Single-Layered Films of Diblock Copolymer Micelles Containing Quantum Dots and Fluorescent Dyes and Their Fluorescence Resonance Energy Transfer

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Fluorescence resonance energy transfer (FRET) involves the nonradiative energy transfer from excited-state donors to ground-state acceptors by dipole−dipole interactions, which strongly depends on the nanometer-scale distance between donors and acceptors.[1] The FRET between donors and acceptors has been utilized notably in biological and optoelectronic applications such as biological assays and organic light-emitting diodes.[2] For example, effective transportation of the incident energy to emitting acceptors in light-emitting devices can be achieved by close placement of donors to acceptors within their Förster radius.[3] In FRET applications, as an attractive donor in conjunction with conventional fluorescent dyes, quantum dots (QDs) can offer unique optical advantages such as broad absorption with large molar extinction coefficients, narrow symmetric emission spectra, and high optical and chemical stabilities.[4] There have been many reports to develop biological assays with QDs as effective donors, the surface of which was modified for specific interactions with the targeting acceptor species.[5–9] FRET was also studied in the systems where QD donors were incorporated into acceptor-labeled polymers.[10,11] To examine QDs working as donors and acceptors, small and large QDs were independently integrated into layer-by-layer assembled films with fluorophores, in which the FRET between QDs and fluorophores was investigated.[12]

In this communication, we demonstrate the nanoscale arrangement of QD donors and fluorescent dye acceptors in a single-layered film of diblock copolymer micelles to control the FRET. In the film, fluorescent dyes were effectively incorporated into the cores of the micelles, whereas QDs were arranged around their periphery. With large micelles, the dominant emission of QDs was observed because the FRET between QDs and dyes was effectively prohibited due to the fact that the size of the micellar coronas was larger than the Förster radius of QD donors and dye acceptors. By employing micelles with smaller coronas, however, the FRET from QDs to dyes was enabled, resulting in decreased emission of QD donors and increased emission of dye acceptors.

Polystyrene−poly(4-vinylpyridine) (PS-PVP) diblock copolymers spontaneously assemble into spherical micelles consisting of a soluble PS corona and an insoluble PVP core in toluene, which is a selective solvent for PS blocks.[14–17] We employed three copolymers of PS(93)-PVP(33), PS(48)-PVP(21), and PS(32)-PVP(13) (Polymer Source Inc.), for which the polydispersity indices were 1.13, 1.14, and 1.08, respectively. The values in the parentheses next to each block are the number average molecular weights of the blocks in kg/mol. To yield a micellar solution (typically 0.5 wt %), PS-PVP copolymers were dissolved in toluene at 70 °C for 3 h and then cooled down to room temperature. From micellar solutions of PS-PVP copolymers with various molecular weights, single-layered films of micelles were produced by spin-coating (typically 2000 rpm, 60 s) on a quartz plate or a freshly cleaved mica substrate. For transmission electron microscopy (TEM), the film coated on the mica substrate was floated on water and transferred onto a carbon-coated grid. TEM images of micellar films are shown in Figure 1.

PVP cores were selectively stained with I_2 and appeared as dark spheres with a pseudohexagonal arrangement in a bright PS matrix. In the single layer of PS(93)-PVP(33) micelles (Figure 1a), the average diameter of the PVP core and the average center-to-center distance between micelles were 35 nm (±7.7 nm, 22%) and 69 nm, respectively. We can control these values effectively by adjusting the molecular weights of PS-PVP copolymers.[15,16] In Figure 1b,c, the average core diameters and center-to-center distances were

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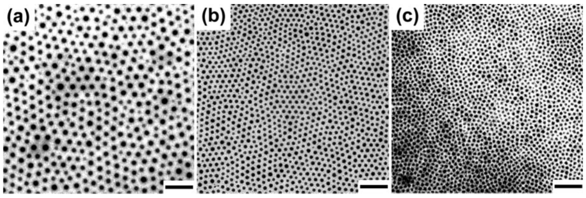

Figure 1. TEM images of single-layered films of PS-PVP micelles: (a) PS(93)-PVP(33); (b) PS(48)-PVP(21); and (c) PS(32)-PVP(13). PVP cores were stained with I_2. The scale bars are 200 nm.

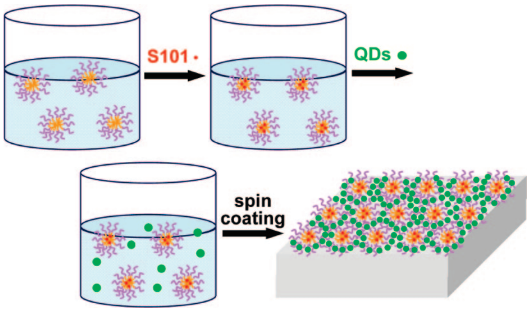

Figure 2. Schematic of the fabrication of a single-layered film of PS-PVP micelles containing S101 in the core and QDs in the periphery of micelles.

24 nm (±2.6 nm, 11%) and 40 nm for PS(48)-PVP(21) micelles and 17 nm (±1.7 nm, 10%) and 28 nm for PS(32)-PVP(13) micelles, respectively. As the molecular weight of copolymers was reduced, both core diameter and center-to-center distance decreased.

First, into a single-layered film of PS-PVP micelles, we incorporated QDs of core−shell CdS@ZnS capped with oleic acid/trioctylphosphine (OA/TOP), which were synthesized as described in the literature.[13] The diameter of the QDs was 3.8 nm, and the photoluminescence (PL) spectrum was centered at 548 nm with green emission. These QDs were then added to a PS-PVP micellar solution at room temperature. The concentration of QDs in the micellar solution was fixed at 0.4 wt %. From a mixture solution of PS-PVP micelles and QDs, a single-layered film was spin-coated, in which the micelles were surrounded by QDs. The detailed structure of the single-layered film will be discussed along with Figures 2 and 3. For a spin-coated film of PS-PVP micelles with QDs, both absorption and emission spectra of the film (Supporting Information Figure S1) were almost identical to those of QDs in toluene, implying that the optical characteristics of QDs were retained in the micellar film.

As an acceptor of the FRET from QD donors, we selected sulforhodamine 101 (S101) because its absorption spectrum well overlaps with the emission spectrum of QDs (Supporting Information Figure S1). In addition, S101 can be selectively incorporated into the PVP core of PS-PVP micelles.[17] Essentially S101 dyes are not soluble and remain as powders in toluene without PS-PVP micelles. From a toluene solution of PS-PVP micelles with S101 in the core, we again spin-coated a single-layered film of the micelles. The molar ratio of S101 to vinylpyridine of copolymers was fixed at 0.006, which yielded reasonable PL intensities below the self-quenching concentration. The PL spectrum of the micellar film at 601 nm with red emission (Supporting Information Figure S1) was not much different from that of S101 in ethanol, indicating that the dye molecules were effectively loaded into the solid film with the assistance of the micellar structure. As a donor−acceptor pair of QDs and S101 dyes based on the Förster formalism,[1,6,7] the Förster radius was estimated to be 5.2 nm with spectral overlap (Supporting Information Figure S1) and a donor quantum yield (~0.37) in the micellar film.

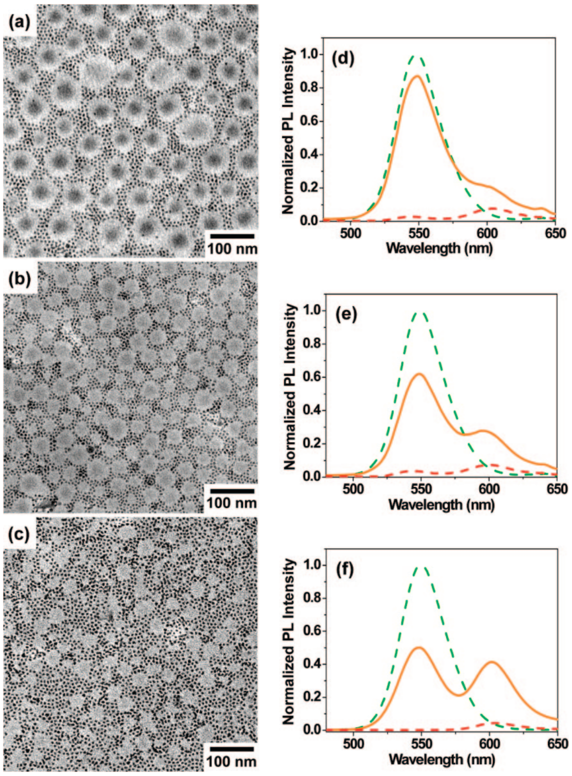

Figure 3. TEM images and PL spectra of single-layered films of PS-PVP micelles containing S101 in the cores and QDs in the periphery of micelles: (a, d) PS(93)-PVP(33); (b, e) PS(48)-PVP(21); and (c, f) PS(32)-PVP(13). PL spectra of PS-PVP micellar films with only QDs in the periphery (green dashed line) and with only S101 in the cores (red dashed line) are also displayed. The excitation wavelength was 360 nm.

We simultaneously incorporated QDs and S101 into a single layer of PS-PVP micelles, as shown in the schematic of Figure 2, to investigate the controllable FRET between QDs and S101 by the micellar nanostructure. S101 was first loaded into the PVP cores of PS-PVP micelles in toluene.[17] Then, QDs were added to the solution, from which a single-layered film was spin-coated. OA/TOP-capped QDs cannot be miscible with polar PVP blocks or aromatic PS blocks. Thus, they can be physically arrested between the micelles due to the fast evaporation of solvent during spin coating. TEM images in Figure 3 clearly show that QDs are distributed around the PS-PVP micelles which contained S101 in their cores. A similar structure of alkanethiol-protected gold nanoparticles surrounding PS-PVP micelles was demonstrated in our previous report.[18]

As shown in Figure 3a, PS-PVP micelles were indirectly visualized as the region surrounded by QDs. In addition, QDs themselves were organized with a regular spacing due to OA/TOP groups on the QD surface. Although PS-PVP micelles

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were not stained with I_2, the central part of the micelles appeared dark due to the thick center of the spherical micelle in plan-view TEM. The dark central part in Figure 3a was larger than the core observed in Figure 1a because the stained image of Figure 1a only visualized the PVP core without the PS corona from the micellar structure. In the film shown in Figure 3a, the acceptor S101 dyes were incorporated in the core of the micelles, and the donor QDs were located around them, that is, the acceptor in the center and the donor in the periphery with the PS gap between them. Such an arrangement of donors and acceptors can be considered analogous to a light-harvesting structure for the energy transfer from the peripheral donors to the central acceptors.[19] Moreover, in the micellar structure, the energy transfer between QDs and S101 can be controlled by changing the nanometer-sized PS gap with micelles of different molecular weights.

Figure 3d shows the PL spectrum of a single layer of PS(93)-PVP(33) micelles containing S101 in the cores and QDs in the periphery of the micelles shown in Figure 3a. PL spectra of the micellar films with only QDs in the periphery (green dashed line) and with only S101 in the cores (red dashed line) are displayed together. The excitation wavelength was 360 nm. Strong emissions of QDs centered at 548 nm were observed from the micellar films containing QDs with or without S101. From the micellar film with only S101, however, the emission of S101 was merely noticeable because of the very weak absorption of S101 at the excitation wavelength of 360 nm (Supporting Information Figure S1). In the case of the micellar film containing both QDs and S101 (orange solid line), we still observed the weak emission of S101 around 600 nm with the strong emission of QDs around 550 nm, because the FRET from QDs to S101 did not proceed effectively by the large gap between QDs and S101 as shown in the TEM image of Figure 3a.

To enhance the emission of S101 by the FRET from QDs with the same excitation of 360 nm, the gap between QDs and S101 was controlled with micelles of lower molecular weights of PS-PVP copolymers as shown in Figure 3b,c. Although the arrangement of micelles and QDs was less ordered in the PS(32)-PVP(13) micellar film, the micelles, that is, the region surrounded by QDs, became smaller with the decrease of the molecular weight of copolymers. Thus, QD donors became closer to the core containing S101 acceptors so that the energy transfer proceeded, which was evidenced by the increased emission of S101 and the decreased emission of QDs, as shown in Figure 3e,f. Therefore, the FRET between QDs and S101 was effectively controlled on the micellar nanostructure, in which QD donors and S101 acceptors were located in the periphery and core of the micelles, respectively.

The distance between QDs and S101 in the micellar film can be estimated either by direct measurement from TEM images of Figure 3 or by calculation of the FRET efficiency from the PL spectra of Figure 3. From the TEM images of Figures 1 and 3, the distance between QDs and S101, that is, mainly the PS gap, can be measured by subtracting the core radius (the region stained in Figure 1) from the micellar radius (the region surrounded by QDs in Figure 3). The average distances from the images were 11 nm (±2.4 nm), 6 nm (±0.7 nm), and 5 nm (±0.5 nm) for PS(93)-PVP(33), PS(48)-PVP(21), and PS(32)-PVP(13), respectively. With the Förster formalism,[1,6,7] the distance between QDs and S101 was again estimated by evaluating the decrease of emission of QD donors in the spectra along with the Förster radius (Supporting Information). The distances estimated from the spectra were 6.9 nm, 5.7 nm, and 5.2 nm, for PS(93)-PVP(33), PS(48)-PVP(21), and PS(32)-PVP(13), respectively. These values are in good agreement with those obtained from the images, except in the case of PS(93)-PVP(33) micelles. The discrepancy in the estimated distance could be attributed to a relatively broad size distribution of PS(93)-PVP(33) micelles, as shown in Figures 1a and 3a.

In conclusion, we demonstrated the nanoscale arrangement of QD donors and S101 acceptors in a single-layered film of PS-PVP micelles, which enabled the controlled FRET. S101 dyes were incorporated in the cores of micelles, whereas QDs were arranged in the periphery. With large micelles, the dominant emission of QDs was observed because the FRET between QDs and S101 was effectively prohibited due to the larger size of micellar coronas than the Förster radius. By employing micelles with smaller coronas, however, the FRET from QDs to S101 proceeded, so that the increased emission of S101, as well as the decreased emission of QDs, was observed. Thus, the nanoscale positioning of QD donors and dye acceptors enables an effective control of the energy transfer from QDs to dyes in a single-layered film of diblock copolymer micelles, which can find potential applications in FRET-based sensors and nanodevices.

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Supporting Information Available: Figure S1 and calculation of the distance between QDs and S101 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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