

# 博士論文

Control of Electronic Properties of Quantum

Dot Assemblies by Ligand Chemistry

(配位化学による量子ドットの電子物性制御)

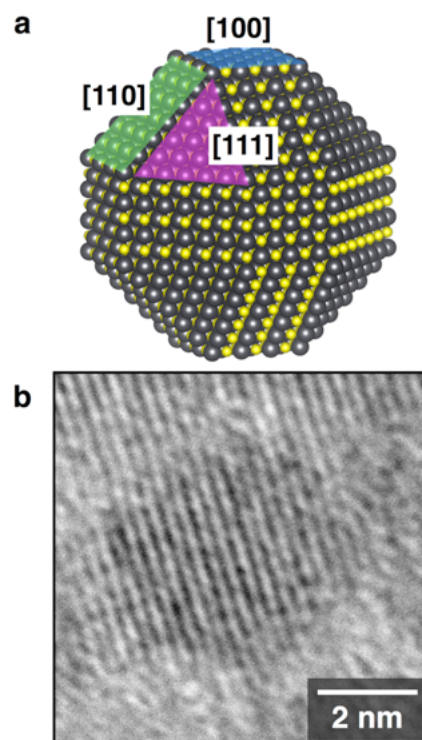
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## [1] Introduction

A quantum dot (QD) is a single crystal of semiconductor (Figure 1a,b) with an electronic wave function that is quantum-confined in all three dimensions. This quantum confinement of carrier wave functions in QDs leads to the formation of discrete electronic energy levels and to the tunability of their electronic bandgaps through alteration of the size of the QD. Among the broad variety of QDs, lead sulfide (PbS) is one of the most attractive materials because of the well-developed control of its synthesis, leading to high quality, high absorbance, and fine-tuning of bandgaps. It is also especially appealing for solar cell applications due to its large confinement effect with a large excitonic Bohr radius (20 nm). To date, PbS QDs can be treated as a model material for investigations of charge carrier transport properties in colloidal QD assemblies, from which any gained knowledge can be translated to other QDs of different compounds. Furthermore, the PbS QDs are of remarkable research interest because of their possible wide range of applications as components of energy-generating devices, such as solar cells, thermoelectrics, or low-power-consumption electronic devices, such as photodetectors and light-emitting devices.<sup>[1]</sup>

In order to improve the performance of these electronic devices used by QDs, well-controlled electronic properties of QD films are highly necessary. However, the QD films always show very bad electronic transport properties due to the hard control of QD assembly structure and its original long insulating ligands [e.g., oleic acid], which block charge carrier transport between the QDs.<sup>[2]</sup> This thesis aims to enhance the conductivity of QD films by ligand chemistry. In detail, we improve the conductivity of QD films by using different short conjugated ligands (1), controlling the ligand coverage and assembly structures (2), and alternating the conjugation length of ligands (3).

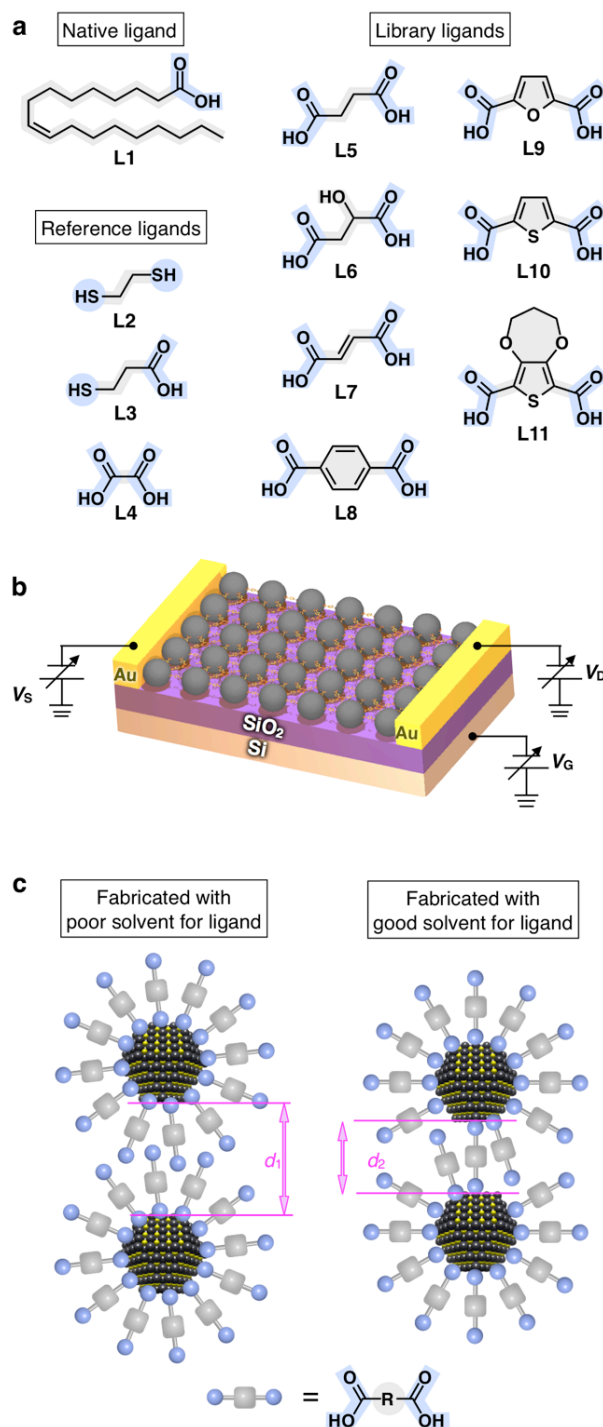
- (1) **[Short Conjugated Ligands]** PbS QDs capped with a novel short thiophene based ligand demonstrate significantly enhanced hole transport and show the highest hole mobility values reported for PbS QD FETs.
- (2) **[Ligand Coverage Control]** A precise ligand coverage control is achieved by a modified liquid/air assembly technique. The degree of ligand coverage influences both the assembly structure and electronic properties of QD films.
- (3) **[Long Conjugated Ligands]** The conjugation length of the ligand is tuned by the number of thiophenes. These long conjugated ligands give QDs both long-range order assemblies and good electronic properties.



**Figure 1.** (a) A schematic image of the PbS quantum dot, which show its different facets. (b) A TEM image of one single PbS quantum dot with high crystallinity.

## [2] Ligand and Solvent Effects on Hole Transport in QD Assemblies<sup>(1)</sup>

As-synthesized PbS QDs are generally covered with long-chain insulating ligands [e.g., oleic acid] that act as native capping agents to stabilize the QDs in dispersions. However, from a device application perspective, these long ligands effectively block charge carrier transport. To impart electronic conductivity in the QD film, these insulating ligands should be replaced by short-chain ligands to enhance the electronic coupling.<sup>[3]</sup> While several n-type ligands for QDs with excellent conductivity have been successfully demonstrated, in general, p-type ligands for QDs have shown poor conductivity. In this [Short Conjugated Ligands] part, we demonstrate high-performance hole transport in PbS QD assemblies with a record high mobility value. To achieve this, we investigate variations of ligands that enable efficient hole transport between the QDs. Bifunctional ligands can bind neighboring QDs, causing effective cross-linking. We screened variations of ligands with bidentate dicarboxylic acid to enable hole transport in field effect transistors (Figure 2a,b). The library contains a ligand with a thiophene core, whose polymer and oligomer derivatives are known to show p-type transport characteristics in organic field effect transistors and solar cells. Furthermore, we emphasize the importance of choosing proper solvents for the ligand exchange process in a solid-state phase (Figure 2c). This choice significantly affects the degree of ligand exchange and the final morphology of the QD assemblies. We observed that PbS QDs capped with a novel short bifunctional ligand based on thiophene (L10 in Figure 2a) demonstrated significantly enhanced hole transport. Through a combination of this ligand and proper ligand-exchange solvent in optimized conditions, we realized p-type dominant ambipolar field effect transistors (FETs) with a high hole mobility of  $0.20 \pm 0.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is among the highest values reported for PbS QD FETs. This result can provide a new foundation for ligand-design strategies to

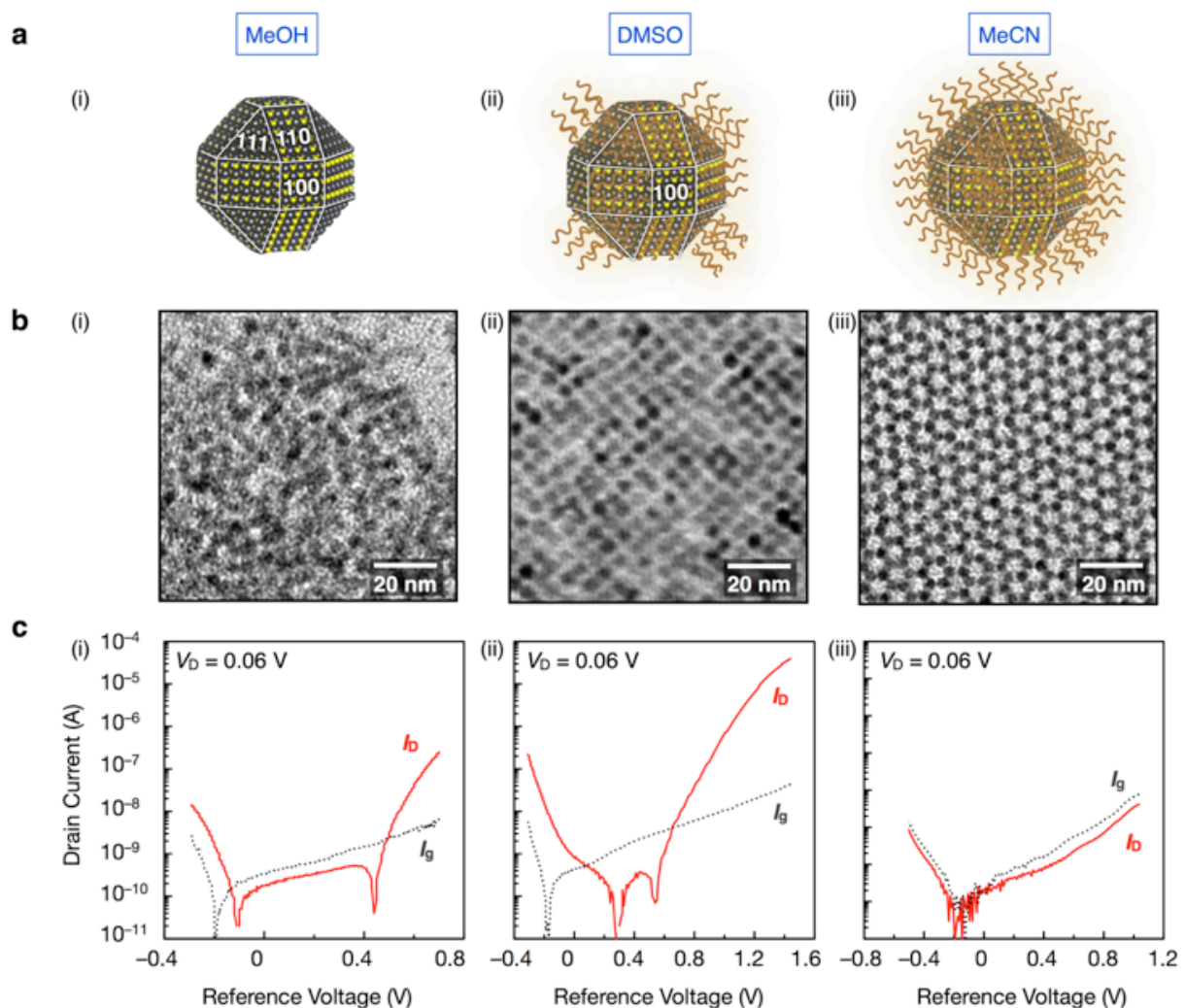


**Figure 2.** (a) Chemical structures of ligands for capping lead sulfide (PbS) quantum dots (QDs). (b) Schematic illustration of a FET device of a PbS QD film. (c) Effect of the solvent used for fabrication of the FETs on the packing of PbS QDs.

control the electronic states and transport in PbS QDs. Furthermore, we also found that the choice of solvent for the fabrication of FETs had an unexpectedly crucial effect on the properties of the resultant devices, irrespective of the type of ligand.

### [3] Tunable Electronic Properties by Ligand Coverage Control in PbS QD Assemblies<sup>(2)</sup>

Colloidal QDs have recently attracted increasing attention due to their wide range of applications, such as solar cells,<sup>[4]</sup> thermoelectrics, photodetectors, and so on. This attractiveness stems from the quantum-confinement-related properties and their solution-process ability. However, for many of these applications, well-controlled electronic transport properties of QD assemblies are necessary. Up to now, controlling the electronic properties is mostly achieved by selections and modifications of the types of ligands that attach to the QD surface. On the other hand, the effects of ligand coverage on the surface of QDs are still mostly ignored for tuning the electronic properties of QD assemblies.



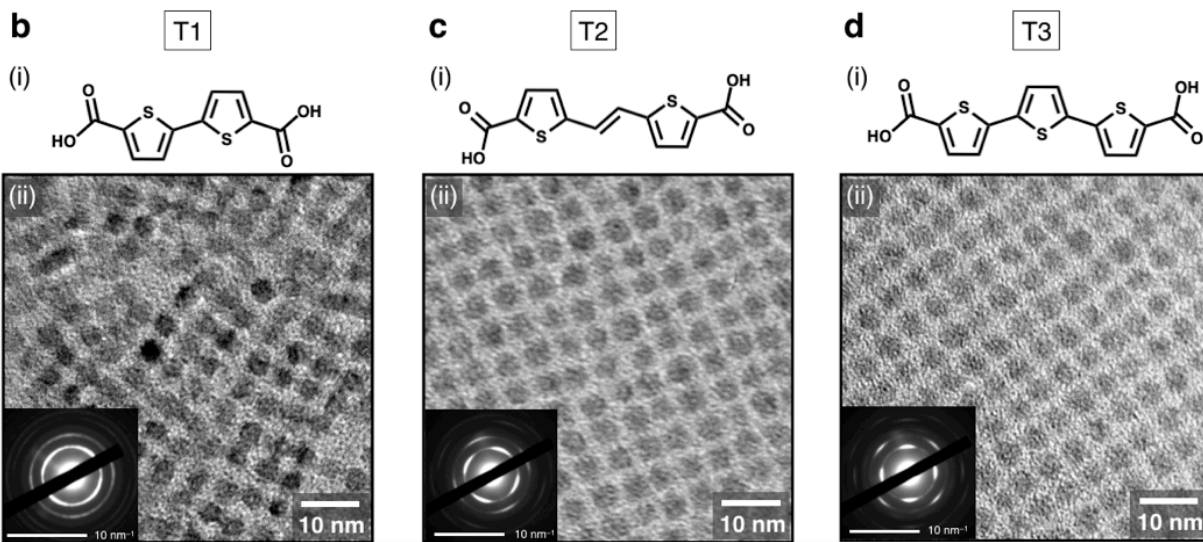
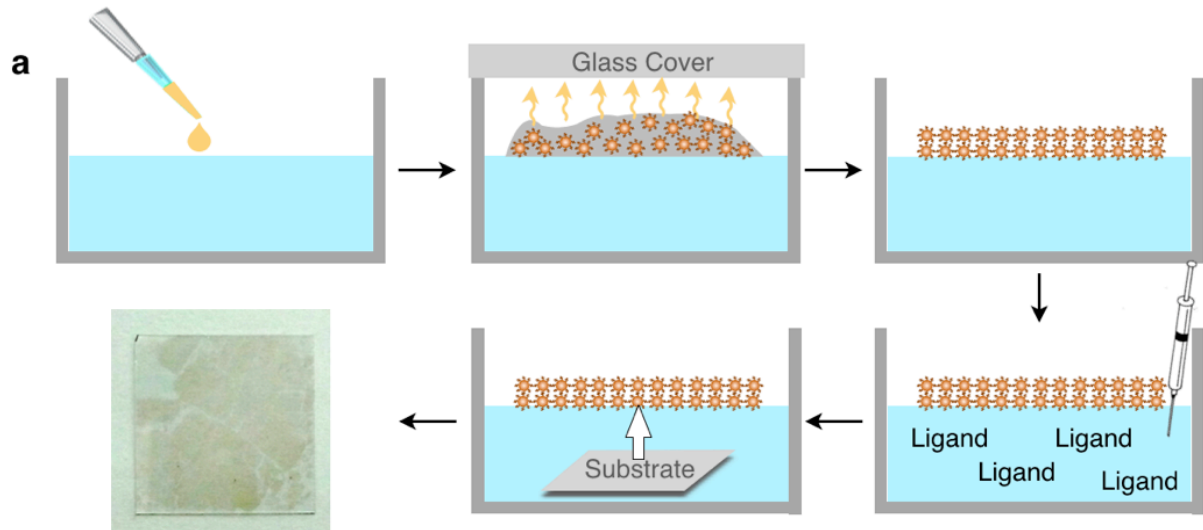
**Figure 3.** (a) Schematic images of different ligand coverage on PbS QDs fabricated by different bottom liquids, where (a-i) methanol (MeOH) gives the smallest ligand coverage; (a-ii) dimethyl sulfoxide (DMSO) gives moderate ligand coverage; (a-iii) acetonitrile (MeCN) gives full ligand coverage. (b) TEM images of corresponding assembly structures by different ligand coverage. (c) The  $I_D$ - $V_G$  transfer curve of the corresponding QD films, where the solid line shows drain current and the dashed line shows gate (leak) current.

There are mainly three following reasons why the effects of ligand coverage have not been scrutinized during the fabrication of electronic devices based on QDs. Firstly, most researchers perceive that the full ligand coverage on the surface of QDs is the best for electronic devices, as the ligands could protect the QD surface from oxidation, and coalescence. Therefore, in many of previous reports, efforts to introduce the full coverage of the newly designed ligands on the surface of QDs are always demonstrated. Therefore, almost no attempts to control the coverage of these ligands have ever been reported. Secondly, the accurate quantitative evaluation of the ligand amounts on the surface of QDs is still lacking. The FTIR (Fourier transformed infrared spectroscopy) technique, which is the most often used in this field, could only offer a qualitative comparison of the ligand exchange ratio, but it could not provide the quantitative analyses to show the exact amount of ligands on the surface of QDs. Thirdly, the ligand coverage control itself needs a precise control of ligand binding on the surface of QDs in nanoscale, which is still very challenging.

In this [Ligand Coverage Control] part, we found that the electronic properties of the monolayer films of PbS QDs can be tuned by the ligand (oleic acid) coverage on the surface of QDs, where neither the full-coverage ( $2.4 \text{ ligand/nm}^2$ ) nor sparse coverage ( $0.7 \text{ ligand/nm}^2$ ) of ligands, but the medium ligand coverage ( $2.1 \text{ ligand/nm}^2$ ) can give the best electronic transport properties for QD assemblies. The degree of ligand coverage on the surface of QDs was precisely controlled by using various bottom liquids (acetonitrile (MeCN), dimethyl sulfoxide (DMSO), methanol (MeOH)) in the liquid/air assembly technique. These bottom liquids with different solubility of oleic acid can remove oleic acid from specific QD facets to control the oleic acid coverage and therefore control the assembly structures (full coverage: quasi-honeycomb lattice; medium coverage: square lattice; sparse coverage: random lattice). We believe that the fabrication and characterization methods of ligand coverage controlled assemblies here will give new insights in both the basic science of ligand quantification of QDs and the applications of electronic devices based on QDs.

#### **[4] Dependence of Carrier Mobility on Ligand Conjugation Length in QD Assemblies <sup>(3)</sup>**

Coupled organic-inorganic nanostructures (COINs) exploit electronic interactions between an inorganic QD core and its organic ligand shell.<sup>[5]</sup> By replacing the insulating surface molecules typically introduced during synthesis with molecules of tailored functionalities, new functional, e.g. optical and electronic, properties can be obtained. As a result, enhanced photovoltaic conversion efficiencies, increased catalytic activity, facilitated energy transfer and photon upconversion have been realized. Specifically, COINs based on lead chalcogenide QDs are widely applied in optoelectronics due to a large size-tunability of the bandgap and high intrinsic charge carrier mobilities. Although there are a few reports, which show finely designed conjugated ligands for perfect energy level alignment between QDs and ligand molecules, the systematic study of the effects of ligand conjugation length, ligand energy levels on electronic transport properties in QD assemblies is still lacking. This is partly due to the difficulty of ligand synthesis, the hard assembly control after ligand exchange, the uncertainty of ligand exchange ratio and various unknown parameters in the devices to affect the final electronic transport properties (e.g., the surface traps on the SiO<sub>2</sub> substrate for FET devices, etc.).



**Figure 4.** (a) PbS QD film growth and transfer processes by a modified liquid air assembly technique. The photograph shows a typical liquid air assembly film transferred to a glass slide. Molecule chemical structures of different conjugated ligands T1 (b-i), T2 (c-i), T3 (d-i). TEM images of superlattices fabricated with different long conjugated ligands T1 (b-ii), T2 (c-ii), T3 (d-ii), where the inset selected area electron diffraction (SAED) images show that longer conjugated ligands give better-ordered QD assemblies.

In order to solve the problems mentioned above and give reliable comparison of the conjugation length and energy level effects on QD assemblies, (i) a modified liquid air assembly technique (Figure 4a) is used in this study to ensure the same ligand exchange ratio and well-ordered QD assembly structure; (ii) an electric double layer transistor is used to compare the electronic transport properties between different ligands capped QD assemblies to exclude the influence of the unknown surface traps in SiO<sub>2</sub> substrate. From the systematic study by using these two above-mentioned techniques, we find that (i) the QD lattice after ligand exchange always give square lattice due to the low binding strength of the oleic acid on [100] facet; (ii) long ligands show better assembly structures than short ligands; (iii) the energy level and the conjugation length of the ligands definitely influence the carrier mobility of QD assemblies. We believe that this study provide a new toolkit of ligands to align QD energy levels and give a new ligand design strategy for QD electronic devices.

## [5] Conclusions

In this thesis, well-controlled electronic properties of QD assemblies are achieved by ligand chemistry: the type of the ligands, the coverage of the ligands, and the conjugation length of the ligands. We carefully studied every small parameter of the ligand exchange process to understand what really happened during ligand exchange. Therefore, we can control these parameters to improve the conductivity of QD films. The newly designed *short conjugated ligands* based on thiophene put a new item to the researcher's toolbox to control the electronic transport properties for electronic devices based on QDs. The *degree of ligand coverage* can control both the assembly structure and electronic properties of QD assemblies. The *long conjugated ligands* show both long-range order assemblies and good electronic properties. We believe that the designed ligands and the ligand exchange method used in this thesis will show big impact on improving the electronic properties and open new application possibilities for QD assemblies.

## [6] References

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## [7] Publications

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- (2) L. Liu, S.Z. Bisri, Y. Ishida, T. Aida, Y. Iwasa, *Nanoscale*, submitted.
- (3) L. Liu, S.Z. Bisri, Y. Ishida, T. Aida, Y. Iwasa, to be submitted.