

DOI: 10.1002/adfm.200701201

Hybrid CdSe Nanoparticle–Carbazole Dendron Boxes: Electropolymerization and Energy-Transfer Mechanism Shift**

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Carbazole containing ligand dendrons are designed based on second generation polybenzyl ether dendrons (2GPO). This is subsequently used for directly synthesizing and capping CdSe nanoparticles in contrast to ligand exchange for introducing functionality. The stable hybrid CdSe-2GPO quantum dot nanoparticles have characteristic energy-transfer properties from the donor carbazole peripheral groups to the acceptor CdSe nanoparticles, i.e., overlap of the fluorescence of the carbazole with the absorbance of the CdSe nanoparticle resulting in an enhanced fluorescence with concentration through Förster resonance energy transfer (FRET). However, electropolymerization of the peripheral electroactive carbazole units result in a red-shift in absorbance and quenching in fluorescence. This is attributed to a reversed molecular orbital energy order with respect to the electropolymerized carbazole dendron and CdSe nanoparticle. The hole-transfer results in fluorescence quenching and charge transfer between the CdSe nanoparticles and the polycarbazole peripheral units. The photoelectric alteration may yet provide for an interesting electro-optical or sensing device application based on electrochemical properties of the hybrid material.

1. Introduction

Hybrid organic-inorganic nanoparticles with electroactive organic ligands are of high interest for their semiconducting properties and various electro-optical applications including:^[1,2] light-emitting diodes,^[3–6] photovoltaic cells,^[7–9] and bio-sensors.^[10–12] A main function for the organic ligands on the surface of these inorganic nanoparticles (quantum dots) is to stabilize the system towards long-term aggregation effects. While linear ligand structures have been widely investigated, reports on the use of dendronic ligands are relatively few.^[13] These ligands can be advantageous in that they create a tight shell structure on the surface of the nanoparticles resulting in slow diffusion kinetics between solution and the surface of the nanoparticles. The synthesis of conjugated polythiophene dendron ligands and their hybridization with CdSe nanoparticles has been previously reported by our group.^[14] The phosphonic acid derivatives of these polythiophene dendrons were introduced to the surface of the quantum dots primarily through ligand exchange procedures. These hybrid materials showed interesting photo-current behavior which eventually

should find utility in the preparation of photovoltaic devices.^[15]

Although, ligand exchange is the usual method for functionalizing the surface of nanoparticles, the direct synthesis of these quantum dots using dendronic ligands is desirable. This results in a more homogenous shell structure for the as-grown particles since it is based on a one component system.^[16–18] Furthermore, cross-linking of the ligand shell of the nanoparticles should further increase the stability of the nanoparticles and ligand complex.^[19] It has also been previously reported that hydrophilic organic dendron ligands stabilizes high quality semiconductors and noble metal nanoparticles (e.g., Au) nanoparticles.^[19]

Electropolymerization of linear precursor polymers results in the formation of conjugated polymer networks and thin films primarily through inter- and intramolecular crosslinking reactions.^[20] We have recently reported the synthesis of dendrimeric precursors based on convergent and divergent synthesized dendrimers in which peripheral carbazole units are present.^[21] These dendrimers are capable of forming individual conjugated polymer nanoparticles as well as being incorporated in thin film devices for sensor applications.^[22]

In this work, carbazole containing dendrons were synthesized based on second generation Frechet-type polybenzyl ether dendrons (**2GPO**) which were subsequently derivatized with phosphonate (Fig. 1). This was subsequently used for directly synthesizing and capping CdSe nanoparticles in-situ. This resulted in the formation of stable hybrid **CdSe-2GPO** quantum dot nanoparticles having characteristic electronic interactions between organic molecules of carbazole peripheral groups and hybrid nanoparticles of CdSe. This is in

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[**] The authors gratefully acknowledge the partial funding from the Robert E. Welch Foundation (E-1551), NSF DMR-0602896 and the Alliance for Nanohealth of Texas. Supporting Information is available online from Wiley InterScience or from the authors.

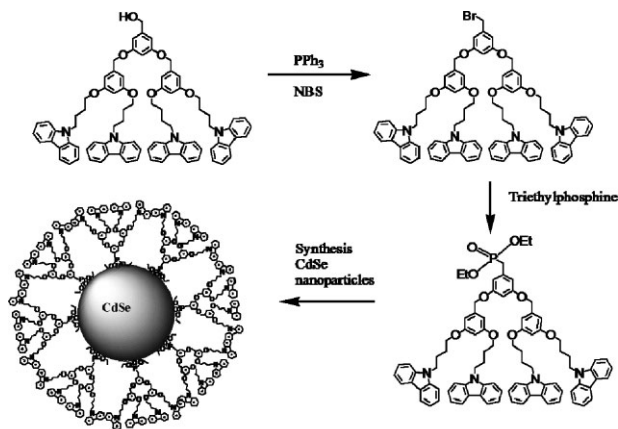


Figure 1. Schematic synthesis of the ligands and hybrid nanoparticles and nanoparticles. Nanoparticles were directly synthesized with the ligands, which were functionalized to phosphonate.

contrast to most methods reported in literature which usually involve ligand exchange to introduce functionality. Spectroscopic and microscopic analysis techniques were used to confirm the size and nature of the hybrid-nanoparticles. Absorbance and fluorescence spectroscopy studies indicated that energy-transfer properties originating from the fluorescence overlap of the dendron with the absorbance of the nanoparticle. However, upon electropolymerization of the peripheral electroactive carbazole units, a red-shift in absorbance and fluorescence quenching was observed. This resulted in a reversed charge transfer by hole-transfer from the CdSe to the polycarbazole peripheral units. Thus, the hybrid CdSe nanoparticles capped with 2GPO itself can be tuned for either energy-transfer or charge-transfer applications.

2. Results and Discussion

2.1. Synthesis of hybrid CdSe Nanoparticle

Synthesis of the benzyl alcohol focal dendron has been previously reported^[23] and is also described in the Supporting Information. Derivatization of these starting dendrons is described below (Fig. 1).

A fixed amount of **2GPO** (50 mg) was put in the schlenk flask with different equivalent ratios of cadmium oxide and dodecylamine under vacuum at 120 °C until no bubbles appeared followed by adding hexylphosphonic acid under nitrogen atmosphere (Supporting Information, Table 1). This flask was heated under nitrogen atmosphere at 270 °C until the yellow solution turned colorless. Depending on the ratio, exact amounts of the solution of selenium (0.1 g) and trioctylphosphine (2 mL) was injected quickly to the flask. After injection of the solution, the flask was removed from the heat when the desired size of nanoparticle is obtained. 10–20 mL of degassed chloroform was added to the solution when the flask was cooled down to around 60 °C. The solution was centrifuged to

remove unreacted precursor and unbounded organic materials with chloroform, methanol and toluene. The process of redispersal and precipitation were repeated until no reactant was detected from UV-vis in the wash solution.

2.1.1. UV-vis and Fluorescence Studies

The UV-vis (λ_{max} at 332 nm and 346 nm) and fluorescence spectrum (peak centered at 360 nm) shown below (Fig. 2a) are typical for the carbazole unit and CdSe nanoparticle (inset). NMR also confirmed the successful bromination and phosphorylation procedures. The CdSe nanoparticles capped with the **2GPO** were then synthesized directly (Fig. 2b). It has both the carbazole absorbance and nanoparticle absorbance band.

Initially, the absorbance of the mixture showed a broad spectrum with a λ_{max} at 560 nm (1 equiv.). As more reagents were added with the fixed amount of **2GPO** (50 mg, 3 equiv.), the UV-vis spectra of the typical CdSe nanoparticle, a long UV-vis absorbance with a peak centered at 570 nm became more prominent. It shows that the amount of metal incorporated in

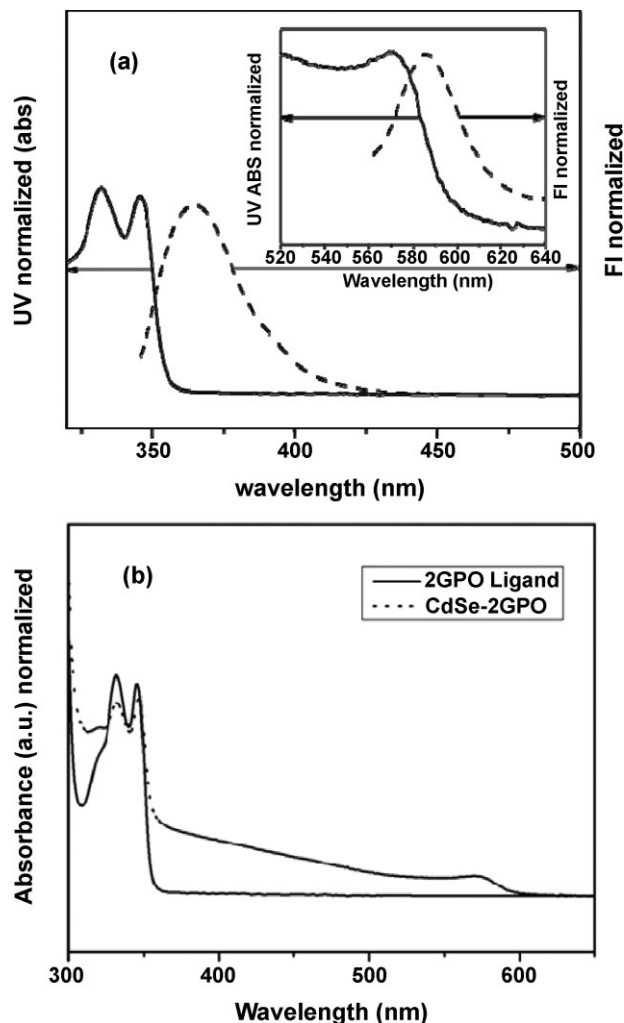


Figure 2. UV-vis and fluorescence spectra of a) the 2GPO, CdSe (inset) and b) CdSe-2GPO.

the nanoparticle was increased with a fixed amount of ligand of up to 3 equivalents (see Supporting Information, Table 1). However, the nanoparticle was not uniformly made at the 5 equivalent ratio suggesting that an excess of the nanoparticle reagents result in a non-stoichiometric condition in which the nanoparticle did not form at the right size or polydispersity.^[19] It is also possible that the large dendron ligands are aggregated as amphiphiles at this concentration, failing to cap the nucleated nanoparticles.^[19] Thus, the optimum ratio for the direct synthesis of the nanoparticles was established to be 3:1 equivalent ratio with respect to CdSe and **2GPO**. From the absorption band of the UV-vis spectra (λ_{max} at 570 nm), the size of the CdSe nanoparticles was calculated to be at (2.4 ± 0.5) nm indicating the size of the nanoparticle alone.^[18] The dendron dimension (radii) is ca. 1.4 nm (using ChemDraw) which is larger than the standard deviation for this estimation method.^[17]

The UV-vis absorption spectra increased linearly with increasing concentration of the hybrid nanoparticles (Fig. 3). The peak at 332 and 346 nm linearly increased because of the corresponding increase in the number of dendron ligands in solution. The fluorescence spectra of the nanoparticle solution were obtained by excitation at 346 nm (absorbance maxima for carbazole) (Fig. 3, inset). Interestingly, by increasing the concentration of the nanoparticle solution, the fluorescence of the carbazole was observed to decrease, while the fluorescence of CdSe nanoparticle increased simultaneously. The emission spectrum has a maximum at 570 nm and the quantum yield of the nanoparticle is 5% since the quantum yield of ligand is 14.5%. This may be explained by the role of energy transfer from the **2GPO** ligands to the CdSe nanoparticles. It should be noted that shell-type nanoparticles are known to transfer energy from the inner shell to the outer shell.^[23,24] Similarly, organic ligands capped with nanoparticles can have energy transfer from the outer ligands to the inner metal nanoparticles.^[14,25]

Since the CdSe-2GPO nanoparticle was directly synthesized with the ligand, the fluorescence of the acceptor itself was not

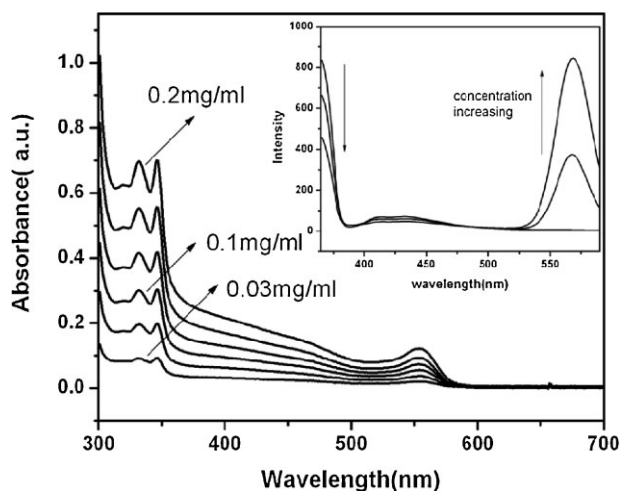


Figure 3. UV-vis absorbance peaks increased linearly with increasing concentration of the nanoparticle precursor solution. Inset: fluorescence spectra as a function of increasing nanoparticle concentration.

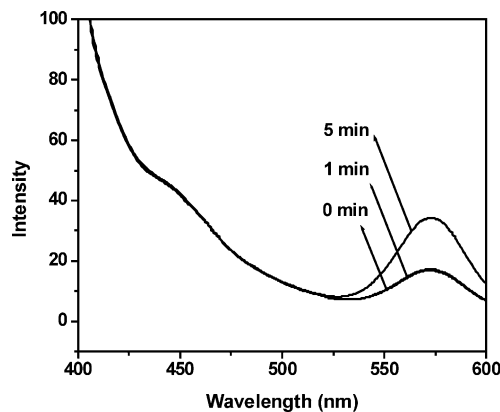


Figure 4. Fluorescence spectra of CdSe-TOPO nanoparticles and CdSe-TOPO and 2GPO blend (50:50). $t=0$ min indicates the solution of CdSe-TOPO only, $t=5$ min indicates the blend stored for 5 min to allow better mixing.

obtained. To verify this, CdSe capped with TOPO (CdSe-TOPO) was prepared as an acceptor without the donor to compare with the CdSe-2GPO solution. Shown in Figure 4 is the fluorescence change of CdSe-TOPO in the presence and absence of 2GPO ligands. The CdSe-TOPO exhibited a peak at 570 nm, which indicates the nanoparticle region when the system was excited at 350 nm. Moreover, the intensity of the nanoparticle region is increased with the presence of 2GPO. The difference was only slightly observed after 1 min, but prolonging the mixing time to 5 min allowed the peak to double in intensity.

Distance dependent Förster resonance energy transfer (FRET) occurs when emitted energy from a donor is absorbed and then emitted by the acceptor. A donor chromophore in its excited state transfers energy to the acceptor unit. In this case, the organic dendron carbazole moiety acts as a donor and the inorganic CdSe nanoparticle as an acceptor.^[26] The absorbance and fluorescence spectra showed energy-transfer properties originating from the overlap of fluorescence of the dendron with the absorbance of the nanoparticle. Thus, the emitted energy from the ligands of **2GPO** would be absorbed again by CdSe nanoparticles. A non-radiative transfer of excitation energy occurs as the emission spectrum of the **2GPO** donor overlaps with the absorption spectrum of the CdSe acceptor, so that several vibronic transitions in the donor have the same energy as the corresponding transitions in the acceptor. However, self quenching cannot be ruled out especially in a very dense fluorophoric condition.^[15] This spectroscopic and energy-transfer behavior is further discussed after the electropolymerization experiments.

2.1.2. Atomic Force Microscopy (AFM) Studies

The hybrid nanoparticles were directly imaged by AFM profilometry to confirm agreement with the calculated dimensions of the nanoparticle and account for the dendron ligand contribution. Very dilute THF solutions of the hybrid nanoparticles were coated on flat Si-wafer substrate (with

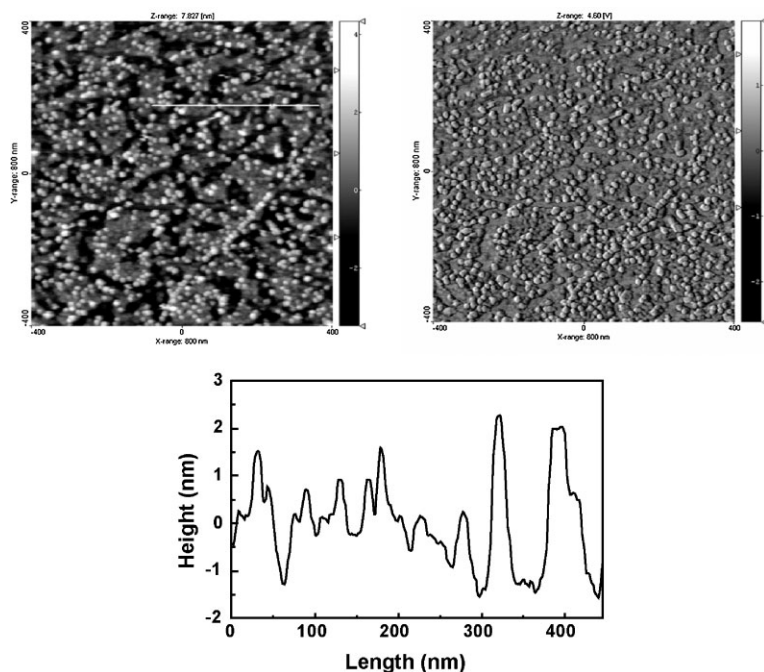


Figure 5. AFM images of **CdSe-2GPO**. The spin-coated film was scanned with AFM (topological and phase images). The height was measured at $\sim(3.5 \pm 1.3)$ nm, which is consistent with the value calculated based on the absorbance, λ_{max} , and the dimensions of the dendron ligand.

oxide layer) by spin-coating (3000–4000 rpm) in order to characterize the height and distribution of the **CdSe-2GPO**. A monolayer distribution of the particles was observed on the substrate (Fig. 5) as confirmed from the phase image. The average height observed was found to be $\sim(3.5 \pm 1.3)$ nm, which accommodates for the actual dimensions of the nanoparticle plus the dendron ligand.

Note that the distribution of the ligand around the particle needs to be determined independently. In principle, the absorbance spectrum can be deconvoluted using the molar absorption coefficients of the two species (**CdSe** and **CdSe-2GPO**) and subtracting out the nanoparticle absorbance. Previous estimations on a terthiophene dendron (P3T) and heptathiophene (P7T) ligands reveal that an average of 53 units of P3T and 30 units of P7T ligands can be packed for a nanocrystal (with 3.17 nm average diameter).^[14] Since the 2GPO dendrons are larger than that of P3T and P7T, the actual number for the **CdSe-2GPO** are expected to be less than 30 dendrons.

2.1.3. FTIR Studies

The IR spectra of the ligand **2GPO** and **CdSe** nanoparticle capped with **2GPO** are shown below, where the P=O (1165 cm^{-1}), Ar–P–O (1055 cm^{-1} , 1026 cm^{-1}) and Ar–P–O (962 cm^{-1}) peaks are assigned for 2GPO ligand itself and the P=O (1151 cm^{-1}), Ar–P–O (1088 cm^{-1} , 1052 cm^{-1}) and Ar–P–O (942 cm^{-1}) peaks are assigned for **CdSe** nanoparticle with ligand **2GPO** (Fig. 6). Thus the peaks present on the hybrid nanoparticle corresponded with the native ligand IR

spectra. Simple mixing can be ruled out since the synthesis of the nanoparticles was done in situ.

2.2. Electropolymerization Studies with CdSe Nanoparticle

2.2.1. Cyclic Voltammetry Studies

The carbazole units on the dendron ligand shell of the nanoparticles can also be electropolymerized and cross-linked in a thin film structure. For example, we have recently reported the synthesis of dendrimeric precursors in which peripheral carbazole units are present.^[21] These carbazole units are essentially electroactive monomer units which are capable of forming individual conjugated polymer nanoparticles as well as being incorporated in thin film devices for sensor applications.^[22,27] The latter involved the electrochemical crosslinking of the carbazole units on an electrode substrate resulting in a highly cross-linked structure of a conjugated polymer network film.^[27] In this case, a polymerized (polycarbazole) network constitutes a dendron box and helps to stabilize the hybrid **CdSe** nanoparticle. The electrochemical activity of these macromolecules has been recently investigated and has been found to have generation dependent electrochemical activity and cross-linking properties.^[28]

To this end, solutions of the **CdSe-2GPO** in chloroform were drop-cast amorously on an ITO substrate which was used as a working electrode in a cyclic voltammetry experiment (CV). Pt was used as a counter electrode and Ag/Ag⁺ as reference electrode. A 20 mL of 0.1 M of tertbutylammonium hexafluoride in acetonitrile was used as electrolyte. The CV experiment was scanned from -0.2 to 0.8 V. In principle with

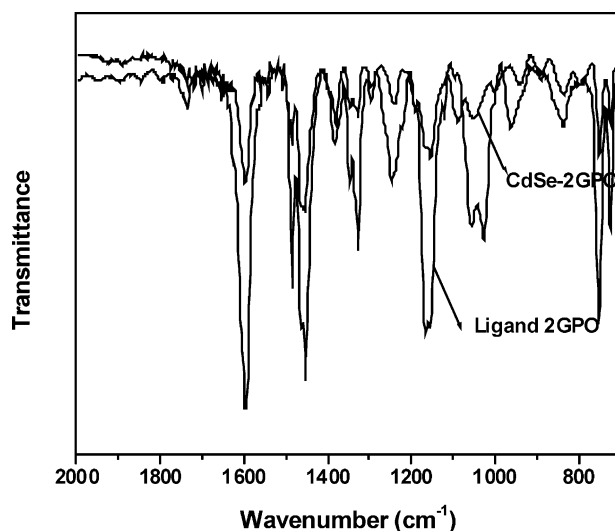


Figure 6. IR spectrum of the 2GPO ligand and the **CdSe** nanoparticle capped with 2GPO.

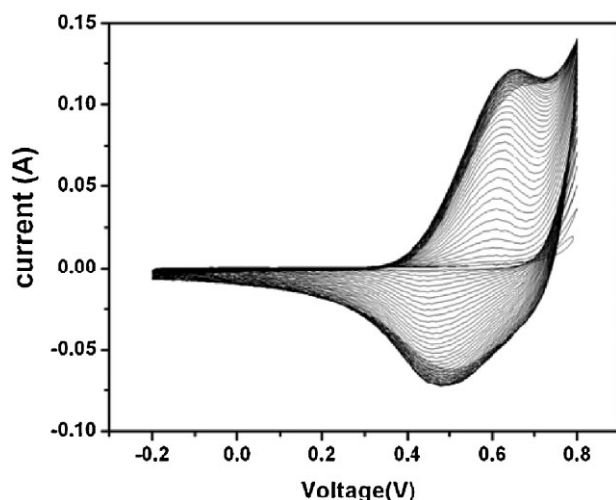


Figure 7. CV curve for CdSe nanoparticles capped with 2GPO. It shows that oxidation and reduction peaks are increased with each cycle.

this procedure, the carbazole units could be cross linked *intra*-molecularly and *inter*-molecularly within a film structure. The current linearly increased with increasing number of cycles and is well behaved as shown in Figure 7. The first cycle showed an oxidation onset at around 0.39 V. After the second cycle, the oxidation peak was then observed around 0.6 V and was found to slightly shift to higher potentials as the number of cycles was increased, but not greater than 0.05 V. The reduction peak likewise was observed to shift from 0.44 to 0.5 V (Fig. 7). Both the linear increase and the shift to lower oxidation potential after the first cycle indicated the formation of higher conjugated polycarbazole species. Saturation was observed beginning at 40 cycles, in which the current started to drop. This CV behavior showed unequivocally that cross linking has occurred. By contrast, linear polyvinylcarbazole (PVK) has a higher oxidation and reduction potentials at 0.9 and 0.7, respectively. It also has a larger shift towards lower potentials with more cycles. This indicates a unique property for dendrimeric precursors which have a higher density of electro-active monomers available per unit surface area.^[27] Similar studies are being made as a function of size and generation for several carbazole functionalized dendrimers synthesized in our group.^[27]

2.2.2. UV-vis and Fluorescence Studies

Polymerization of the carbazole units was also verified from the UV-vis and fluorescence spectra. As the number of cycles was increased, the UV-vis peak at 334 nm attributed to the carbazole units was overlapped by a strong UV-absorption and shifted towards a longer absorbance tail in the visible region (Fig. 8a).^[21] The UV-vis peaks of the nanoparticles were not shifted and were found to be independent of the number of CV cycles. This indicated the formation of more conjugated polycarbazole species in which the ligands remained attached to the surface of the nanoparticles. The absence of any change

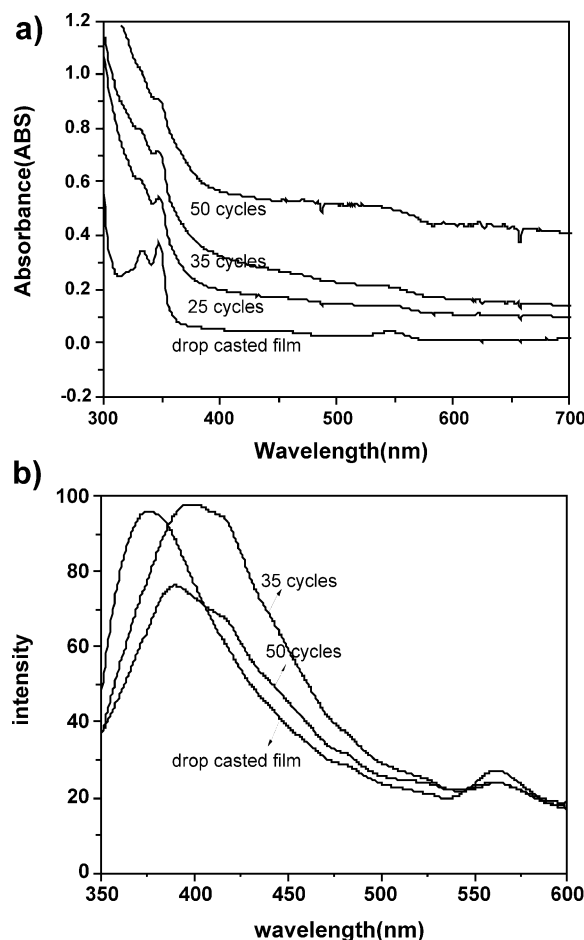


Figure 8. UV-vis (a) and fluorescence (b) spectra after polymerization of the carbazole units. a) UV-vis spectra of the carbazole units overlapped and shifted as the number of cycles increased, whereas the peak attributed to the nanoparticles retained its position. b) The fluorescence spectra showed a similar pattern shift as the UV spectra.

at $\lambda_{\text{max}} = 560$ nm indicated that no electrochemical degradation effects on the CdSe nanoparticles were present.

It was also possible to observe the fluorescence of the cross-linked film when the film was excited at 346 nm. Firstly, the fluorescence of carbazole was red-shifted to the polycarbazole (PCZ) region which indicates the carbazole units on the ligands of **2GPO** were polymerized and no wavelength shift was detected on the 570 nm peak attributed to the nanoparticle with increasing number of CV cycles. However, the fluorescence intensity dramatically decreased after electropolymerization with 25 and 50 cycles (Fig. 8b). To explain this phenomenon, it was calculated that the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap was decreased from 3.5 eV to 2.48 eV (25 cycles) and 2.38 eV (50 cycles) as the number of cycles was increased (Fig. 9) with the data of cyclic voltammetry and UV-vis spectra.^[28,29]

Electropolymerized 2GPO was mixed with CdSe-TOPO nanoparticles. The fluorescence of polymerized 2GPO in the present and absence of CdSe-TOPO is shown in Figure 9. The

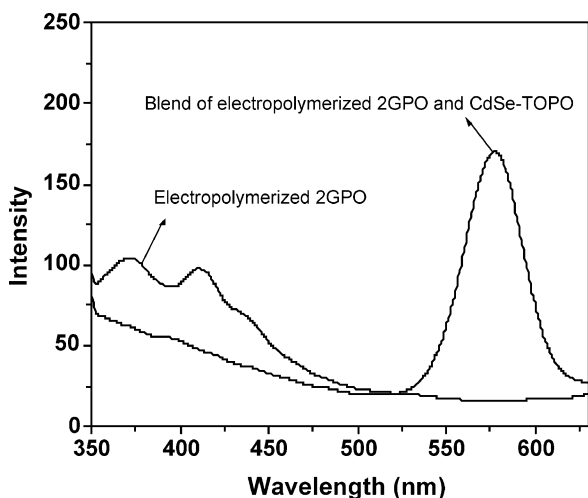


Figure 9. Fluorescence spectra of the electropolymerized 2GPO and the electropolymerized blend of 2GPO and CdSe-TOPO. The blend still showed emission of nanoparticles that were not bleached by polymerized 2GPO.

blend of polymerized 2GPO and CdSe-TOPO still showed the emission of the nanoparticle. Furthermore, the emission of the nanoparticle was not bleached by the polymerized 2GPO units.

At this point, a detailed discussion of these changes in the fluorescence behavior before and after electropolymerization is needed in the context of a FRET mechanism. The FRET efficiency can be calculated from the fluorescence experiments (also see Supporting Information). The FRET efficiency is commonly defined as:^[30–32]

$$E = 1 - \frac{F_{DA}}{F_D} \quad (1)$$

where F_D is the fluorescence intensity integration of the donor itself and F_{DA} is the fluorescence intensity integration of donor with acceptor. The fluorescence intensity of 2GPO (donor) and CdSe nanoparticle capped with 2GPO dendrons (donor-acceptor) were integrated in order to calculate the FRET efficiency. The FRET efficiency of the nanoparticle system before and after electropolymerization was calculated to be 0.81 and 0.51 respectively. The FRET efficiency can also be expressed from fluorescence lifetime as:^[30–32]

$$E = 1 - \frac{\tau_{DA}}{\tau_D} \quad (2)$$

in which τ is the fluorescence lifetime. In principle, based on the previously calculated efficiency, the fluorescence lifetime of dendrons capped with CdSe nanoparticles can be reduced to about 20% compared to the dendron itself while the fluorescence lifetime of dendrons on nanoparticles can be decreased to approximately 50% compared to the dendron itself after electropolymerization. Future experiments of the fluorescence lifetime decay can be done to support the calculated theoretical values.

Förster radius can be calculated with the calculated FRET efficiency. The Förster radius, R_o , is defined as^[30–32]

$$E = \frac{nR_o^6}{nR_o^6 + r^6} \quad (3)$$

where r is the distance between donor-acceptor pair and n is the average number of acceptor paired with one donor. Assuming that the CdSe nanoparticle is capped with around 30 dendrons, while each dendron has four carbazole subunits, the size of the CdSe nanoparticle and dendron were calculated as approximately 2.4 nm and 1.4 nm, respectively. Using $n = 1/120$ and $r = 2.6$ nm, R_o can be calculated with these values as 7.4 nm and 5.8 nm for before and after electropolymerization. The overlap integral J which is defined as:^[30–32]

$$J = \int f_D(\lambda) \epsilon_D(\lambda) \lambda^4 d\lambda \quad (4)$$

indicates quantitatively the integrated area under the spectral overlap function. As determined, the J value before electropolymerization is 28% smaller than that after the electropolymerization (Supporting Information).

2.2.3. Molecular Orbital Studies

Without electropolymerization, the emission of the carbazole unit was absorbed by the core of CdSe and was emitted again. However, the fluorescence is quenched when the polycarbazole units were produced after the electropolymerization. In this case, a charge transfer phenomenon was determined to be the best mechanism to explain the fluorescence quenching. After electropolymerization, the HOMO level of the polycarbazole goes to a higher energy state than the HOMO level of the CdSe nanoparticles. By contrast, the HOMO level of carbazole was originally lower than that of the CdSe nanoparticles.^[33] When carbazole units were excited and the excited electron relaxed, the emitted energy would be absorbed by CdSe nanoparticle units to excite the CdSe nanoparticle moiety. However, the electron from CdSe nanoparticle is excited faster than the

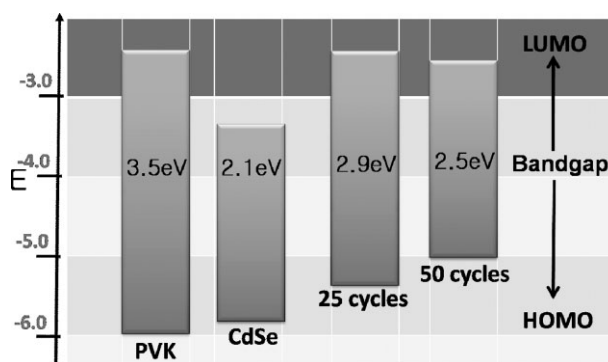


Figure 10. HOMO–LUMO gaps of polycarbazole (PCZ), CdSe, 25 cycles, and 50 cycles of electropolymerization.

polymerized carbazole moieties when the system is irradiated. The electron on the ground state of the electropolymerized moiety moves into the empty space of the HOMO orbital of the excited polymerized carbazole (Fig. 10).^[34] This indicates a type of energy-transfer system for the CdSe-2GPO, which transforms to a charge-transfer system for the CdSe-2GPO as a consequence of the electropolymerization of the surface ligand dendrons.^[33] Clearly, there are other possible consequences of a shift from energy transfer to a charge-transfer phenomenon as previously reviewed by Kamat et al. including intermolecular interaction (aggregation), electron transfer, energy transfer, and non-radiative energy loss.^[34] In this case, the shift to charge transfer is also facilitated by a change from a ligand-fluorophore-nanoparticle to a conducting polymer- ligand (HOMO shift)-nanoparticle interaction as facilitated by the electropolymerization of the carbazole units of the dendrons.

3. Conclusions

In summary, the applied dendron ligands facilitate efficient capping of quantum dot CdSe nanoparticles showing high stability and energy-transfer properties. In contrast to most methods reported in literature involving ligand exchange for the introduction of functionality, the direct synthesis of the hybrid CdSe nanoparticles has been successfully demonstrated. Lastly, the electropolymerization of the peripheral electroactive carbazole units resulted in lifting up the ground state molecular orbital of electropolymerized carbazole, which was higher than the ground state of CdSe nanoparticles. This reversed molecular orbital process quenches the fluorescence of the hybrid CdSe nanoparticles and transforms the system to a charge-transfer mechanism. Fluorescence lifetime-decay experiments are underway to further probe the energy-transfer mechanism of the CdSe-2GPO nanoparticle system.

4. Experimental

Synthesis of the benzyl alcohol focal dendron has been previously reported [23] and is also described in the Supporting Information.

¹H NMR spectra were recorded on a General electric QE 300 spectrometer (300MHz). UV-vis was recorded using Agilent 8453 Spectrometer. Fluorescence spectra were obtained using Perkin-Elmer LS45 luminescence spectrometer. FT-IR spectra were obtained on Digilab FTS 7000 equipped with HgCdTe detector at a range from 4000 cm⁻¹ to 700 cm⁻¹.

All chemicals were purchased from Aldrich Chemical Company and were used directly without further purification. Tetrahydrofuran (THF) was freshly distilled over sodium and benzophenone before use. All solvents were aspirated with nitrogen gas before use.

The electropolymerization was done in a potentiostat (AMEL Instruments, model 2049) using the conventional three electrode set-up wherein the ITO substrate served as working electrode, platinum wire as counter electrode, and Ag/AgCl as reference electrode. The carbazole units on the dendron ligand shell of the nanoparticles can be electropolymerized and cross-linked in a thin film structure. Solutions of the CdSe-2GPO in chloroform were drop-cast amorphaously on an ITO substrate which was used as a working electrode in a cyclic

voltammetry (CV) experiment. Pt was used as a counter electrode and Ag/Ag⁺ as a reference electrode. 20 mL of 0.1 M of tertabutylammonium hexafluoride in acetonitrile was used as electrolyte. The CV experiment was performed with window of -0.2 to 0.8 V at scan rate of 20 mV s⁻¹ for 50 cycles.

Atomic force microscopy (PICOSCAN SPM, Molecular Imaging Inc., now Agilent 5500 AFM/SPM System (Agilent Technologies) was used to investigate surface morphologies and surface analysis. The AFM measurements were carried out using with a piezoscanner capable of scanning an area of ~10 μm × 10 μm at room temperature. Commercially available tapping mode tips (TAP300-10, Silicon AFM Probes, Tap 300, TedPella, Inc.) were used on cantilevers with a resonance frequency in the range of 290–410 kHz. All images (AFM topography, tapping mode) were filtered and analyzed by using SPIP software (Scanning Probe Image Processor, Imagemet.com). All data in the dimensions of surface aggregates were collected and averaged by at least 20 measurements from the line profilometry of AFM images. Lateral size and height of the aggregate were determined after calibration of AFM tips using a defined patterned surface (MIKRO MASCH, size: 100 nm).

Received: October 18, 2007

Revised: January 29, 2008

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