Quantum Dots

Semiconductor Nanocrystals with Adjustable Hole Acceptors: Tuning the Fluorescence Intensity by Metal–Ion Binding**

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Semiconductor nanocrystals (NCs) are robust inorganic chromophores that combine an efficient broadband absorption with a narrow-band fluorescence spectrum. Hence, they have a great potential as photoactive systems in attractive applications such as biolabeling,[1] solar cells,[2,3] light-emitting diodes,[4] and even in sensor systems.[5–7] Whereas most of these applications rely on the tunability of the fluorescence wavelength and thus on the size of the particles, sensor devices require a change of the fluorescence intensity, which strongly depends on surface effects in NCs. As the fluorescence arises from the recombination of photoexcited electron–hole pairs (excitons) within the inorganic NC core, its intensity is lowered if charge carriers are transferred to surface-bound ligands. This process, involving a photoinduced electron transfer (PET), strongly depends on the energetic position of the electronic levels of the NC with respect to those of the molecular orbitals (MOs) of the ligands.

It has been known for many years that ligands may either increase or decrease the fluorescence intensity of NCs. For example, for the well-known CdSe NCs, prepared by standard methods in trioctylphosphine oxide (TOPO),[8] the replacement of TOPO ligands by amines increases the fluorescence intensity,[9] whilst that by thiols leads to a complete fluorescence quenching.[10] For CdTe NCs, prepared by similar methods, the situation is reversed: ligand exchange of TOPO by thiols leads to an increase of the fluorescence intensity.[10] The fluorescence quenching is assumed to be due to a transfer of the photoexcited hole from the top of the NC valence band (VB) to the highest occupied molecular orbital (HOMO) of the attached ligand.[10]

We have investigated the electronic interaction between NC and ligand in detail by optical and electrochemical measurements of similarly sized CdSe and CdTe NCs in combination with different surface ligands, including the phenanthroline ligand 1 (Figure 1). Specifically, we compared
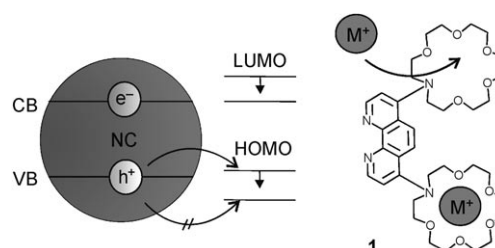

Figure 1. Ligand 1 attached to a CdTe NC. Ion complexation at the aza crown ether sites of the surface-bound ligand suppresses hole transfer from the photoexcited CdTe NC, thus increasing emission. VB = valence band, CB = conduction band.

the emission intensity of NC–ligand combinations with their respective energy levels of isolated NCs and ligands as determined by cyclic voltammetry (CV). Using the ligand 1, the oxidation potential of which can be adjusted by ion complexation, we could demonstrate that the addition of metal ions modulates the PET between the NC core and the attached ligands. As a consequence, the fluorescence of the NC–1 hybrids is made sensitive to the presence of metal ions.

As depicted in Figure 2a,b, the attachment of octadecylamine (ODA) leads to an enhancement of the CdSe–NC fluorescence and to a decrease of the CdTe–NC emission. For thiol ligands, such as dodecylthiol (DT) or mercaptopropionic acid (MPA), the fluorescence of CdSe NCs is quenched whilst that of the CdTe NCs is enhanced. This result can be understood by comparison with Figure 2c, which shows CV measurements from the NCs and also from the respective ligands. The anodic peaks (positive values) are related to the VB of the NCs or the HOMO of the ligands, whilst the cathodic peaks (negative values) result from the conducting band (CB) of the NCs. From the summary of the measured energy levels shown in Figure 2d, it can be seen that the positions of the thiol HOMOs (MPA and DT) are located between the VB of CdSe and CdTe–NCs. The uncertainty in the measured NC values is only partially due to the NC size distribution (see also Figure 4b) because additional parameters, such as NC deposition conditions, NC concentrations, electrolytes used, scan speeds, or aging of the NCs, can also affect the results of the CV measurements.[11–13] Despite the given experimental uncertainty, the HOMO levels of the thiol ligands lie in the same energy range as the VB levels of the CdTe particles, whilst the VB levels of CdSe NCs are clearly lower. This fact suggests that emission quenching arises by hole transfer from the semiconductor VB to the ligand HOMO, as observed in the case of CdSe NCs with attached thiols.

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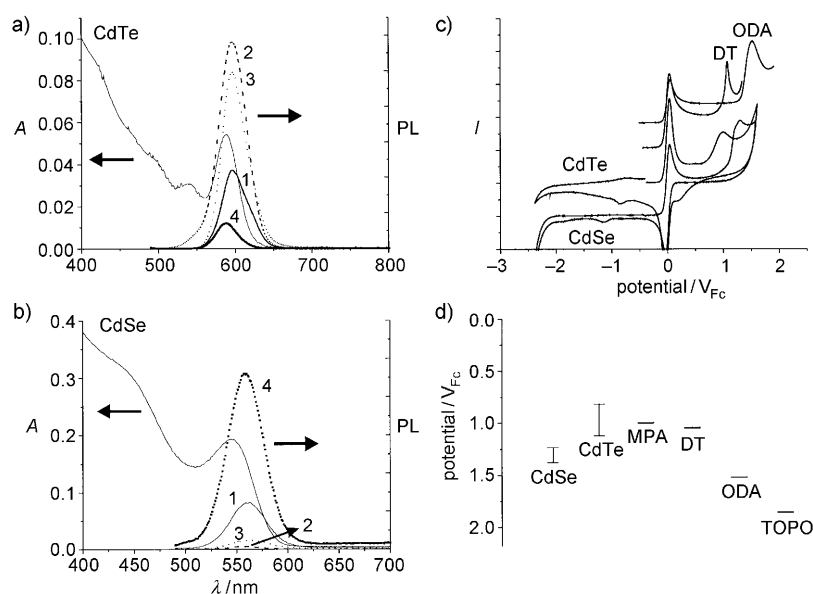Adolf-Reichwein-Strasse 2, 57076 Siegen (Germany)

Figure 2. a,b) UV/Vis and fluorescence spectra of CdTe NCs (a) and CdSe NCs (b) with different ligands: TOPO (1), MPA (2), DT (3), and ODA (4). c) Typical CV measurements of CdSe and CdTe NCs deposited on platinum electrodes and compared to pure ligands measured in solution. d) Range of energy levels for the VB positions for several CdSe and CdTe NC samples compared to the HOMO levels of ODA, MPA, DT, and TOPO. Potentials are given in V versus Fc/Fc^+ (V_{Fc}).

In general, the CV measurements show only the redox potentials of the isolated compounds, but the electronic interaction of the NCs surface orbitals with those of ligands will lead to the formation of new energy levels.[14,15] However, a recent theoretical study has shown that the attachment of thiols to small CdSe clusters indeed inserts sulfur orbitals above the Se 4p orbitals of the clusters, which could act as hole traps for CdSe nanocrystals.[16] Additional results from the same study concerning the interaction of CdSe clusters and ammonia revealed much less change of the frontier orbitals due to the wider gap of the organic molecule. Thus, although the details of the electronic interaction are subject of high-level quantum-mechanical calculations, it is reasonable to argue that charge-transfer processes between NCs and strongly interacting ligands can be discussed based on the redox levels of the isolated compounds.

Similarly, NC fluorescence may be used to record the relative energies of the oxidation levels of NCs and attached ligands. For example, if a chemical signal shifts the oxidation potential of a surface-bound ligand, the resultant alterations should manifest themselves in a change of the NC fluorescence. As a candidate for a NC surface receptor we chose the crown ether ligand 4,7-di(1-aza-4,7,10,13,16-pentaoxacyclooctadecyl)1,10-phenanthroline (**1**; Figure 1), which has already shown its potential for metal ion recognition as part of optical molecular sensor systems.[17] Both ruthenium(II) and iridium(III) complexes with ligand **1** acted as luminophores for selective and quantitative analysis of Pb^{2+} and Ba^{2+}. As the event of ion complexation led to shifts both in the redox potentials and changes in the optical spectra, quadruple-channel detection that combined UV/Vis, PL, CV, and ECL was used to set up a lab-on-a-molecule.[18] It was

thus decided to combine the **1**/Ba^{2+} system with NCs, especially since in earlier work we had shown that diazaperylene ligands with a similar complexing motif as phenanthroline could readily be attached to semiconductor NC surfaces.[19] Variation of redox potential is achieved by complexation of Ba^{2+} ions in the crown ether groups.

First, we developed several strategies to chemically couple ligand **1** to CdSe and CdTe NCs. The process was followed by spectroscopic methods, such as UV/Vis, PL, and NMR spectroscopy (see Supporting Information), and also by changes in solubility upon formation of the NC–ligand complexes. The adjustment of the desired concentrations of NCs and ligands was based on their respective UV/Vis absorption cross-sections.[20] An elegant way of preparing NC–**1** complexes is the phase-transfer reaction using methanol as a solvent for ligand **1** and hexane as a solvent for the NCs. If a solution of TOPO NCs in hexane is brought together with another solution consisting of ligand **1** in methanol and stirred for several minutes, the ligand-covered NCs transfer to the methanol layer owing to a change of surface polarity upon attachment of ligand **1**.[21] Unfortunately, this strategy only works with a large excess of **1** in methanol (50-fold), thus making the separation of **1** and NC–**1** complexes very difficult.

As an alternative, we performed ligand-attachment experiments in chloroform, which is a good solvent for TOPO NCs, NCs covered with ligand **1**, and also for ligand **1**. As NCs covered with ligand **1** were insoluble in heptane, but molecules of **1** could easily be dissolved in a mixture of heptane and chloroform, the NCs covered with ligand **1** were precipitated by addition of heptane. Therefore, they could be separated and redissolved in methanol or chloroform for purification. The corresponding ^{1}H NMR spectra show characteristic shifts and broadenings of the signals for **1** upon attachment (Supporting Information, Figure S1). Thus by integrating the relative signal intensity of free and attached ligands, we determined that up to 30 molecules of ligand **1** were attached to the surface of CdSe or CdTe NCs, depending on the size of the NCs. This value is in agreement with an estimated required space of 1 nm^2 for one upright ligand on the surface of the NCs. When small relative ratios of **1**/NC are reacted in chloroform, the ligands attached quantitatively to the NC surface, as judged from the ^{1}H NMR spectra being devoid of signals for the free ligands. Therefore, for the following experiments we prepared the respective compounds in chloroform with **1**/NC ratios of 5:1 and 10.1.

Figure 3 shows the evolution of the PL spectra of CdSe and CdTe nanocrystals upon attachment of ligands **1** and subsequent addition of stoichiometric amounts of barium ions (two Ba^{2+} ions per ligand **1**). For clarity, only the absorption spectra of TOPO NCs are depicted, and the luminescence spectra show the NC PL at different stages of surface
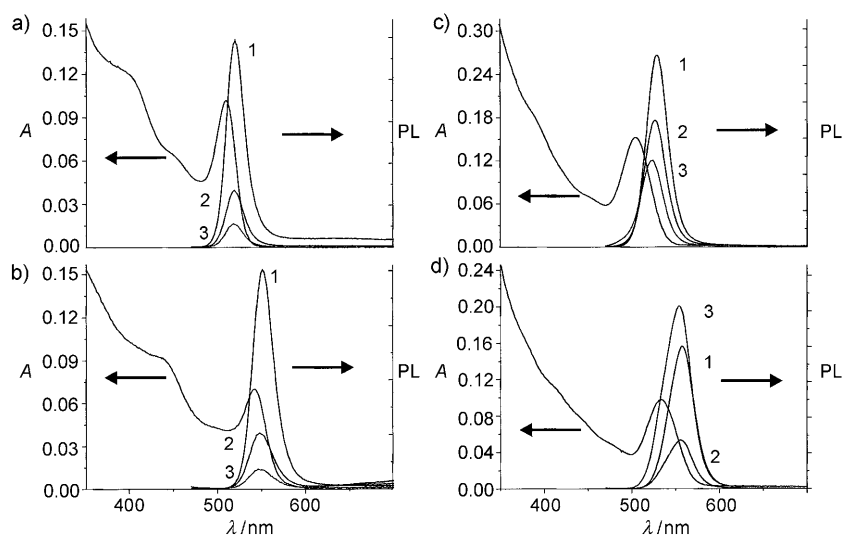
Figure 3. UV/Vis and PL spectra ($\lambda_{ex} = 460$ nm) of CdSe and CdTe NCs after various surface modifications: a,b) CdSe NCs with a diameter of 2.5 nm (a) and 3 nm (b) with TOPO ligands (1) and after addition of ligand **1** (2) and stoichiometric amounts of Ba^{2+} ions (3). The respective PL intensity decreases. c,d) CdTe NCs with a diameter of 2.5 nm (c) and 3 nm (d) with TOPO ligands (1) and after addition of ligand **1** (2) and stoichiometric amounts of Ba^{2+} ions (3). Similar to the situation in (a) and (b), the PL intensity decreases upon attachment of ligand **1** in (c) and (d). Whilst further addition of Ba^{2+} ions leads to an additional decrease of the PL intensity for smaller CdTe NCs (c), it enhances the PL intensity for larger CdTe NCs (d).

CdSe particles are located in a range of 1.2–1.4 V_{Fc} (see Figure 2d), the fluorescence of CdSe particles is always quenched for both: ligand **1** with and without Ba^{2+} ions. In contrast, for 2.5 and 3 nm CdTe NCs we measured VB potentials in the range of 1.0–1.15 V_{Fc} and 0.8–1.0 V_{Fc}, respectively. Even though the exact values are subject to experimental uncertainties, as mentioned above, it is reasonable to argue that the complexation of Ba^{2+} ions within the aza crown ether groups shifts the oxidation potential of the ligands **1** across the VB levels only for larger CdTe particles. This leads to a suppression of the PET process mediated by the presence of the Ba^{2+} ions and thus to the fluorescence increase of larger CdTe NCs.

In summary, we have shown that the fluorescence of semiconductor NCs is sensitive to the electronic interaction between the inorganic NC cores and the attached ligands. Specifically, we have used a receptor ligand for which the oxidation potential can be manipulated by ion complexation, leading ultimately to a change of electronic

modification. For excitation, we choose a wavelength of 460 nm, at which only the NCs absorb (for details, see the Supporting Information). Figure 3a,b show the spectra of CdSe NCs of 2.5 nm and 3 nm in diameter, respectively. It can be seen that their fluorescence is decreased upon attachment of ligand **1** and further decreased upon addition of barium ions, independent of the size of the CdSe particles. Similarly, the fluorescence intensity of small CdTe NCs (2.5 nm) is decreased upon attachment of ligand **1** and even further decreased upon addition of Ba^{2+} ions (Figure 3c). This behavior is decisively different for the larger CdTe NCs (diameters of more than 3 nm), as the PL intensity firstly decreases after attachment of ligand **1**, but strongly increases after Ba^{2+} ion addition (Figure 3d). This size-dependent effect was reproduced for more than ten different samples and could also be observed if ligand **1** was preloaded with Ba^{2+} ions before surface attachment. Time-dependent fluorescence measurements (see Supporting Information) showed a combination of static and dynamic quenching behavior; that is, both the fluorescence lifetimes and also the initial intensity is changed upon surface modification. Moreover, we observed a complex time dependence of the fluorescence intensity changes upon addition of ligand **1** and barium to the NC solutions. This effect is probably due to intricate ligand-attachment and barium-complexation dynamics (see Supporting Information).

Typical CV waves for different-sized CdTe NCs compared to ligand **1** (with and without Ba^{2+} ions) are depicted in Figure 4. The anodic peak of ligand **1** shifts from 0.8 V_{Fc} to (1.06 ± 0.01) V_{Fc} if different amounts of Ba^{2+} ions are complexed within the crown ether site. As the VB levels for

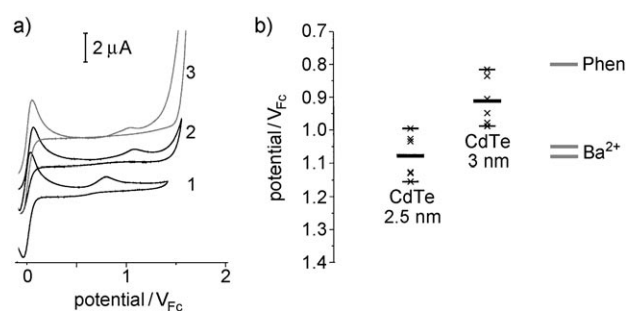**Figure 4.** a) CV waves of pure ligand **1** in solution (1), **1** with one Ba^{2+} ion (2), and more than two Ba^{2+} ions on average (3). b) Energy levels of the VB positions of different-sized CdTe NCs compared to the HOMO levels of ligand **1** with and without Ba^{2+} ions.

interactions and fluorescence. In combination with the size dependence of the electronic levels in CdTe NCs, we could show that small and large particles react differently towards the presence of Ba^{2+} ions. This principle is a first step into the development of metal ion sensors based on the fluorescence of nanocrystals. Further experiments are aimed at varying the material and size of nanocrystals to combine diverse functional ligands at different NCs towards the construction of sensor arrays for multi-analyte mixtures.

Experimental Section

Communications

reacted in TOPO (4.0 g), whilst for preparation of CdTe NPs, CdO (0.0514 g, 0.400 mmol) and TDPA (0.2232 g, 0.802 mmol) were reacted in TOPO (1.0 g) and ODE (15 mL). All reactants were degassed in a three-neck flask for 30 min at 80°C. For ligand exchange of TOPO by MPA, DT, or ODA, standard precipitation methods were used. For attachment of ligand **1**, the respective solutions of NCs and ligand were mixed and stirred at room temperature for 5 h before the UV/Vis and PL spectra were obtained. After addition of the calculated amounts of Ba^{2+} ions, the solutions were further stirred for 4 h before measuring the UV/Vis and PL spectra. The CV measurements were performed in acetonitrile (0.1 M nBu$_4$N PF$_6$) using a platinum working electrode and the Fc/Fc$^+$ couple as a reference system. Whereas the ligands were dissolved in the electrolyte solution, the NCs were deposited on the cleaned electrodes as a submonolayer and immediately measured at a scan rate of 100 mV s^{-1}.

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