Summary

The main focus of this work was the phase transfer of nanoparticles from non-polar organic solvents into water. The method chosen to achieve phase transfer was the exchange of the native capping ligands with water-soluble polymers. The employed polymers were based on highly water-soluble poly(ethylene oxide), PEO, which was functionalised so that it contained suitable functional groups which could bind to the nanoparticle. Amino and mercapto functionalities were used as binding groups.

This work deals mostly with the phase transfer of semiconductor nanoparticles based on CdSe. The CdSe nanoparticles were synthesised by the hot-injection technique in a “greener” chemical approach. The influence of the amount of phosphonic acid (tetradecylphosphonic acid, TDPA), employed as one of the coordinating ligands during the synthesis of CdSe, on the kinetics of the growth and properties of the CdSe nanoparticles was investigated. With decreasing amount of TDPA, the particle growth was faster, for very low amounts often uncontrollable, and the luminescence yields were lower. For all further syntheses of the CdSe nanoparticles used in this work, the highest investigated amount of TDPA investigated (0.9 wt%) was employed. The core CdSe nanoparticles were covered with an inorganic shell of CdS, a higher band gap material, to produce more robust CdSe/CdS nanoparticles. In addition, even more stable, CdSe/CdS/ZnS, core/shell/shell nanoparticles were synthesised using a one pot synthetic method. All the synthesised nanoparticles were characterised by absorption and luminescence spectroscopy, as well as XRD and TEM analysis.

To obtain poly(ethylene oxide) ligands possessing amino functional groups, two types of synthetic routes were utilised. In one, block copolymers poly(ethylene oxide)-*b*-(ethylene imine), PEO-*b*-PEI, were synthesized by the cationic ring opening polymerization of 2-ethyl-2-oxazoline, starting from tosyl-PEO as the macroinitiator. Three polymers with varying length of the PEI block (5, 10 and 20 PEI units) were synthesised. In the second approach, PEO was coupled with different amino group bearing molecules by the diisocyanate coupling reaction. In the second approach, in addition to linear polymers, produced by coupling PEO and diethylenetriamine or pentaethylenehexamine, branched ones were also synthesized by coupling two PEOs to a small molecular weight PEI core.

Ligands with mercapto groups as binding groups were also produced in two different ways. In the first approach, esterification of mercaptopropionic acid with PEO monomethyl ether was performed resulting in linear polymers of different length with a mercapto group at one end of the polymer chain. In this way, starting from PEO with two hydroxyl groups at one end of polymer chain, a ligand with two mercapto groups was also synthesised. PEO based ligands possessing more mercapto groups and with branched structures were prepared through the Michael type reaction between the acrylate end group of acrylate-functionalised PEO and the mercapto group of a molecule with four mercapto groups. Three types of ligands were produced with one two or three PEO branches possessing three, two or one mercapto group, respectively. The PEO ligands with mercapto and with amino functionalities were characterised by NMR spectroscopy and SEC, in order to confirm the desired structure.

Ligand exchange was achieved by exposure of the nanoparticles to a large excess of amino-functionalised PEO-based ligands. Subsequent addition of a non-solvent for the new capping groups enabled the nanoparticles covered with PEO to be separated from the native ligands. The obtained PEO covered nanoparticles were readily soluble in water, whereby all their properties were retained. The solutions of nanoparticles were stable for months and insensitive to a change in the ionic strength of the medium. In solutions of low pH values, the nanoparticles exhibited lower photoluminescence efficiencies due to the protonation of the amino groups, and such solutions were less stable than those of higher pH value. The luminescence efficiencies of nanoparticles transferred into water were generally lower compared to those of nanoparticles in chloroform. The efficiencies were not decreased only in the case of the ligand with a small binding part and with the lowest

molecular weight PEO block, and were sometimes even higher than those measured for the nanoparticles in chloroform. Using the same method for ligand exchange, in addition to semiconductors, magnetic Fe_3O_4 and $CoPt_3$ nanoparticles could also be made water-soluble with the amino-functionalised PEOs.

Depending on the [amino-functionalised polymer]/nanoparticle ratio employed during the ligand exchange, which dictates the number of attached polymers to the nanoparticles, the structure of the nanoparticle-polymer conjugate can be directed. For low ratios, worm-like, while for the high ratios spherical conjugates were present in the respective aqueous solutions. The type of the structure can also be varied by changing the type of the employed ligand. The formation of worm-like conjugates is promoted when the binding amino part of the PEO ligand is small. All the observed changes could be qualitatively described by the packing parameter theory.

In an attempt to further increase the stability of the polymer-nanoparticle conjugate, the crosslinking reaction of the PEO2000-PEI-branched around the nanoparticles with hexamethylenediisocyanate was investigated. Although the reaction, which was followed by IR spectroscopy, was successfully performed without any deleterious effect on the nanoparticles, the stability, as judged from chemical and long-term stability experiments, was not improved. Further optimization of the ligand architecture, as well as the use of a more suitable crosslinking agent is necessary for the nanoparticles with a crosslinked polymeric shell to show better characteristics.

The same method for ligand exchange was applied in the case of mercapto-functionalised PEO ligands. Aqueous solutions of nanoparticles covered with mono-mercapto-functionalised PEOs were more stable than those containing nanoparticles bearing mono-amino ligands. This behaviour is due to the stronger binding of the mercapto group and its more difficult dissociation from the nanoparticle surface, which are the result of the less pronounced hydrogen bonding of the mercapto group. The luminescence efficiencies were lower for the nanoparticles stabilised with mercapto-functionalised PEOs, however, they were still high enough for these nanoparticles to be employed in further experiments of interest. The size of the nanoparticle-polymer conjugates, measured by dynamic light scattering, increased with increasing polymer chain length. Nanoparticles covered with branched PEO ligands of the smallest molecular weight exhibited hydrodynamic radii in water which were insignificantly larger than the hydrodynamic radii of the native nanoparticles in chloroform.

The photochemical stability of the nanoparticles covered with mercapto-functionalised PEOs was investigated and compared to the properties of nanoparticles covered with mercaptopropionic acid. In all cases, nanoparticles covered with a dense polymer coating were more stable than the nanoparticles stabilised with mercaptopropionic acid.

The attachment of PEO based ligands, different with respect to the binding group and the overall molecular architecture, to nanoparticles allows for the properties of the nanoparticle-polymer conjugate to be chosen as desired. The different ligand molecular architecture also allows the final structure of the conjugate to be predicted and dictated.