



Poly(ether) dendrons possessing phosphine focal points for stabilization and reduced quenching of luminescent quantum dots

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Dedicated to Professor Gerard van Koten.

Abstract

Hydroxyl terminated, poly(alkyl ether) dendrons possessing single site phosphine functional groups at their focal points have been synthesized. These single site reactive dendrons are then used in ligand exchange reactions to produce stabilized surface capped CdSe/core CdS-shell quantum dots that exhibit high quantum yield, non-quenching photoluminescence (PL) properties. These enhanced features are in sharp contrast to quantum dots capped with analogous single site thiol functionalized dendrons that exhibit substantially quenched photoluminescence. These new dendron constructions begin with protected pentaerythritol moieties which are used as the initiator core as well as the branch cells. By protecting one of the four hydroxyl groups in the pentaerythritol moiety, the remaining three hydroxyl groups are utilized as divergent growth sites for the poly(ether) dendron construction. Desired generation levels (i.e., generations 1, 2) are synthesized, followed by deprotection of the focal point hydroxyl group to expose appropriate functional groups suitable for conversion to sulfhydryl, phosphine or other desired functional groups.

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1. Introduction

Semiconductor nanocrystals or quantum dots (QDs) exhibit interesting size-tunable optical properties due to the confinement of their electronic wave functions [1,2]. Extensive research has been reported on the synthesis and characterization of such II–VI semiconductor nanoparticles [1,2]. The widely established approach for the production of QDs (mainly CdS and CdSe) is by synthesis in organic solvents using suitable stabilizers to pacify and protect against aggregation [3,4]. Subsequent ligand exchange procedures can be employed to vary the surface chemistry of the QDs [5,6]. Either traditional monofunctional ligands or more recently, polyfunctional dendron

type ligands may be utilized [3,7,8]. Chemical functionalization of the QD's may be important to facilitate processing, stabilize against oxidation or for compatibilization and incorporation into various substrates/devices [7,9]. Ligand-exchange with various thiol-containing materials has been extensively studied [9]. However, ligand exchange with thiols usually diminishes the quantum yield of the as-grown QD photoluminescence. For example, the photoluminescence (PL) of CdSe core nanocrystals were substantially reduced after utilizing single site, focal point thiol-based dendron ligands in such a ligand exchange procedure [3,4,8,10]. Encapsulating QDs and their initial ligands with traditional polymers can preserve the quantum yield (QY), but is less controllable and may substantially enhance the volume of the QDs, to a final size that may be much larger than desired. More recently, oligomeric phosphine ligands have been used to stabilize QDs while maintaining PL [5]. However, the hydrophobic functionality utilized in this

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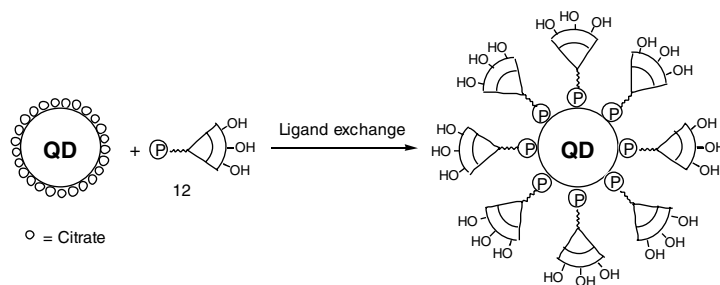


Fig. 1. Illustration of ligand exchange of phosphine dendron with citrate protected QDs.

report limits potential applications and precludes use of these QDs in aqueous systems or as biological labels.

We report here the synthesis of a novel hydroxyl-terminated poly(ether) dendron possessing an aryl phosphine at the focal point and demonstrate that it provides a stabilizing sheath for QDs in aqueous systems without associated reduction in PL normally observed for thiol functionalized ligands [8] (Fig. 1).

Dendrimers/dendrons are well-defined, highly branched macromolecules that are of intense interest as new materials in many important application areas [11]. The convergence of architecturally driven “dendritic effects” with the ability to control nanoscale sizes, shapes and chemical functionality of these dendritic constructs has led to many new unprecedented properties [12,13]. Dendrimers/dendrons possess three key architectural features; namely, an initiator core, interior branching units (branch cells), and mathematically defined numbers of functional surface groups, as a function of generation level. Peng et al. [3] have studied the use of single site, focal point thiol functionalized dendrons to stabilize QDs, however, no PL studies were described in their report [3,9].

The structure of a dendron ligand is uniquely suited for stabilizing the QDs. Firstly, their dendritic architectures provide a closely packed matrix, as well as dimensionally quantized ligand shells that can be controlled as a function of the generation level. Each generation level manifests mathematically defined numbers of functional groups (i.e., precise stoichiometries) in contrast to traditional sheaths formed by capping with ligands derived from long, floppy single chains or traditional polymer shells. Furthermore, the steric crowding of a surface ligated dendron is ideally suited for filling the spherical QD ligand interface since the dendron ligand can naturally pack into a conical shape at the surface of nanocrystals. Secondly, the inter- and intramolecular chain tangling of a dendron possessing relatively flexible branches may further repress the diffusion of small molecules (i.e., oxygen) or ions from the bulk solution into the interface between a nanocrystal and its ligand [7].

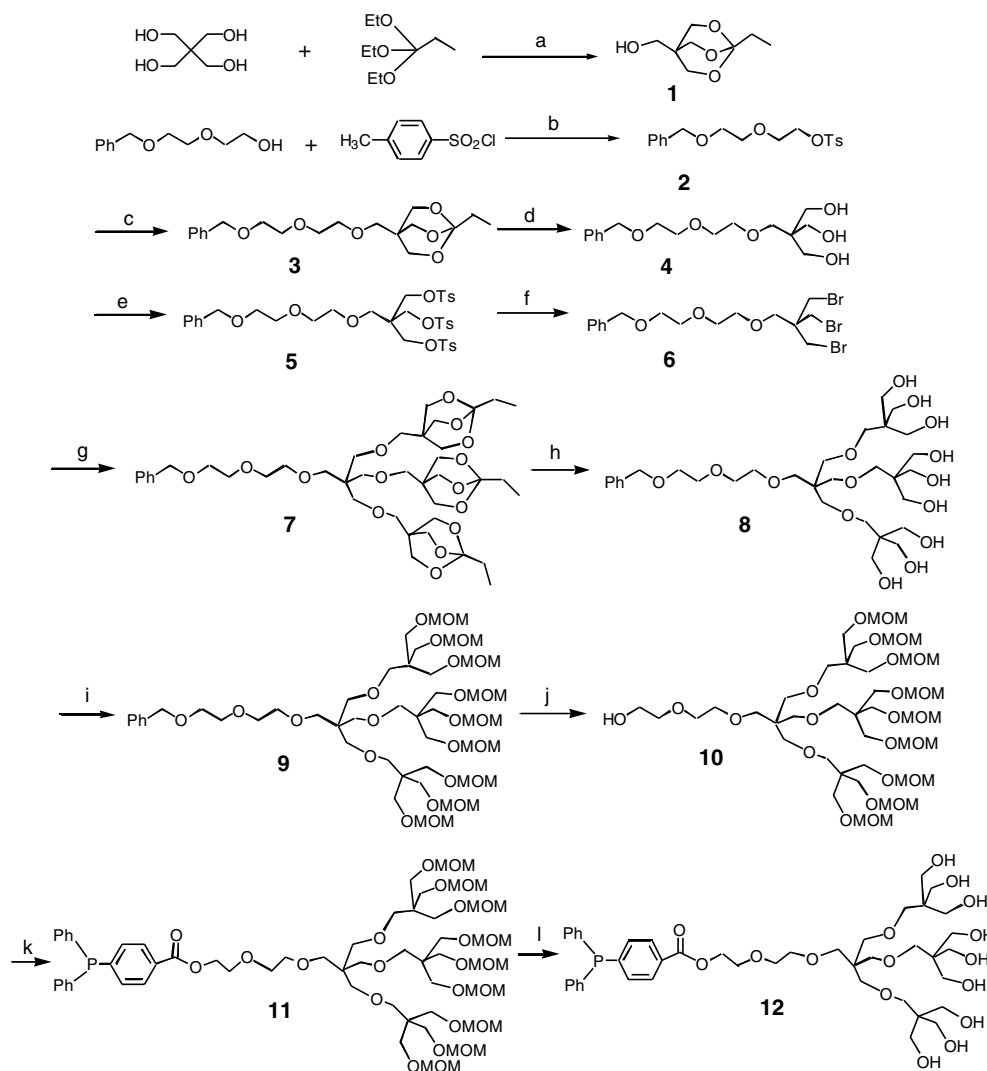
2. Results and discussion

Design of the present dendron ligand is based on the following considerations: (1) An aryl phosphine is used as a single site, focal point binding site to QDs since it is stable

in air and less toxic than alkyl phosphines. The aryl groups, which are UV active at 200 nm, would not block any photoluminescence (above 500 nm). Most importantly, phosphine pacification may not quench the PL, which is essential for bio-labeling. (2) The two units of ethylene diglycol chain between the focal point and the dendritic structure provide enhancement of aqueous solubility. (3) The pentaerythritol moiety (i.e., an AB_3 type branch cell unit) was chosen since it will attain a dense packed state earlier (i.e., at a lower generation) than an AB_2 type branch cell [11–13]. (4) Methoxymethyl ether protection of the dendron hydroxyl surface groups was used. After deprotection this allows subsequent modification to present either hydrophobic or hydrophilic type properties. Synthesis of the dendritic poly(ether) phosphine ligands (generation 2) is as shown in Scheme 1.

The desired phosphine focal point, functionalized poly(ether) dendrons were synthesized by a multistep strategy. The first step involved chemically blocking of three hydroxyl groups on neopentyl alcohol via conversion to give a cyclic orthoester, structure **1** (step a). Covalent attachment of a polyether linker (steps b and c) followed by deprotection (step d) provided a benzyl protected triol, structure **3**. This triol was used as a substrate from which to divergently amplify interior branching and surface groups according to dendritic growth protocol reported earlier by Tomalia et al. [14,15] (steps e–h). Protection of the hydroxyl surface groups (step i) with chloromethyl ether (MOMCl) allowed the carbodiimide assisted conjugation of 4-(diphenylphosphino) benzoic acid to the focal point of the dendron (step k). Finally, acidic deprotection (step l) gave the desired, generation = 2, phosphine functionalized, poly(ether) dendron bearing hydroxylic surface groups. All structures were characterized by NMR, TLC and mass spectrometry (MALDI-TOF).

The water-soluble citrate stabilized core-shell (CdSe/CdS) quantum dots were synthesized using previously reported methods [9]. The luminescence spectrum exhibits a sharp [full width at half maximum (fwhm) 36 nm], symmetrical emission at 563 nm (indicative of a 3.5 nm CdSe core) [16]. The core-shell QDs showed a narrow size distribution with no detectable surface trap emission (Fig. 2). To demonstrate the non-quenching property of the phosphine poly(ether) dendron on QDs, we compared the photoluminescence of phosphine protected QD's with the PL's of QD's pacified by a thiol focal point functionalized PAMAM



Scheme 1. (a) Pyridinium *p*-toluenesulfonate, 130 °C; (b) pyr., -12 °C; (c) NaH (1) DMF, 100 °C; (d) trace HCl, MeOH; (e) TsCl, pyr., rt; (f) NaBr, DMAc, 130 °C; (g) NaH (1) DMF, 100 °C; (h) trace HCl, MeOH; (i) MOMCl, diisopropylethylamine/CH₂Cl₂; (j) H₂/Pd-C, MeOH; (k) 4-(diphenylphosphino)benzoic acid, DCC, DMAP, CH₂Cl₂; (l) 0.1 M HCl, MeOH, 40 °C.

dendron [8]. This comparison showed that the thiol functionalized dendron quenched the PL of the QD's approximately 60%. In dramatic contrast, the phosphine

functionalized poly(ether) dendron pacified QD's exhibited no quenching. Moreover, the nanocrystals retained their original high quantum yields and narrow emission line

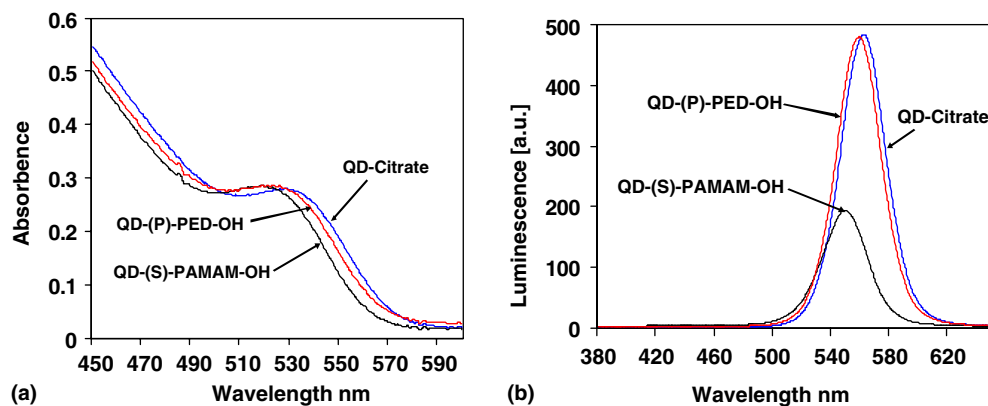


Fig. 2. Absorption (a) and luminescence (b) spectra of CdSe/CdS core-shell QDs stabilized by citrate (blue); G2 poly ether phosphine ligand (12) (red) and G2 PAMAM thiol ligand (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

widths, thus, indicating crystallite growth was accomplished with relatively few electronic defect sites. The sharp luminescence observed, dramatically illustrates the phosphine functionalized dendron efficiency as an optimum capping moiety for electronically pacifying these nanocrystals. The dendron capping moieties also appear to protect the individual crystallites from chemical and oxidative degradation thus yielding chemo/physically robust QD systems.

3. Experimental

3.1. General procedures and methods

All chemicals and solvents were obtained from Acros Organics or Sigma–Aldrich and used as received. Silica gel 60, particle size 0.040–0.063 mm, 230–400 mesh ASTM was obtained from EM Sciences. Thin layer chromatography (TLC) was performed using Whatman Adsorption plates, 60 Å silica gel, 250 mm layer thickness. The ^1H NMR and ^{13}C NMR spectra were obtained using either a Varian Unity 300 or a Bruker WM 360 SF instrument. MALDI-TOF mass spectrometry was performed on a Thermo-Bioanalysis Vision Mass Spectrometer. UV–Vis spectra were measured using a Hewlett Packard model 8543 and a software made by Agilent Technologies. FT-IR spectra were measured using Nicolet, MAGNA-IR-560. PL spectra were measured using a Shimadzu Spectrofluorophotometer RF-1501.

3.2. Synthetic procedures

3.2.1. 1-Ethyl-4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]-octane, compound 1

Pentaerythritol (27.2 g, 0.2 mol), triethyl orthopropionate (35.3 g, 0.2 mol) and pyridinium *p*-toluenesulfonate (PPTS, 1.0 g, 0.004 mol) were combined in a 250 mL round bottom flask equipped with a Dean-Stark trap fitted and a reflux condenser. The mixture was heated at 140 °C, with periodic stirring, under nitrogen. The solid slowly dissolved after heating for 1 h and the mixture became homogenous. After heating 3.5 h, the reaction produced almost a quantitative amount of ethanol (32 mL, theoretical). The reaction mixture was placed under vacuum to remove residual ethanol. The reaction residue was distilled under vacuum at 140–150 °C to give a colorless oily product which solidified in the freezer as white crystals (23 g, 73%). ^1H NMR (DMSO- d_6 , 300 MHz) δ : 0.8 (t, $J = 7.5$ Hz, 3H), 1.54 (q, $J = 7.5$ Hz, 2H), 3.21 (d, $J = 5.7$ Hz, 2H), 3.85 (s, 6H), 4.75 (t, $J = 5.4$ Hz, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 7.67, 29.63, 35.41, 59.53, 68.89, 108.93 ppm; MALDI-TOF: Calc. 174.19, found: 175.11% (M + H).

3.2.2. Tosylation of di(ethylene glycol) benzyl ether, compound 2

Di(ethylene glycol) benzyl ether (5.016 g, 25.56 mmol) was dissolved in 30 mL pyridine and cooled to 0 °C. Tosyl chloride (5.36 g, 28.12 mmol) was added and the reaction

was stored in a freezer (12 °C) overnight. Pyridine was removed and the residue was taken up in dichloromethane followed by washing with diluted HCl and brine. After evaporation of solvent product **2** was obtained as a colorless oil (8.1 g, 91.3%). ^1H NMR (CDCl_3 , 300 MHz) δ : 2.39 (s, 1H), 3.52–3.61 (m, 4H), 3.66 (t, $J = 7.5$ Hz, 2H), 4.51 (s, 2H), 7.22–7.34 (m, 7H), 7.77 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 21.35, 68.40, 69.11, 69.14, 70.51, 72.97, 127.38, 127.45, 127.69, 128.14, 129.60, 132.74, 137.95, 144.58 ppm; MALDI-TOF: Calc. 350.43, found: 373.26% (M + Na).

3.2.3. Bn-G0-(ethyl orthoester), compound 3

The cyclic orthoester (EHTBO, structure **1**) (3.83 g, 22 mmol) was dissolved in 10 mL anhydrous DMF and then slowly added to a suspension of NaH (581 mg, 24.2 mmol; 968 mg of 60% NaH dispersed in mineral oil washed with hexanes) in 10 mL of DMF. The mixture was stirred for 45 min after which a solution of **2** (7.0 g, 20 mmol) in DMF (5 mL) was added dropwise. The reaction was then stirred at room temperature over night. Solvent was removed using a rotary evaporator and the residue was taken up in 30 mL of dichloromethane and washed with 5% NaHCO_3 . After removal of solvent, the product was purified by silica gel chromatography (ethyl acetate:hexanes = 2:1) to give (3.5 g, 50%) of compound **3** which was used directly in the next step.

3.2.4. Bn-G0-(OH)₃, compound 4

Bn-G0-(ethyl orthoester) (**3**) (2.42 g, 6.88 mmol) was dissolved in 17 mL methanol. To this solution 0.5 mL concentrated HCl was added and the reaction was heated to 70 °C for 2 h. After solvent was removed, the residue was placed on a high vacuum over night to give Bn-G0-(OH)₃ (**4**) as a slightly yellow oil (2.159 g, 100%). ^1H NMR (CDCl_3 , 500 MHz) δ : 3.48 (s, 2H), 3.58–3.65 (m, 14H), 4.27 (s, 3H), 4.54 (s, 2H), 7.26–7.33 (5H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 45.13, 63.33, 69.16, 70.04, 70.31, 70.44, 71.89, 73.07, 127.54, 127.65, 128.23, 137.83 ppm; MALDI-TOF: Calc. 314.37, found: 316.70% (M + H).

3.2.5. Bn-G0-(OTs)₃, compound 5

Following the tosylation procedure, Bn-G0-(OH)₃ (**4**) (2.028 g, 6.46 mmol) was used to give Bn-G0-(OTs)₃ (**5**) as a white solid (4.88 g, 97%) after silica gel chromatography purification. ^1H NMR (CDCl_3 , 500 MHz) δ : 2.39 (s, 9H), 3.26 (s, 2H), 3.30–3.32 (m, 2H), 3.38–3.40 (m, 2H), 3.50–3.55 (m, 4H), 3.86 (s, 6H), 4.50 (s, 2H), 7.21–7.29 (m, 5H), 7.64–7.65 (m, 4H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 21.55, 43.68, 66.77, 67.21, 69.32, 69.99, 70.49, 70.73, 73.10, 127.50, 127.64, 127.83, 128.26, 129.93, 131.84, 138.14, 145.18 ppm; MALDI-TOF: Calc. 776.94, found: 816.23% (M + K).

3.2.6. Bn-G0-(Br)₃, compound 6

Bn-G0-(OTs)₃ (**5**) (1.12 g, 1.44 mmol) was dissolved in dimethyl acetamide (10 mL). Sodium bromide (1.11 g,

10.8 mmol) was added and the reaction was heated to 130 °C for 2.5 h. Solvent was removed and the residue was taken up in dichloromethane (20 mL). The organic layer was washed with water (3 × 20 mL) and brine. Evaporation of solvent gave Bn-G0-(Br)₃ (**6**) as a colorless oil (690 mg, 96%). ¹H NMR (CDCl₃, 500 MHz) δ: 3.51 (s, 6H), 3.52 (s, 2H), 3.60–3.67 (m, 8H), 4.56 (s, 2H), 7.24–7.34 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ: 34.84, 43.70, 69.43, 69.77, 70.34, 70.58, 70.93, 73.19, 127.53, 127.64, 128.29, 138.18 ppm; MALDI-TOF: Calc. 503.06, found: 504.77% (M + H).

3.2.7. Bn-G1-(ethyl orthoester)₃, compound 7

The cyclic orthoester EHTBO (**1**) (825 mg, 4.71 mmol) was added slowly to a suspension of NaH (133 mg, 5.54 mmol, 218 mg 60% NaH in mineral oil) in 2 mL anhydrous DMF. The mixture was stirred for 45 min till all the gas was released. A solution of Bn-G0-(Br)₃ (**6**) (586 mg, 1.167 mmol) in 2 mL DMF was added dropwise to the alkoxide solution. After addition, the reaction was heated to 100 °C for 10 h under nitrogen. Solvent was removed and the residue was taken up in 20 mL dichloromethane, washed with 5% NaHCO₃ (100 mL), water (200 mL) and saturated NaCl. The product was obtained as a pale yellow oil (868 mg, 95%) after the evaporation of solvent as ¹H NMR (CDCl₃, 500 MHz) δ: 0.93 (t, *J* = 7.5 Hz, 9H), 1.68 (q, *J* = 7.5 Hz, 6H), 3.07 (s, 6H), 3.22 (s, 6H), 3.28 (s, 2H), 3.50–3.62 (m, 8H), 3.93 (s, 18H), 4.54 (s, 2H), 7.33 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ: 7.39, 29.73, 35.16, 45.59, 69.24, 69.45, 69.51, 69.65, 70.07, 70.30, 70.54, 70.98, 73.16, 109.70, 127.54, 127.63, 128.27, 138.15 ppm; MALDI-TOF: Calc. 782.91, found: 805.95% (M + Na).

3.2.8. Bn-G1-(OH)₉ poly(ether) dendron, compound 8

Bn-G1-(ethyl orthoester)₃ (**7**) (470 mg, 0.602 mmol) was dissolved in 5 mL methanol, and concentrated HCl (0.12 mL) was added. The reaction was heated at 70 °C for 2 h. After removal of solvent, the residue was placed on high vacuum over night to give the deprotected dendron **8** (420 mg, 100%). This material was used for the next step reaction without further purification.

3.2.9. Bn-G1-(MOM)₉, compound 9

Diisopropylethyl amine (4.0 mL) and anhydrous dichloromethane (1.0 mL) was added to the flask containing Bn-G1-(OH)₉ poly(ether) dendron **8** (402 mg, 0.601 mmol). This suspension was cooled to 0 °C using an ice–water bath. Methoxymethyl chloride (1.31 g, 16.23 mmol) was added dropwise. After addition the reaction was allowed to warm to room temperature and stirred over night. Solvent was removed and the residue was taken up in 10 mL dichloromethane followed by washing with saturated NaHCO₃ (4 × 20 mL) and brine. After silica gel purification the product is a colorless oil (245 mg, 38%). ¹H NMR (CDCl₃, 500 MHz) δ: 3.31 (s, 27H), 3.349 (s, 6H), 3.354 (s, 6H), 3.40 (s, 2H), 3.50 (s,

18H), 3.51 (m, 2H), 3.58–3.65 (m, 6H), 4.56 (s, 2H), 4.57 (s, 18H), 7.45–7.64 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz) δ: 44.48, 45.90, 54.97, 66.90, 69.46, 70.06, 70.39, 70.50, 70.61, 71.08, 73.12, 96.77, 127.51, 127.66, 128.30, 138.28 ppm; MALDI-TOF: Calc. 921.25, found: 944.76% (M + Na).

3.2.10. HO-G1-(MOM)₉, compound 10

Following the Parr hydrogenation procedure, Bn-G1-(MOM)₉ (**9**) (190 mg, 0.178 mmol) was used and the product HO-G1-(MOM)₉ (**10**) was obtained as a colorless oil (167 mg, 96.2%). ¹H NMR (CDCl₃, 500 MHz) δ: 3.32 (s, 27H), 3.35 (s, 6H), 3.36 (s, 6H), 3.42 (s, 2H), 3.51 (s, 18H), 3.52–3.53 (m, 2H), 3.55–3.57 (m, 2H), 3.59–3.60 (m, 2H), 3.68–3.70 (m, 2H), 4.58 (s, 18H); ¹³C NMR (CDCl₃, 125 MHz) δ: 44.50, 45.91, 55.00, 61.81, 66.93, 70.08, 70.43, 70.51, 70.53, 71.11, 72.50, 96.80 ppm; MALDI-TOF: Calc. 831.12, found: 834.50% (M + H).

3.2.11. Focal point, phosphine functionalized poly(ether) dendrons, compound 11

The focal point deprotected dendron, HO-G1-(MOM)₉ (**10**) (122 mg, 0.125 mmol) and 4-(diphenylphosphino)benzoic acid were dissolved in 0.5 mL dichloromethane under nitrogen and cooled to –5 °C using a NaCl–ice–water bath. Then a solution of dicyclohexyl carbodiimide (DCC) (39 mg, 0.375 mmol) and DMAP (5 mg, 0.075 mmol) in 0.5 mL dichloromethane was added. The reaction was stirred at 0 °C for 5 h followed by filtration of the white precipitate which was formed. The crude product was purified using a silica gel column (1% methanol in dichloromethane) to give the pure compound **11** as an oil. ¹H NMR (CDCl₃, 500 MHz) δ: 3.32 (s, 27H), 3.362 (s, 2H, overlapped), 3.415 (s, 2H), 3.512 (s, 18H), 3.524 (m, 2H), 3.796 (m, 2H), 4.445 (m, 2H), 4.575 (s, 18H), 7.295–7.991 (m, 14H); ¹³C NMR (CDCl₃, 125 MHz) δ: 44.51, 45.92, 55.00, 64.22, 66.92, 69.15, 70.10, 70.43, 70.48, 70.54, 71.09, 96.80, 128.63, 128.68, 128.73, 129.12, 129.35, 129.40, 130.00, 132.04, 132.12, 166.27 ppm; MALDI-TOF: Calc. 1263.40, found: 1286.61% (M + Na).

3.2.12. Compound 12

Compound **11** (76 mg, 0.06 mmol) was dissolved in 2 mL of methanol followed by addition of 20 μL concentrated hydrochloric acid. The reaction was then stirred at 50 °C for 3 h. TLC showed that all starting material was consumed. Removing of solvent gave the product **12** as a pale oil. ¹H NMR (CDCl₃, 500 MHz) δ: 3.24 (m, 2H, overlapped), 3.28 (s, 2H), 3.512 (s, 18H), 3.524 (m, 2H), 3.786 (m, 2H), 4.445 (m, 2H), 4.75 (s, 18H), 7.295–7.991 (m, 14H); ¹³C NMR (CDCl₃, 125 MHz) δ: 55.37, 64.52, 67.53, 69.85, 70.18, 70.44, 70.49, 70.84, 74.965, 96.80, 128.54, 128.89, 128.12, 129.43, 129.70, 129.98, 130.78, 132.96, 133.82, 168.33 ppm; MALDI-TOF: Calc. 866.92, found: 890.26% (M + Na).

4. Conclusions

Earlier efforts to pacify quantum dots with thiol functionalized ligands (i.e., both traditional and dendron types) have invariably led to substantial quenching of the QD photoluminescence. We now report virtual elimination of such quenching by utilizing phosphine focal point functionalized poly(ether) dendrons. A recent examination of phosphine, focal point functionalized poly(amidoamine) (PAMAM) dendrons as capping agents for quantum dots has clearly demonstrated that these enhanced (non-quenching) photoluminescence properties are influenced by the phosphine ligation parameter and not the interior composition or surface groups of the ligating dendron [17].

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