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Water-Soluble CdSe Quantum Dots Passivated by a Multidentate Diblock Copolymer

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ABSTRACT: We describe a process for transferring trioctylphosphine oxide-stabilized CdSe semiconductor nanocrystals (CdSe/TOPO quantum dots, QDs) from toluene into water through a ligand exchange process with a poly(ethylene glycol-*b*-2-*N*,*N*-dimethylaminoethyl methacrylate) (PEG-*b*-PDMA) diblock copolymer. In this polymer, the DMA units serve as multidentate ligands for the QD. While we expected the protruding PEG layer to enhance the water-solubility of the polymer/QD adduct, it was not sufficient, upon initial exposure to the QDs, to impart water solubility. Residual TOPO groups remained at the particle surface. Multiple exchanges with the polymer accommodated the slow dissociation of TOPO groups from the CdSe surface, and allowed the particles to achieve water solubility (dispersibility). Transfer to water was accompanied by a 10-fold decrease in the quantum yield of photoluminescence (PL), but this intensity could be recovered by photoactivation. Before photoactivation, the QDs in water showed a small decrease in PL intensity as the solutions were warmed from 25 to 55 °C, which was fully reversible when the solutions were cooled. After photoactivation, the QDs showed a similar decrease in PL intensity upon warming, but only a fraction of this loss of intensity was recovered when the sample was cooled to room temperature. At high ionic strength (0.2−1.0 M NaCl) the PL emission intensity decreased, accompanied by an increase in trap emission at longer wavelength.

Introduction

Semiconductor nanocrystals, known as quantum dots (QDs), are photoluminescent probes that have several advantages over organic dyes.[1−3] They have broad and continuous absorption with high molar extinction coefficients, a narrow and symmetric emission, often with a high photoluminescence (PL) quantum yield (QY), as well as a strong resistance to photobleaching. As a consequence, QDs show great promise for applications in which bright emission and photostability are important. Many of these applications, for example biological imaging, require QDs that form stable colloidal solutions in water.

One method to prepare water-soluble QDs is to perform the synthesis directly in water in the presence of hydrophilic ligands,[4] but it is generally difficult to obtain high QY QDs through this approach. The best way to prepare high-quality QDs is to use an organometallic synthesis at high temperature in the presence of coordinating organic ligands such as trioctylphosphine and trioctylphosphine oxide (TOPO).[5] Various research groups have shown that this approach leads to highly crystalline and photoluminescent II−VI nanocrystals, e.g., CdSe, core/shell CdSe/ZnS, and CdSe/CdS QDs, with controlled sizes and shapes.[6,7] The QDs synthesized in this way are hydrophobic. To be transferred into water, they must be modified via ligand exchange[8] or micellar encapsulation.[9]

In previous publications,[10] we examined the use of poly(2-*N*,*N*-dimethylaminoethyl methacrylate) (PDMA) homopolymer as a multidentate ligand for CdSe and CdSe/ZnS core−shell QDs. We showed that PDMA was able to displace TOPO groups from the surface of these nanoparticles. This led to a substantial enhancement in colloidal stability and a preservation or modest increase in the intensity of photoluminescence (PL). The most interesting result is that the polymer bound to the surface of the nanoparticles allowed the particles to be dissolved (dispersed as a colloidal solution) in a much broader range of solvents (e.g., methanol, toluene, tetrahydrofuran, chloroform) than the original TOPO coated particles. A curious feature of these particles is that they would not dissolve in water even though PDMA itself is water-soluble. Very recently, we found that CdSe QDs covered by PDMA could be transferred from toluene to water after a post modification of the polymer corona with a methylating agent (methyl iodide or methyl tosylate).[10c]

Over the past 30 years, many experiments have been carried out on polymer-stabilized organic and inorganic nanoparticles. The book by Napper[11] provides a good review of the basic principles. For particles sterically stabilized by flexible chains covalently bound or tightly adsorbed to the surface, one expects the particles to form stable colloidal solutions in any solvent which is a good solvent for the surface chains. Thus, our inability to disperse or dissolve PDMA-stabilized CdSe QDs in water was surprising and in need of further investigation.

We began these studies with the idea that we could improve the water solubility of the particles containing surface-adsorbed polymer by employing a poly(ethylene glycol-*b*-*N*,*N*-dimethylaminoethyl methacrylate) (PEG-*b*-PDMA) diblock copolymer. We synthesized one such polymer, and ligand exchange experiments with PEG-*b*-PDMA resulted in the adsorption of the polymer to the surface of CdSe QDs. Unfortunately, the modified particles from these intial ligand exchange experiments still could not be dispersed in water. Careful ^{1}H NMR measurements identified the source of the problem, a substantial fraction of TOPO groups at the particle surface after the initial ligand exchange. By manipulating the ligand exchange conditions, we could replace a large fraction of these TOPO groups with ligands from the PDMA polymer, and as a consequence the polymer-coated QDs became water-soluble.

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In this paper, we are primarily interested in factors that enable the polymer ligand exchange to produce water-soluble QDs. Furthermore, we wish to characterize directly the surface passivation efficacy conferred by the polymer ligands. As a consequence, we report experiments carried out on CdSe QDs, rather than core−shell CdSe/ZnS QDs. The latter would, of course, demonstrate the attainment of higher quantum yields for photoluminescence, but by investigating CdSe we can better quantify the ligand coverage and binding which should be related directly to the photoluminescence quantum yield[8b]. We describe the details of the ligand exchange process and examine the properties of the CdSe QDs in aqueous solution, including their susceptibility to photoenhancement of the PL intensity, and the variation of this intensity with changes in temperature and ionic strength.

Experimental Section

Materials and Methods. Cu^IBr (98%, Aldrich) was washed repeatedly with acetic acid and ether, then dried, and stored under nitrogen. 2-(Dimethylamino)-ethyl methacrylate (DMA, 98%, Aldrich) was passed through a short silica column to remove the radical inhibitor. MeO−PEG, 2-bromoisobutyryl bromide (98%), 2,2′-bypyridine (98%), and triethylamine (99.5%) were purchased from Aldrich and used without further purification. TOPO/TOP-capped CdSe QDs were prepared through an organometallic approach[5,10a] at high temperature and purified by precipitation in methanol before use.

^1H NMR spectra were recorded at 300 MHz using a Varian Mercury spectrometer. Optical absorption spectra were collected at room temperature on a Perkin-Elmer Lambda 25 spectrometer using 1.00 cm quartz cuvettes. Photoluminescence spectra were measured using a SPEX Fluorolog-3 spectrofluorometer (Jobin Yvon/SPEX, Edison, NJ). The emission spectra were corrected using an algorithm built into the software. The PL QY of the CdSe QDs (CdSe−TOPO in toluene and CdSe/PEG-*b*-PDMA in water) were measured using fluorescein (QY = 0.95) in 0.1 M NaOH as a standard. Solutions of similar optical density (ca. 0.06) at the excitation wavelength (440 nm) were prepared for both CdSe QDs and fluorescein. Fluorescence spectra were recorded from 460 to 650 nm and integrated on a wavelength scale. The TEM images were taken using a Hitachi 5200 STEM instrument.

Ligand Exchange of CdSe/TOPO with PEG-*b*-PDMA and QD Transfer into Water. Ligand exchange was performed in toluene at room temperature by stirring the mixture of excess PEG-*b*-PDMA and freshly purified CdSe/TOPO QDs overnight. In a typical procedure, polymer (41 mg) containing 3.38×10^{-2} M $N(Me)_2$ groups was mixed with CdSe/TOPO (4.3×10^{-6} M) in 8 mL toluene. The concentration of CdSe/TOPO was calculated through the Beer−Lambert law ($c = A/(\epsilon \times L)$),[12] and the extinction coefficient (ϵ) of CdSe QDs was determined by the empirical equation: $\epsilon = 5857 \times D^{2.65}$ (D is the diameter of CdSe QDs measured by TEM). Unexpectedly, the residue left upon removal of the solvent under vacuum could not be dispersed in water, but was easily soluble in methanol. The same result was obtained when the ligand exchange reaction was performed in THF.

This problem could be overcome in two ways: In one approach, excess PEG-*b*-PDMA (41 mg) was mixed with CdSe/TOPO (4.3×10^{-6} M) in toluene (8 mL) and stirred overnight at room temperature. Then hexane (ca. 20 mL) was added to the mixture. Both the polymer and the ligand-exchanged CdSe QDs precipitated as a viscous mixture. Sedimentation was rapid even without centrifugation, and the supernatant was clear and colorless. The colorless supernatant was decanted, and the residue was redispersed in toluene (4 mL). This precipitation/redispersion process was repeated for another two cycles. Then the sediment was dried under a N_2 flow (or in vacuum) at room temperature. The dry solid obtained at this point could be dissolved (dispersed) in distilled water, leaving only a trace of insoluble material behind. No obvious increase of the water-dispersibility of this material was observed upon increasing the number of precipitation−redispersion cycles to four or five.

In the second approach, excess PEG-*b*-PDMA (41 mg) was mixed with CdSe/TOPO (4.3×10^{-6} M) in toluene (8 mL) and stirred overnight at room temperature, and then subjected to sonication for 30 min with the flask containing the sample immersed into water contained in a 60 W ultrasonic cleaning bath (Branson 1510). Then hexane (ca. 20 mL) was added to the mixture. After the precipitate was filtered and dried, it could be dissolved directly in water.

Ligand Exchange of CdSe/TOPO with Pyridine Prior to Treatment with PEG-*b*-PDMA. Freshly purified CdSe/TOPO QDs (6.0×10^{-6} M) were dispersed in 3 mL pyridine. The mixture was heated in a 90 °C oil bath for 24 h under stirring. Then the mixture was cooled down to room temperature for optical measurements and further ligand exchange with polymer. The solution was always clear during the heating and cooling process.

Ligand Exchange of Pyridine-Coated CdSe with PEG-*b*-PDMA and QD Transfer into Water. The CdSe/pyridine solution (0.4 mL) was mixed with PEG-*b*-PDMA (2.0 mL, 4.3 mg/mL, in toluene). The mixture was stirred at room temperature overnight. Then excess hexane (ca. 3 mL) was added to the mixture. The QD/polymer precipitate was separated, dried first under a N_2 flow for 2 min, and then further dried in vacuum at room temperature for 30 min. Finally, distilled water was added to dissolve the dried QD/polymer.

Photoactivation of CdSe/PEG-*b*-PDMA in Water. An aqueous dispersion of CdSe/PEG-*b*-PDMA (3 mL, containing 2.8×10^{-7} M CdSe QDs) was placed in a fluorescence cell and irradiated in a Luzchem LZC-UVA or UVC reactor with 8 overhead lamps. The irradiation wavelength of the UVA reactor was in the range 316−400 nm with a peak at 365 nm. The dose was 53 W m^{-2}. For the UVC reactor, the range of irradiation wavelength was 235−280 nm with a peak at 254 nm, and the dose was 75 W m^{-2}.

Photoluminescence Decay Measurements. PL decays of aqueous dispersions of CdSe/PEG-*b*-PDMA were measured using a single photon timing instrument from IBH. The samples were excited with a pulsed diode at 456 nm, and the emission was monitored by a monochromator at 550 nm. PL decays were fitted to sums of three to five exponential terms. The resulting fits and weighted residual plots are shown in the Supporting Information.

Effect of Ionic Strength on PL of CdSe/PEG-*b*-PDMA Water Dispersion. The samples were prepared by adding CdSe/PEG-*b*-PDMA aqueous dispersions (0.2 mL, containing 4.8×10^{-6} M CdSe QDs) to NaCl solutions (3.8 mL) with different concentrations (0.1−1.0 M). For the sample at 0 M NaCl, 3.8 mL water was added to dilute the original CdSe/PEG-*b*-PDMA aqueous dispersion (0.2 mL).

Dynamic Light Scattering Measurements. Dynamic light scattering (DLS) measurements were performed using a wide angle light scattering photometer from ALV. The light source was a JDS Uniphase He−Ne laser ($\lambda_0 = 632.8$ nm, 35 mW) emitting vertically polarized light. The cells were placed into the ALV/DLS/SLS-5000 Compact goniometer System and sat in a vat of thermostated *cis*-decahydronaphthalene, which matched the index of refraction of the glass cells. The scattered light was detected by a Dual ALV−High Q.E. APD avalanche photodiode module, interfaced to the ALV-5000/EPP multiple τ digital. All measurements were carried out at room temperature and at an angle of 90°. The resulting autocorrelation function was analyzed using both the second cumulant and CONTIN analysis.

Results and Discussion

We synthesized PEG-*b*-PDMA by atom-transfer radical polymerization (ATRP) with a methoxy-PEG derivative as the macroinitiator. We based our approach on the work reported in ref 13, which described the use of methoxy−PEG macroinitiators to prepare PEG-methacrylate diblock copolymers by ATRP. A similar series of block copolymers (PEG-*b*-PDMA) with a diethylacetal at the end of the PEG block was synthesized by

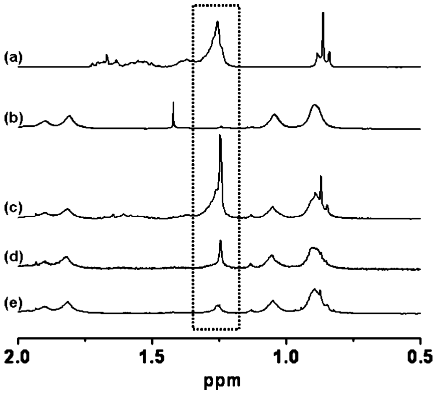


Figure 1. ^{1}H NMR (solvent: $CDCl_3$) spectra: (a) TOPO; (b) PEG-*b*-PDMA; (c) CdSe/TOPO/PEG-*b*-PDMA mixture before precipitation in hexane, in which a strong signal of TOPO appears around 1.3 ppm; (d, e) the mixture of CdSe/TOPO with PEG-*b*-PDMA after the first and fourth precipitation in hexane respectively.

the Nagasaki group[14] in Japan using anionic polymerization. This group then used these polymers in aqueous media as stabilizers to synthesize in situ PEGylated Au nanoparticles[14b] and CdS QDs.[14c] We have not found any report of the use of this kind of block copolymer for surface modification of preformed QDs through ligand exchange.

Using methoxyPEG-2-bromoisobutyrate of $M_n = 2000$ with a narrow molar mass distribution as a macroinitiator for polymerization of 2-dimethylaminoethyl acrylate (DMA), we synthesized a sample of PEG-*b*-PDMA block copolymer of M_n(NMR) = 9000, M_w/M_n(GPC) = 1.5. Filtration of a solution of the polymer through basic alumina, followed by several precipitations with hexane of the block copolymer solution in THF not only served to remove unreacted macroinitiator, as monitored by GPC. It also served to reduce the residual Cu ion concentration to such a low level ($\ll$1 ppm) that no Cu could be detected by ICP-AES. This result is important. In a previous publication,[10c] we showed that a PDMA homopolymer containing 89 ppm of Cu displaced TOPO from the surface of CdSe QDs in toluene, but the presence of the Cu ion impurity reduced the QY of photoluminescence compared to samples of PDMA prepared by traditional solution polymerization (i.e., free of the Cu impurity).

Ligand Exchange of CdSe/TOPO with PEG-*b*-PDMA. When samples of CdSe/TOPO QDs in toluene or tetrahydrofuran (THF) were treated with an excess of this PEG-*b*-PDMA polymer, the resulting particles could be dissolved in methanol, but not in water. This was the same type of result obtained earlier with PDMA homopolymer. In Figure 1 we provide experimental evidence indicating that treatment of CdSe–TOPO QDs with PEG-*b*-PDMA produced material with residual TOPO groups on the surface.

In curve a, we present part of the ^{1}H NMR spectrum of TOPO itself in $CDCl_3$, and curve b is that of the block copolymer. Ligand exchange was carried out in toluene solution. Curve c is from an unpurified mixture of CdSe–TOPO QDs with PEG-*b*-PDMA after stirring in toluene, drying and redissolving the sample in $CDCl_3$. Peaks due to TOPO can be seen at 0.8 and 1.2–1.3 ppm. Curve d presents the spectrum of this sample after addition of hexane to precipitate the QDs, removal of the supernatant liquid, and redispersion of the QDs in $CDCl_3$. These steps should remove almost all of the free TOPO liberated through ligand exchange; nevertheless, a peak due to residual TOPO groups can still be seen at 1.25 ppm. These results are consistent with a number of reports in the literature that ligand exchange of CdSe–TOPO with pyridine[15] or with other low-molecular-weight ligands[8a] does not displace all TOPO molecules from the particle surface. These TOPO groups make parts of the CdSe surface hydrophobic and are likely responsible for the insolubility in water.

Multiple Precipitation–Redispersion Cycles. If the problem with the ligand exchange is that dissociation of some of the TOPO from the QDs is slow, then a series of precipitation–redispersion cycles, which removes free TOPO in each cycle, should promote polymer replacement of TOPO in the sample. To test this idea, we designed the protocol shown in Figure 2. Samples like that shown in Figure 1d were redispersed in toluene, stirred overnight, and then reprecipitated with hexane. The precipitation, which occurs in the presence of excess polymer, is fast.

As shown in Figure 2b, a viscous precipitate forms, and one does not need to centrifuge the sample in order to decant the colorless supernatant liquid. The supernatant remained clear and colorless, indicating that almost all the QDs had PEG-*b*-PDMA bound to the surface and precipitated from the hexane-rich solution. The same result was obtained when a homopolymer PDMA (M_n = 9500, PDI = 1.6) was used for the ligand exchange. This process for the block copolymer was repeated a total of three times. The TOPO peak at 1.2–1.3 ppm decreased in intensity compared to the polymer peak at 1.0–1.1 ppm with the increase of the precipitation cycles. The ^{1}H NMR spectrum after the final (fourth) precipitation with hexane shows a reduced peak intensity at 1.2–1.3 ppm, suggesting that number of surface bound TOPOs has been significantly reduced. This sample, after drying, is easily dissolved in water, but a noticeable amount of material remains undissolved. Using the QD absorbance at 530 nm (see Supporting Information), we calculate that ca. 75% of the QDs could be transferred into water. The remaining 25% of material remained insoluble in water. The situation could not be improved by increasing the number of reprecipitation steps. In addition, for samples dissolved in $CDCl_3$, the peak at 1.2–1.3 ppm in the ^{1}H NMR spectrum persisted without any noticeable reduction in intensity when we carried out two additional precipitation–redispersion cycles. This approach has to be considered a partial success. A mechanism for the precipitation–redispersion process is presented in Scheme 1.

With the success of multiple exchanges with PEG-*b*-PDMA in transferring these QDs to water, we returned to the example of PDMA homopolymer (M_n = 9500, PDI = 1.6). After multiple exchanges as described above, followed by sample drying, ca. 67% of the resulting QD/PDMA adduct could be transferred into water. The aqueous phase became photoluminescent, but the solution did not appear to be as transparent as the QD/PEG-*b*-PDMA aqueous solution. To test whether particle aggregation was responsible for slight turbidity, the solution was passed through a 0.45 μm filter. Approximately 80% of the QDs were trapped by the filter for CdSe/PDMA, whereas only 20% QDs were trapped when an aqueous solution of CdSe/PEG-*b*-PDMA was filtered in this way (see Supporting Information). On the basis of this result, we conclude that PEG-*b*-PDMA provides better colloidal stability than PDMA homopolymer for CdSe QDs in water.

As a control experiment, we also examined the interaction of CdSe/TOPO with poly(ethylene glycol). We mixed a sample of the CdSe/TOPO in toluene with excess MeO–PEG (M_n = 2000). When hexane was added to this solution, only the MeO–PEG precipitated. Essentially all of the CdSe QDs remained in the supernatant. These results establish that, in the block copolymer system, only the PDMA block binds to the CdSe QDs.

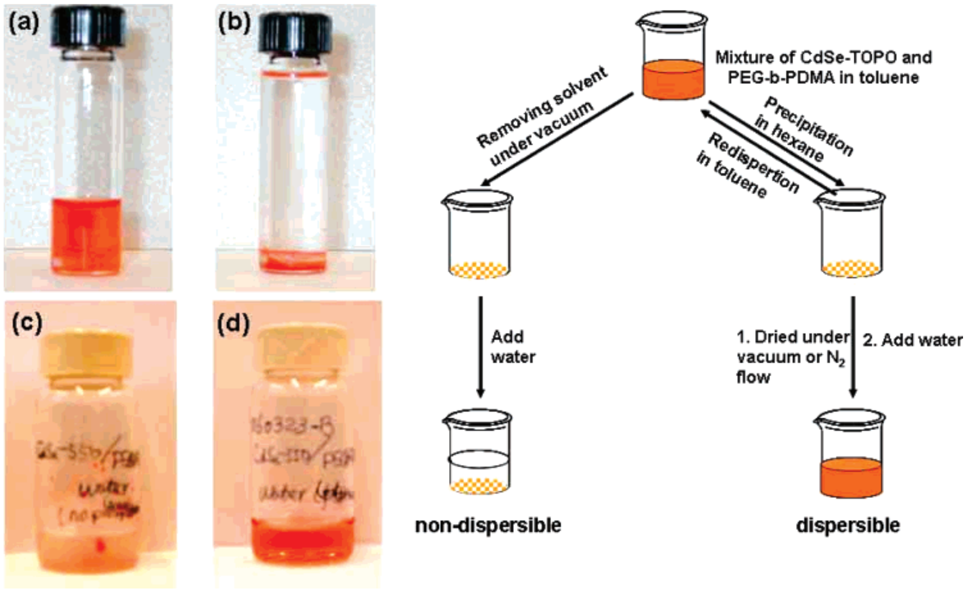
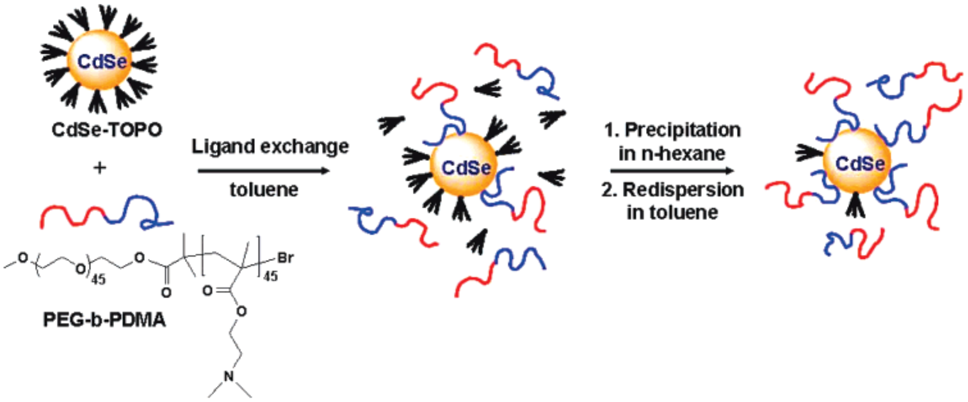


Figure 2. Photographs (left) of CdSe/PEG-*b*-PDMA QDs and the sample preparation procedures (right) show the effect of process on the dispersibility of QDs in water: (a) mixture of PEG-*b*-PDMA with CdSe/TOPO in toluene; (b) viscous precipitate of the CdSe QDs in sample a upon addition of hexane; (c) CdSe/PEG-*b*-PDMA following procedure I added to water; (d) CdSe/PEG-*b*-PDMA following procedure II, which is well dispersible in water.

Scheme 1. Ligand Exchange between CdSe−TOPO and PEG-*b*-PDMA Block Copolymer



Preexchange with Pyridine. Another possible strategy for driving the replacement of TOPO from the QD surface is to carry out a preliminary exchange with another ligand that might be more easily replaced by the dimethylamino groups of the block copolymer. Following a procedure developed by Emrick et al.,[8e] we attempted a replacement of TOPO with pyridine groups by heating the CdSe QDs in excess pyridine. Then the pyridine-coated QDs were mixed with PEG-*b*-PDMA in toluene. We found that only one precipitation in hexane followed by drying was enough to disperse the QD/polymer adduct into water. The ^{1}H NMR spectrum (not shown) indicated that only a trace amount of TOPO remained in the final sample. This result demonstrates that the prior exchange of TOPO by pyridine makes it easier for the QDs to be transferred into water. Unfortunately, QDs prepared in this way have very low photoluminescence quantum yields. The optical properties of these materials are described in more detail later in this paper.

Using Sonication To Enhance the Ligand Exchange Rate. We examined the influence of relatively mild sonication on the exchange efficiency of PEG-*b*-PDMA with CdSe/TOPO QDs. When a mixture of CdSe/TOPO with PEG-*b*-PDMA in toluene was sonicated for 0.5 h in a 60 W ultrasonic cleaning bath, there were no apparent changes to either the absorption spectrum or to the maximum emission wavelength of the QDs. There was, however, a 50% decrease of the PL intensity from the QDs. After a single precipitation with hexane, followed by separation from the solvent and drying, a large fraction (ca. 90%) of the particles could be dissolved directly in water, and only 5% QDs were trapped when the aqueous solution passed through a 0.45 μm filter. ^{1}H NMR measurements established that the remaining amount of TOPO in these sonicated samples was lower than in the samples without this sonication treatment. We found similar results when a PDMA homopolymer ($M_n = 9500$, PDI $= 1.6$) was used (see Supporting Information). Thus, sonication serves to enhance the efficiency of ligand exchange, and the ^{1}H NMR results support our hypothesis that the insolubility of the QD/polymer in water following the initial exchange with PEG-*b*-PDMA was caused by the significant amounts of TOPO that remained bound to the particle surface.

Characterization of CdSe/TOPO in Toluene and CdSe/PEG-*b*-PDMA in Water. Figure 3 shows the size and optical properties of the CdSe/PEG-*b*-PDMA QDs in water. These particular samples were prepared by the multiple precipitation−redispersion method. For comparison, we also performed the same characterization for the original CdSe/TOPO QDs in toluene. Figure 3a shows that the diameter of CdSe/TOPO in toluene is 4.0 ± 0.4 nm. After treatment with PEG-*b*-PDMA and transfer into water, the size and shape of the CdSe particles did not change. In Figure 3b, we present a transmission electron microscope (TEM) image of these particles, which can be

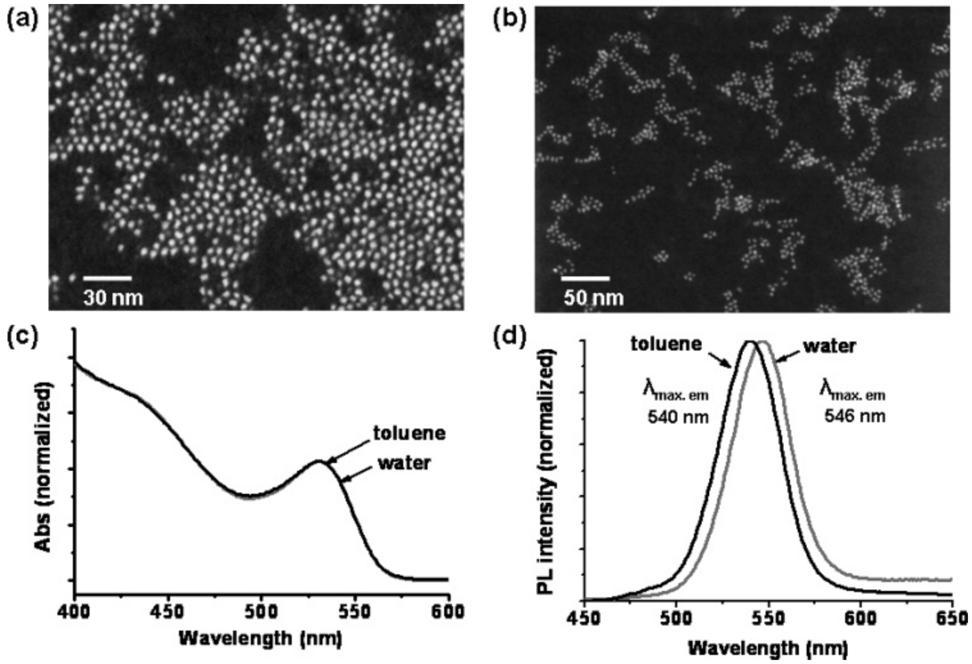


Figure 3. TEM images of (a) CdSe/TOPO QDs from toluene, (b) CdSe/PEG-*b*-PDMA QDs from water. These show that the size and shape of the QD are preserved after the ligand exchange and transfer into water. (c) Normalized absorption and (d) photoluminescence spectra of CdSe/PEG-*b*-PDMA dispersion in water and CdSe/TOPO QDs in toluene.

compared to that of the original particles shown in Figure 3a. A further indication that the particle size is unchanged can be seen in the absorption spectra shown in Figure 3c, in which the normalized spectra of the precursor particles and the CdSe/PEG-*b*-PDMA particles are superimposible. The band edge peak at 530 nm is a very sensitive measure of the diameter of the CdSe nanocrystals. Dynamic light scattering measurements (not shown) gave a hydrodynamic radius $R_h = 10$ nm for the PEG-*b*-PDMA-coated CdSe particles in water, a value consistent with polymer adsorption on the QD particles.

In contrast, we observed clear differences between the PL spectra of the particles in water and in toluene. There was a small red shift (ca. 6 nm) of the emission maximum of the CdSe/PEG-*b*-PDMA particles upon transfer from toluene to water (Figure 3d), accompanied by a substantial decrease in PL intensity. The QY of the QDs decreased by about 1 order of magnitude in the aqueous dispersions. The QY of the as-prepared CdSe/TOPO in toluene was approximately 2.2% and decreased to 0.26% after the addition of PEG-*b*-PDMA followed by the transfer into water using the multiple precipitation−redispersion procedure. The PL decay profiles showed that the excited-state decay rate of CdSe/PEG-*b*-PDMA particles became much faster in water compared to that in toluene. By fitting these decays to a sum of exponential terms, we calculated a mean lifetime of 11.2 ns for the CdSe/PEG-*b*-PDMA QDs in toluene and 0.5 ns for this sample in water. We provide further comments on these changes in PL decay profiles later in the paper.

We also monitored the optical changes for the samples prepared by a pretreatment with pyridine (see Supporting Information). After heating CdSe/TOPO in excess pyridine for 24 h and then cooling down to room temperature, the first absorption peak of the QDs shifted from 531 to 527 nm. The emission peak of CdSe/pyridine became significantly broader than that of CdSe/TOPO in toluene, accompanied by a 34 nm blue shift and an over 10-fold decrease of the PL quantum yield. After ligand exchange of CdSe/pyridine with PEG-*b*-PDMA and then transfer into water, the first absorption peak of the QDs further shifted to 521 nm. Interestingly, the emission peak became narrower than that of CdSe/pyridine and moved back to 542 ± 2 nm, but the QY decreased by approximately 2 orders of magnitude. An even lower QY (ca. 0.005%) was obtained for the water-soluble CdSe/PEG-*b*-PDMA particles prepared by sonication. In comparison, we can see that the optical properties of QDs are better preserved for the sample with a direct ligand exchange with PEG-*b*-PDMA. Therefore, in the following discussions we mainly focus on the sample prepared through the multiple precipitation−redispersion process.

Luminescence Photoenhancement of CdSe/PEG-*b*-PDMA in Water. Because of the pronounced decrease in the PL quantum yield upon transfer of the QDs into water, we attempted to restore the emission intensity by photoactivation. Photoenhancement of CdSe QD luminescence has been reported for several colloidal QD systems.[16] For example, the Kotov group[16d] found that exposure of citrate-stabilized CdSe or CdSe/CdS core/shell QDs in aqueous media to ambient light significantly enhanced the PL quantum yield. The extent of the PL increase was related to the exposure time. No PL enhancement was observed when either light or oxygen was absent. Kotov et al.[16d] proposed a mechanism for the photoactivation of CdSe PL in which photooxidation of CdSe QDs eliminates surface defects and roughness, resulting in a size reduction coupled with an enhanced luminescence efficiency.

We subjected aqueous dispersions of CdSe/PEG-*b*-PDMA to irradiation with UV light. Figure 4 shows the evolution of the QD absorption and emission as a function of exposure time during the irradiation of the sample with a 365 nm light source. With increasing irradiation time, there was a gradual blue-shift for the first absorption peak of the QD from an initial value of 520 nm to ca. 505 nm after 4.5 h irradiation, accompanied by a slight decrease of the absorption intensity. The PL spectra of the CdSe/PEG-*b*-PDMA in water showed a much stronger response to the UV irradiation, as shown in Figure 4b. The PL intensity increased approximately 7-fold during the first 1 h irradiation, with a smaller and slower increase over the next 2.5 h. Further irradiation of the sample led to a decrease in the

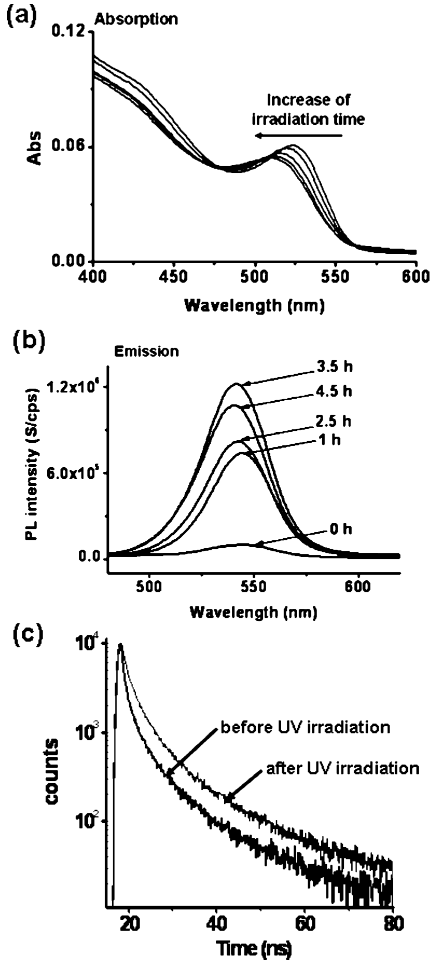


Figure 4. Effect of UV irradiation ($\lambda = 365$ nm, dose = 53 000 mW m^{-2}) on the absorption and photoluminescence of CdSe/PEG-*b*-PDMA dispersion in water. Part a shows that there is an obvious gradual blue-shift for the first absorption band around 530 nm with the increase of the irradiation time. Part b shows the change of the emission spectra of the QDs during the irradiation process. Part c shows the photoluminescence decay of CdSe/PEG-*b*-PDMA aqueous dispersion before and after 3.5 h UV irradiation.

PL intensity. The emission peak also showed a slight blue-shift of ca. 4 nm after 3.5 h irradiation. The quantum yield in water before photoactivation is 0.26%. On the basis of the absorption and emission spectra before and after photoactivation (Figure 4), we estimate that the maximum quantum yield after photoactivation is 3.1%.

We found a similar spectral shift and an increase of PL intensity when the CdSe/PEG-*b*-PDMA aqueous dispersion was irradiated at 254 nm. The irradiation time required to reach the maximum PL intensity was shorter (ca. 2 h) than for 365 nm irradiation because of the higher energy and higher dose at 254 nm. A shoulder appeared at ca. 490 nm in the PL spectra of the sample irradiated at 254 nm, which was not observed in the sample irradiated at 365 nm.

For comparison, we also investigated the UV-irradiation effect on the PL spectra of CdSe/TOPO in toluene (Figure S7 in Supporting Information). The PL intensity of CdSe/TOPO showed a 4-fold decrease after 1 h irradiation at 365 nm, accompanied by a slight decrease and blue-shift of the absorption peak around 520 nm. Thus, for this sample in toluene, we observed only photodeactivation.

The PL photoactivation of CdSe/PEG-*b*-PDMA in water was also accompanied by a striking change in the PL decay profile, as shown in Figure 4c. After UV irradiation for 3.5 h, the PL decay rate of CdSe/PEG-*b*-PDMA became slower compared to that of the nonirradiated sample. By fitting these decay profiles to sums of exponential terms, we calculated a mean lifetime of 0.5 ns for the sample prior to UV irradiation, and 2.0 ns after irradiation. The two decay curves in Figure 4c are remarkably similar in shape in the latter part of the decay. One might speculate that the UV irradiation removed sites that lead to the weak rapid decay that appears at short times in the decay profile of the nonirradiated sample.

These results indicate that the PL of the CdSe/PEG-*b*-PDMA dispersion in water can be dramatically enhanced after the photoactivation process, accompanied by a longer lifetime, thus providing a new way to obtain water-soluble and highly photoluminescent CdSe QDs. The change of the optical properties of our QDs under the UV irradiation can be rationalized by the photooxidation mechanism proposed by Kotov et al. [16d]

PL Sensitivity of CdSe/PEG-*b*-PDMA Water Dispersion to Temperature and Ionic Strength. The properties of QDs in an aqueous environment are often strongly affected by changes in the environment. For example, Silver and Ou[17] reported that CdSe/ZnS core–shell QDs coated with cationic peptides lost substantial PL intensity following endocytosis and transport to lysosomes. Much of this PL intensity could be restored by intense irradiation of the cells with visible light in the chamber of a confocal microscope. The authors proposed that the dark state is induced by the interaction of QDs with cellular molecules. It may also be affected by a change in pH within the lysosomes. With these results as background, we chose to explore the sensitivity of PEG-*b*-PDMA-stabilized CdSe QDs to changes in their aqueous environment. The obvious variables to examine are pH, temperature, and ionic strength. Our preliminary experiments in which we varied pH gave very complicated results that require much more detailed investigation. Here we report the response of PEG-*b*-PDMA-coated CdSe QDs to modest changes in temperature and to changes in ionic strength, comparing samples prior to and after photoenhancement of the PL quantum yield.

Several groups have investigated the sensitivity of QD PL intensity to changes in temperature.[18] Walker et al. [18a] studied the steady-state PL properties of CdSe/ZnS core/shell QDs in poly(lauryl methacrylate) matrices. They found that when the temperature was decreased from 315 to 100 K, the PL intensity of the 5 nm QDs increased and the peak of the emission band was blue-shifted by 20 nm. Labeau et al. [18b] studied the temperature dependence of the luminescence decay of individual CdSe/ZnS QDs between 2 and 140 K. They prepared samples by spin-coating a glass coverslip with a 10^{-9} M solution of QDs in toluene, followed by an overcoat of a 2% weight poly(methyl methacrylate)/toluene solution. In time-resolved experiments, a biexponential decay of the QDs was observed, and the decay rate of the long time component was found to depend strongly on temperature. Recently, Biju et al.[18c] reported studies of the temperature response of CdSe QD clusters in *n*-butanol. The PL intensity of the QD clusters showed a gradual decrease with the increase of the temperature from 25 to 55 °C, accompanied by a red-shift of the PL spectral maximum. The temperature response was reversible. They attributed these changes to the reversible thermal trapping of electrons at inter-QD interfaces within individual clusters.

Our objective in carrying out similar experiments is to examine whether the photoenhancement process affects the thermal response of the QDs. For PEG-*b*-PDMA-stabilized CdSe particles in water, both the non-photoactivated and irradiated QDs show a decrease in PL intensity with an increase in

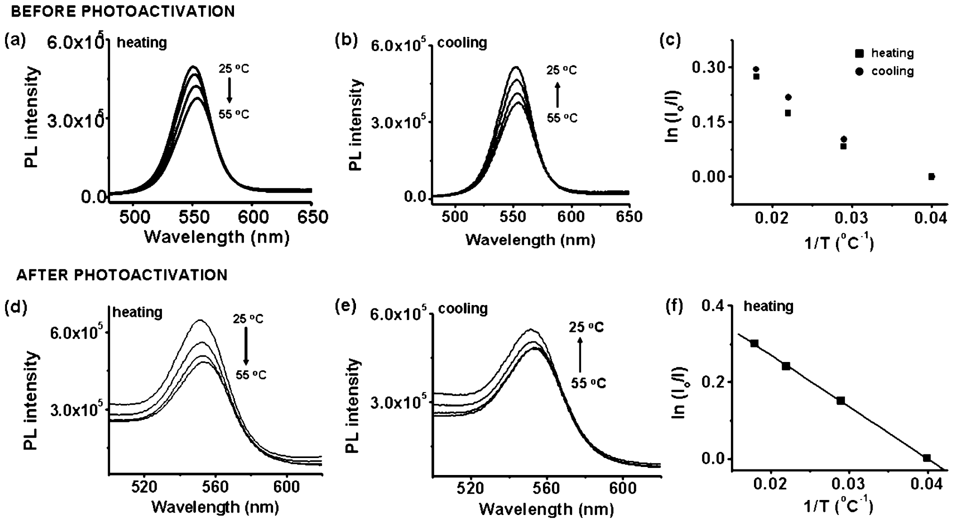


Figure 5. Temperature-sensitivity of the photoluminescence of CdSe/PEG-*b*-PDMA dispersion in water. Parts a and b show the evolution of the photoluminescence spectra of the nonphotoactivated sample during the heating and cooling process, respectively. Parts d and e show the evolution of the photoluminescence intensity of the sample after irradiation at 254 nm for 3.5 h. Arrhenius plots ($\ln(I_o/I)$ with $1/T$) of CdSe/PEG-*b*-PDMA aqueous dispersion before and after photoacitivation are shown in parts c and f, respectively.

temperature from 25 to 55 °C similar to the response reported by Biju et al. [18c] The results are presented in Figure 5, and they show that the decrease in intensity is accompanied by a slight red-shift (3−4 nm) of the PL peak ($\lambda_{\mathrm{max,em.}}$). For the nonphotoactivated samples, when the temperature of this solution was decreased from 55 to 25 °C (Figure 5b), the intensities returned to their original values, and the PL emission peak shifted back to 550 nm. Under these conditions, the CdSe/PEG-*b*-PDMA sample that had been irradiated at 254 nm in water for 3.5 h to increase the luminescence quantum yield exhibited a different response. As shown in Figure 5e, the intensities did not recover fully upon cooling.

If this “thermal quenching” is an activated process, it should follow an Arrhenius-type behavior. To examine this idea, we take 25 °C as a reference temperature corresponding to an intensity I_o and plot $\ln(I_o/I)$ vs $1/T$ in Figures 5c and 5f. Before photoactivation of CdSe/PEG-*b*-PDMA, the response of the PL intensity on temperature changes is reversible, but the plot $\ln(I_o/I)$ vs $1/T$ is not linear (Figure 5c). What we found (not shown) was that I decreased linearly with T in this range. After the photoactivation, the plot of $\ln(I_o/I)$ vs $1/T$ during the heating process is linear and can be fitted by Arrhenius equation. This Arrhenius plot gives an effective activation energy of 0.11 kJ/mol. However, the temperature response of PL intensity in the cooling process is different because of irreversible changes that occurred during the heating process.

We then investigated the effect of ionic strength on the PL of aqueous solutions of CdSe/PEG-*b*-PDMA. In this experiment, the QD concentration was kept constant and various amounts of NaCl solution were added. As shown in Figure 6, over the range of 0 to 1.0 M NaCl, the band-edge emission intensity of the QDs at 550 nm decreased, while the trap-state emission at 650−700 nm showed a corresponding increase. These changes are much larger than those reported by Uyeda et al.,[8g] who studied the optical response of PEG-DHLA-capped CdSe/ZnS core/shell QDs to changes in ionic strength. They found little change in either the PL intensity or the characteristics of the emission spectra over the concentration range from 0 to 1 M NaCl. From a comparison of these two sets of experiments, we learn that the ZnS overcoat provides the QDs with a strongly reduced sensitivity to ionic strength in aqueous solution.

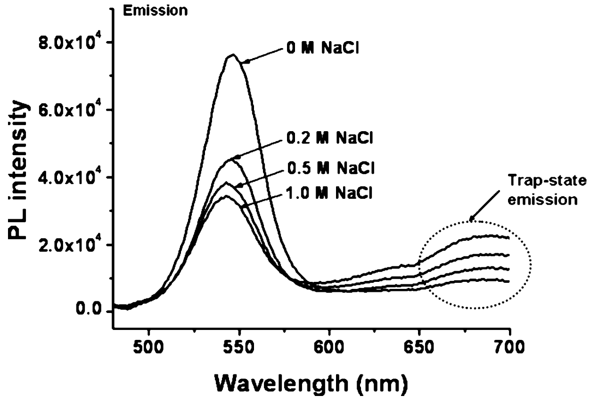


Figure 6. Photoluminescence spectra of CdSe/PEG-*b*-PDMA dispersion at different concentrations of NaCl in water. With the increase of NaCl concentration, the band-edge emission at 550 nm decreases accompanied by a gradual increase of the trap-state emission in the range of 650−700 nm.

Summary

We synthesized a water-soluble diblock copolymer (PEG-*b*-PDMA) by ATRP and demonstrated that this polymer could be employed to transfer TOPO-capped CdSe QDs into water through a ligand exchange process. The PDMA block acts as a multidentate ligand for the QD, while the PEG block enhances the water-solubility and provides potential biological compatibility for the QD/polymer colloidal system. A key finding is that a series of precipitation−redispersion steps in the presence of excess block copolymer promotes the ligand exchange of CdSe/TOPO with the polymer and reduces the amount of residual TOPO at the QD surface. After three such cycles, the dried CdSe/PEG-*b*-PDMA mixture could be dissolved easily in water. This enhanced ligand replacement of TOPO groups with amine groups of the polymer could be carried out more effectively by subjecting the polymer-QD mixture in toluene to mild sonication in an ultrasonic cleaning bath. Another potentially interesting route is initial replacement of TOPO with pyridine, followed by treatment with the block copolymer. While the ease of the ligand exchange was increased in both sonication and pyridine-pretreatment approaches, the QDs obtained in water had PL quantum yields much lower than those obtained by the multiple precipitation−redispersion process.

The CdSe QD particles retained their size and shape after the direct ligand exchange and transfer to water. In the transfer of the CdSe/PEG-*b*-PDMA QDs from toluene to water, the optical properties were basically preserved, but there was a strong (10-fold) decrease in the PL intensity. The PL intensity could be significantly enhanced through UV photoactivation, and the QY could be increased to a level close to that of the as-prepared CdSe/TOPO QDs in toluene. Photoactivation appeared to suppress a fast component in the PL decay profile, so that the increase in QY was accompanied by a lengthening of mean PL decay time. The PL of the CdSe/ PEG-*b*-PDMA dispersion in water before photoactivation shows linear and reversible sensitivity to the temperature change over the range from 25 to 55 °C. This reversibility was lost for the photoactivated samples. In the presence of NaCl, the PL intensity of the band-edge emission of CdSe/ PEG-*b*-PDMA in water was reduced, accompanied by an increase in trap-state emission.

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Supporting Information Available: Text giving experimental conditions for ligand exchange with pyridine and figures showing UV−vis spectra for quantifying the fraction of QDs transferred into water, determination of residual TOPO on the particle surface for CdSe/PDMA, synthetic scheme and characterization of PEG-*b*-DMA, and PL decay traces for CdSe/PEG-*b*-PDMA before and after UV irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

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