J|A|C|S
COMMUNICATIONS

# Control of the Optical Properties of Quantum Dots by Surface Coating with Calix[*n*]arene Carboxylic Acids

Takashi Jin,*,† Fumihiko Fujii,† Eiji Yamada,‡ Yoshinobu Nodasaka,§ and Masataka Kinjo†

*Research Institute for Electronic Science, Hokkaido University, Sapporo 060-0812, Japan, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan, and Faculty of Dental Medicine, Hokkaido University, Sapporo 060-8586, Japan*

Received March 24, 2006; E-mail: jin@imd.es.hokudai.ac.jp

Semiconductor quantum dots (QDs) have become a new class of fluorescent probes that can be used for biological labeling,[1] in vivo bioimaging,[2] and multi-color optical encoding of biomolecules.[3] Since the optical properties of semiconductor QDs can be continuously tuned by changing the particle size, a variety of QDs (II−IV and III−V semiconductor materials) that emit in the visible to the near-infrared regions have been developed.[4] Recent advances in the synthesis of QDs have led to the development of smaller QDs,[5,6] where the optical properties can be tunable without a change in the particle size.[6] Several groups have reported alloyed semiconductor QDs for size-independent tuning of the emission properties.[6] Bailey and Nie showed that the emission peaks of ternary $CdSe_xTe_{1-x}$ QDs can be controlled by varying the composition of Se and Te.[6c] Here, we report a new method for the control of the optical properties of CdSe/ZnS (core−shell) QDs by changing the surface coating layer with different oligomer sizes of calixarene derivatives.

Recently, we have found that the surface of CdSe/ZnS QDs can be modified with amphiphilic calixarene derivatives to give water-soluble QDs.[7] In this work, we examined the optical properties of CdSe/ZnS QDs coated with calix[*n*]arene carboxylic acids (**1**−**3**). The calixarene coating was performed by mixing trioctylphosphine oxide (TOPO)-capped CdSe/ZnS QDs and **1**−**3** in tetrahydrofuran at room temperature. Deprotonation of the carboxyl groups of the calix[*n*]arene resulted in water-soluble QDs (Scheme 1). The QDs were highly fluorescent (quantum yield = 0.1−0.34) and stable for more than 1 month in aqueous solution.

***Scheme 1.*** Preparation of Water-Soluble CdSe/ZnS QDs by Surface Coating with Calix[*n*]arene Carboxylic Acids (**1**−**3**)

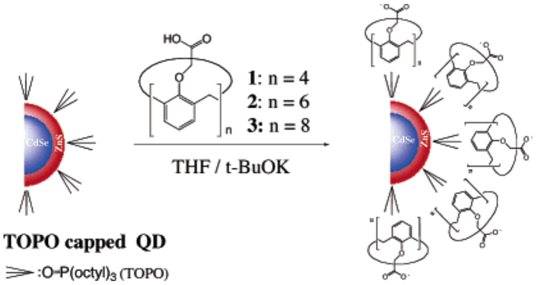

Figure 1a−c shows the fluorescence spectra of CdSe/ZnS QDs before and after the surface coating with **1**−**3**. The emission peak of QDs shifted to longer wavelengths with increasing the oligomer size of the calix[*n*]arene used. In the case of the CdSe/ZnS QD with a 530 nm emission peak, the red shifts were observed to be 8, 21, and 35 nm for **1**-, **2**-, and **3**-coated QDs, respectively. When the QDs with longer emission peaks were coated, the red shifts became smaller. The dependences of oligomer sizes of the calixarene on the peak shifts are shown in Figure 1d. The result indicates that the emission peaks of CdSe/ZnS QDs can be controlled by the surface coating of the QDs with calix[*n*]arene carboxylic derivatives.

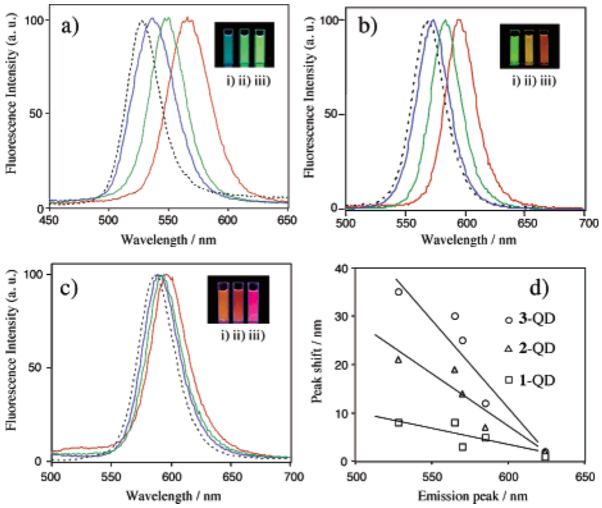

***Figure 1.*** Fluorescence spectra (a−c) of TOPO-capped CdSe/ZnS QDs in chloroform (broken line) and their surface-coated QDs with **1**−**3** in water (blue for **1**, green for **2**, and red for **3**). The inset shows the fluorescence image of the calix[*n*]arene-coated QDs exited at 365 nm (i for **1**-QD, ii for **2**-QD, and iii for **3**-QD). The peak shifts of the calix[*n*]arene-coated QDs compared to the initial QDs are shown in (d).

To understand the mechanism of the red shifts, we first examined the absorption spectra of the QDs. Figure 2a shows the absorption spectra of TOPO-capped QDs (565 nm emission) and their surface-coated QDs with **1**−**3**. It should be noted that the band edge absorption shifts to longer wavelengths depending on the oligomer size of calixarenes used for the surface coating. This result shows that the band gap energy decreases in the calixarene-coated QDs compared to that of the initial TOPO-capped QDs. It is well-known that the band gap energy in CdSe/ZnS QDs decreases with increasing particle size.[4a] In the calixarene-coated QDs, however, the particle sizes of the CdSe/ZnS moiety could not be changed because the surface coating procedure was performed at room temperature.

To characterize the structure of the calixarene-coated QDs, we determined their particle size using TEM and fluorescence correlation spectroscopy (FCS).[7,8] The inset in Figure 2b shows a TEM image of the TOPO-capped CdSe/ZnS QDs (565 nm emission). The TEM image shows that the size of the core−shell moiety of the QDs is ca. 5 nm. For each of the QDs coated with **1**−**3**, we attempted to measure their particle sizes using TEM, but we failed

---

† Research Institute for Electronic Science.
‡ Faculty of Engineering.
§ Faculty of Dental Medicine.

10.1021/ja062021k CCC: $33.50 © 2006 American Chemical Society

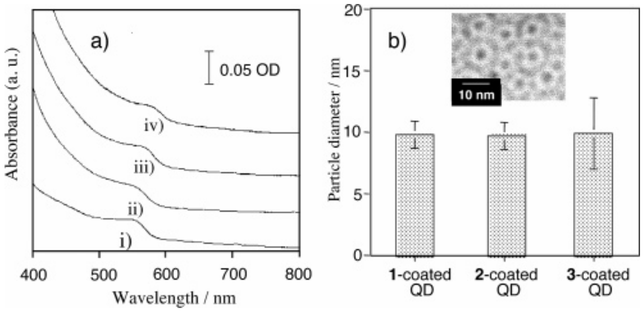

***Figure 2.*** (a) Absorption spectra of CdSe/ZnS QDs (565 nm emission) before and after coating with calix[*n*]arene carboxylic acids: (i) TOPO-coated QDs in chloroform; (ii) **1**-coated QDs; (iii) **2**-coated QDs; and (iv) **3**-coated QDs in water. (b) TEM images (inset) for TOPO-coated QDs (565 nm emission) and the hydrodynamic particle diameter of **1**-, **2**-, and **3**-coated QDs determined by FCS.

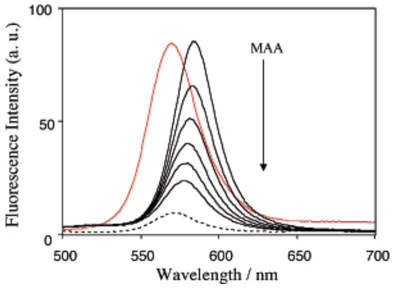

***Figure 3.*** Changes in the fluorescence spectra (solid lines) of **3**-coated CdSe/ZnS QDs by ligand-exchange with mercaptoacetic acid (MAA) in borate buffer (pH = 9.2). MAA was added to the QD solution (o.d. = 0.05 at 480 nm) as an aqueous solution (2 mg/mL). For comparison, the fluorescence spectra of TOPO-capped QDs before coating by **3** in chloroform (red line) and MAA-coated QDs in water (broken line) prepared separately are shown.

to obtain, due to the aggregation during dryness of QD colloids on the Cu grid. Instead, we measured hydrodynamic diameters of the calixarene-coated QDs by using FCS. Interestingly, the hydrodynamic diameters of the QDs were calculated to be similar values (ca. 10 nm) for **1**-, **2**-, and **3**-coated QDs (Figure 2b). This result indicates that the thickness of the organic surface layer is 2.5 nm long for all of the QDs coated with **1**−**3**. The molecular lengths of TOPO and calix[*n*]arene carboxylic acids along their alkyl chains are estimated to be 1.3 and 0.95 nm, respectively. Thus it is reasonable to assume that the surface layer of the QDs forms a bilayer structure, as shown in Scheme 1 (see Supporting Information).

If the surface organic layer induces the emission shifts in the calixarene-coated QDs, their emission properties should be affected by compositions of the surface layer of QDs. To confirm the surface coating effect of **1**−**3** on the optical properties of QDs, we performed a ligand-exchange experiment. The surface organic layer of **3**-coated QDs was exchanged with mercaptoacetic acids (MAA). Figure 3 shows the changes in the fluorescence spectra of **3**-coated QDs upon addition of MAA. With increasing the concentration of MAA, the emission peak of **3**-coated QDs shifted to shorter wavelengths and the emission spectra became close to that of MAA coated QDs. Thus, the red shift observed in the **3**-coated QDs can be attributed to the surface coating effect by the calixarene derivative of **3**.

The theoretical study of the factors that influence the excitonic states in semiconductor QDs has shown that dielectric confinement effects[9] are also important as well as quantum (size) confinement effects.[10] It has been predicted that the change in the dielectric constant of the medium surrounding the QDs results in the change in the exciton binding energy.[9] We believe that the difference in dielectric nature of the surface layer (TOPO and calixarene) plays an important role in the red shifts of the emission of QDs coated with **1**−**3**. Recently, Feng et al. reported a red shift of over 15 nm in the TOPO-capped QDs upon complexation of $\gamma$-cyclodextrin, and on the basis of first-principles calculations, they suggested that the S atom in the ZnS shell is exchanged with the hydroxyl oxygen atom of the cyclodextrin.[11] In the case of the calixarene-coated QDs, the possibility that the change of the ZnS surface due to the binding of calixarene derivatives may have resulted in the red shifts cannot be ruled out.

In conclusion, we have presented a new method for the control of the optical properties of QDs by surface coating with the calix[*n*]arene derivatives. Although the coating effect on the shifts of the emission peak of QDs decreases with increasing the particle sizes (emission wavelengths) of QDs, this method is useful for the preparation of water-soluble multi-colored QDs from an initial TOPO-coated QD. We expect that the surface coating method using calix[*n*]arene carboxylic acids can be applied to other semiconductor QDs for the control of the optical properties of QDs without changing the particle sizes.

**Acknowledgment.** We thank Prof. M. Tamura for continual encouragement.

**Supporting Information Available:** Synthetic procedures for **1**−**3** and QDs, surface coating procedure, TEM and FCS measurements, and additional characterization results. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) (a) Bruchez, M., Jr.; Moronne, M.; Gin, P.; Weiss, S.; Alivisantos, A. P. *Science* **1998**, *281*, 2013−2016. (b) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016−2018.
(2) (a) Gao, X.; Yang, L.; Petros, J. A.; Marshall, F. F.; Simons, J. W.; Nie, S. *Curr. Opin. Biotechnol.* **2005**, *16*, 63−72. (b) Pinaud, F. F.; Michalet, X.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Iyer, G.; Weiss, S. *Biomaterials* **2006**, *27*, 1679−1687.
(3) Han, M.; Gao, X.; Su, J. Z.; Nie, S. *Nat. Biotechnol.* **2001**, *19*, 631−635.
(4) (a) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463−9475. (b) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, *28*, 538−544.
(5) Zimmer, J. P.; Kim, S.-W.; Ohnishi, S.; Tanaka, E.; Frangioni, J. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2006**, *128*, 2526−2527.
(6) (a) Petrov, D. V.; Santos, B. S.; Pereira, G. A.; Donegá, C. D. M. *J. Phys. Chem. B* **2002**, *106*, 5325−5334. (b) Wang, W.; Germanenko, I.; El-Shall, M. S. *Chem. Mater.* **2002**, *14*, 3028−3033. (c) Bailey, R. E.; Nie, S. *J. Am. Chem. Soc.* **2003**, *125*, 7100−7106. (d) Zhong, X.; Feng, Y.; Knoll, W.; Han, M. *J. Am. Chem. Soc.* **2003**, *125*, 13559−13563.
(7) (a) Jin, T.; Fujii, F.; Sakata, H.; Tamura, M.; Kinjo, M. *Chem. Commun.* **2005**, 2829−2831. (b) Jin, T.; Fujii, F.; Sakata, H.; Tamura, M.; Kinjo, M. *Chem. Commun.* **2005**, 4300−4302.
(8) (a) Yoshida, N.; Kinjo, M.; Tamura, M. *Biochem. Biophys. Res. Commun.* **2001**, *280*, 312−318. (b) Tsay, J. M.; Doose, S.; Weiss, S. *J. Am. Chem. Soc.* **2006**, *128*, 1639−1647.
(9) Takagahara, T. *Phys. Rev. B* **1993**, *47*, 4569−4584.
(10) (a) Rosseti, R.; Nakahara, S.; Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 1086−1088. (b) Alivisatos, A. P. *Science* **1996**, *271*, 933−937.
(11) Feng, J.; Ding, S.-K.; Tucker, M. P.; Himmel, M. E.; Kim, Y.-H.; Zhang, S. B.; Keyes, B. M.; Rumbles, G. *Appl. Phys. Lett.* **2005**, *86*, 033108−033111.

JA062021K