

Semiconductor Nanocrystals with Multifunctional Polymer Ligands

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The color tunability of semiconductor nanocrystals (NCs) as a function of size could lead to many applications that rely on color multiplexing.¹ For example, it has been shown that differently sized NCs can be used as fluorescence labels to stain biological samples.² For this purpose, the surface chemistry of the nanocrystals is of major importance, because functional surface ligands can serve as linkers between the particles and an appropriate docking site.

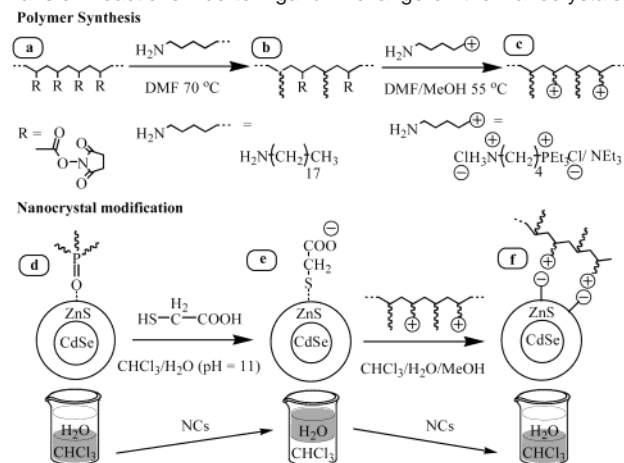
In principle, a functional surface linker consists of an anchor group that attaches to the nanocrystal, a functionality, and a spacer in between. Possible organic anchor groups for semiconductors such as CdSe or ZnS are provided by amines, oxides, and thiols, which have different affinities to the NC surface and alter the fluorescence properties to a different degree. For example, the use of amines as anchors increases the fluorescence quantum yield up to 70–80%,³ but only if the solution contains an excess of these ligands. We found that the quantum yield is considerably reduced if the excess ligands are removed by precipitation techniques, probably related to a dynamic exchange equilibrium between the ligands on the NC surface and in the solution.⁴ A more stable bond can be formed with thiols, although these groups reduce the fluorescence of CdSe particles.⁵ However, it has been shown that even thiol covered NCs can precipitate after some time,⁶ which was explained by photo-induced dimerization of close packed thiol groups on the particle surface.⁷

The purpose of the functionality is to render the particles soluble or to provide the “right” reactivity when the NCs are used as chemical agents. For example, aliphatic chains provide solubility of the particles in nonpolar solvents,⁸ while deprotonated carboxylic functions will lead to charged particles that are soluble in water.⁹

A major problem in linker chemistry is that the stability of the complex relies on the strength of only one chemical bond. If either the anchor to the NC surface or the functional docking bond breaks, the whole complex will dissociate. To avoid this problem, we developed a versatile polymer ligand based on a polyreactive ester,¹⁰ which can be substituted by multiple anchors and functionalities. As an example, we show that poly(acrylamide) ionomers with a certain ratio of ionic and aliphatic chains can be attached to CdSe/ZnS nanocrystals by a phase transfer reaction.¹¹ The resulting polymer-coated NCs can be dispersed in many organic solvents and are characterized in terms of structure and photostability.

The synthesis of the polymeric ligand is shown in the top part of Scheme 1. It starts from polymer (a), which could be obtained by polymerization of *N*-acryloyloxysuccinimide in benzene/dioxane with azo-bis-isobutyronitrile (AIBN) as initiator. The monomer was prepared by reaction of acryloyl chloride with *N*-hydroxysuccinimide. The mean number of repeating units of this polymer was determined from an appropriate derivative by gel permeation chromatography (GPC)¹² to be about 290 monomers. This polymer of reactive esters can, in principle, be statistically substituted with any compound containing amino-functionalities. In our experiments,

Scheme 1. (Top) Synthesis of the Functional Ligand Starting from a Chain of Reactive Esters, Which Are Subsequently Substituted by Unpolar and Charged Side Chains, and (Bottom) Phase Transfer Reactions Due to Ligand Exchange on the Nanocrystals^a



^a The TOPO ligands of ZnS covered CdSe nanocrystals are first substituted by mercapto acetic acid, which leads to water-soluble NCs after deprotonation. Attachment of charged side groups from the amphiphilic polymer transfers the NCs back to chloroform.

we performed a stepwise substitution of the reactive esters by charged and nonpolar side groups.¹³ In the first step, a certain amount of the reactive esters (50, 70, or 90%) was substituted by octadecylamine chains (b). In the second step, the remaining reactive sites were substituted by an aliphatic phosphonium salt, which led to the amphiphilic polymer (c).

The CdSe nanocrystals were prepared following standard procedures¹⁴ and nominally covered with 2 monolayers of ZnS.¹⁵ Because of the synthesis, the particles are initially covered with trioctylphosphineoxide (TOPO) (d) and are soluble in chloroform. These particles can be transferred from the chloroform into the water phase via attachment of deprotonated mercapto acetic acid (MAA) at pH = 11 (e).⁹ The thiols replace the TOPO from the NC surface to an extent of more than 80%,⁵ and the deprotonated negatively charged carboxylic functions provide the solubility in water.

The NC coverage by the polymer (f) was again accomplished by a phase transfer reaction, where an excess of the polymer was dissolved in chloroform and mixed with the water solution of the NCs.¹⁶ After addition of small portions of methanol¹¹ and vigorous stirring, the particles transferred into the chloroform phase, which could directly be observed by the color change. This corresponds to the known adsorption of polyelectrolytes on charged surfaces.¹⁷ Obviously, the positively charged sites of the polymer are attracted by the negatively charged NC surface ligands, while the aliphatic chains stick out into the solvent to provide the solubility change. We found that this reaction worked only when the amount of charged groups within the polymer was adjusted to about 30–50%. No transfer reaction could be observed for lower amounts of polar chains, probably because of uncompensated negative charges on

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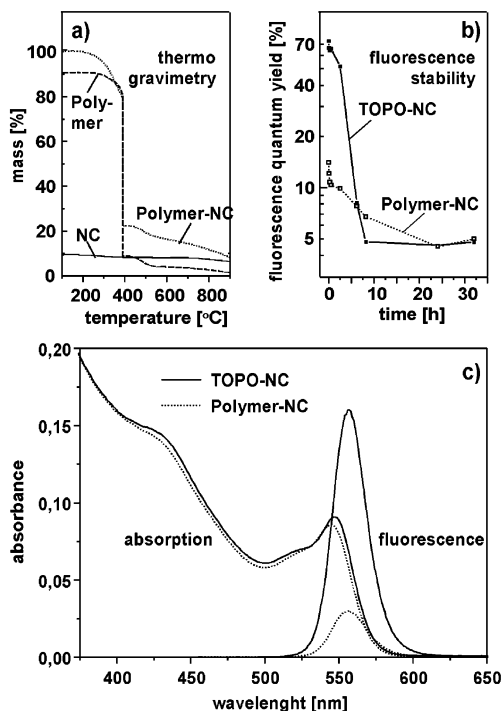


Figure 1. (a) Determination of the mass ratio of polymer versus NC by thermogravimetry. (b) Fluorescence degradation of TOPO-NCs and polymer-NCs in oxygen saturated chloroform solutions under UV illumination. The fluorescence of both samples is decreasing but converges at approximately 5% quantum yield after several hours. (c) Absorption and fluorescence spectra of the TOPO covered CdSe/ZnS NCs (solid line) and of polymer covered particles in chloroform (dotted line). The fluorescence intensity is decreased by a factor of 4 upon surface modification.

the NC surface, while polymers with a higher ratio of charged groups are not soluble in chloroform.

To investigate the amount of polymers that covered the NC surface, we performed a thermogravimetric analysis (TGA), which shows that the mass of the polymer shell is about 9 times higher than that of the NC itself (Figure 1a). Because a CdSe-NC, which is 3 nm in diameter and covered by 2 monolayers of ZnS, has approximately the same molar mass as that of the polymer (~90.000 g/mol),⁴ each NC is presumably covered by about 9 polymer chains. For comparison, one can assume that every MAA molecule covers a surface area of 13 \AA^2 ¹⁸ and hence each NC is covered with 425 MAA molecules. Because a polymer chain with 30% positively charged end groups could compensate approximately 90 negative charges, only about 5 polymers could be attached to one NC, according to these considerations. However, most likely the polymers are not wrapped smoothly around the surface, and hence the coverage is somewhat higher as can be seen from the TGA experiments.

In view of possible applications of the polymer/NC composites, we investigated the stability of the colloidal solutions. While pure MAA covered NCs precipitate after some time,⁶ the NC/polymer composites described in this work did not precipitate even when the oxygen-saturated solution was exposed to UV light for more than a day. This is most likely due to the fact that the possible

ligand dimerization happens at the inorganic particle surface while the stabilizing polymer stays attached to the NC due to the multiple bonding and strong ionic interaction.

The photophysical properties of the particles are compared in Figure 1b and c. While the absorption spectrum does not show a remarkable change after surface modification, the fluorescence intensity drops by a factor of 4 (Figure 1c). This decrease results most likely from the attachment of the MAA. If both solutions are saturated with oxygen and exposed to UV light, the fluorescence quantum yield decreases strongly due to photooxidation effects (Figure 1b). However, it can be seen that in both cases the quantum yield levels out at a value of approximately 5% after 1 day. We assume that the long-term quantum yield is similar because the outermost inorganic shell might be oxidized in both cases.

In summary, we have presented a new versatile polymer ligand that can be attached to semiconductor nanocrystals via a phase transfer reaction. The ligand consists of a chain of reactive esters, which can be substituted with different molecules containing amino-functionalities.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (SFB625).

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- (12) To obtain a GPC-compatible derivative, poly(*N*-acryloyloxysuccinimide) was brought to reaction with *N*-methyl hexylamine. The GPC analysis of the resulting poly(acrylamide) (THF, light-scattering detection) gave the following values: $M_n = 28\,000 \text{ g/mol}$; $M_w = 48\,700 \text{ g/mol}$, where the number of repeating units (290) is based on the M_w value. The calculated molecular weight for the poly(acrylamide) ionomer used in the TGA experiment (see below) is $M_w = 89\,300 \text{ g/mol}$.
- (13) For the synthesis of the poly(acrylamide) ionomers with 30% of ionic amines, 1.00 g (5.93 mmol repeating units) of poly(*N*-acryloyloxysuccinimide) was dissolved in 72 mL of DMF and heated to 70 °C. After that, 1.12 g (4.15 mmol) of octadecylamine was added. The mixture was stirred for 5 h at 70 °C and then cooled to 55 °C. After that, a solution of 1.17 g (4.46 mmol) of 4-aminobutyltriethylphosphoniumchloride hydrochloride in 24 mL of methanol and 8 mL of triethylamine was added. The mixture was stirred for another 16 h at 55 °C. The solvent was evaporated, and the resulting residue was washed three times with 50 mL of methanol. 4-Aminobutyltriethylphosphonium-chloride hydrochloride was synthesized by reaction of *N*-(4-bromobutyl)phthalimide with triethyl phosphine in toluene for 48 h under reflux. The resulting phosphonium salt was refluxed for 7 days with concentrated hydrochloric acid.
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JA028641C