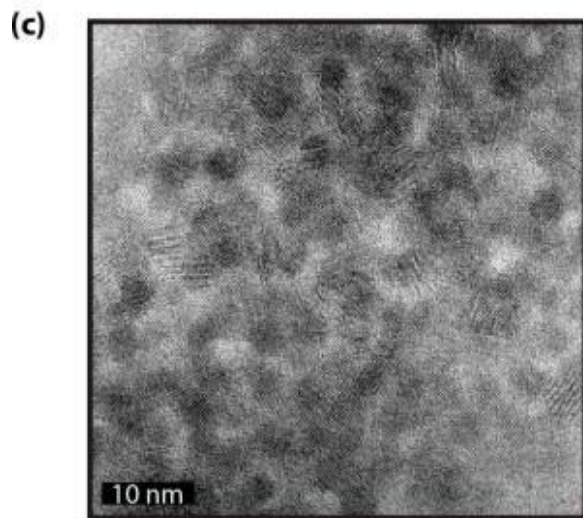
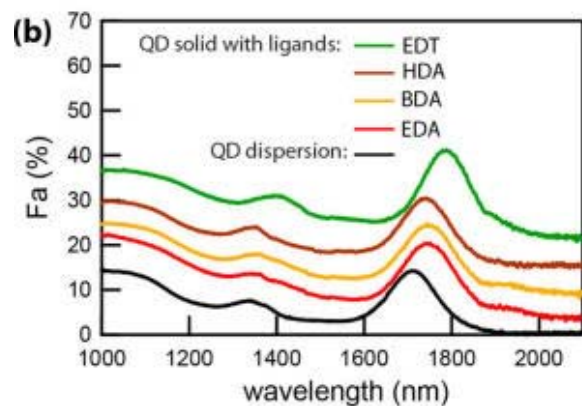
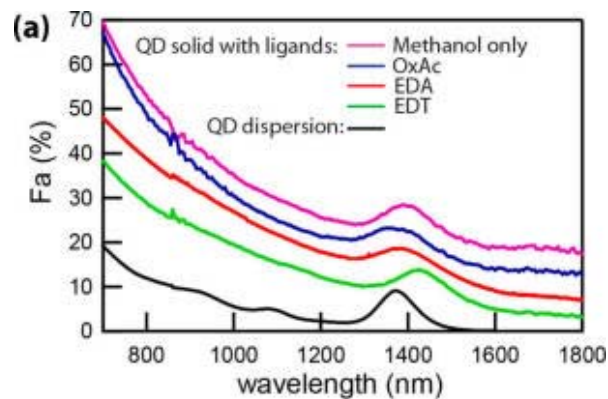
Results and discussion



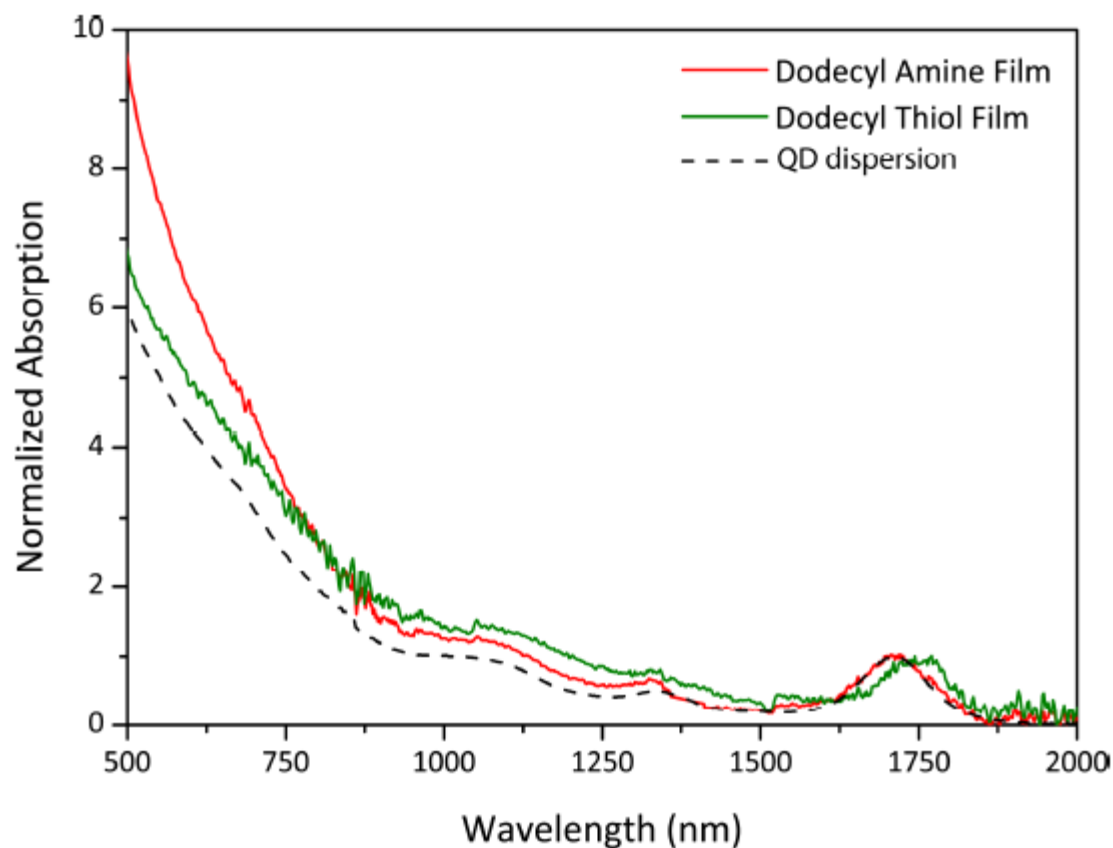
Scanning electron microscope image of a QD solid made by dip-coating shows smooth, crack free films.



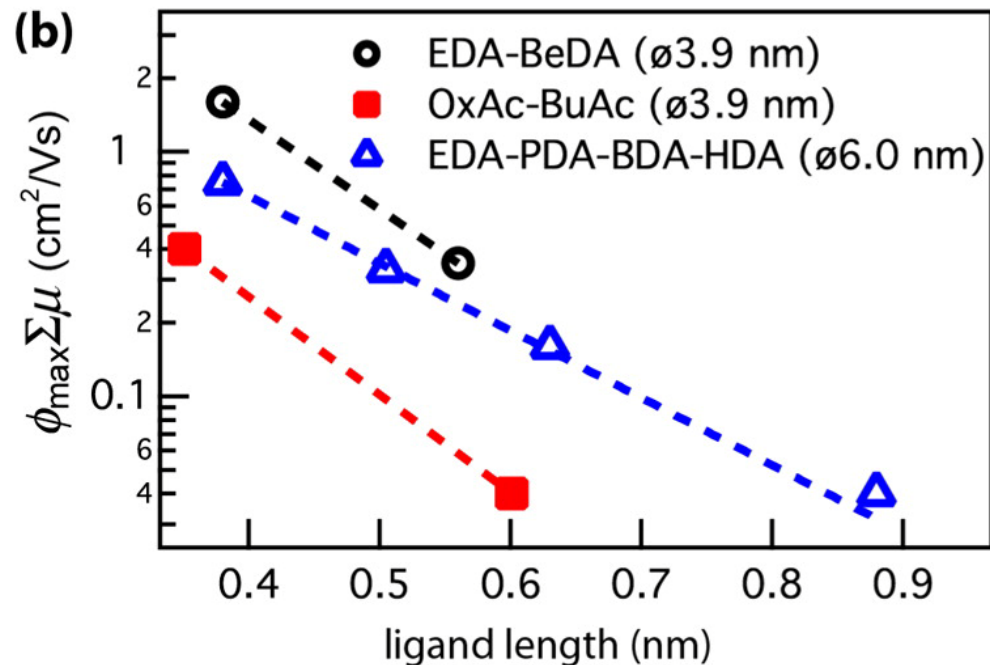
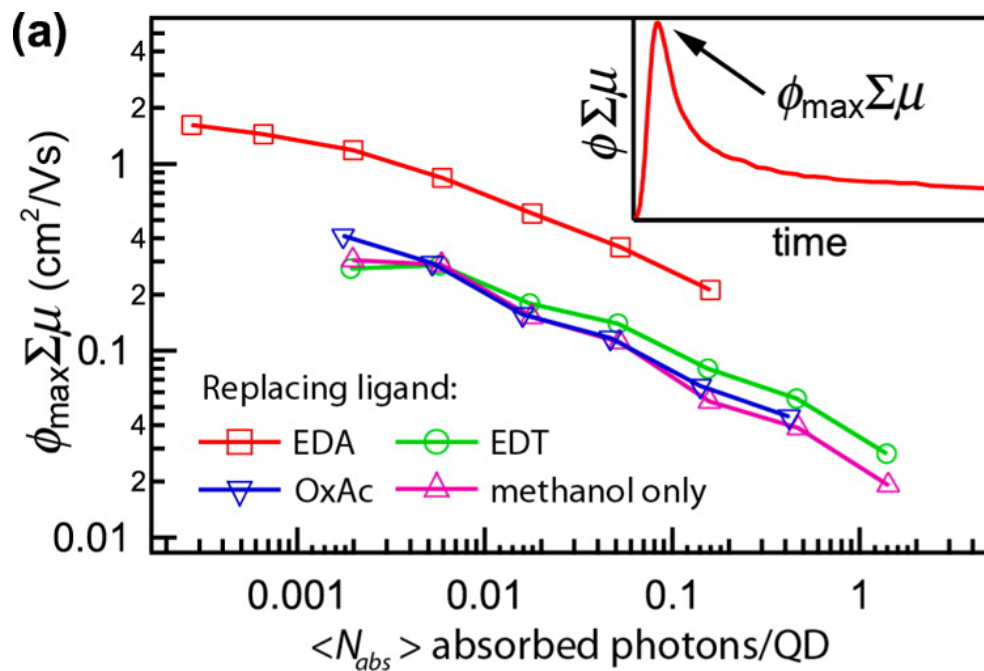
a) FTIR spectra of PbSe QD solids made by drop casting (purple) and dip-coating using various replacing ligands as indicated. The reduction of the CH_2 peaks at 2852 cm^{-1} and 2924 cm^{-1} indicates removal of native oleylamine ligands. b) and c) are zoom-ins on the absorbance in the treated films.



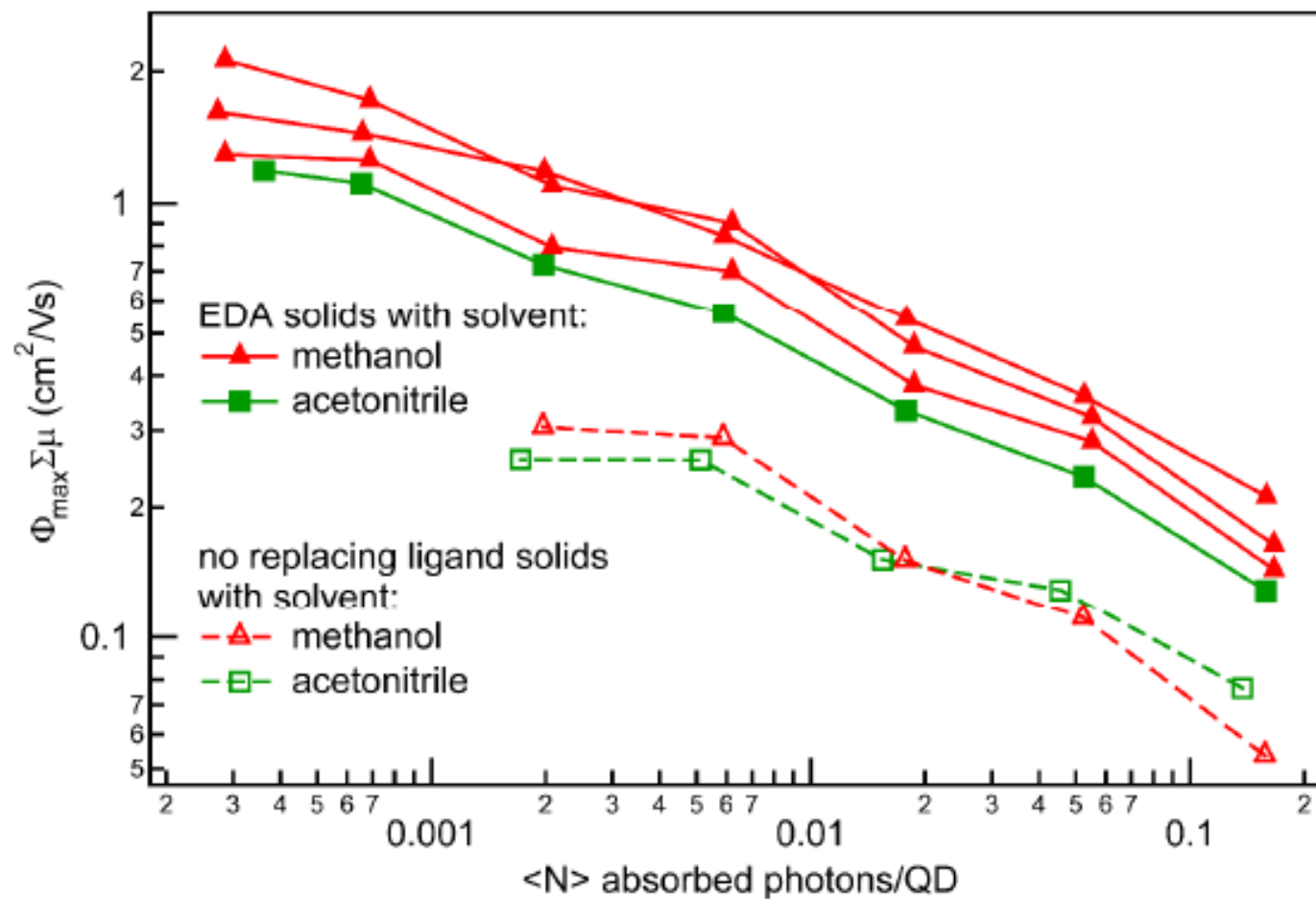
(a) Absorptance spectra of 3.9 nm PbSe QD solids prepared using the layer-by-layer dip-coating method on quartz substrates with various replacing ligands: EDA (red line), EDT (green line), OxAc (blue line) and without ligands (rinsed with pure methanol, magenta line). The spectra are offset for clarity. (b) Absorptance spectra of 6.0 nm PbSe QD solids with a series of alkydiamine ligands: EDA (red line), BDA (orange line), HDA (brown line), and EDT (green line). (c) High-resolution TEM image of a PbSe EDA QD film prepared by a single dip-coating cycle.



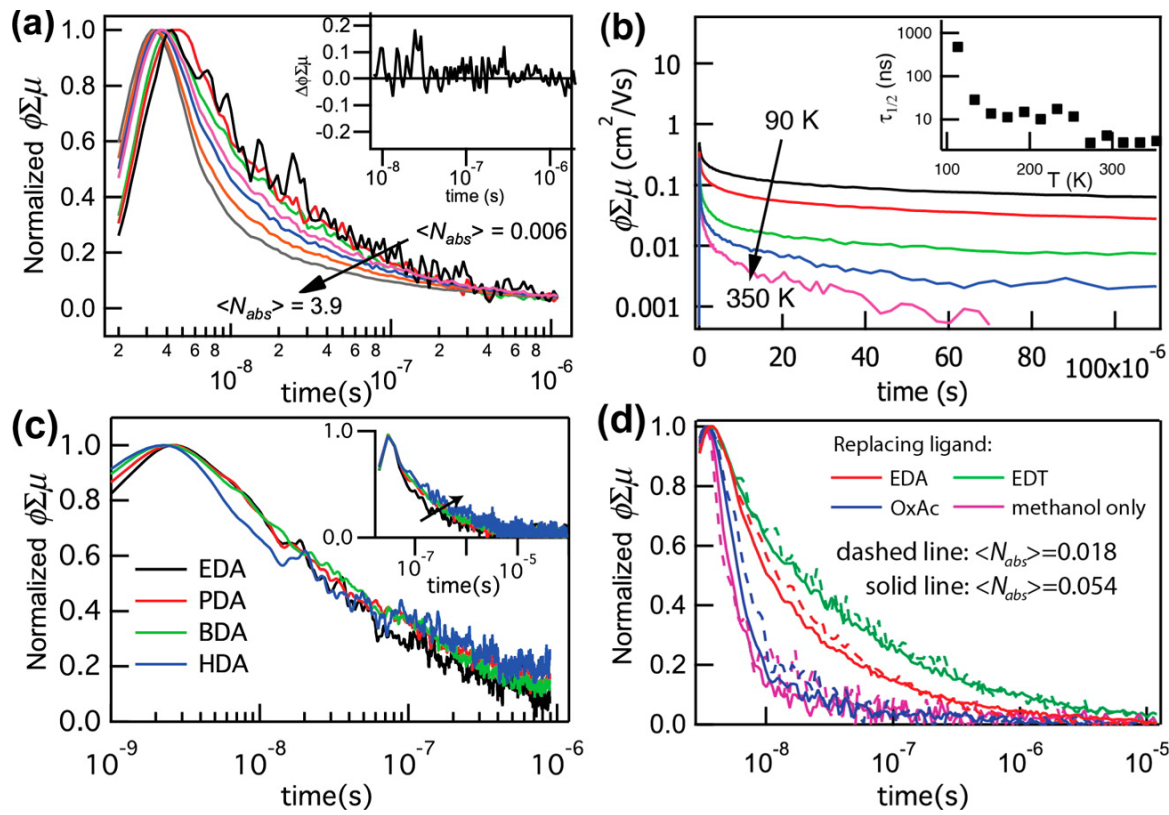
Absorption spectra of a 6.0 nm PbSe QD dispersion (black dashed curve) and films grown with dodecyl amine and dodecyl thiol ligands. The dodecyl thiol treated film shows a pronounced red shift that is not observed in the dodecyl amine treated film.



TRMC photoconductivity of PbSe QD solids with different replacing ligands, as indicated in the figure. (a) $\phi_{\max} \Sigma \mu$ values as a function of the average photoexcitation density for QD solids with different replacing ligands. The inset shows a photoconductivity transient and the corresponding value of $\phi_{\max} \Sigma \mu$. (b) Overview of the effect of ligand length on the $\phi_{\max} \Sigma \mu$ values for various series of ligands: 1,2-ethanediamine and 1,4-benzenediamine (black circles), oxalic acid and butanedioic acid (red squares), and 1,2-ethanediamine, 1,3-propanediamine, 1,4-butanediamine, and 1,6-hexanediamine (blue triangles). The dashed lines are exponential fits to the data.



TRMC photoconductivity of PbSe quantum dot solids fabricated with 1,2-ethanediamine (EDA) as replacing ligands (solid line with results from three samples) and without any replacing ligands (dashed lines), and within these traces up triangle (▲) is for methanol used as solvent, square (■) is for acetonitrile used as solvent.



(a) Normalized photoconductivity transients for a PbSe QD solid with EDA replacing ligands at various excitation densities: 0.006 (black), 0.018 (red), 0.054 (green), 0.15 (purple), 0.45 (blue), 1.3 (orange), and 3.9 (gray) absorbed photons per QD. The inset shows the difference between the two transients at the lowest fluences, demonstrating that within the noise of the experiments these transients are the same. (b) Temperature-dependent photoconductivity transients for PbSe QD solids with EDA ligands. The inset shows the extracted half-lifetime at low excitation density ($\langle N_{abs} \rangle = 0.001$) as a function of temperature. (c, d) Normalized photoconductivity for PbSe QD solids with ligands of various length (c) or various anchor groups (d). The inset in (c) shows the transients on a longer time scale. The solid and dashed lines in (d) correspond to $\langle N_{abs} \rangle = 0.054$ and $\langle N_{abs} \rangle = 0.018$ absorbed photon per QD, respectively.

TABLE 1. Summary of Charge Carrier Properties in PbSe QD Solids with Various Replacing Ligands at Room Temperature

replacing ligands	$\Phi_{\max} \Sigma \mu$ ($\text{cm}^2/(\text{V s})$)	$\tau_{1/2}$ (ns)	diffusion length (nm)
EDA	1.6	12.5	550
EDT	0.27	18.5	280
OxAcid	0.41	<5.0	
methanol only	0.30	<7.5	

Summary

- The anchor group of replacing ligands strongly affects the carrier mobility and lifetime. With amine anchor groups the QD solids show higher carrier mobilities, while with thiol groups the QD solids possess a longer carrier lifetime.
- The carrier lifetime at low excitation density is determined by trapping processes on a nano- to microsecond time scale.
- Carrier mobility decreases exponentially with ligand length.

Thank You