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# Dendron-Tethered and Templated CdS Quantum Dots on Single-Walled Carbon Nanotubes

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***Abstract:*** CdS nanoparticles on the surface of single-walled carbon nanotubes (SWNTs) were templated and stabilized through the initial attachment of 1 → 3 C-branched amide-based dendrons and were both photophysically and morphologically characterized. The CdS clusters were shown to be ca. 1.4 nm in diameter as calculated from their optical absorption spectra and exhibited reduced fluorescence emission intensity at 434 nm compared to that of CdS quantum dots stabilized by untethered dendrons due to partial emission quenching by the SWNT. Unchanged UV absorption behavior of these materials indicated that they are stable $>$ 90 days at 25 °C.

## I. Introduction

Functionalization of single-walled and multiwalled carbon nanotubes (CNTs) has attracted increasing attention due to their outstanding structural, chemical, electrical, and thermal properties.[1−5] Methods developed for functionalizing CNTs include the formation of noncovalent as well as covalent assemblies.[6−20] Among these, the modification of CNTs with metal nanoparticles can provide unique properties leading to advanced catalytic systems, very sensitive electrochemical sensors, and highly efficient fuel cells.[21,22] Up to now, only a few protocols have been devised for attaching metal particles onto CNTs; these have included chemical binding through DNA double-helix linkages,[19] electrochemical deposition,[23] electroless deposition with and without the aid of reducing agents,[23,24] and physical/chemical deposition on CNTs with and without surface activation.[25−27]

Quantum dots provide a functional platform for the creation of novel materials and devices that benefit from the unique physical properties arising from their quantum-confined nature and properties, which are intermediate between those of the molecular and bulk size scales.[28,29] They have also formed the basis for new photovoltaic cells,[30,31] light-emitting diodes,[32,33] biosensors,[5,34] and other hybrid materials prepared by directed-

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(1) Kovtyukhova, N. I.; Mallouk, T. E.; Pan, L.; Dickey, E. C. *J. Am. Chem. Soc.* **2003**, *125*, 9761−9769.
(2) Martin, B. R.; St. Angelo, S. K.; Mallouk, T. E. *Adv. Funct. Mater.* **2002**, *12*, 759−765.
(3) Sun, Y.-P.; Fu, K.; Lin, Y.; Huang, W. *Acc. Chem. Res.* **2002**, *35*, 1096−1104.
(4) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253−1256.
(5) Chan, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **2005**, *282*, 95−98.
(6) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P. *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*; Springer: Berlin, 2001.
(7) Hirsch, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1853−1859.
(8) Dyke, C. A.; Tour, J. M. *Chem.*−*Eur. J.* **2004**, *10*, 813−817.
(9) Bettinger, H. F. *Chem. Phys. Chem.* **2003**, *4*, 1283−1289.
(10) Georgakilas, V.; Voulgaris, D.; Vázquez, E.; Prato, M.; Guldi, D. M.; Kukovecz, A.; Kuzmany, H. *J. Am. Chem. Soc.* **2002**, *124*, 14318−14319.
(11) Khabashesku, V. N.; Billups, W. E.; Margrave, J. L. *Acc. Chem. Res.* **2002**, *35*, 1087−1095.
(12) Stevens, J. L.; Huang, A. Y.; Peng, H.; Chiang, I. W.; Khabashesku, V. N.; Margrave, J. L. *Nano Lett.* **2003**, *3*, 331−336.
(13) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536−6542.
(14) Maultzsch, J.; Reich, S.; Thomsen, C.; Webster, S.; Czerw, R.; Carroll, D. L.; Vieira, S. M. C.; Birkett, P. R.; Rego, C. A. *Appl. Phys. Lett.* **2002**, *81*, 2647−2649.
(15) Marcoux, P. R.; Hapiot, P.; Batail, P.; Pinson, J. *New J. Chem.* **2004**, *28*, 302−307.
(16) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *313*, 91−97.
(17) Balasubramanian, K.; Friedrich, M.; Jiang, C.; Fan, Y.; Mews, A.; Burghard, M.; Kern, K. *Adv. Mater.* **2003**, *15*, 1515−1518.
(18) Knez, M.; Sumser, M.; Bittner, A. M.; Wege, C.; Jeske, H.; Kooi, S.; Burghard, M.; Kern, K. *J. Electroanal. Chem.* **2002**, *522*, 70−74.
(19) Moghaddam, M. J.; Taylor, S.; Gao, M.; Huang, S.; Dai, L.; McCall, M. J. *Nano Lett.* **2004**, *4*, 89−93.
(20) Cui, J.; Burghard, M.; Kern, K. *Nano Lett.* **2003**, *3*, 613−615.
(21) Kong, J.; Chapline, M. G.; Dai, H. *Adv. Mater.* **2001**, *13*, 1384−1386.
(22) Ye, X.-R.; Lin, Y.; Wang, C.; Engelhard, M. H.; Wang, Y.; Wai, C. M. *J. Mater. Chem.* **2004**, *14*, 908−913.
(23) Quinn, B. M.; Dekker, C.; Lemay, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 6146−6147.
(24) Choi, H. C.; Shim, M.; Bangsaruntip, S.; Dai, H. *J. Am. Chem. Soc.* **2002**, *124*, 9058−9059.
(25) Xing, Y. *J. Phys. Chem. B* **2004**, *108*, 19255−19259.
(26) Azamian, B. R.; Coleman, K. S.; Davis, J. J.; Hanson, N.; Green, M. L. H. *Chem. Commun.* **2002**, 366−367.
(27) Kim, B.; Sigmund, W. M. *Langmuir* **2004**, *20*, 8239−8242.
(28) Brus, L. *J. Phys. Chem. Solids* **1998**, *59*, 459−465.
(29) Alivisatos, A. P. *Science* **1996**, *271*, 933−937.
(30) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425−2427.
(31) Leatherdale, C. A.; Kagan, C. R.; Morgan, N. Y.; Empedocles, S. A.; Kastner, M. A.; Bawendi, M. G. *Phys. Rev. B* **2000**, *62*, 2669−2680.
(32) Lee, J.; Sundar, V. C.; Heine, J. R.; Bawendi, M. G.; Jensen, K. F. *Adv. Mater.* **2000**, *12*, 1102−1105.
(33) Schlamp, M. C.; Peng, X.; Alivisatos, A. P. *J. Appl. Phys.* **1997**, *82*, 5837−5842.
(34) Pathak, S.; Choi, S.-K.; Arnheim, N.; Tompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4103−4104.

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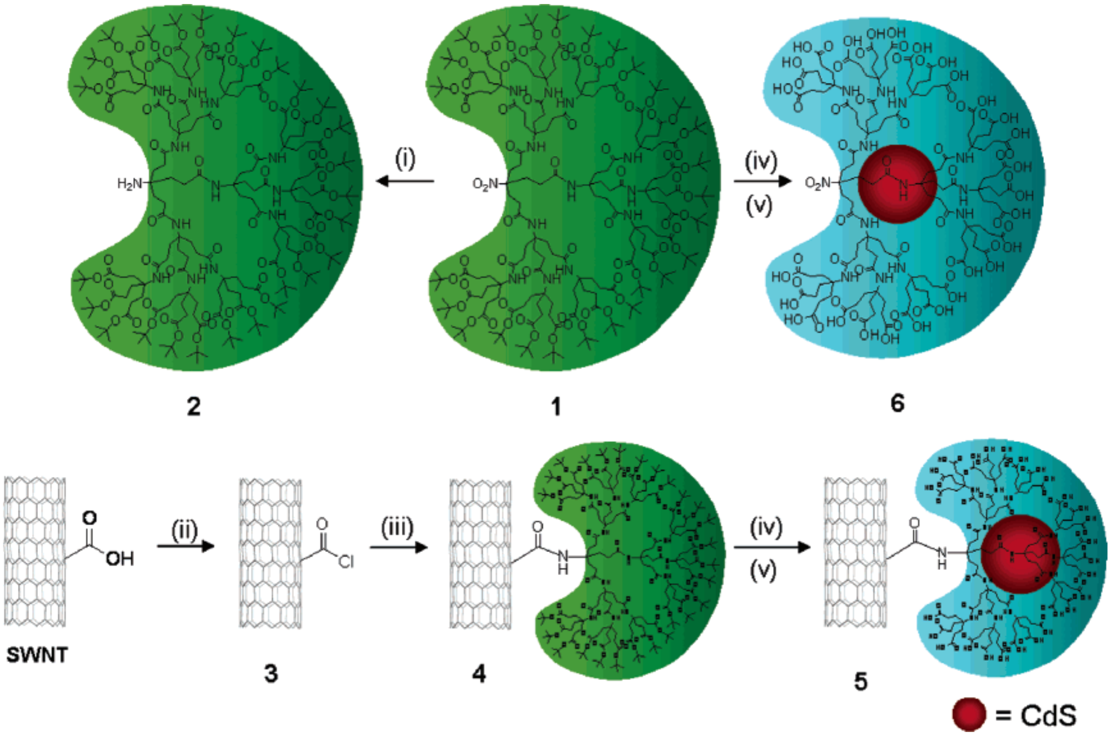
***Scheme 1.*** Synthesis of the Tethered (**5**) and Untethered (**6**) CdS-Based Quantum Dots[a]



[a] Reagents and Conditions: (i) Raney Ni, EtOH, $H_2$ (65 psi), 50 °C, 24 h; (ii) $SOCl_2$, THF, 0 °C; (iii) G3-amino-dendron **2**, $Et_3N$, $CH_2Cl_2$; (iv) $HCO_2H$ 25 °C; (v) $Cd(NO_3)_2{\cdot}4H_2O$, $Na_2S$, MeOH

and self-assembly techniques.[35−37] These semiconducting nanoparticles have photophysical properties that are superior to many organic-based materials, and the use of dendrimers as nanoreactors, stabilizers and templates for their preparation presents advantages, such as temperature and size control.[38−40]

We herein describe the preparation of stable CdS quantum dots onto the surface of single-walled carbon nanotubes (SWNTs) templated and stabilized by means of attached 1 → 3 C-branched amide-based dendrons, along with their photooptical properties.

## II. Results and Discussion

The 3rd-generation 1 → 3 C-branched amino-polyester dendron **2** was prepared by following an improved literature procedure.[41] Its structure was confirmed ($^{13}C$ NMR) by the presence of a quaternary carbon peak at 52.3 ppm ($R_3CNH_2$) and the molecular ion peak (MALDI-TOF MS) at $m/z$ 4537.3 ($[M + Na]^+$ calcd $m/z = 4535.8$). Scheme 1 illustrates the basic strategy for the preparation of the dendron-tethered and templated CdS quantum dots on SWNTs. Treatment of commercial, oxidized SWNTs $[(HO_2C)_n\text{-SWNT}]$s with excess $SOCl_2$ under anhydrous conditions gave $[(ClOC)_n\text{-SWNT}]$s (**3**) that were then treated with the amino-polyester dendron **2** in the presence of $Et_3N$ in dry $CH_2Cl_2$ to afford $[(Den)_n\text{-SWNT}]$ (**4**). TGA analysis of the initial $[(HO_2C)_n\text{-SWNT}]$s showed excellent thermal stability below 600 °C under a nitrogen atmosphere (Figure 1A); whereas, dendronized SWNT **4** exhibited a weight loss at >ca. 200 °C (Figure 1B) that is well-known to be associated with *tert*-butyl esters, which undergo a quantitative thermal loss of *iso*butylene.[42] This degradation also provided a facile way to ascertain the presence of the dendron on the SWNT's surface and an estimated percentage (ca. 15%) of its overall composition. Cleavage of the ester groups using formic acid at 25 °C gave the desired carboxylic-acid-coated dendronized SWNTs $\{[(HO_2C)_{27}\text{-Den}]_n\text{-SWNT}\}$, which were then treated with alternating dropwise addition of $Cd(NO_3)_2$ and $Na_2S$, both in methanol at 0 °C to generate the encapsulated CdS quantum dots tethered to the

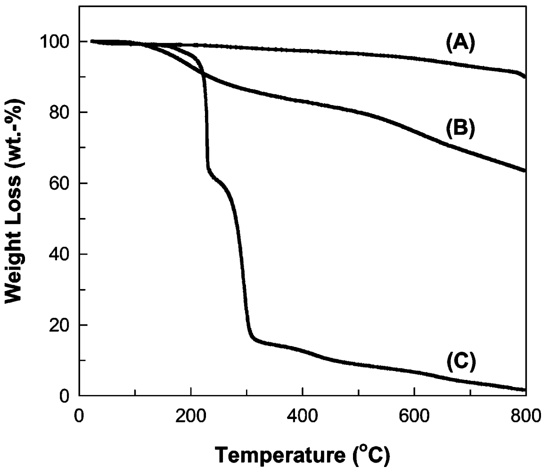


***Figure 1.*** TGA thermograms: (A) pure $[(HO_2C)_n\text{-SWNT}]$; (B) $[(Den)_n\text{-SWNT}]$; (C) pure G3-amino-dendron **2**.

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(35) Thompson, R. B.; Ginzbrug, V. V.; Matsen, M. W.; Balazs, A. C. *Science* **2001**, *292*, 2469−2472.
(36) Lin, Y.; Skaff, H.; Emrick, T.; Dinsmore, A. D.; Russell, T. P. *Science* **2003**, *299*, 226−229.
(37) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1338.
(38) Lemon, B. I.; Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 12886−12887.
(39) Wang, R.; Yang, J.; Zheng, Z.; Carducci, M. D.; Jiao, J.; Seraphin, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 549−552.
(40) Sooklal, K.; Hanus, L. H.; Ploehn, H. J.; Murphy, C. J. *Adv. Mater.* **1998**, *10*, 1083−1087.
(41) Newkome, G. R.; Kotta, K. K.; Moorefield, C. N. *J. Org. Chem.* **2005**, *70*, 4893−4896.
(42) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183−188.

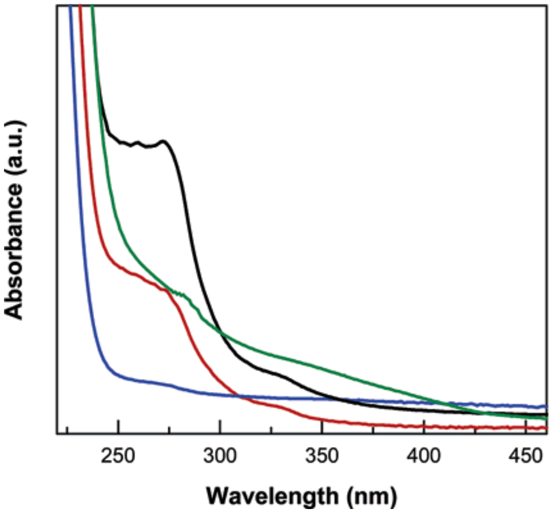

***Figure 2.*** UV aborption spectra for [$(HO_2C)_n$-SWNT] (blue line); CdS/Den-SWNT hybrid **5** (red line); CdS/dendron hybrid **6** (green line); after 90 days of CdS/Den-SWNT hybrid **5** (black line).

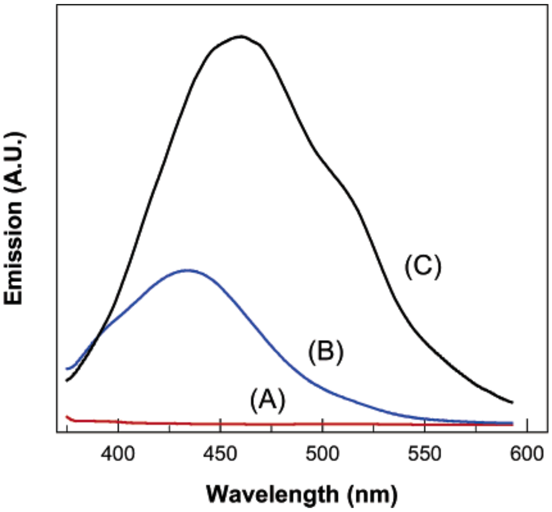

***Figure 3.*** Photoluminescence spectrum for [$(HO_2C)_n$-SWNT] (A); CdS/Den-SWNT hybrid **5** (B); CdS/dendron hybrid **6** (C).

SWNT surface. Filtration, followed by repeated washing with MeOH, $H_2O$, and acetone, gave the nanoparticles free of bulk reagents and surface attached ions.

As shown in Figure 2, UV absorbance behavior for the CdS/Den-SWNT hybrid **5** revealed significant absorption of UV light at 273 nm (calculated by using the Lorentzian multipeak analysis method) with a 242 nm blue shift when compared with the characteristic absorption of the corresponding band gap of bulk CdS (515 nm). This indicates the quantum confinement effect of the CdS nanocrystal, produced under this environment, corresponding to the first optically allowed transition between the electron state in the conduction band and the hole state in the valence band. For comparison, the [$(HO_2C)_n$-SWNT]s, which were analogously treated with $Cd^{2+}$ and $S^{2-}$ solutions and followed by copious washing, do not exhibit any absorption at the same wavelength; this result implies that there is no CdS nanoparticle tethered to the SWNT surfaces.

Since particle size is directly related to the absorption wavelength of quantum-sized particles due to a size quantization effect,[43] the diameter of the CdS particles was predicted to be ca. 1.4 nm from their optical absorbance spectrum. These results agree with measurements based on molecular modeling of the fully expanded dendron (ca. 1.9 nm; focal point to periphery distance), while the absorption peak (Figure 2C) of the CdS/dendron hybrid **6** occurred at somewhat higher wavelength than that of CdS/Den-SWNT hybrid **5**. This red shift of the absorption indicated that CdS/dendron hybrid **6** contains larger CdS nanoparticles than those of the CdS/Den-SWNT hybrid **5**. A UV absorption peak of CdS/Den-SWNT hybrid **5** appeared at nearly the same wavelength (∼272 nm) (Figure 2D) even after 90 days. Thus, the SWNT surface-anchored dendrons stabilize the CdS nanoparticles against coalescence into bulk CdS particles by their mutual van der Waals attraction.

Upon light excitation at 350 nm, the CdS/Den-SWNT hybrid **5** exhibits photoluminescence with a maximum emission at 434 nm (Figure 3B), which is assigned to an electron−hole recombination in the CdS nanoparticles and is further indicative of the quantum size effect. There was no observable luminescence peak in the case of [$(HO_2C)_n$-SWNT] after treatment with $Cd^{2+}$ and $S^{2-}$ solutions. Based on studies by Kamat et al.,[44] the luminescence of CdS quantum dots, attached directly to the SWNTs, is totally quenched by the charge-transfer mechanism that occurs between the CdS quantum dots and the SWNTs. In contrast, CdS/Den-SWNT hybrid **5** showed a significant luminescence but a decreased emission intensity when compared to that of CdS/dendron hybrid **6** (Figure 3C). A possible origin for this phenomenon is based on the known properties of SWNTs and quantum dots. In the hybrid system (i.e., **5**) of SWNT and quantum dots, electron−hole recombination competes with the electron-injection mechanism, and this competition should depend on the distance between the quantum dot and the SWNT. Thus, the electrons of the excitons could be partially transferred to SWNTs by an electron-injection mechanism while the remainder of electrons provides for a reduced emission by an electron−hole recombination process.

Figure 4 shows transmission electron microscope (TEM) images of carboxylic acid-coated dendronized SWNT with/without the CdS nanoparticles. It can be seen that the quantum dots [black spots in Figure 4C, D, and F] are well-dispersed and attached to the SWNTs. Figure 4E shows a corresponding selected area electron diffraction (SAED) pattern for the CdS/Den-SWNT hybrid **5**. Calibration of the SAED spacing was conducted using standard evaporated thallous chloride, which has the largest first-order spacing diffraction of 0.384 nm. In Figure 4E, several diffused diffraction rings appeared with five different *d*-spacings: 0.358, 0.336, 0.245, 0.207, and 0.176 nm, which belong to the (100), (002), (102), (110), and (112) Miller indices of CdS wurtzite, respectively; this agrees with literature.[45] The electron diffraction pattern of the CdS at (101) and (103) is weak but supports the fact that the black spots of **5** are randomly oriented, small CdS crystals.

X-ray photoelectron spectroscopic (XPS, monochromatic Mg Kα radiation at a power of 250 W, 93.90 eV) measurements for the CdS/Den-SWNT hybrid **5** showed new peaks attributed to N1s at 398 eV along with other expected peaks assigned to Cd (3d5 at 405.0 eV and 3d3 at 412.1 eV) and S (2s at 229.4

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(43) Qingqing, W.; Gang, X.; Gaorong, H. *J. Solid State Chem.* **2005**, *178*, 2680−2685.

(44) Robel, I.; Bunker, B. A.; Kamat, P. V. *Adv. Mater.* **2005**, *17*, 2458−2463.

(45) Yang, J.; Zeng, J.-H.; Yu, S.-H.; Yang, L.; Zhou, G.-E.; Qian, Y.-T. *Chem. Mater.* **2000**, *12*, 3259−3263.

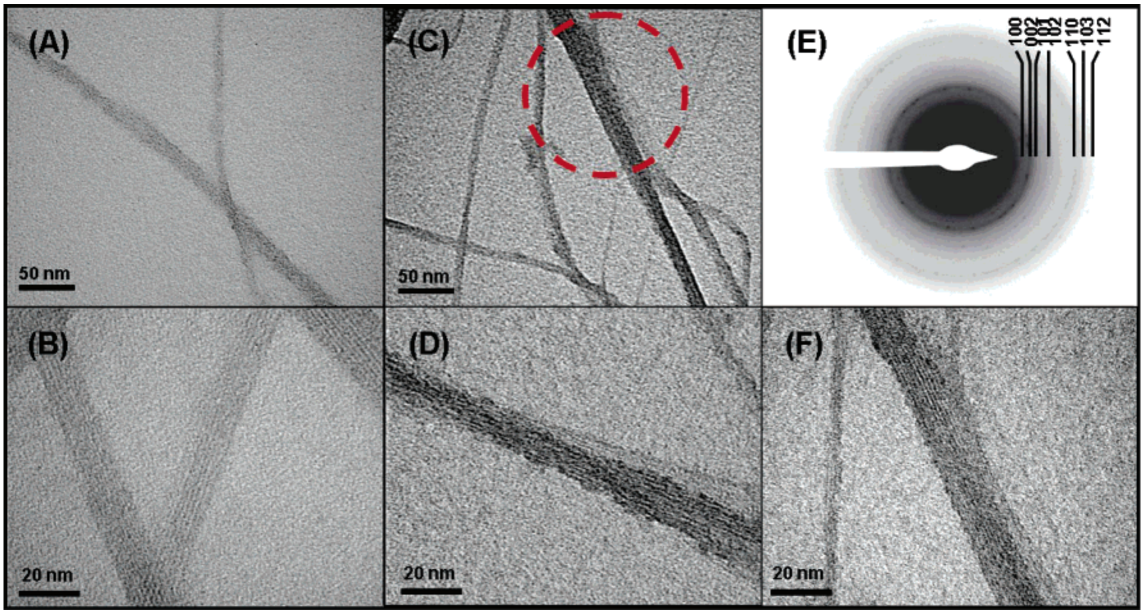

***Figure 4.*** Transmission electron micrograph for pure {[$(HO_2C)_{27}$-Den]$_n$-SWNT} (A, B); CdS/Den-SWNT hybrid **5** (C, D, F); selected area electron diffraction pattern taken from red circle in image C (E).

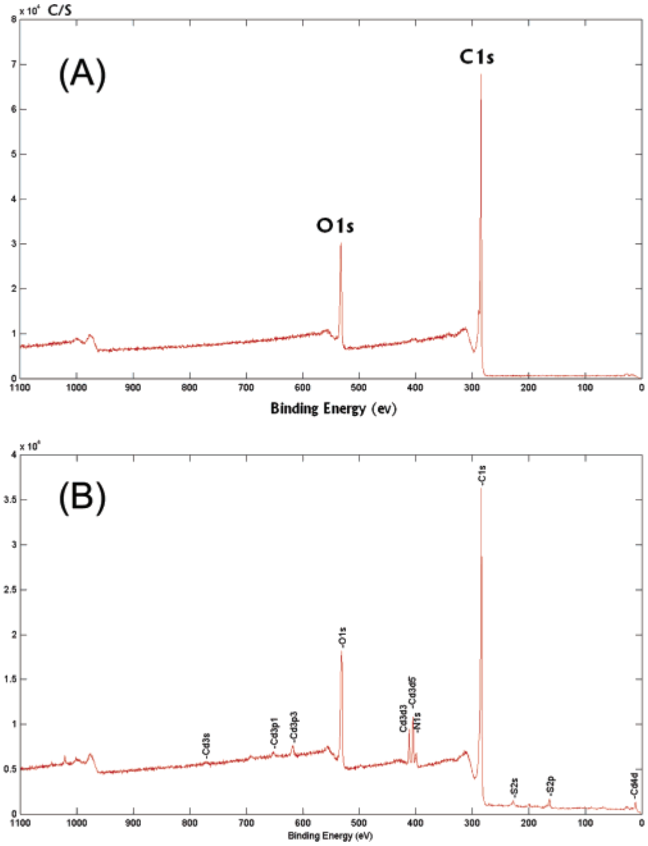

***Figure 5.*** XPS spectra for (A) pure [$(HO_2C)_n$-SWNT] and (B) CdS/Den-SWNT hybrid **5**.

eV and 2p at 165.3 eV) [Figure 5B]. The binding energies were calibrated for a backbone carbon peak at 284.8 eV. The small shift of the Cd peak (from 405.5 to 405.0 eV) is in full agreement with the formation of CdS particles.[46]

The un-ionized and uncoordinated carboxylic acid C═O stretching band appears at 1750−1700 cm$^{-1}$, whereas the ionized C═O stretching band occurs at 1650−1590 cm$^{-1}$.[47] As shown in Figure 6, the IR spectrum of the carboxylic-acid-coated dendron showed a strong asymmetric vibration characteristic of carboxyl groups at 1715 cm$^{-1}$ and a weak broad peak at 1660 cm$^{-1}$ attributed to hydrogen bonding between carboxyl groups in the film state. The IR spectrum of CdS/dendron hybrid **6** exhibited an ionized carbonyl frequency at the usual position near 1660 cm$^{-1}$ with an increased intensity. The intensity of the asymmetric carboxylate stretching vibration band at ∼1540 cm$^{-1}$ attributed to complexed carboxylates with metal ions or CdS clusters also increased.

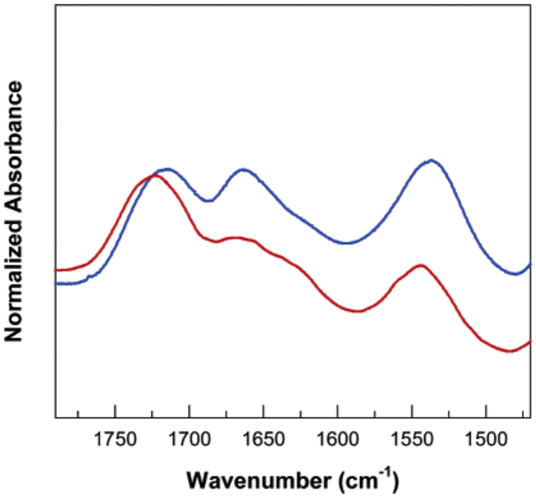

***Figure 6.*** FT-IR spectra for the pure acid-terminated dendron (red line) and CdS/dendron hybrid **6** (blue line).

Comparison of the UV/vis spectra gives insight into the cluster size-distribution differences. In an otherwise ideal local environment, the position of the observed dispersion peak for the nanoparticles is a function of both domain size and aspect ratio.[29] Consequently, one would expect a single distribution

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(46) Guo, S.; Konopny, L.; Popovitz-Biro, R.; Cohen, H.; Porteanu, H.; Lifshitz, E.; Lahav, M. *J. Am. Chem. Soc.* **1999**, *121*, 9589−9598.

(47) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1970.

curve in the electromagnetic spectrum for a homogeneous nanoparticle and a multimodal distribution curve (broader and much less defined)[48] for heterogeneous nanoparticles. Thus, from the broad UV/vis spectra and IR band at ~1540 $cm^{-1}$ for the CdS/dendron hybrid **6**, we speculated that CdS clusters were produced in the void regions of single and aggregated dendrons; this is in agreement with other dendrimer composites.[49] In contrast, the CdS/Den-SWNT hybrid **5** exhibited a more narrow single distribution curve (as shown in Figure 2) suggesting that these CdS nanoparticles were produced in the void region of the dendrons tethered to the SWNT's surface.

## III. Conclusion

We have fabricated unique CdS quantum dot composite assemblies using dendronized SWNTs. The resulting nanohybrids have been characterized by UV/vis, XPS, TEM, and SAED; the size of these materials appears to be in the quantum-confined regime, and they exhibit novel luminescence properties. Templated CdS quantum dots also show long-term stability (>90 days) at ambient temperatures. These features suggest that these and other quantum dot assemblies with $\{[(HO_2C)_{27}\text{-Den}]_n\text{-SWNT}\}$ may be useful for fabricating molecular electronic devices predicated on their unique nanoscale electronic properties.

## IV. Experimental Details

**General Comments.** Chemicals were purchased and used without further purification. Thin-layer chromatography (TLC) was conducted on flexible sheets precoated with $SiO_2$ (IB2-F). Column chromatography used $SiO_2$ (60−200 mesh). The melting points were determined on an Electrothermal 9100 heater. $^1H$ and $^{13}C$ NMR spectra were recorded on a 300 MHz NMR spectrometer using $CDCl_3$. Mass spectra were obtained by Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) using *trans*-3-indoleacrylic acid (IAA), as the matrix. UV/vis absorption spectra were obtained on a Hewlett-Packard UV/vis spectrophotometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS55 luminescence spectrometer. A Digilab Win-IR Pro FTS 3000 Fourier transform infrared spectrometer (FT-IR) was used on film samples prepared via film-casting from solution onto the KBr plates. TEM images were obtained by using scanning transmission electron microscopy at an acceleration voltage of 120 kV. TEM samples were prepared by casting a MeOH suspension on a carbon-coated mica surface. After 12 h, the films were removed from the glass slide, floated on a water surface, and recovered using copper grids. Thermogravimetric analysis (TGA) was conducted with a DuPont model 2950 at a heating rate of 10 °C/min under a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) was performed using a Perkin-Elmer PHI-5600 system with a Mg anode (Mg $K\alpha = 93.90$ eV) operating at 250 W and a 50 cm hemispherical electron energy analyzer.

**Synthesis of the 3rd Generation Dendron 2.**[50] This dendron possessing an amino focal site was obtained (73%) from the nitro dendron **1** using T-1 Raney Ni catalyst as described in previous literature:[41] mp 105−106 °C (lit.[41] mp 106−107 °C); $^1H$ NMR $\delta$ 6.14 (s, 12H), 2.00 (br m, 78H), 1.77 (br m, 78H), 1.22 (s, 243H); $^{13}C$ NMR $\delta$ 27.6, 29.5, 31.3, 52.4, 57.0, 57.5, 80.1, 172.3, 172.9; MALDI-TOF MS: $m/z$ 4537.4 $[M + Na]^+$ (Calcd $m/z = 4535.8$).

**Synthesis of the 3rd Generation Carboxyl-Coated Dendron 6.** A solution of 3rd generation predendron **1**[50] [mp 161−162 °C (lit.[41] mp 161−162 °C) 100 mg, 22 $\mu$mol] in formic acid (7 mL) was stirred for 24 h at 25 °C. After the reaction, the excess formic acid was removed in vacuo, and $H_2O$ (10 mL) and acetone (50 mL) were added to dissolve the resulting oil. After concentration in vacuo, the 3rd generation carboxyl-coated dendron **6** was isolated in nearly quantitative yield, as a white solid: mp 134−136 °C; $^1H$ NMR ($CD_3OD$) $\delta$ 7.49 (s, 3H), 7.30 (s, 9H), 5.14 (br, s, 27H), 2.27 (br m, 78H), 2.02 (br m, 78H); $^{13}C$ NMR ($CD_3OD$) $\delta$ 177.4, 175.8, 58.9, 58.7, 32.0, 20.6, 29.4; MALDI-TOF MS: $m/z$ 3064.3 $[M + Na]^+$ (Calcd $m/z = 3065.3$).

**Preparation of the Chlorocarbonyl-Functionalized SWNT $[(ClOC)_n\text{-SWNT}]$ (3).** Dry oxidized SWNTs $[(HO_2C)_n\text{-SWNT}$; Aldrich No. 652490, 80 mg] were suspended in $SOCl_2$ (5 mL) and stirred at 65 °C for 24 h. The solid was then separated by filtration, washed with anhydrous THF, and then dried in vacuo at 25 °C for 6 h to give the chlorocarbonyl-functionalized SWNT $[(ClOC)_n\text{-SWNT}]$ (70 mg), which was used without further purification.

**Preparation of the Dendronized SWNT $\{[(HO_2C)_{27}\text{-Den}]_n\text{-SWNT}\}$.** To a stirred suspension of $[(ClOC)_n\text{-SWNT}]$ **3** (70 mg), anhydrous $CH_2Cl_2$ (10 mL), and dry $Et_3N$ (several drops), the 3rd generation amino-dendron[41] (**2**; 200 mg) was added dropwise at 0 °C and then stirred at 25 °C for 48 h. The solid was filtered and washed several times with excess $H_2O$ and $CH_2Cl_2$. The crude product was dispersed in excess $CH_2Cl_2$, filtered, and washed again to remove any adsorbed unreacted dendron. The black solid was collected and dried in vacuo overnight at 40 °C to afford the dendronized SWNT $[(\text{Den})_n\text{-SWNT}]$: 75 mg. The suspension of $[(\text{Den})_n\text{-SWNT}]$ (**4**; 75 mg) in formic acid (10 mL) was stirred for 24 h at 25 °C, and then the excess formic acid was removed in vacuo. To ensure the total removal for residual traces of formic acid, $H_2O$ (25 mL) and acetone (25 mL) were added to suspend the $\{[(HO_2C)_{27}\text{-Den}]_n\text{-SWNT}\}$, followed by concentration in vacuo to give the $\{[(HO_2C)_{27}\text{-Den}]_n\text{-SWNT}\}$.

**Preparation of the CdS Quantum Dots.** Stock solutions (2.0 mM) of $Cd^{2+}$ and $S^{2-}$ were freshly prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ (12.4 mg) in MeOH (20 mL) and dissolving $Na_2S$ (3.0 mg) in MeOH (20 mL), respectively. In the incremental addition procedure,[51] a 0.5 mL aliquot of $Cd^{2+}$ methanolic solution was added to 10 mL of either a $\{[(HO_2C)_{27}\text{-Den}]_n\text{-SWNT}\}$ (60 mg) or $[(HO_2C)_n\text{-SWNT}]$ (50 mg) methanolic suspension at 0 °C and then sonicated, followed by the addition of a 0.5 mL aliquot of $S^{2-}$ methanolic solution. This procedure was repeated several times. After complete addition of $Cd^{2+}$ and $S^{2-}$ stock solutions, the suspension was kept at 0 °C overnight, then filtrated, and washed sequentially with MeOH, $H_2O$, and acetone.

**Preparation of the CdS quantum dots** with the carboxyl-coated dendron **6** followed an analogous manner, as described above, without further filtration and washing steps.

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(48) Martin, C. R. *Science* **1994**, *266*, 1961−1966.

(49) Balogh, L.; Valluzzi, R.; Laverdure, K. S.; Gido, S. P.; Hagnauer, G. L.; Tomalia, D. A. *J. Nanopart. Res.* **1999**, *1*, 353−368.

(50) Available from Frontier Scientific, Inc., Logan, UT (www.frontiersci.com).

(51) Sooklal, K.; Hanus, L. H.; Ploehn, H. J.; Murphy, C. J. *Adv. Mater.* **1998**, *10*, 1083−1087.