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Comparison and Stability of CdSe Nanocrystals Covered with Amphiphilic Poly(Amidoamine) Dendrimers

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This paper describes the surface modification of CdSe nanoparticles (NPs) with amphiphilic and flexible poly(amidoamine) (PAMAM) dendrimers carrying different numbers of hydrophobic aliphatic chains. Although hydrophilic full generation dendrimers with primary amine termini caused aggregation of the CdSe particles, the amphiphilic dendrimers proved to be useful caps for the CdSe nanocrystals and solubilized them in chloroform. Complete exchange of the original TOPO/TOP caps was achieved through a CdSe/pyridine intermediate. It was found that both amine groups (which interact with the nanoparticle surface) and hydrophobic chains (which provide the particles with solubility in the solvent) were necessary to stabilize the CdSe NPs. The PAMAM covered CdSe nanocrystals were characterized using NMR, UV−visible absorption, photoluminescence (PL), and TEM. UV−vis absorption and PL of such CdSe/PAMAM systems were studied during a two month period, and it was found that PAMAM derivatives with only secondary and tertiary amines provided a better protection for the nanocrystals than those with primary amines.

Introduction

Research on semiconductor nanoparticles has been expanded tremendously during the past couple of decades.[1−4] Semiconductor nanocrystals possess unique optical and electronic properties because of size quantization effect on the nanometer scale. Such NPs are usually capped with organic molecules containing an electron donating ligand, such as trioctylphosphine oxide (TOPO) or pyridine, to provide chemical and electric passivation.[5,6] Surface modification of NPs is an important issue because surface ligands not only determine the stability of the nanoparticles but also influence their optical properties and control their compatibility with the actual physical environment. Although TOPO/TOP and long chain aliphatic primary amine passivated CdSe QDs are relatively stable when properly stored, they cannot be supplied with additional functionalities. CdSe/TOPO preparations also usually contain a high excess of TOPO, which makes them impossible to use them directly in biologic systems.

The mechanisms of this "capping" appear to be similar to metal ion complexation by organic molecules, i.e., a donor−acceptor type interaction between the NP surface and the ligand site of the organic molecule. If surface caps are bound covalently, dry nanoparticles remain soluble when only solvent is added. However, in case of a dynamic equilibrium, an excess of organic molecules must be present in the solution. On the basis of analogy with metal ion chelation, we assumed that multiligand polymers should form more stable surface caps than molecules with a single ligand if bound by noncovalent interactions.

In the meantime, enormous research efforts have been devoted to the synthesis and characterization of dendrimers as well. Polymers with dendritic architectures have large numbers of functional terminal groups, which are exposed on their surface when in solution. We have selected poly(amidoamine) PAMAM dendrimers[7−11] to carry electron donating amine ligands as they have a predetermined size with narrow molecular weight distributions and their molecular weight can be varied systematically from generation to generation. Physical properties of PAMAM dendrimers, such as solubility and interactions with the surrounding environment,[12−15] can be altered by changing the characteristics of terminal groups. Introduction of additional surface functionalities should be relatively simple by using dendritic polymers because of their multifunctionality.

PAMAMs have been used as templates for semiconductor particles[16−21] and metal nanoparticles[22−26] where hybrid nanocomposites were formed in situ in the presence of dendrimers. In a study on CdS nanocomposites,[18] it was suggested that PAMAM dendrimers retard the growth of the nanoparticles thereby producing small CdS nanocrystals, although these composite particles proved to be unstable and underwent further aggregation to form micrometer scale flocs.

In our work, instead of using dendrimers as templates, we introduce dendrimer caps on preformed CdSe nanocrystals synthesized by a well-known wet chemistry procedure in TOPO/TOP.[27,28] Using dendrimers as surface ligands, we wish to develop a universal method for adjusting the nanoparticle surface in a controlled manner and for adding further functionality to the nanoparticles. TOPO covered particles proved to be stable and have a long shelf life if stored properly. However, it is not possible to add further moieties to the TOPO passivated NP surface that would empower us to target specific cell-receptors and use the particles for biomedical research. Dendritic molecules, with an exact number of functional groups, should provide excellent model compounds to study surface passivation of NPs. These multifunctional dendrimer caps possess "heads"

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that bind to the NP surface, whereas other parts of the molecule increase the solubility and provide stability against aggregation and crystal growth. Dendrimers also have been used as targeted nanodevices. We hereby report the preparation of the surface modified dendrimers and the preliminary results on the characterization and stability of such amphiphilic PAMAM passivated CdSe nanocrystals.

Experimental Section

Materials. Generation 2 PAMAM dendrimer (ethylenediamine core) was obtained from Dendritech, Inc. (Midland, MI) as a 19.17 wt %/wt solution in methanol. 1,2-Epoxyhexane (97%), 1-hexadecanol (99%), octadecylamine (97%), trihexylamine (96%), ethylenediamine (99.5+%), pyridine (99%), and the solvents were obtained from Sigma-Aldrich (Milwaukee, WI). Tetraethylenepentamine (TEPA, 99%) was received from Air Products as a gift. *N*-Octadecoylacetamide and *N*,*N*′-dihexadecoyltetraethylenepentamine were synthesized from octadecylamine and TEPA following standard acylation procedures.

General Procedures. All ^{1}H, ^{13}C, and ^{31}P NMR analyses were recorded on a Bruker 500 spectrometer. ^{1}H NMR spectra were collected at 500.1 MHz using $CHCl_3$ (7.259 ppm) as an internal reference. ^{13}C NMR spectra were obtained at 125.8 MHz using $CDCl_3$ (77.23 ppm) as an internal reference. ^{31}P NMR spectra were obtained at 202.4 MHz using phosphoric acid (0 ppm) as an external reference. ESI-MS spectra were acquired on a VG Platform (SISONS Instrument, UK) with continuous extraction. Samples (10 mL, 50 pmol/mL) were flow-injected through an autosampler, using acetonitrile with 0.2% (V/V) formic acid as the carrier solvent. UV−vis absorption spectra were recorded on a Perkin-Elmer Lambda 20 UV−vis spectrometer using pure solvent in the reference beam. Photoluminescence spectra were collected on a Fluoromax-2 photofluorometer at 90° in ambient atmosphere at room temperature. Transmission electron microscopy (TEM) images were obtained on a Philips EM100 instrument.

Amphiphilic PAMAM Dendrimers. PAMAM dendrimers terminated by aliphatic chains were made via reacting full generation ethylenediamine (EDA) core PAMAMs with various amounts of 1,2-epoxyhexane, resulting in various degrees of surface substitution.[15] Starting with 8, 16, 24, and 32 equivalents of 1,2-epoxyhexane, we obtained PAMAMs with 8, 16, 24, and 28 respective sidearms attached on average, designated as PAMAM_E2R$_8$, PAMAM_E2R$_{16}$, PAMAM_E2R$_{24}$, and PAMAM_E2R$_{28}$, respectively. The reaction with 16 equivalents of 1,2-epoxyhexane is used here as an example of the general procedure: a methanol solution of PAMAM_E2.NH$_2$ (2.08860 g, 19.17 wt %/wt, 400.0 mg dendrimer, 0.1228 mmol) was measured out into a 25 mL round-bottom flask. 1,2-Epoxyhexane (0.1987 g, 1.984 mmol) in 2 mL of methanol was added dropwise under vigorous stirring. The reaction was stirred at room temperature for 3 days and refluxed for 1 h. Methanol and unreacted 1,2-epoxyhexane were removed by rotary evaporation, and the product was dried in a vacuum to give the modified dendrimer PAMAM_E2R$_{16}$ as a viscous oil at a near quantitative yield. (See the Supporting Information for ESI-MS spectra.)

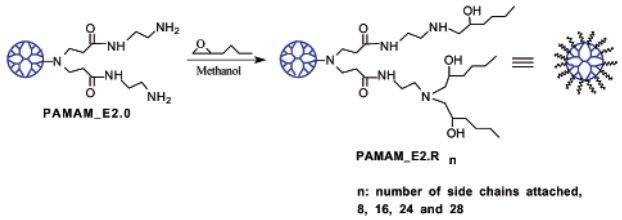
CdSe/TOP/TOPO. CdSe nanocrystals capped with trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) surface were synthesized following the procedure based on growth and annealing of organometallic compounds at high temperature, a technique developed by Murray et al.[27]

CdSe nanoparticles were prepared by injection of a trioctylphosphine (TOP) solution of Cd$(CH_3)_2$/TOPSe into TOPO at 300 °C. Provided that favorable conditions of temperature, injection, and nanocrystal growth time were employed, size-selective precipitation was not necessary. Average nanoparticle diameter and size distribution were also determined from optical absorption spectroscopy. Comparisons with published optical absorption data correlated well with electron microscopy studies of size. The final average particle diameter was 5.5 nm, deduced from optical absorption spectroscopy, TEM, and AFM (see the Supporting Information). The resultant CdSe/TOP/TOPO (10.9 mg) was subjected to NMR analysis. ^{1}H NMR ($CDCl_3$, ppm): 1.65 (t, 2H, $-CH_2CH_2\mathit{CH}_2PO$), 1.55 (p, 2H, $-CH_2\mathit{CH}_2CH_2$-PO), 1.38 (p, 2H, $-\mathit{CH}_2CH_2CH_2PO$), 1.27 (m, 8H, the rest of the CH_2s), 0.87 (t, 3H, CH_3). ^{31}P NMR gives multiple peaks at 20−60 ppm, in addition to two broad peaks at ∼25 and 0 ppm, indicating a complex chemical environment of several phosphorus compounds. Using P(OMe)$_3$ as an internal standard and based on both ^{1}H and ^{31}P NMR integration, the amount of TOP/TOPO (expressed as pure TOPO) was calculated to be 4.6 mg, and hence, the amount of CdSe was 6.3 mg. The weight ratio of CdSe:"TOPO" = 10 mg:7.3 mg.

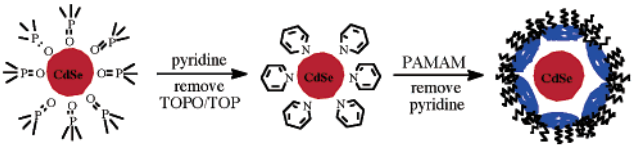
CdSe/Pyridine. CdSe/TOP/TOPO in hexane (10 mL) was measured into a 50 mL round-bottom flask, and then the solvent was removed by rotary evaporation. The resultant CdSe/TOP/TOPO solid (109 mg) was dissolved in 5 mL of pyridine and allowed to stir at 65 °C for 1 h. Hexane (30 mL) was added to reprecipitate CdSe. The orange/red suspension was centrifuged to collect the solid, which was again redissolved in ∼5 mL of pyridine. This cycle was repeated seven times, while being monitored by both ^{1}H and ^{31}P NMR. The final CdSe/pyridine solid was redissolved in 10 mL of pyridine to make the CdSe/pyridine stock solution. Of this solution, 1 mL was dried (first in dry N_2 stream followed by vacuum at room temperature until constant weight) to give 8.5 mg of solid which was subjected to NMR analyses. ^{1}H NMR (pyridine, ppm): 8.73 (dd, 2H, H ortho to N in pyridine), 7.58 (t, 1H, para), 7.22 (dd, 2H, meta), 1.0−1.8 (b, aliphatic protons from residual phosphorus compounds). ^{31}P NMR shows broad peaks at around 25 and 0 ppm, indicating the presence of residual phosphorus. This is in agreement with other literature data suggesting that 10−15% "TOPO" remains on the surface.[29,30] Using P(OMe)$_3$ as an internal standard and based on both ^{1}H and ^{31}P NMR integration, the amounts of residual phosphorus compounds (expressed as TOPO) and pyridine were calculated to be 1.1 and 1.4 mg, respectively, and hence, CdSe was 6.0 mg. The weight ratio of CdSe:"TOPO":pyridine = 10.0 mg:1.8 mg:2.3 mg.

CdSe/PAMAM_E2.R$_n$. The standard cap exchange procedure of CdSe/pyridine with modified PAMAM dendrimers is as follows: CdSe/pyridine (1.0 mL, 3.0 mg CdSe) stock solution was measured into a 2 dram vial. PAMAM_E2.R$_{16}$ (25.6 mg, 5.27×10^{-6} mol) was added and dissolved instantly. The pyridine was removed first under N_2 stream and then under vacuum. The solid was then redissolved in ∼1 mL of $CHCl_3$, and the solvent was again removed. This cycle was repeated three times until ^{1}H NMR indicated complete removal of pyridine by the disappearance of the aromatic proton peaks of pyridine (see the Supporting Information). The resultant CdSe/PAMAM_E2.R$_n$ particles were characterized using UV−vis absorption, photoluminescence (PL) spectrometry, and TEM. To ensure that the observed changes in optical measurements were intrinsic to the sample, optical samples were carefully prepared as follows. Equal aliquots (0.025 mL) of a CdSe/PAMAM stock solution containing 0.6 mg (8.75×10^{-11} mol) of CdSe and 5 mg ($(3-5) \times 10^{-8}$ mol) of PAMAM in 500 mL of $CHCL_3$ were distributed into positive sealing glass (2 mL)

SCHEME 1: Derivatization of Terminal Functionalities of the PAMAM G2.0 Dendrimer (For Simplicity, Only Two Different Terminal Branches Are Shown)



SCHEME 2: Surface Modification of CdSe Nanoparticles by Amphiphilic PAMAM Dendrimers



vials, diluted to 500 mL using $CHCL_3$, and capped with Teflon-lined screw caps. The vials were then sealed with Parafilm and kept in a refrigerator in the dark. Only one set of samples was removed each time, when the solutions were transferred into closed quartz cuvettes for PL and UV−vis absorption measurements. Optical measurements were conducted on days 1, 5, 9, 14, 27, and 65.

Results and Discussion

PAMAM Dendrimer Surface Modification. When generation 2.0 PAMAM with $-NH_2$ terminal groups was added directly to the CdSe/TOP/TOPO system or to the CdSe/pyridine solution, a solid precipitate formed instantaneously, which was insoluble in any solvents. This precipitation is most likely induced by the strong interactions between the primary amino groups on the multifunctional dendrimer surface and the CdSe surface. To decrease the interparticle interaction through terminal amine groups and avoid physical cross-linking, we have modified the surface properties of the PAMAM dendrimers by reacting it with 1,2-epoxyhexanes. The resultant CdSe/PAMAM systems were well soluble in common organic solvents.

The reaction between aliphatic epoxides and terminal amino groups provides a simple way to synthesize amphiphilic PAMAM dendrimers[15] (Scheme 1).

To tailor the amphiphilic properties of PAMAMs, we varied the 1,2-epoxyhexane/dendrimer ratio and obtained PAMAMs with 8, 16, 24, and 28 respective sidearms attached on average. The number averages of attached sidearms have been calculated from ^{1}H NMR integration. Mass spectra of the partially modified dendrimers indicated a statistical distribution of similarly substituted entities (typically ± 3 hexyl chains) centered on the calculated average substitution (see the Supporting Information).

Cap Exchange and Passivation of CdSe NPs. In the cap exchange process, pyridine was first used to replace the TOP/TOPO bound to the original NPs,[28,29] and then amphiphilic PAMAM dendrimers were used to replace the pyridine on the CdSe surface (Scheme 2). CdSe/pyridine is an essential intermediate because neither TOP/TOPO nor PAMAM is volatile, and a direct cap exchange from CdSe/TOP/TOPO to CdSe/PAMAM is impossible. *Pyridine capped dry CdSe/pyridine particles were insoluble in any solvent including chloroform and toluene, and they were only soluble in pyridine as solvent.* However, by adding amphiphilic PAMAMs to the solution of CdSe/pyridine, the weakly bound pyridine[30] can be replaced easily because of its volatility, and the resultant CdSe/PAMAM solids were soluble in common organic solvents. Complete exchange of pyridine with PAMAM was monitored using ^{1}H NMR and was indicated by the disappearance of the aromatic proton peaks corresponding to pyridine.

Although the fully modified PAMAM has only tertiary amines, PAMAM_E2.R_8 has also unreacted primary amine termini, and PAMAM_E2.R_n ($n = 16$, 24, and 28) have tertiary and secondary amines, in addition to hydroxyl and amide functional groups as part of their structure. To elucidate which functional group interacts with the nanoparticles, we have tested several linear model compounds such as ethylenediamine, 1-hexadecanol, 1-octadecylamine, *N*-octadecylacetamide, tetraetheylenepentamine, *N,N′*-dihexadecanoyl-tetraethylenepentamine, and trihexylamine. Ethylenediamine dissolved the CdSe/TOPO/TOP particles. When 1-hexadecanol or *N*-octadecylacetamide was added to CdSe/pyridine and the pyridine was subsequently removed, the CdSe residue was insoluble in any solvent. We concluded that hydroxyl and amide functional groups do not interact with the CdSe surface, and hence, ligands containing only hydroxyl (e.g., 1-hexadecanol) or amide (e.g., *N*-octadecylacetamide) functionalities are unable to stabilize the CdSe nanocrystals. In addition, we found that both 1-octadecylamine and trihexylamine can keep the particles in solution after the pyridine was removed. (Characterization of such amine-passivated particles will be reported in a forthcoming paper.) Furthermore, tetraethylenepentamine (TEPA), with both primary and secondary amine groups, caused aggregation of CdSe, but its acylated derivative, *N,N′*-dihexadecanoyltetraethylenepentamine, provided a clear nanoparticle solution after the pyridine was removed.

Summarizing of the above scouting experiments, we confirmed that the presence of both polar "anchors" (that bind to the nanoparticles surface) and hydrophobic "chains" (that provide solubility and compatibility in a solvent) were essential for efficient solubilization of the polar CdSe particles in chloroform.

In the case of *N,N′*-dihexadecanoyltetraethylenepentamine, clearly the amine groups bind to the CdSe surface, whereas the aliphatic chains provide the solubility of the passivated CdSe NPs. This binding is likely due to the interaction of the Lewis bases (electron donating amines) with the Lewis acids (electron deficient Cd sites). On the basis of the above experiments, it is reasonable to conclude that stabilization of CdSe by PAMAM_E2.R_n is the result of interactions between the dendrimer amine groups (both tertiary and residual primary/secondary amines) with the CdSe surface as well, and the aliphatic terminal chains provide the essential solubility. Complete solubilization of CdSe in $CHCl_3$ by dendritic PAMAM_E_2.R_n indicates that the dendrimers are sufficiently interacting with the CdSe nanoparticles. Efficient binding to the polar CdSe surface is possible only between the amine groups and the electron deficient particle surface sites. To make the internal amines accessible, PAMAM_E_2.R_n molecules, spherical in solution, have to undergo a considerable distortion upon absorption. It has to be noted that, although dendrimers have a spherical architecture, lower generation PAMAMs ($G < 4$) are very flexible and are able to assume even platelike conformations on solid planar surfaces. This was predicted by theoretical considerations[31] and was corroborated later by AFM observations of PAMAMs adsorbed on a mica surface.[32] In a similar case, it was also suggested that amphiphilic poly(propyleneimine) dendrimers became highly distorted with all aliphatic end groups pointing upward when spread on air−water

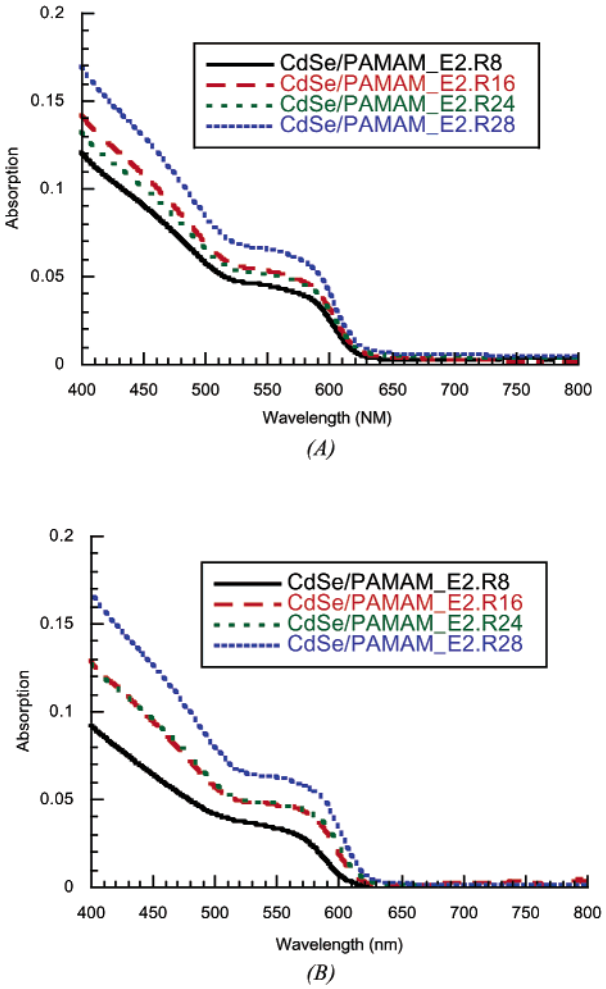


Figure 1. Comparison of UV−vis absorption spectra of for the CdSe/PAMAM_E2.R_n series taken on days 1 (A) and 65 (B).

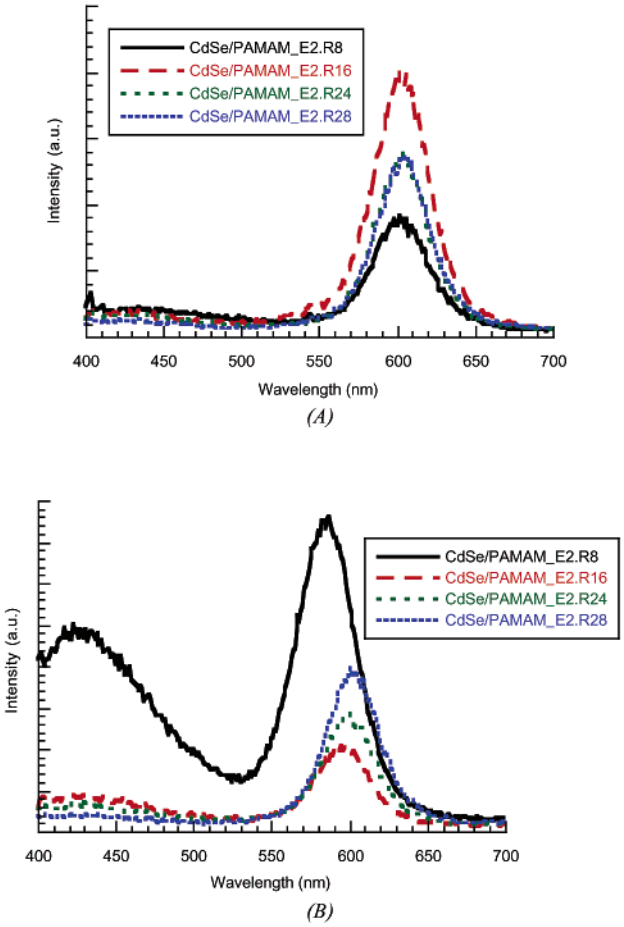


Figure 2. Comparison of photoluminescence spectra of for the CdSe/PAMAM_E2.R_n series taken on days 1 (A) and 65 (B).

interfaces.[33] So, it is expected that the modified PAMAM dendrimer molecules (d = 2−3 nm) become asymmetric because of the interaction with a 5.5 nm solid particle. As a consequence, the aliphatic chains "phase-separate" and form a hydrophobic halo around the surface endowing with solubility and stability of the CdSe nanoparticles inside (Scheme 2).

Optical Properties of CdSe/PAMAM. The crucial experimental problem in acquiring the CdSe optical spectra is the unknown exposure of the samples to a minute, but uncontrolled, amount of oxygen and moisture. In line with a recent report on the photooxidation of single CdSe/ZnS quantum dots,[6] all current experiments were performed in closed vials. In our approach, we have used a constant amount of nanoparticles and preset an identical amount of air present in each vial. We also used chloroform as a solvent, which does not favor the absorption of moisture. Therefore, we assume that short-term changes are dominated by the exchange of ligands and their donacity, but later data are informative of the protection of nanoparticles by the various dendrimer caps. We followed the optical properties of the CdSe/PAMAM systems for over two months. Because of the multiligand structure of the PAMAM_E2.R_n, all accessible functionalities will contribute to the final optical properties.

According to literature studies, amine surface ligands, as hole acceptors, quench the photoluminescence of NPs through eliminating the surface trapped electron−hole recombination via binding to the hole trapping emission sites on the surface.[6,34,35] This quenching effect was also observed in our current dendritic PAMAM passivated CdSe systems, compared with the original TOPO passivated NP. Exchange of surface bound moieties from TOPO/TOP to pyridine and then PAMAM_E2.R_n only slightly changed the UV−vis adsorption characteristics of CdSe nanoparticles, i.e., peak and band edge positions were within the experimental error on day 1. However, by day 65, a considerable difference developed between the samples (Figure 1): whereas adsorption characteristics of CdSe/PAMAM_E2.R_{28} was practically unchanged, the absorption intensity of the CdSe/PAMAM_E2.R_8 sample considerably decreased, and its absorption edge blue shifted, with CdSe/PAMAM_E2.R_{28} and CdSe/PAMAM_E2.R_{28} falling between (see the Supporting Information).

Comparison of the photoluminescence (PL) spectra of the CdSe/PAMAM_E2.R_n nanoparticles (Figure 2 parts A and B) is shown in Figure 2. On day 1, the position of the PL peak maxima of all of the CdSe/PAMAM systems were practically identical, whereas on day 65, all of the PL spectra showed a blue shift with CdSe/PAMAM_E2.R_8 shifted the most, ∼15 nm.

Comparing the change of the PL wavelength and the PL intensity of the various derivatives, there is a significant difference between the spectra of CdSe/PAMAM_E2.R_8 and the other PAMAM modified CdSe nanoparticles (Figure 3). As indicated above, PAMAM_E2.R_8 possesses primary amines in its structure, different from the rest of PAMAM_E2.R_n (n = 16−28). The blue shift in PL peak correlates well with the degree of substitution of PAMAM, and this shift was increasing in the order of $n = 8 > n = 16 > n = 24 > n = 28$. Interestingly, PL intensity values for PAMAMs containing only secondary and tertiary amines decreased in the order of

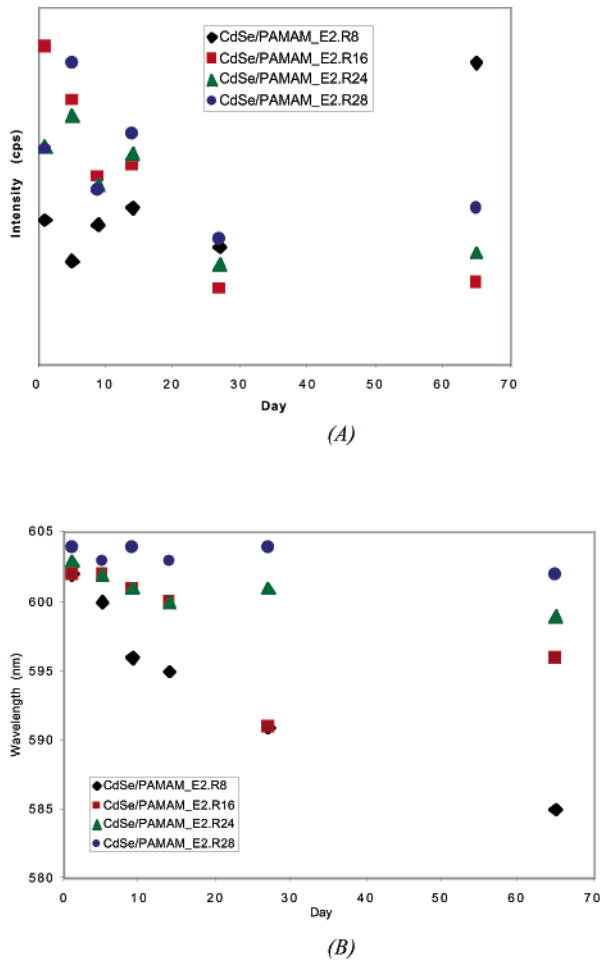


Figure 3. Comparison of change in peak wavelength (A) and PL intensity (B) of the CdSe/PAMAM_E2.R_n series as a function of time.

CdSe/PAMAM_E2.R_{16} > CdSe/PAMAM_E2.R_{24}, > CdSe/PAMAM_E2.R_{28} and leveled off after day 27, whereas the primary amine-containing PAMAM_E2.R_8 system kept increasing. At present, we have not identified the origin of the shorter wavelength peak that developed at ~430 nm in the PL spectra of CdSe/PAMAM_E2.R_8.

On the basis of our current data and previous literature results,[6] the authors are convinced that oxidation of the particles plays an important role in the observed change of absorption and photoluminescence over time. Particle oxidation will lead to virtual size shrinkage of NPs and, hence, the blue shifts in both band-edge absorption and photoluminescence. Evaluated similarly to the previous report,[37] the shift of ~15 nm in PAMAM_E2.R_8 corresponds to an shrinkage of 1 layer of CdSe (~0.5 nm) from the surface. However, when the particles were examined under TEM and compared to the original CdSe/TOPO, no significant change in size was observed (see the Supporting Information). As the photooxidation product was identified to be $CdSeO_x$ ($x = 2$ or 3),[36,37] it appears that the oxidized surface layer is responsible for the changes in the optical spectra. At the moment, it cannot be decided whether this layer remains on the NP surface or it is partially removed.

Most importantly, even though all of these amphiphilic PAMAM dendrimers have very similar structure, they provide different protections for the NPs. We suggest that this is due to the difference in chemical structure, e.g., the number and nature of amine groups of the modified PAMAMs involved in the capping. As mentioned above, CdSe NPs dissolve in ethylenediamine. Taking into account the increasing PL intensity of CdSe/PAMAM_E2.R_8 accompanied with the considerable decrease in the respective UV−vis absorption by day 65, our observations suggest that primary amines (just like ethylenediamine) probably slowly react with the surface of the CdSe nanoparticles making them smaller. This derivative provides much less protection for the CdSe nanoparticles than PAMAMs without primary amines do. In a very recent study,[38] Peng et al. also demonstrated the importance of surface ligands, using hydrophilic thiols capped CdSe NPs.

To gain a better insight into the mechanism of the change of the CdSe/PAMAMs, a more detailed study under strictly controlled conditions is in order. We are presently investigating the optical properties of CdSe nanoparticles modified by various surface ligands that are bound to linear and dendritic molecules. These results will be reported in a forthcoming paper.[39] In another similar study, higher generation and hence more rigid PAMAM dendrimers are to be used to provide further insight into the utilization of amphiphilic dendritic ligands as nanoparticle surface modification agents.

Conclusions

Generation 2 poly(amidoamine) dendrimers were successfully used as multifunctional organic surface modification molecules for CdSe nanocrystals. Complete exchange of TOPO/TOP caps was achieved through a CdSe/pyridine intermediate. Although unmodified PAMAM dendrimers cross-linked the nanoparticles, a series of hydrophobically modified PAMAM_E2.R_n provided transparent nanoparticle solutions. We suggest that these simultaneous actions of passivation, stabilization, and compatibilization are due to the adsorption of the amphiphilic dendrimers on the surface of the nanoparticles. The absorption occurs as the interaction of the electron donating amines with the electron deficient Cd sites. The flexible network of the PAMAM_E2.R_n molecules undergo a conformational change upon adsorption, and the carbon chains form a hydrophobic halo around the CdSe nanoparticle making it soluble in solvents. Following the absorption and PL change over a two month period, we have found that the PAMAM_E2.R_{28} provided the most effective protection of the NPs against oxidation. In the long run, nanoparticles that are stable in air will be essential for many different applications. To achieve this stabilization will be a challenge for both physical chemists and material scientists. This work has clearly shown the important role of surface ligands and the potential of surface modification in stabilizing NPs.

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Supporting Information Available: ESI-MS spectra of PAMAM_E.2R_n (n = 8, 16, 24, and 28; Figures 1−4). Comparisons of UV-vis spectra of CdSe/PAMAM_E.2R_n (n = 8, 16, 24, and 28; Figures 5−8). TEM images of CdSe/TOPO/TOP starting material (Figure 9), CdSe/pyridine nanoparticles (Figure 10), and CdSe/PAMAM_E2R_{28} nanoparticles (Figure 11). This material is available free of charge via the Internet at http://pubs.acs.org.

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