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Controlled Aqueous Synthesis of CdSe Quantum Dots using Double-Hydrophilic Block Copolymers as Stabilizers

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Abstract: We present a simple experimental procedure to obtain CdSe quantum dots from aqueous solution with a controllable size. Double-hydrophilic block copolymers consisting of a poly(ethylene glycol) block and a block of either poly(ethylene imine) or polylysine are used as stabilizers. UV/VIS absorption spectroscopy, analytical ultracentrifugation and transmission electron microscopy are used to examine the resulting quantum dots. The particle size can be simply controlled by adjusting the polymer concentration during synthesis for both block copolymers.

Keywords: CdSe; double hydrophilic block copolymer; quantum dot; size control.

Dedicated to: Prof. Alexander Eychmüller on the occasion of his 60th birthday.

1 Introduction

Due to their size-dependent properties, semiconductor nanoparticles, also known as quantum dots (QDs), are interesting materials for various applications, such as solar cells [1–3], light-emitting diodes [4–6], lasers [7, 8] and bioimaging [9, 10]. CdSe is of special interest since its band gap can be adjusted from 1.7 eV for the bulk material to 2.4 eV by reducing the particle size to 2 nm [11]. Therefore, CdSe QDs can cover a large part of the visible spectrum, which is desired for many of their applications.

CdSe QDs of high uniformity can be obtained by reaction at 300 °C in trioctylphosphine [12]. The resulting QDs can only be dispersed in organic solvents, which disqualifies them for many biological applications. One way to overcome

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this limitation is to exchange the hydrophobic phosphine ligands for water-soluble stabilizers, such as mercapto acids [13] or hydrophilic polymers [14–16]. However, these approaches still use phosphine capped QDs as starting material. The toxicity of the phosphine reagents and the high energy use during the QD formation reduce the appeal of this route, which has led to the development of aqueous syntheses at low temperatures [17–22].

Since water-soluble quantum dots can potentially enter the organism [23], their toxicity has to be carefully evaluated. Any application of CdSe Qds has to ensure that no cadmium is released to the environment. Especially when using QDs for cell labeling, it would be undesirable if the particles are cytotoxic. There are three ways QDs can have toxic effects [23]. First, there might be toxic residues from the synthesis process, such as trioctylphosphine for QDs, which were prepared by the hot-injection method and then transferred to the aqueous medium by ligand exchange. Second, capping agents such as mercaptoundecanoic acid can cause cytotoxic effects [24]. Third, if QDs are degraded by oxidation or photolysis, cadmium ions can be released from them [23]. Therefore, the ideal quantum dots for these applications are highly stable, use non-toxic capping agents and were synthesized directly in water.

Common Se^{2-} sources for QD synthesis in water are H_2Se and NaHSe [21]. The former is a toxic gas that requires the use of inert gas techniques, the latter is generated *in situ* by reaction of $NaBH_4$ with either elemental Se or Na_2SeO_3 [19, 20]. Another suitable precursor is Na_2SO_3Se. It is formed by reaction of elemental Se and Na_2SO_3 and can be stored in aqueous solution [18, 25]. This property allows for the preparation of a stock solution that only needs to be mixed with a Cd^{2+} solution in the presence of a stabilizing agent to form CdSe quantum dots. The use of Na_2SO_3Se therefore simplifies the experimental set-up compared to other Se^{2-} sources.

Double-hydrophilic block copolymers (DHBCs) consist of two blocks, which are both water-soluble [26]. They have been used to stabilize ZnS [27], CdS [28, 29] and CdSe QDs [14] in water, where one of the blocks binds to the QD, while the other block mediates the dispersibility (see Figure 1). Of particular interest are the results of our group regarding CdS. When using poly(ethylene glycol)-poly(ethylene imine) (PEG-b-PEI) block copolymers as stabilizers for CdS QDs, the particle size depends on the stabilizer concentration, leading to smaller particles with higher concentrations [28]. To our knowledge, this approach to QD size-control is unique in the literature. Here, we report the successful transfer of this method to synthesize CdSe QDs of different sizes. We also used poly(ethylene glycol)-α-poly-L-lysine (PEG-b-pLys) as an example of a DHBC with only primary amine groups, opposed to the PEG-b-PEI with branched binding block, which consists of a mixture of primary, secondary and tertiary amine groups. According to previous investigations on the stabilizer capacity of DHBCs with linear,

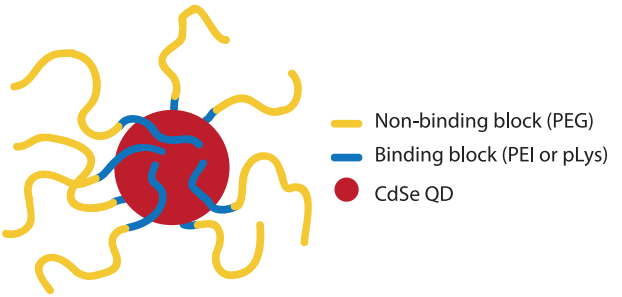

Fig. 1: Scheme of a CdSe QD, stabilized by a DHBC. One block binds to the QD, while the other block mediates the dispersibility in water. In our case, the non-binding block consists of PEG, while the binding block was either PEI or pLys.

branched and dendritic binding blocks, the branched binding blocks were found to be most efficient resulting in the smallest particle sizes at the same concentration [28], so that we would expect the PEG-b-PEI with a branched binding block to be a better stabilizer than the PEG-b-pLys block.

2 Materials and methods

PEG-b-PEI (Sigma-Aldrich Chemie GmbH, Munich, Germany) (Figure 2) with a PEG block of 5000 g/mol and a block of branched PEI of 2000 g/mol was synthesized according to Ref. [30]. Briefly, PEG monomethyl ether was reacted with epichlorohydrin in the presence of an excess of sodium hydroxide and small amounts of hydroquinone and water at 60 °C over 10 h and then at 90 °C for 1.5 h. The resulting MeO-PEG glycidyl ether was extracted with dichloromethane. After removing the majority of the solvent under reduced pressure, the product was precipitated in cold diethyl ether. PEG glycidyl ether and PEI were mixed in methanol. After distilling off the solvent, the reaction mixture was heated to 80 °C for 8 h. The product

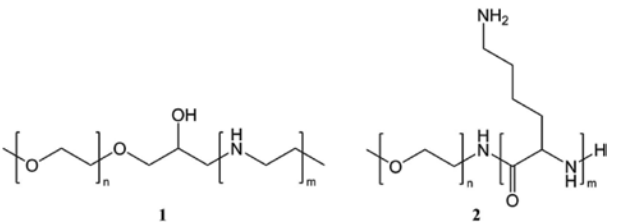

Fig. 2: Structures of PEG-b-PEI (1) and PEG-b-pLys (2). The PEG-b-PEI used for QD synthesis consists of a branched PEI block with primary, secondary and tertiary amine groups.

was purified by dialysis against distilled water. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich Chemie GmbH, Munich, Germany.

The protocol for synthesizing PEG-b-pLys (Figure 2) with a PEG block of 1800 g/mol and a α-poly-L-lysine block of 3200 g/mol was adapted from Ref. [31]. Z-protected L-lysin was transformed to an *N*-carboxyanhydride (NCA) by reaction with triphosgene in THF at 50 °C for 4 h. The product was purified by recrystallization. The NCA was then used in a ring opening polymerization with amino-PEG methyl ether in DMF at room temperature for 5 days to yield Z-protected PEG-b-pLys. The protecting groups were then cleaved with trifluoroacetic acid and hydrobromic acid. The length of the pLys block was determined by ^{1}H-NMR (data not shown).

A Na_2SO_3Se stock solution was prepared by heating 20 mmol Na_2SO_3 (Merck KGaA, Darmstadt, Germany, 95% purity) and 5 mmol Se powder (99.5% purity, 100 mesh) in 100 mL MilliQ water to 65 °C for 6 h [18]. This solution was stored in the dark at 9 °C and diluted as required. CdSe QDs were obtained by adding 5 mL of a 2 mM $CdCl_2$ (Fluka, Fisher Scientific GmbH, Schwerte, Germany, 99% purity) solution to 10 mL copolymer solution of the desired concentration. After stirring for 1 min, 5 mL of a 2 mM Na_2SO_3Se solution were added. The solution was stirred for 30 s at room temperature, then it was stored at 9 °C in the dark. The resulting QDs were characterized after 24 h of aging.

UV/VIS spectra were recorded on a Varian Cary 50 spectrometer (Agilent Technologies, Santa Clara, CA, USA), using 1 cm quartz cuvettes. The band gap positions were determined by extrapolating the steep section of the absorption edge and finding an intersection with the extension of the linear part at shorter wavelengths. AUC measurements were carried out at 25 °C on a Beckman Coulter Optima XL ultracentrifuge (Beckman Coulter, Palo Alto, CA, USA) with multi wavelength detector [32, 33]. The data was evaluated with Sedfit 14.4d (Peter Schuck: http://www.analyticalultracentrifugation.com), using the ls-g*(s) model, which assumes non-diffusing species, and the Continuous c(s) Distribution model, which performs a diffusion broadening correction. For the partial specific volume, we assumed the inverse of the bulk density of CdSe, for the buffer density and viscosity, we used the values for water. High resolution transmission electron microscopy (HR-TEM) images were recorded on a JEOL JEM-2200FS electron microscope (JEOL Ltd., Tokyo, Japan) with a 220 kV accelerating voltage. Carbon coated Quantifoil S7/2 TEM grids (Quantifoil Micro Tools GmbH, Großlöbichau, Germany) were used.

3 Results

Using the PEG-b-PEI copolymer, different batches of CdSe QDs were synthesized. At a concentration of 2 g/L PEG-b-PEI, no quantum dots were formed. Using 1 g/L

PEG-b-PEI yields particles with a band gap at 429 nm (2.89 eV), while lowering the stabilizer concentration stepwise to 0.03 g/L gradually shifts the band gap to 544 nm (2.28 eV), as can be seen in Figure 3. The empirical formula

$$E_g = 1.858\ \text{eV} + \frac{\text{eV}}{0.220 d^2/\text{nm}^2 + 0.008 d/\text{nm} + 0.373}$$

was used to determine the diameters d from the band gaps E_g of the CdSe QDs [34]. Table 1 shows the band gaps of the particles and the corresponding sizes. It is evident that smaller particles are formed at higher concentrations of the stabilizer.

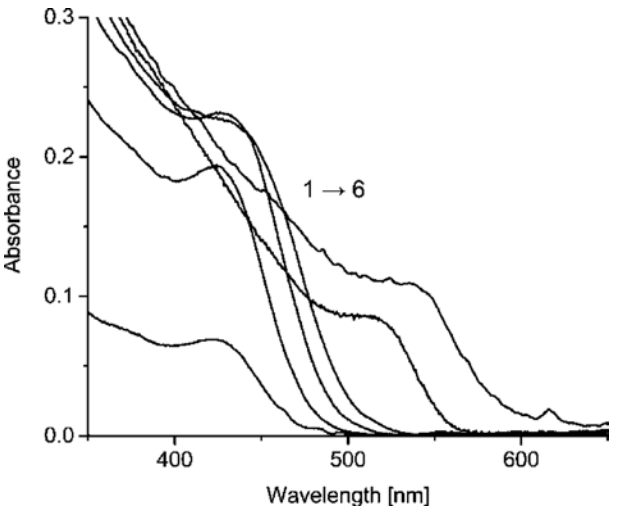

Fig. 3: UV/VIS absorption spectra of CdSe QDs, prepared with PEG-b-PEI concentrations of 1) 1.0 g/L, 2) 0.5 g/L, 3) 0.25 g/L, 4) 0.13 g/L, 5) 0.06 g/L and 6) 0.03 g/L.

Tab. 1: Band gap energies and particle sizes of PEG-b-PEI stabilized CdSe QDs.

PEG-b-PEI concentration (g/L)	Band gap (eV)	Particle size by UV/VIS (nm)	Particle size by AUC (nm)
1.00	2.89	1.6	1.6
0.50	2.86	1.7	1.6
0.25	2.83	1.7	1.8
0.13	2.78	1.8	2.1
0.06	2.38	2.6	5.0
0.03	2.28	3.0	N.A.

Sizes were determined from the band gaps (UV/VIS) and by analytical ultracentrifugation (AUC).

Analytical ultracentrifugation (AUC) measurements confirm this trend. The particle size distributions can be seen in Figure 4. The samples with PEG-b-PEI concentrations of 1 g/L–0.25 g/L have very narrow size distributions, with full widths at half maximum (FWHM) of only 0.1 nm–0.2 nm. This high uniformity explains the distinct exciton transitions that are visible in the UV/VIS spectra of these samples. The QDs with 0.13 g/L and 0.06 g/L PEG-b-PEI have much wider size distributions and no distinct exciton transitions in their UV/VIS spectra. The QDs with 0.03 g/L PEG-b-PEI could not be analyzed by AUC, as they precipitated in the sample cell before the measurement started.

The QDs prepared with 0.06 g/L PEG-b-PEI were investigated with HR-TEM. Figure 5a,b show that particle sizes range from 2 nm to 6 nm, which is in accordance with the particle size distribution obtained from AUC measurements. It can also be seen that the particles are slightly elongated. Evidence of the crystallinity of the QDs is presented in form of the lattice fringes in Figure 5a,b and as further evidence the diffraction rings for the most common CdSe faces in the Fourier transform in Figure 5c. A Fourier transform of an HR-TEM image with many particles results in a series of concentric circles. By taking the inverse of the radius of such a circle, the lattice spacing is obtained [35]. This was done for the three most prominent circles. By comparison with literature values from the Crystallography Open Database [36], it is confirmed that the CdSe QDs have wurtzite structure (see Table 2).

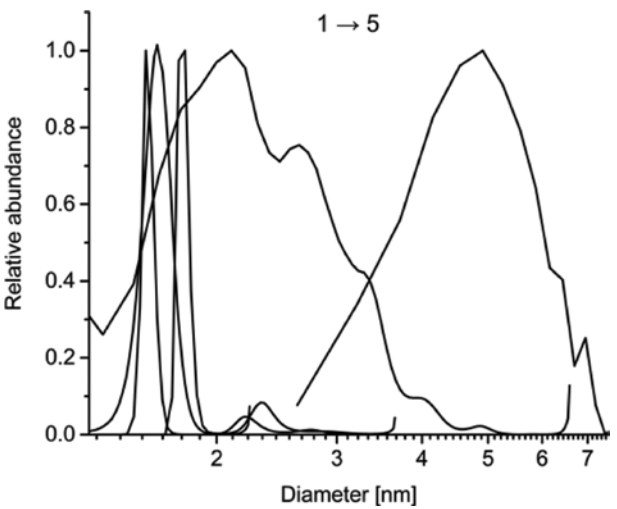

Fig. 4: Particle size distributions determined by AUC for CdSe QDs, prepared with PEG-b-PEI concentrations of 1) 1.0 g/L, 2) 0.5 g/L, 3) 0.25 g/L, 4) 0.13 g/L and 5) 0.06 g/L. The c(s) model was used.

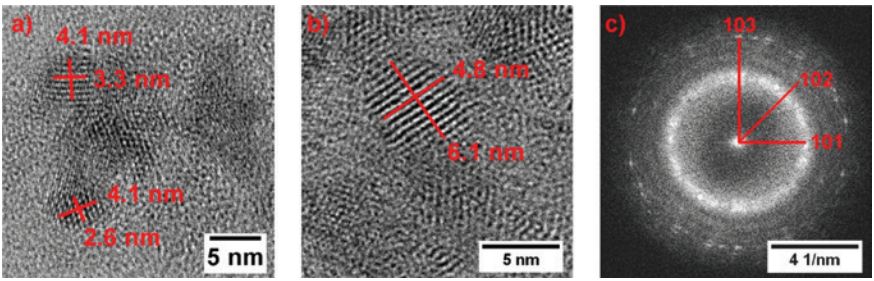

Fig. 5: The lattice fringes and diffraction rings show the crystallinity of the QDs. (a,b) HR-TEM images of CdSe QDs prepared with 0.06 g/L PEG-b-PEI. (c) Fourier transform of an overview image with lots of particles. Miller indices of lattice planes, which correspond to the most prominent rings, are denoted.

Tab. 2: Radii of the rings in Figure 5c and corresponding lattice spacings.

Radius (1/nm)	Calculated lattice spacing (nm)	Literature lattice spacing (nm)	Miller index
3.1	0.32	0.33	101
3.9	0.26	0.26	102
4.9	0.20	0.20	103

Comparison with literature values allows assignment of Miller indices.

We were also interested in the long term stability of the QDs synthesized in presence of PEG-b-PEI since for the CdS case, excellent stability was reported also against photocorrosion due to the high concentration of amine groups in the stabilizer shell [28]. Repeating the UV/VIS spectra after 1 year storage in the refrigerator in the dark revealed still typical spectra of a QD. However, the band gap was red shifted for all applied polymer concentrations with the smallest shift for the highest polymer concentration (0.1 nm) and the largest shifts for the lower polymer concentrations (up to 1.0 nm) (see Figure S3–S8 Supporting Information). This shows a lower stability compared to the CdS case [28], but still a reasonable stability from the viewpoint of application.

We also used PEG-b-pLys in the aforementioned procedure to synthesize CdSe QDs of varying sizes. Figure 6 shows the UV/VIS spectra of the resulting particles. It is evident that the band gap is blue-shifted with increasing stabilizer concentration. For the same stabilizer concentration, QDs formed in the presence of PEG-b-pLys have band gaps at higher energies than PEG-b-PEI stabilized QDs. However, the absorption edges for PEG-b-pLys QDs are less distinct and assigning precise values for the band gaps is not easy. Table 3 shows estimated values for

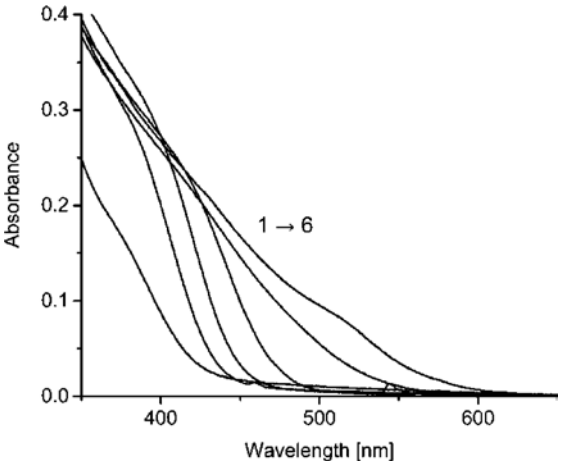

Fig. 6: UV/VIS absorption spectra of CdSe QDs, prepared with PEG-b-pLys concentrations of 1) 1.0 g/L, 2) 0.5 g/L, 3) 0.25 g/L, 4) 0.13 g/L, 5) 0.06 g/L and 6) 0.03 g/L.

Tab. 3: Band gap energies and particle sizes of PEG-b-pLys stabilized CdSe QDs.

PEG-b-pLys concentration (g/L)	Band gap (eV)	Particle size by UV/VIS (nm)	Particle size by AUC (nm)
1.00	3.32	1.2	3.2
0.50	3.22	1.3	4.0
0.25	3.12	1.4	5.5
0.13	2.99	1.5	N.A.
0.06	2.93	1.6	5.1
0.03	2.43	2.5	N.A.

Sizes were determined from the band gaps (UV/VIS) and by analytical ultracentrifugation (AUC).

the band gaps, along with the corresponding particle sizes. PEG-b-pLys appears to be able to stabilize smaller CdSe QDs than PEG-b-PEI.

This size difference is very interesting, as it cannot be attributed solely to the different molar masses of the polymers (ca. 5000 g/mol for PEG-b-pLys and ca. 7000 g/mol for PEG-b-PEI). The higher mass of PEG-b-PEI leads to a 1.4 times higher number of PEG-b-pLys molecules at the same mass concentration if only the number of polymer chains determined the particle size, particles formed with a certain amount of PEG-b-pLys should be just as big as particles formed with the 1.4 fold amount of PEG-b-PEI. However, the particles formed at a certain concentration of PEG-b-pLys are even smaller than QDs formed at twice that concentration of PEG-b-PEI. Even though the mass of the pLys block is bigger than that of

the PEI block, the chain length of pLys is shorter (ca. 25 lysine repeating units, compared to ca. 46 PEI units in PEG-b-PEI). In combination with the difference in molecular mass, this leads to a concentration of amine groups of 5 mmol/L for a solution of 1 g/L PEG-b-pLys and 6.5 mmol/L for a solution of 1 g/L PEG-b-PEI. These numbers show that the concentration of amine groups also cannot be responsible for the size differences. These findings are in contrast to earlier works, where we found that PEG-b-PEI with a linear PEI chain is not as effective at stabilizing CdS QDs as PEG-b-PEI with a branched PEI block and results in slightly larger particles at the same concentrations [28]. Since PEG-b-pLys contains a linear pLys block with a slightly rigid peptide backbone, we would have expected it to form larger particles than PEG-b-PEI. However, the amine groups in pLys are located on alkyl side chains. The flexibility of these alkyl chains might compensate for the less flexible polymer backbone.

Tarasov et al. [27] prepared ZnS QDs in the presence of a poly(acrylic acid)-poly(acryl amide) (PAA-PAM) block copolymer. In their work, they propose that this DHBC forms micelles in the presence of Zn^{2+} kations, which incorporate S^{2-} anions and form crystals. They further conclude, that the crystal growth is limited by the size of the micelles and that PAA-PAM stabilizes the resulting QDs by binding to them with the PAA block. They employed PAA-PAMs of different lengths and observed, that bigger polymers led to the formation of smaller particles. We suspect that a similar mechanism explains our findings regarding CdSe QDs. Despite its similar mass, the PEG-b-pLys copolymer has significantly fewer repeating units than the PEG-b-PEI we used. Even though the pLys block contributes a lot of mass, it is relatively compact, as most of its mass is located in the flexible side chains. The formation of smaller particles at similar concentrations of PEG-b-pLys might then be explained by the shorter length of the polymer, which leads to the formation of smaller micelles. Furthermore, it seems plausible that at higher concentrations of the polymer, smaller micelles are formed. This would explain why PEG-b-pLys forms smaller particles than PEG-b-PEI, for a given polymer concentration, and why higher concentrations of each polymer lead to smaller particles.

The lack of distinct exciton bands in the UV/VIS spectra of PEG-b-pLys stabilized QDs indicates a lower quality compared to QDs prepared with PEG-b-PEI. Even at 9 °C, the particles seem to be only metastable and agglomerate over time. The low stability of the QDs complicated AUC measurements, so that we could not use the c(s) model for evaluation. For this reason, we used the ls-g*(s) model here, which does not take diffusion effects into account. Figure 7 shows the particle size distributions for four of the samples, the other two precipitated in the sample cells before enough data for an evaluation was collected. The particle size distributions show multiple trailing peaks, which are caused by agglomeration

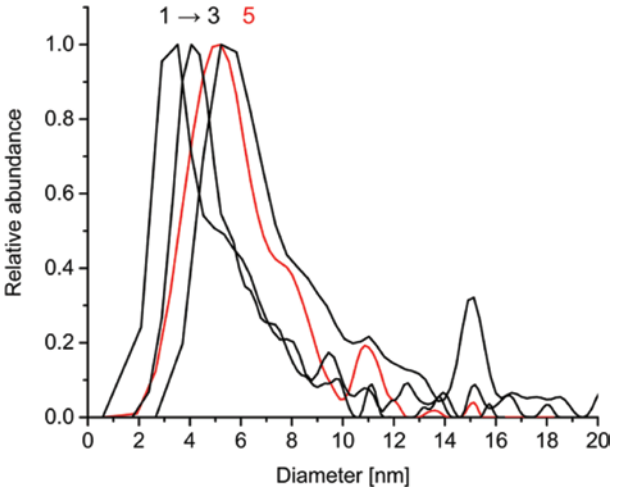

Fig. 7: Particle size distributions determined by AUC for CdSe QDs, prepared with PEG-b-pLys concentrations of 1) 1.0 g/L, 2) 0.5 g/L, 3) 0.25 g/L and 5) 0.06 g/L. The ls-g*(s) model was used.

of the QDs. The modal sizes determined by AUC (Table 3) are also bigger than the sizes calculated from the band gaps. We suspect that the polymer chain extends into the solution, so that the hydrodynamic radius of the particles is bigger than the core diameters determined by UV/VIS spectra but this should also be the case for PEG-b-PEI. Since the particle size distributions were calculated on basis of the bulk CdSe density, the particle sizes are potentially calculated too small, since the real particle density is smaller than that of the bulk due to the contribution of the stabilizer shell. Therefore, it cannot be excluded that small aggregates are formed even at high polymer concentrations leading to larger sizes in the AUC as the ones determined for their separate cores from UV/VIS. The size distributions are also broader than that of PEG-b-PEI stabilized QDs hinting at the aggregation of nanoparticles. The FWHM of the PEG-b-pLys particles range from 2 nm to 3 nm. When the QDs prepared with PEG-b-PEI are evaluated with the same model, FWHM values range from 0.2 nm to 2.0 nm (see Figure S9 Supporting Information) which leads us to the conclusion, that the broader distributions of PEG-b-pLys QDs are not entirely caused by diffusion broadening effects, but represent a real difference in particle sizes. The lower stability and uniformity of QDs prepared with PEG-b-pLys is explained by the shorter PEG block of only 1800 g/mol (compared to 5000 g/mol in PEG-b-PEI), which is at the threshold of steric stabilization of ca. 2000 g/mol [37]. A longer PEG chain might lead to better stabilization and QDs of higher quality and uniformity. Since the stability of the PEG-b-pLys stabilized

QDs was lower compared to those stabilized by PEG-b-PEI, no long term stability tests were conducted for these samples.

4 Conclusions

CdSe QDs of different sizes were synthesized via a simple mixing approach in aqueous solution under ambient conditions using DHBCs with a non-binding block of PEG and a binding block containing amine groups. Particle sizes range from 1 nm to 5 nm, depending on the stabilizer used and its concentration during QD formation. The reaction is a simple one-step procedure, using precursors which can be stored in solution. This approach simplifies the experimental set-up for the formation of CdSe QDs extremely and allows for a very simple control of the particle size via the block copolymer concentration. This shows that the approach is not only applicable to CdS [28], but seems more generally applicable to QD synthesis in aqueous solution and possibly also to other nanoparticle systems. Also, the DHBC choice does not seem to be restricted for this approach as long as a sufficient binding block (for the CdSe system amine containing) can be applied.

When using PEG-b-PEI as stabilizer in higher concentrations, small QDs of high quality can be obtained, with distinct exciton bands and narrow size distributions. Lower PEG-b-PEI concentrations lead to bigger particles with broader size distributions since the block copolymer amount is not sufficient anymore for nanoparticle stabilization. The particles show good to reasonable stability and after 1 year, the core particle size increased between 0.1 nm for high PEG-b-PEI concentrations to 1.0 nm for the lower polymer concentrations. HR-TEM measurements reveal that the QDs have wurtzite structure. Higher polymer concentrations also lead to smaller QDs when using PEG-b-pLys as stabilizer. For the same mass concentrations of the polymer, QDs formed with PEG-b-pLys are smaller than QDs formed with PEG-b-PEI. However, the QDs formed with PEG-b-pLys are of lower quality, which is evident by the lack of exciton bands and broader size distributions. This could be explained by the smaller chain length of the PEG-b-pLys leading to less efficient steric stabilization. By increasing the size of PEG-b-pLys, higher quality QDs might be obtained.

In terms of toxicity, PEG is known to be non-toxic and therefore it is used in multiple drug delivery applications [38]. Since pLys and PEI bind to the quantum dot, they are shielded by the PEG corona and therefore non-toxic. This situation is similar to shielding of DNA structures by such DHBCs [39] or their use for gene delivery applications in the body [40]. Therefore, our strategy implies the here described DHBCs to be non-toxic. On the other hand, because CdSe has a very low solubility product of 1.4×10^{-35} [41], it can be considered as insoluble. Since

it has been reported that the basic PEI block protects CdS QDs against oxidation and photolysis [28], a similar effect can be expected for the CdSe QDs and thus, no release of toxic Cd^{2+} is expected in biological environment. Therefore, the here reported CdSe QDs are especially promising for biological applications.

In this work, we could show that our method to prepare CdS QDs in aqueous solution, using PEG-b-PEI as stabilizer and controlling the particle size by adjusting the polymer concentration, can be transferred not only to CdSe, but also to another DHBC. This procedure offers a versatile and facile approach to QD size control and we expect it to be applicable to even more systems.

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