Designing electronic materials have been in the focus of scientists for the last several decades, trying to avoid the huge energy cost of forming the highly pure, single crystalline silicon wafers required for modern electronics. Solution-processed organic materials (fullerenes and polymers) were developed first, and took over some applications from the classical, inorganic semiconductors, especially in the screens of mobile phones and TVs. However, their high sensitivity to heat and ambient conditions, and the low carrier mobilities and light absorption limits their use in large-scale energy harvesting and electronic devices. Consequently, solution-processed inorganic semiconductors, especially colloidal quantum dots (CQDs) have gained significant attention.

The interest in CQDs stems from the prospects of fully tunable electronic and optical properties and easy fabrication. However, for a very long time, the prospects remained unexploited in lack of deep knowledge on the chemistry and physics of the materials. Due to the large surface of the nanocrystals, different processes get the emphasis compared to bulk samples, and different characterization and treatment methods had to be developed to test and control the relevant properties. The general knowledge in colloid chemistry had to be expanded making it suitable for the fabrication of highly pure, electronic-grade materials.

The properties can be deliberately controlled by modifying the surface, as shown in this thesis. The curial step in fabricating CQD solids, electronically coupled arrays of CQDs, is the ligand-exchange: the initial surfactants have to be replaced by shorter ones to induce coupling. At the same time, the chemistry of the new ligands determines the electronic properties of the solids, giving a tool for proper control. Aspects of this control are discussed in Chapters 2, 3 and 5. The process requires lots of optimization and suitable equipment; a solution to this problem is offered in Chapter 4. CQDs are not only relevant for large-scale applications, but for their confined nature and the related unique physical properties as well; related experimental results are discussed in Chapter 6.

In the work reported in Chapter 2, we established the conditions for reproducible fabrication of high performance, thiol-treated PbS CQD FETs. We showed that the fabrication and measurement plays a crucial role in the process; ambient conditions can lead to a switch from n-type to p-type behavior. Interestingly, this effect was found to be largely reversible under mild annealing, suggesting an origin related to the physisorption of oxygen and water in the CQD film. This finding also highlights the importance of the large surface area in controlling the electronic properties of CQD solids.

The known air-sensitivity of the thiol-capped CQDs was targeted by using atomic, halide ligands in Chapter 3. We observed the formation of ordered PbS CQD superlattices with common orientation and epitaxial merger of the CQDs both in mono- and multilayers. The order depends on the counterion used with the iodide ligands, pointing to its influence in the ligand exchange process. We shed light to the mechanism of the ligand exchange by
creating a non-reactive environment for the ligand exchange, and tune the reactivity of solutions, showing the presence of an acidic catalytic process. With this, we showed that FETs are not only useful to test physical properties, but such a characterization also delivers indirect data on chemical processes in the material.

Designer materials are technologically interesting only if there is a large-scale fabrication method that results in the same properties as the lab-scale samples. For CQD solids, solution-phase ligand exchange and blade coating are the prospective methods replacing the layer-by-layer spin coating and thin film ligand exchange, as shown in Chapter 4. We showed that single-step blade-coated FETs can be on par with the best layer-by-layer processed ones regarding charge carrier mobility and on/off ratio with an additional post-deposition washing step. The fabrication method can be directly upscaled showing the prospects of CQD solids in (opto)electronic devices.

Besides the facile film formation, controlling the electronic properties is also crucial for practical applications. In Chapter 5, we showed that the typical dominance of electron transport in halide-capped PbS CQD solids is mainly caused by the off-stoichiometry inherent to the particles. By adjusting the lead-sulfur balance, we achieved changes in the hole mobility, while the electron mobility remained similar, suggesting a changing electronic structure in the thin film. Such flexibility in the properties is only achievable in nanostructured materials with large surface area, demonstrating the relevance of CQD solids in designing electronic materials for applications.

Most current application of CQDs rely on disordered arrays of CQDs. On the other hand, long-range translational order is predicted to result in coherent transport, offering new possibilities for observing and exploiting unique, confinement-based phenomena. Having investigated and discussed the different aspects of controlling the properties of disordered CQD solids, we expanded the research to ordered superlattices. In Chapter 6, the effect of different ligands on the nanostructure and electrical transport in large area PbSe CQD superlattices is investigated. We measured electron mobilities up to 24 cm²/Vs, the highest ever reported in quantum confides systems, and observed a clear improvement compared to a disordered reference sample. The implications of these findings are including the prospects of achieving coherent transport in CQD superlattices, exploiting confinement-based phenomena such as enhanced Seebeck-effect, and fabrication of highly efficient optoelectronic devices operating in the near infrared wavelengths.

In summary, this thesis demonstrates several ways of controlling the electronic properties of electronically coupled CQD arrays, the so-called CQD solids. These materials show much larger tunability of the electronic, electrical and optical properties than the bulk semiconductors, and show greater promises than the organic semiconductors. Several questions are still open, but the discoveries and developments of the last couple years strongly suggest that researchers will soon be in full control of the properties, and the commercialization of CQDs solids will bring a new era in energy harvesting and (opto)electronics.