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Charge extraction from colloidal inorganic nanocrystals

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Chapter 3

Surface modification of semiconductor nanocrystals

Abstract

*In this chapter we report on successful binding of a fullerene derivative, namely 3,4-dihexyloxyphenyl-C₆₁-butyric-acid (dPCBA) to the surface of PbS and CdSe nanocrystals (NCs). This molecule is an excellent candidate to serve as electroactive ligand for NCs and form novel complexes, which could be very promising building blocks for optoelectronic devices. The surface modification was followed by steady-state and time-resolved photoluminescence (PL) experiments. The dramatic PL quenching in the case of both NCs indicates photoinduced charge transfer from NCs to dPCBA molecules as a result of effective coordination of dPCBA to the NC surface. The electrically active nature of the new complexes is proven by current-voltage measurements on thin films of the NC-dPCBA complexes.**

* K. Szendrei, D. Jarzab, M. Yarema, M. Sytnyk, S. Pichler, J.C. Hummelen, W. Heiss, M. A. Loi, *Journal of Materials Chemistry*, **2010**, 20, 8470

3.1 Introduction

Colloidal inorganic nanocrystals (NCs) have recently received increasing attention due to their unique photophysical properties,¹ resulting in promising applications in biological labeling²⁻⁴, light-emitting diodes^{5,6} and photovoltaic devices⁷⁻¹⁰. For most of these applications the key issue is to be able to control the surface chemistry of the NCs, since a ligand shell is needed to prevent aggregation. NCs are generally stabilized with commercially available ligands such as carboxylic acids, amines, phosphines, phosphine oxides and alkyl thiols, which are all electrical insulators. It has been shown that integrating semiconducting NCs with insulating ligands into polymer-based photovoltaic cells could lead to good performance by partially removing the ligands from the NCs during film processing. However, controlling the appropriate morphology and dispersion of the NCs within the polymer matrix remains challenging⁷. Therefore, the integration of NCs into optoelectronic devices requires direct surface modification of the NCs. Via surface design, many crucial features of the NCs can be tuned, such as solubility, reactivity, processability and most importantly electronic properties with direct effects on the conduction and optical activity.

Several strategies, starting from the simplest ligand exchange^{11,12} to attachment of end-functionalized polymers¹³⁻¹⁵ and small molecules¹⁶⁻²¹, as well as layer-by-layer assemblies²² have been explored so far. The most interesting attempts are based on binding of organic electronically active ligands to the NCs' surface to form hybrid complexes. Milliron et al. have designed an electrically active oligothiophene ligand and succeeded to attach it to CdSe NCs¹⁷. Here changes in the fluorescence quantum yield revealed photoexcited hole transfer from the CdSe NCs to the oligothiophenes. Few examples of attached^{16,18,19} or adsorbed²³ fullerenes (C₆₀, C₇₀) on the NCs' surface are also reported. To bind fullerenes to the NCs' surface, fullerene derivatives have to be designed with proper end-functionalization, which has high affinity for the NCs surface. In the most promising cases C₆₀ molecules were used to create C₆₀-CdSe and C₆₀-PbSe conjugates. However, the major drawbacks of conjugating C₆₀ to NCs are the very low solubility of C₆₀ and the need of attaching a long dithiocarbamate functionalized co-ligand to C₆₀^{18,19}. The photo-electrochemical properties of C₆₀-NC conjugates revealed enhanced photocurrent suggesting photoinduced electron transport from NCs to the conjugated C₆₀, but without deeper insights in the optical properties of NC-C₆₀ conjugates.

In the current work, we report on successful binding of a fullerene derivative, namely 3,4-dihexyloxyphenyl-C₆₁-butyric-acid (dPCBA)²⁴ to PbS and CdSe NCs. This molecule is an excellent candidate to serve as electroactive ligand, having

carboxylic acid as functional end-group which has a high affinity to the NCs' surface. In addition, dPCBA (Figure 3.1) is a semiconductor with similar structure and properties to its famous sibling PCBM (phenyl-C₆₁-butyric-acid-methyl-ester), which is widely used as electron acceptor in bulk heterojunction photovoltaic devices²⁵. To the best of our knowledge, attachment of such C₆₀ derivatives to NCs without co-ligands has not yet been reported.

3.2 Results and discussion

3.2.1 Optical characterization of dPCBA-NC complexes

An idealized sketch of the NC surface modification is shown in Figure 3.1. The as-prepared PbS and CdSe NCs are stabilized by oleate (o-PbS) and oleylamine (o-CdSe), respectively. These compounds are two of the most often used coordinating ligands for colloidal NCs.

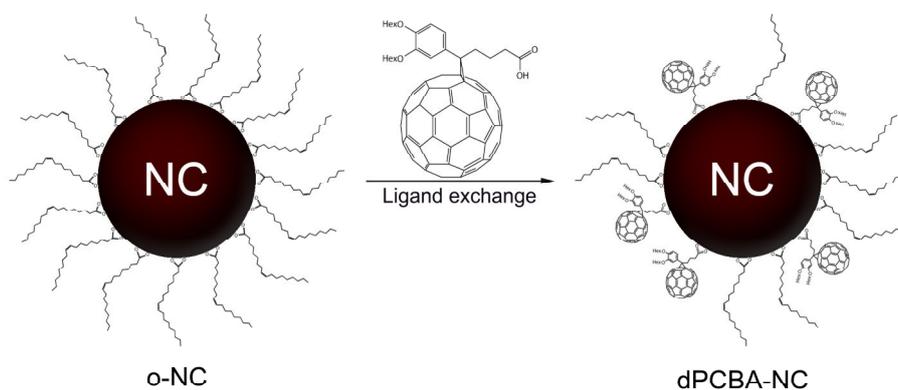


Figure 3.1 Schematic illustration of the surface modification of NCs using dPCBA molecules

The simple ligand exchange reaction is carried out by adding various amounts of dPCBA molecules to PbS and CdSe NC solutions. The optical density (OD) spectra of the as-prepared PbS and CdSe NCs, as well as of the ligand-modified NCs are presented in Figure 3.2. The inset (Figure 3.2 (b)) shows the optical density of dPCBA which is very similar to previously reported data for PCBM²⁶⁻²⁸. As a result of the ligand exchange, the first excitonic peak of PbS NCs, which is located ~930 nm, is blue-shifted by about 40 nm, as well as the first excitonic peak of CdSe NCs (~528 nm) by about 10 nm. Similar shifts have been reported to be evidence of successful surface modification²⁹. We followed the ligand exchange phenomenon by steady-state and time-resolved photoluminescence (PL)

experiments, since the PL quenching can serve as good indicator for NC-ligand interaction¹⁷.

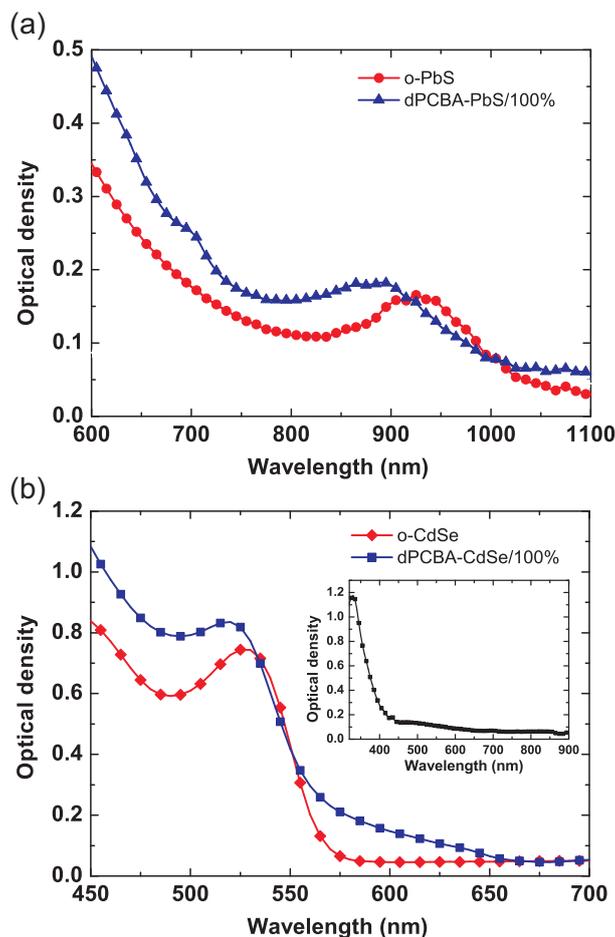


Figure 3.2 Room-temperature OD of a) dPCBA-PbS NCs and b) d-PCBA-CdSe NCs compared to the OD of dPCBA and o-PbS NCs or o-CdSe NCs, respectively. Inset shows the OD spectra of dPCBA molecules

A series of dPCBA concentrations were equilibrated with a certain fixed concentration of as-synthesized PbS and CdSe NCs. Figure 3.3 a) shows the steady-state PL of PbS NCs, which is dramatically quenched with an increasing concentration of dPCBA. An analogous effect was observed for CdSe NCs (Figure 3.3 b)), where the steady-state PL of CdSe NCs is decreasing with increasing dPCBA concentration. To picture the degree of PL quenching, the maximum steady-state PL intensities of dPCBA-NCs are plotted for increasing concentrations of dPCBA and compared to those of NCs:PCBM blends in Figure 3.3 c) and d).

As a control experiment, PCBM was added to as-prepared PbS and CdSe NCs. PCBM does not have free carboxylic acid moiety, therefore it is not expected to cause a dramatic PL quenching of the NCs, since it is unable to coordinate to the NCs' surface. Indeed, when only 10% of dPCBA was equilibrated with NCs, the PL quenching was already more pronounced than in the control sample composed by 1:1 ratio of NCs:PCBM. In solution, PCBM molecules and NCs interact weakly, therefore a higher concentration of PCBM is needed to cause PL quenching. Conversely, when NCs and dPCBA molecules are in close proximity, as is in the case of surface binding, the PL quenching is much more effective even with a limited amount of dPCBA. The much stronger PL quenching in the case of both NCs indicates the effective coordination of dPCBA to the NC surface. It is important to underline that the quenching of the steady state PL in the case of the CdSe crystals could be due to either energy transfer or charge carrier transfer from the excited NCs to dPCBA.

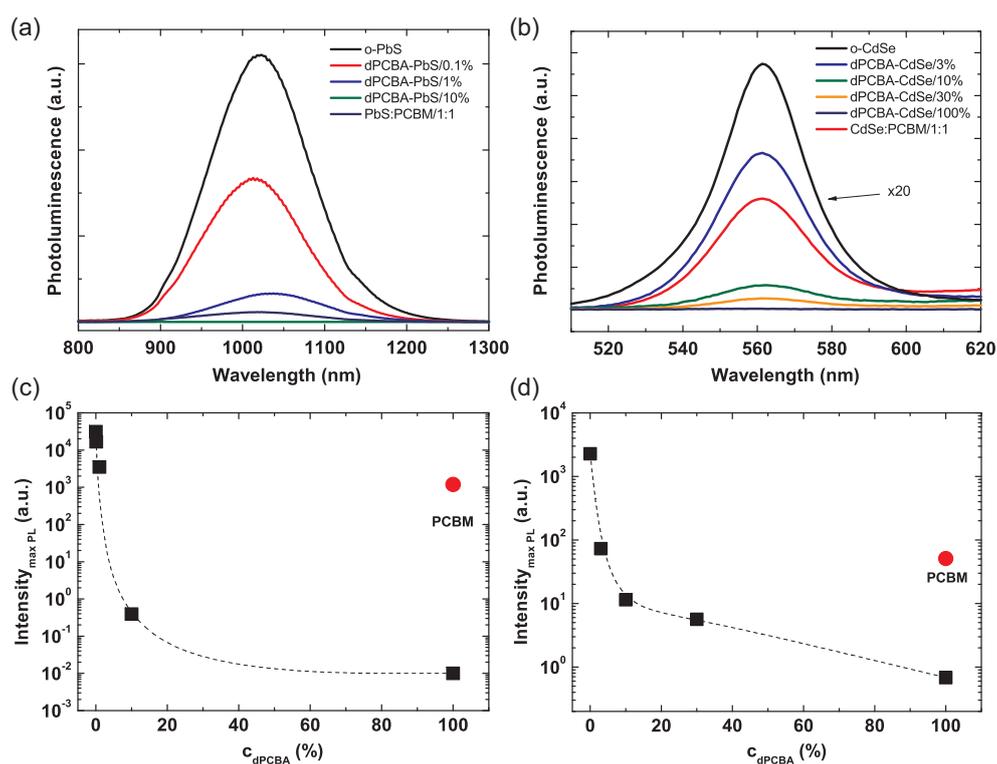


Figure 3.3 Steady-state PL of a) oleate and dPCBA capped PbS NCs and the control sample PbS:PCBM b) oleylamine and dPCBA capped CdSe NCs and the control sample CdSe:PCBM. Steady-state PL maxima of c) oleate and dPCBA capped PbS NCs and the PbS:PCBM control sample and d) oleylamine and dPCBA capped CdSe NCs and the CdSe:PCBM control sample in solution.

Time-resolved PL is an elegant experimental tool to provide more information about the efficiency of the PL quenching. Figure 3.4 a) and b) show the PL decays of PbS and CdSe NCs with increasing dPCBA concentration, respectively. In both cases, the PL decay times are much faster when only 10% of dPCBA is added to NCs solutions compared to the control NCs:PCBM solution.

The PL of the pristine o-PbS decays mono-exponentially with a time constant of $\sim 1.9 \mu\text{s}$, while the PL of PbS with 10% dPCBA shows a bi-exponential behavior with a faster component of $\sim 40 \text{ ns}$ and a slower component of $\sim 430 \text{ ns}$. When PCBM and the as-prepared PbS NCs were co-dissolved in equal amounts, the PL of PbS was quenched as well, but much less compared to the case when 10% dPCBA was used to exchange the original oleate ligand on the NCs. The PL of PbS with equal amount of PCBM shows bi-exponential decays with a faster component of $\sim 130 \text{ ns}$ and a slower component of $\sim 1.2 \mu\text{s}$.

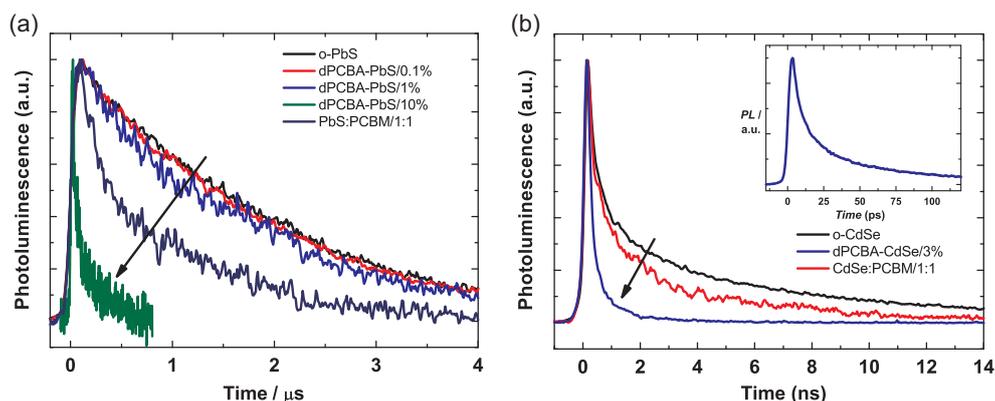


Figure 3.4 Time-resolved PL spectra of a) oleate and dPCBA capped PbS NCs and the PbS:PCBM reference blend and b) oleylamine and dPCBA capped CdSe NCs and the CdSe:PCBM blend in solutions, respectively. Inset shows the magnification of time-resolved PL of CdSe NCs after surface modification with 3% of dPCBA molecules

The same effect was observed for o-CdSe NCs (Figure 3.4 b)). The PL of the as-synthesized CdSe NCs shows a bi-exponential decay with a faster component of $\sim 2.9 \text{ ns}$ and a slower component of $\sim 25.7 \text{ ns}$. After surface modification, the PL decay of CdSe NCs - using 3% of dPCBA - is much faster, showing a mono-exponential decay with time constant of $\sim 4.6 \text{ ps}$ (inset Figure 3.4 b)). Also in this case, the PL quenching is much more efficient than when o-CdSe and PCBM are co-dissolved in equal amounts. Note that it is not possible to measure the PL decay of the NCs above a certain dPCBA concentration (10% for PbS and 3% for CdSe NCs), since the signal is below the instrument sensitivity. Still, we presume from the steady-state PL measurements that using higher concentrations of dPCBA would further speed up the process due to the more efficient ligand exchange.

3.2.2 Electrical properties of dPCBA-NC complexes

To prove the electrically active nature of the new complexes, current-voltage (IV) measurements on thin films of the NC-dPCBA complexes were performed in dark and under illumination. Figure 3.5 a) and b) show that the current under illumination is ~ 3.5 orders of magnitude higher than the dark current in both cases, giving further evidence that photoexcited charge transfer occurs from the semiconductor NCs to the dPCBA molecules. These results are in agreement with previous reports based on electron transfer in NCs/ C_{60} ³⁰ and in NCs/PCBM³¹ blends. Moreover, our devices exhibit surprisingly low dark currents, which could be an advantage for PD and photovoltaic applications.

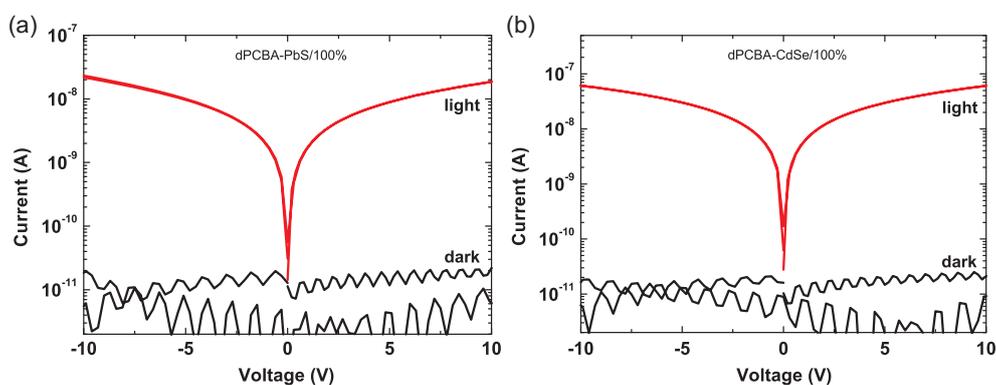


Figure 3.5 Current-voltage characteristics of the thin films formed by a) dPCBA-PbS NCs and b) dPCBA-CdSe NCs

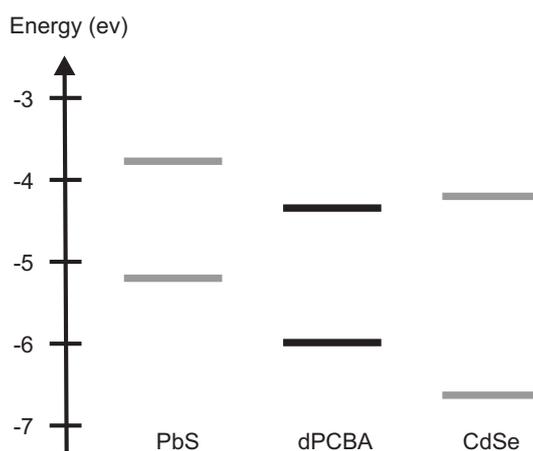


Figure 3.6 The proposed energy level alignment for NC-dPCBA complexes.

The comparison of the relative energy levels of the conduction and valence bands of the NCs and the HOMO-LUMO (highest occupied-lowest unoccupied molecular orbital, respectively) levels of dPCBA provides more information to understand the quenching mechanism. Figure 3.6 show the proposed energy level alignment for both NC-dPCBA complexes. The estimation of conduction and valence bands of the NCs is based on literature data^{32,33}. The value of the energy levels of dPCBA originates from cyclic voltammetry measurements, where the half way potential ($E_{1/2}$) of dPCBA is ~ 0.12 eV below C_{60} , supposing the same shift for the HOMO level of dPCBA²⁴. The energy level alignment between NCs and dPCBA molecules supports the idea of the efficient photoinduced electron and energy transfer from PbS and CdSe to dPCBA molecules, respectively. Consequently, the NCs with the new electroactive ligands have great potential for the fabrication of NC-organic optoelectronic devices. In the case of PbS NCs, energy transfer can be eliminated as the mechanism of PL quenching, since the HOMO of dPCBA lies deeper than the valence band of PbS NCs, with respect to the vacuum level.

3.3 Conclusions

In summary, we have introduced a new surface modification of NCs using electroactive organic C_{60} derivatives. The successful ligand exchange reaction was evidenced by UV-Vis, PL and time-resolved PL measurements indicating photoinduced charge transfer from NCs to dPCBA molecules. Current-voltage characteristics of NC-dPCBA complexes showed enhanced photocurrents due to photoinduced charge carrier transfer and lowering of the potential barrier between NCs, which indicates that NC-dPCBA complexes are promising building blocks for solar cell fabrication.

3.4 Experimental

Synthesis of NCs. PbS NCs with size of ~ 3 nm were synthesized by hot injection method³⁴. CdSe NCs with average size of ~ 5 nm were synthesized by Sytnyk et al.³⁴

dPCBA molecules were synthesized according to ref. 23 and were dissolved in chlorobenzene at concentrations of ~ 30 mgmL⁻¹ for ligand exchange. The solution of dPCBA was sonicated at 70°C for 30 min.

Surface functionalization of NCs. The oleate-capped PbS and oleylamine-capped CdSe NCs were precipitated from the crude solution by adding a polar solvent mixture of hexane and ethanol (1:2). After precipitation, the NCs were

centrifuged and redissolved in chlorobenzene to form stable colloidal solutions. Coordination of dPCBA molecules was performed in a nitrogen-filled glovebox by simple addition of various amounts of dPCBA to the NCs solutions. dPCBA was systematically added to the PbS or CdSe NCs solution. In detail, 0.1% means 1:1000, while 100% means 1:1 weight ratio of dPCBA:PbS and the same strategy applies for CdSe NCs and NCs with PCBM (Solenne) as reference samples. The ligand exchange reaction was equilibrated within approximately 15-20 min after dPCBA addition.

Optical and electrical characterization. Optical density spectra of NCs, NC-dPCBA and dPCBA were taken with a Perkin Elmer Lambda 900 spectrometer. Steady-state and time-resolved PL measurements were performed by photoexciting the NCs with a 150 fs pulse Kerr mode locked Ti-Sapphire laser (Coherent, Mira 900), using an optical pulse selector (APE, Pulse Select) to vary the repetition frequency of the exciting pulse train between 80 MHz and 130 kHz. Samples containing PbS were photoexcited at 770 nm and the spectra were detected at 1020 nm, while samples containing CdSe were photoexcited at 387 nm and PL signal was detected at 560 nm.

The steady-state PL was measured in the near-infrared with an InGaAs detector from Andor and in the visible with a Si-CCD from Hamamatsu. The time-resolved PL was recorded by two Hamamatsu streak cameras working in synchroscan and single sweep mode, one with a photocathode sensitive in the visible and the other in the near-infrared spectral range. All of the measurements were performed at room temperature. For electrical characterization, NC-dPCBA solutions were spin cast (500rpm/s) onto interdigitated gold electrodes with 5 μm spacing. The measurements were carried out in a home-built probe station under high vacuum (10^{-6} mbar) with Keithley 4200 semiconductor analyzer at room temperature. The illumination of the samples was provided by a 532 nm fiber-coupled laser with a power of 11 mW cm^{-2} .

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