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# Photoluminescence ON/OFF Switching of CdSe/ZnS Core/Shell Quantum Dots Coated with Diarylethene Ligands

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CdSe/ZnS core-shell quantum dots coated with diarylethene ligands were successfully synthesized, and the photoluminescence ON/OFF switching behavior of the quantum dots accompanying with the photochromic reactions of the diarylethene was investigated. The quantum dots exhibited a fast speed of photoluminescence ON/OFF switching even in the low photocyclization conversion ratio of the diarylethene.

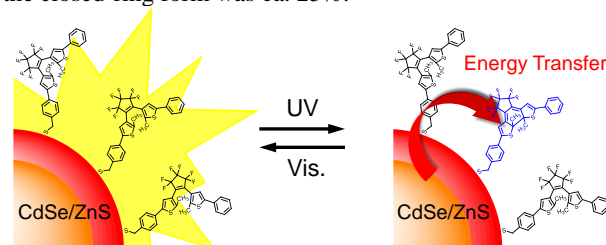
**Keywords:** Diarylethene, Photoluminescence Switching, Quantum Dot, Photochromism

Photoluminescence ON/OFF photoswitchable materials whose intensity changes in response to light have potential applications in sensing materials,<sup>1,2</sup> bioimaging materials for super-resolution microscopy,<sup>3,4</sup> and single-molecule memory materials.<sup>5,6</sup> Green fluorescent protein,<sup>7</sup> carbocyanine dye,<sup>8</sup> and photochromic molecules<sup>9,10</sup> have been widely studied as the materials. Among them, the photoluminescence ON/OFF switchable molecules combining a photoluminescent dye and a photochromic diarylethene are known as one of the most promising materials because of the rapid response, fatigue resistance, and thermal stability of the diarylethene.<sup>9</sup> Diarylethenes undergo thermally irreversible photoisomerization between a colorless open-ring form and a colored closed-ring form upon alternating irradiation with ultraviolet (UV) and visible light. The materials consisting of diarylethenes and photoluminescent dyes exhibit photoluminescence when the diarylethenes are in their open-ring forms. In contrast, when the diarylethenes are converted to their closed-ring forms, the photoluminescence is quenched by an energy transfer from the excited photoluminescent dye to the closed-ring form.

The previous studies mainly used organic molecules as the photoluminescent dye.<sup>11</sup> On the other hand, there are several reports on the photoluminescence switching of quantum dots coated with diarylethenes.<sup>12-14</sup> The quantum dots have excellent properties compared with the organic photoluminescent dyes, such as a narrow, tunable photoluminescent band, a long photoluminescence lifetime, high photostability, and so on. The quantum dots coated with diarylethenes also exhibited the photoluminescence switching behavior accompanying with the photochromic reactions of the diarylethenes, but the photoluminescence of the quantum dots was not completely quenched even in the photostationary state (PSS) although a large number of diarylethenes existed around the single quantum dot.<sup>15</sup> In addition, the materials reported so far have no high repeating

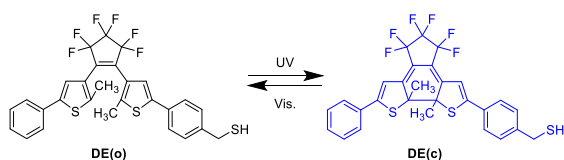
durability. It is not revealed whether this is ascribed to quantum dots or diarylethenes. Moreover, the high contrast of photoluminescence ON/OFF is required for the applications.

Here, to accomplish the efficient photoluminescence ON/OFF switching upon alternating irradiation with UV and visible light, we have synthesized a novel diarylethene ligand and fabricated the quantum dot coated with the diarylethene ligands (QD-DE), as shown in Scheme 1. We have succeeded in fabricating QD-DE that exhibits reversible photoluminescence ON/OFF switching efficiently. The photoluminescence was completely quenched when the photocyclization conversion ratio from the open-ring form to the closed-ring form was ca. 25%.



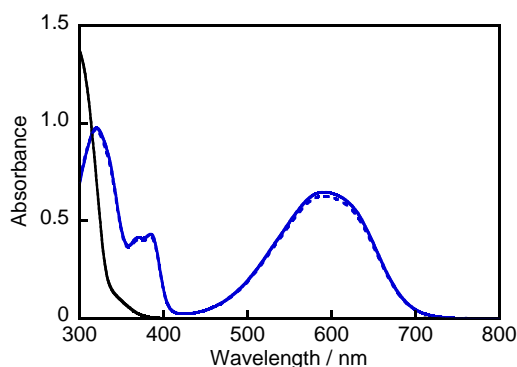
**Scheme 1.** Schematic illustration of photoluminescence ON/OFF switchable quantum dot coated with diarylethene ligands.

First, we designed the molecular structure of the diarylethene ligand. In previous reports on quantum dots combining diarylethenes, the distance between the quantum dot and the diarylethene was too long to occur an energy transfer from the excited quantum dot to the diarylethene closed-ring form with high efficiency.<sup>12-14</sup> This may be the reason why the photoluminescence was not completely quenched even in the PSS. On the other hand, a quantum dot combined with pyridine at the end of diarylethene did not show high ON/OFF contrast.<sup>15</sup> It may be ascribed to a charge transfer through  $\pi$ -conjugation. Therefore, it is necessary to connect quantum dot and diarylethene through a short linker to completely quench the photoluminescence. In addition, quantum dots and diarylethenes are required to be bound without through  $\pi$ -conjugation. From the reasons mentioned here, we designed a diarylethene ligand (DE(o)) bearing a mercaptomethyl group (Scheme 2). We successfully synthesized DE(o) by reducing 1-(2-methyl-5-(4-thiobenzoylsulfanylmethylphenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene<sup>16</sup> with sodium tetrahydroborate in THF in 91% yield (detailed in Supporting information).



**Scheme 2.** Photochromic reactions of DE(o) and DE(c).

To reveal the photochromic reaction behavior of DE(o), the absorption spectral changes of DE(o) in toluene were investigated, as shown in Figure 1. Upon irradiation with 313 nm light, the absorption band of DE(c) appeared at 591 nm ( $\epsilon = 16300 \text{ M}^{-1} \text{ cm}^{-1}$ ). The absorption spectrum returned to the initial one upon irradiation with visible light ( $> 500 \text{ nm}$ ). Thus, DE(o) underwent reversible photochromic reactions between the open-ring isomer and the closed-ring isomer upon alternating irradiation with UV and visible light. The photocyclization conversion ratio from DE(o) to DE(c) was determined to be 97% upon irradiation with 313 nm light. To avoid the absorption of toluene at 313 nm, the photocyclization quantum yield ( $\Phi_{c \rightarrow o}$ ) was measured in *n*-hexane and THF, and was determined to be 0.60 and 0.58, respectively (Table S1). The photocycloreversion quantum yield ( $\Phi_{o \rightarrow c}$ ) was also measured in *n*-hexane and THF, and was determined to be 0.017 and 0.016 upon irradiation with 22579 and 590 nm, respectively. These are values similar to those of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (DE<sub>ref</sub>).<sup>17</sup> Therefore, it was confirmed that the introduction of a mercaptomethyl group to the diarylethene hardly affected the photochromic performance.



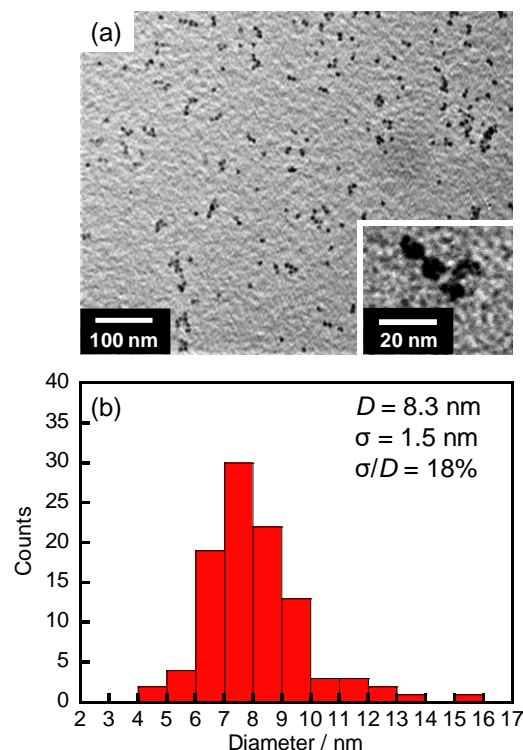
**Figure 1.** Absorption spectra of DE(o) (solid black line), DE(c) (solid blue line), and the solution in the photostationary state upon irradiation at 313 nm (dashed blue line) in toluene.

The absorption and photoluminescence maximum wavelengths of CdSe/ZnS core/shell quantum dot without any diarylethene ligands (QD) in toluene were observed at 542 and 562 nm, respectively (Figure S1). In addition, the photoluminescence quantum yield was 0.48. The particle size was determined to be  $8.0 \pm 1.2 \text{ nm}$  by TEM image (Figure S2).

Next, we have fabricated CdSe/ZnS core-shell quantum dot coated with diarylethene ligands (QD-DE). QD-DE was successfully fabricated by mixing QD ( $[\text{QD}] = 2.36 \times 10^{-7} \text{ M}$ ,

0.5 mL) and DE(o) ( $[\text{DE(o)}] = 2.82 \times 10^{-4} \text{ M}$ , 0.5 mL) in toluene. The QD-DE solution was stirred in the dark for 3 h at room temperature to allow the mercapto group of DE(o) to chemically bond to the quantum dot.<sup>18,19</sup> To the solution was added 2 mL of toluene, and the solution was kept for the next experiments.

Figure 2 shows the TEM image and histograms of the diameter distribution of QD-DE. The particle size was determined to be  $8.3 \pm 1.5 \text{ nm}$ . QD-DE was well-dispersed without agglomeration on the TEM grid, and there was no overlap of QD-DE.

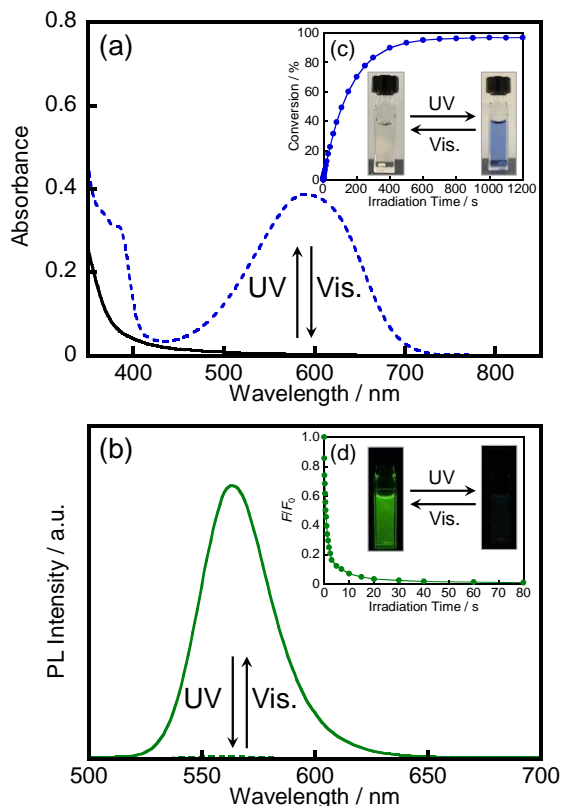


**Figure 2.** (a) TEM image and (b) histograms of diameter distribution of QD-DE.

The photoluminescence switching accompanying with the photochromic reactions of QD-DE was investigated. Figure 3 shows the absorption and photoluminescence spectral changes of QD-DE upon alternating irradiation with UV and visible light. Upon irradiation with 313 nm light, DE(o) underwent the photocyclization reaction, and the absorption band of DE(c) appeared around 591 nm. The absorption band disappeared upon irradiation with visible light. QD-DE exhibited the green photoluminescence at the initial state, as shown in Figure 3b. The photoluminescence intensity drastically decreased accompanying with the photocyclization reaction upon irradiation with 313 nm light. This is ascribed to an energy transfer from the excited QD to DE(c). Upon irradiation with visible light, the photoluminescence intensity returned to the initial one. As expected, the photoluminescence of QD-DE was almost completely quenched in the PSS. Thus, QD-DE exhibited the

1 photoluminescence ON/OFF switching upon alternating  
 2 irradiation with UV and visible light.

3



4 **Figure 3.** (a) Absorption spectra and (b) photoluminescence  
 5 of QD-DE in toluene: open-ring form (solid line) and 80 s  
 6 upon irradiation with 313 nm light (dashed line). (c)  
 7 Photocyclization conversion ratio and (d) normalized  
 8 photoluminescence intensity of QD-DE relative to irradiation  
 9 time upon irradiation at 313 nm (light intensity: 0.28 mW  
 10 cm<sup>-2</sup>). The photoluminescence spectra were recorded upon  
 11 excitation at 410 nm.

12

13  
 14 To confirm that DE(o) unconnected to QD does not  
 15 quench the photoluminescence of QD-DE in solution, the  
 16 change in the photoluminescence intensity upon irradiation  
 17 with 313 nm light to the toluene solution containing QD and  
 18 DE<sub>ref</sub> was monitored (Figure S3). The photoluminescence  
 19 intensity slightly decreased upon irradiation with 313 nm  
 20 light. To clarify whether this decrease is due to the energy  
 21 transfer from excited QD to the diarylethene closed-ring form  
 22 or due to the degradation of QD, the durability of QD was  
 23 examined (Figure S4). The photoluminescence intensity of  
 24 QD without any diarylethene also decreased as well as in the  
 25 previous experiment. Therefore, the slight decrease in the  
 26 photoluminescence intensity is not ascribed to diarylethene  
 27 unconnected to QD. Diarylethene unconnected to QD does  
 28 not affect the photoluminescence switching behavior of QD-  
 29 DE.

30 To estimate the coverage number of DE to QD, the  
 31 theoretical fitting reported previously was performed using  
 32 the photoluminescence intensity change against the

33 photocyclization conversion ratio of DE.<sup>20</sup> The theoretical  
 34 formula is as follows;

35

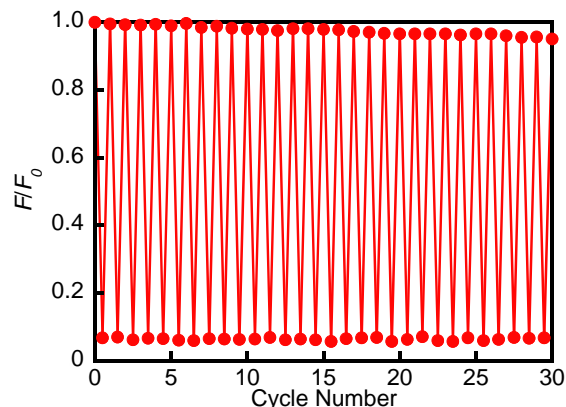
$$F/F_0 = (1 - \alpha)^n \quad (1)$$

37

38 Here,  $F/F_0$  is the relative photoluminescence intensity  
 39 and  $\alpha$  is the photocyclization conversion ratio of DE. Also,  $n$   
 40 is the coverage number of DE to QD. The fitting result is  
 41 shown in Figure S5. When  $n$  is 77, the theoretical curve best  
 42 agreed with the initial experimental points. This result  
 43 suggests that QD was covered with approximately 77  
 44 molecules of DE. In addition, it can be expected that the  
 45 coverage number would be controlled by changing the ratio  
 46 of DE and QD in the feed. Figure S6 shows the  
 47 photoluminescence intensity change relative to the  
 48 photocyclization conversion ratio of DE when the feed ratio  
 49 of DE and QD was changed. As can be seen from Figure S6,  
 50 the photoluminescence intensity change relative to the  
 51 photocyclization conversion ratio of DE is almost the same  
 52 in the feed ratios of [DE]/[QD] = 3400 and 1200 (blue and  
 53 red in Figure S6, respectively). These results suggest that  
 54 QD-DE fabricated in this work has a sufficient amount of DE  
 55 to cover QD.

56 Figure 4 shows repeating cycles of the  
 57 photoluminescence ON/OFF switching of QD-DE upon  
 58 alternating irradiation with UV and visible light, which could  
 59 be repeated 30 times although a decrease in 5 % of the  
 60 photoluminescence intensity for QD-DE was observed after  
 61 30 cycles. From the result of Figure S3, it is considered that  
 62 the decrease in the photoluminescence intensity of QD-DE is  
 63 due to the photodegradation of QD by UV light irradiation.  
 64 We revealed that QD-DE fabricated in this work exhibited  
 65 excellent high repeating durability. Research on  
 66 photoluminescence ON/OFF switching using QD and DE has  
 67 been conducted so far, but there is no report on high repeating  
 68 durability. The application to a super-resolution microscopy  
 69 and so on using such high-durable and high-contrast  
 70 switching materials is expected to expand in the future.

71



72

73 **Figure 4.** Reversible photoluminescence ON/OFF switching  
 74 of QD-DE in toluene upon alternating irradiation with 313  
 75 nm light for 25 s (light intensity: 0.28 mW cm<sup>-2</sup>) and visible  
 76 light for 2 min (> 600 nm)

77

1 In conclusion, we have fabricated CdSe/ZnS core/shell  
2 quantum dots coated with diarylethene ligands (QD-DE).  
3 QD-DE exhibited the reversible photoluminescence  
4 switching accompanying with the photochromic reactions of  
5 the diarylethene upon alternating irradiation with UV and  
6 visible light. In addition, the photoluminescence of QD-DE  
7 was almost completely quenched when the photocyclization  
8 conversion ratio was ca. 25%. Also, QD-DE exhibited the  
9 excellent repeating durability of the photoluminescence  
10 ON/OFF switching. As a result, we accomplished efficient  
11 photoluminescence ON/OFF switching using QD-DE. This  
12 work can be useful for molecular design of  
13 photoluminescence ON/OFF switchable materials.  
14

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21

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## Graphical Abstract

## Textual Information

A brief abstract

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