

Supporting Information for

**Photoluminescence On/Off Switching of a
Single Colloidal Quantum Dot Using
Photochromic Diarylethene**

Nanoka Yano¹, Mitsuaki Yamauchi¹, Daichi Kitagawa², Seiya Kobatake², and Sadahiro

Masuo^{1}*

¹Department of Applied Chemistry for Environment, Kwansei Gakuin University, 2-1

Gakuen, Sanda, Hyogo 669-1337, Japan.

²Department of Applied Chemistry, Graduate School of Engineering, Osaka City

University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan.

1. Synthesis of CdSe/ZnS QDs

Chemicals: Cadmium oxide (CdO, 99.99%), trioctylphosphine oxide (TOPO), hexadecylamine (HDA, 95%), tetradecylphosphonic acid (TDPA, 97%), selenium (Se), 1-octadecene (90%), hexane, EtOH, acetone, zinc oxide (ZnO, 99%), sulfur (S, 98%), oleic acid (90%), and oleylamine (70%).

Synthesis of CdSe core QD¹⁻²: TOPO (3.0 g, 8.0 mmol), HDA (2.0 g, 8.0 mmol), TDPA (0.28 g, 1 mmol), and CdO (64 mg, 0.5 mmol) were loaded into a 100 mL three-necked flask. The mixture was heated to 100 °C, degassed at temperature under vacuum for 20 min, heated to 300 °C under an argon atmosphere and stirred for 60 min. When the CdO dissolved to create an optically clear solution, the temperature was adjusted to 270 °C. In another 50 mL three-necked flask, Se (32 mg, 0.4 mmol) and 2 mL of 1-octadecene were mixed and degassed at 20 °C under vacuum for 30 min and then placed under Ar. 2 mL of the Se suspension was swiftly injected into the prepared 100 mL three-necked flask loaded with the clear Cd solution at 270 °C. After reacting for 1 min at 250 °C under an Ar atmosphere, 5 mL of hexane was added to the mixture to quench the reaction. The resulting suspension was separated by centrifugation (5000 rpm, 5 min, 20 °C) to remove aggregated QDs and insoluble impurities. EtOH was added to the supernatant until the

homogeneous solution became a suspension, and the suspension was separated by centrifugation (5000 rpm, 5 min, 20 °C) to obtain size-separated QDs as precipitates. The QDs were redispersed in CHCl_3 (for spectrochemical analysis) and stored at 5-10 °C. The diameter of the synthesized CdSe QD was estimated to be 3.2 ± 0.2 nm from transmission electron microscope (TEM) image shown in Figure S1(b).

Synthesis of CdSe/ZnS core/shell QD³: Precursor solutions of Zn and S were prepared as follows. The precursor solution of Zn was prepared by mixing ZnO (16 mg, 0.20 mmol) in oleic acid (2 mL) and 1-octadecene (4 mL) at 190 °C under an Ar atmosphere for 60 min to create an optically clear Zn-oleate solution. The precursor solution of S was prepared by mixing S (6.4 mg, 0.20 mmol) in 1-octadecene (3 mL) at 100 °C under an Ar atmosphere for 10 min to create an optically clear S solution. These mixing processes were carried out after degassing the solutions at 100 °C under reduced pressure for 10 min. To the 100 mL three-necked flask, CHCl_3 solution of CdSe core QDs with 3.2 nm in diameter (1 mL, 0.30 μmol), oleylamine (1 mL) and 1-octadecene (4 mL) were loaded and degassed under reduced pressure at 100 °C for 30 min, and then, the mixture was blanketed with Ar. After the temperature was increased to 245 °C, the first injection of the Zn precursor solution (3 mL) was carried out. After 5 min, the S precursor solution (1.5 mL) was injected. The Zn and S precursor solutions were then successively injected

at 5 min intervals. After the reaction, the mixture was cooled to room temperature, and EtOH was added to the suspension, which was separated by centrifugation (5000 rpm, 5 min, 20 °C). The resulting precipitate was dissolved in CHCl₃ and reprecipitated with acetone, followed by separation by centrifugation (5000 rpm, 5 min, 20 °C) to obtain size-separated QDs as precipitates. The QDs were redispersed in CHCl₃ (for spectrochemical analysis) and stored at 5-10 °C. The diameter of the synthesized CdSe QD was estimated to be 4.7 ± 0.2 nm from TEM image shown in Figure S1(c). As the thickness of ZnS monolayer is 0.31 nm, the CdSe core was covered by two monolayers of ZnS shells.

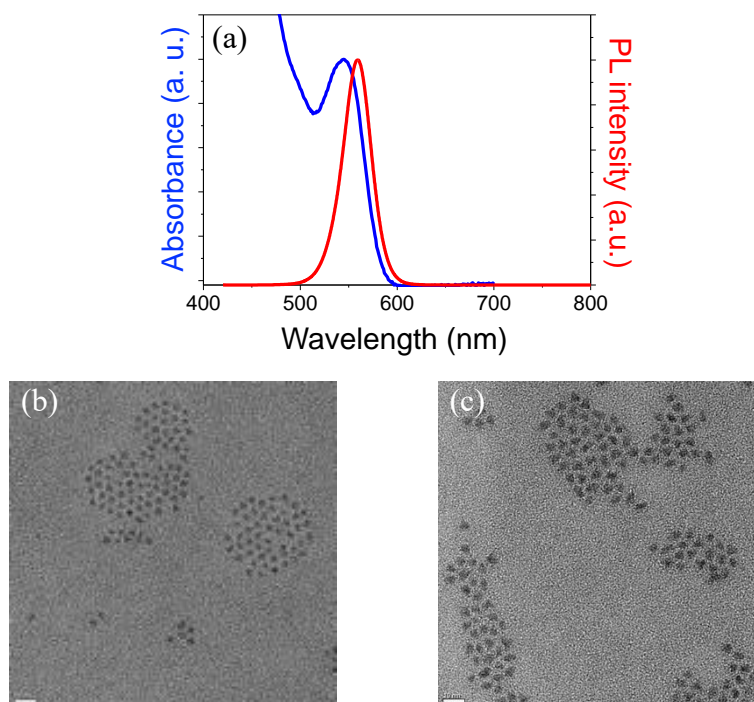


Figure S1. (a) Absorption and PL spectra of the synthesized CdSe/ZnS QD in CHCl₃. (b)(c) TEM images of CdSe QD (b) and CdSe/ZnS core/shell QD (c). The scale bars in the images represent 10 nm.

2. Instrument setup for the PL ON/OFF switching of single QDs

The PL behaviors, i.e., the time trace of PL intensity, PL decay curve, and photon correlation of isolated QDs with the photoisomerization of DAE were measured using a sample-scanning inverted confocal microscope (Olympus, IX-71) in combination with a ps-pulsed laser excitation at 405 nm (10.0 MHz, 90 ps full width at half maximum; PicoQuant). The laser beam was converted to circularly polarized beam by passing a Gran-Thomson polarizer and a $\lambda/4$ wave plate. The laser beam was introduced to the inverted microscope and reflected by a dichroic mirror (Semrock, Di01-R405) in the microscope. Then, the laser beam was focused to a diffraction-limited spot on the sample by an objective lens (Olympus, 100 \times , NA 1.4) and irradiated to the isolated single NC. The PL emission photons from the single NC were collected by the same objective lens and passed through a confocal pinhole (100 μm) with a long-pass (Semrock, LP02-442RU) to remove the excitation laser. Subsequently, half of the photons were detected by a spectrometer (Acton Research Corporation, SpectraPro2358) equipped with a cooled CCD camera (Princeton Instruments, PIXIS400B). The remaining half of the photons were divided equally by a 50/50 nonpolarizing beam splitter cube into two beam paths and then detected by two avalanche single-photon counting modules (APD: PerkinElmer, SPCM-AQR-14). The signals from both APDs were connected to the router of a time-

correlated single-photon counting (TCSPC) PC board (Becker & Hickl, SPC630) to measure the PL lifetime and to collect data for the photon correlation histogram. The signal from one of the two APDs was delayed using a delay generator (Stanford Research, DG535) to compensate for the dead time of the TCSPC board. Time-resolved data were acquired using a first-in-first-out mode, in which the arrival time after the beginning of the acquisition, the time delay between the start and stop pulses, and the detection channel were registered for each detected PL photon. The data were analyzed using a homemade LabVIEW routine that allowed for the simultaneous measurement of PL intensity trajectory, PL lifetime, and the photon correlation histogram of single NCs. The time-resolution of the lifetime measurement, i.e., the instrumental response function (IRF) of the system, was estimated by the deconvolution of the fluorescence decay curve of erythrosine in water, which has a reported fluorescence lifetime of 87 ps.⁴ The estimated IRF was approximately 0.3 ns.

For the wide-field imaging of isolated QDs with the photoisomerization of DAE, continuous wave laser (405 nm, CrystaLaser) as an excitation light was introduced to the inverted microscope (Olympus, IX-71) and focused onto the sample with 30 μ m in diameter through the objective lens (Olympus, 100 \times , NA 1.4). PL image of isolated QDs

was recorded using EM-CCD camera (Hamamatsu photonics, ImagEM X2) by passing through the long-pass (Semrock, LP02-442RU) to remove the excitation laser.

3. Determination of the UV and Vis irradiation times to observe the photoswitching behavior of single QDs

To induce the photoisomerization of DAE in a PMMA film using LED lamps (UV; 300 nm with $100 \mu\text{W}/\text{cm}^2$ at sample surface, Vis; 630 nm with $150 \text{ mW}/\text{cm}^2$ at sample surface), the suitable irradiation times were determined by observing the absorption spectra of the DAE upon UV and Vis irradiation. The sample was prepared by drop-casting the toluene solution containing DAEs and PMMA (concentration of DAE was corresponding to **Conc. 3** in main text) onto a clean coverslip and dried. Figure S2(a) shows the absorption spectra upon UV irradiation. Before UV irradiation, the open-ring isomer, DAE(o), showed no absorption at the visible range. Upon UV irradiation, the absorption bands at 380 nm and 585 nm appeared by the formation of closed-ring isomer, DAE(c). The change of the absorbance at 585 nm against the UV irradiation time is plotted in Figure S2(b). The absorbance reached the maximum value, i.e., photostationary state (PSS), upon UV irradiation for approximately 20 s. Upon UV irradiation for 10 s, the absorbance reached 88% of that at PSS.

Figure S2(c) shows the absorption spectral change upon Vis irradiation onto the sample after UV irradiation for 60 s. Upon Vis irradiation, the absorption of DAE(c) decreased, which indicated the photoisomerization from DAE(c) to DAE(o). The change of the absorbance at 585 nm against the Vis irradiation time is plotted in Figure S2(d). Although the absorption was decreased to 0.033 upon Vis irradiation for 30 s, the absorbance did not return to 0 even by the longer irradiation. In the absorption spectra shown in Figure S2(c)(inset), the broad spectra with a peak at 550 nm were observed even upon the long-time irradiation, for examples, 50 s, 60 s. The origin of the absorption spectrum is attributed to the byproduct during the photoisomerization from DAE(o) upon UV irradiation.⁵ We observed the decrease of the formation of the by-product by decreasing the UV irradiation time. Since the by-product could be an energy acceptor of QD, short UV irradiation time was better to observe the PL photoswitching behavior of single QDs. Therefore, we selected the UV irradiation time below 10 s. On the other hand, Vis irradiation does not damage to the DAE(c). Thus, we selected the Vis irradiation time for 60 s due to the efficient photoisomerization of DAE(c) to DAE(o).

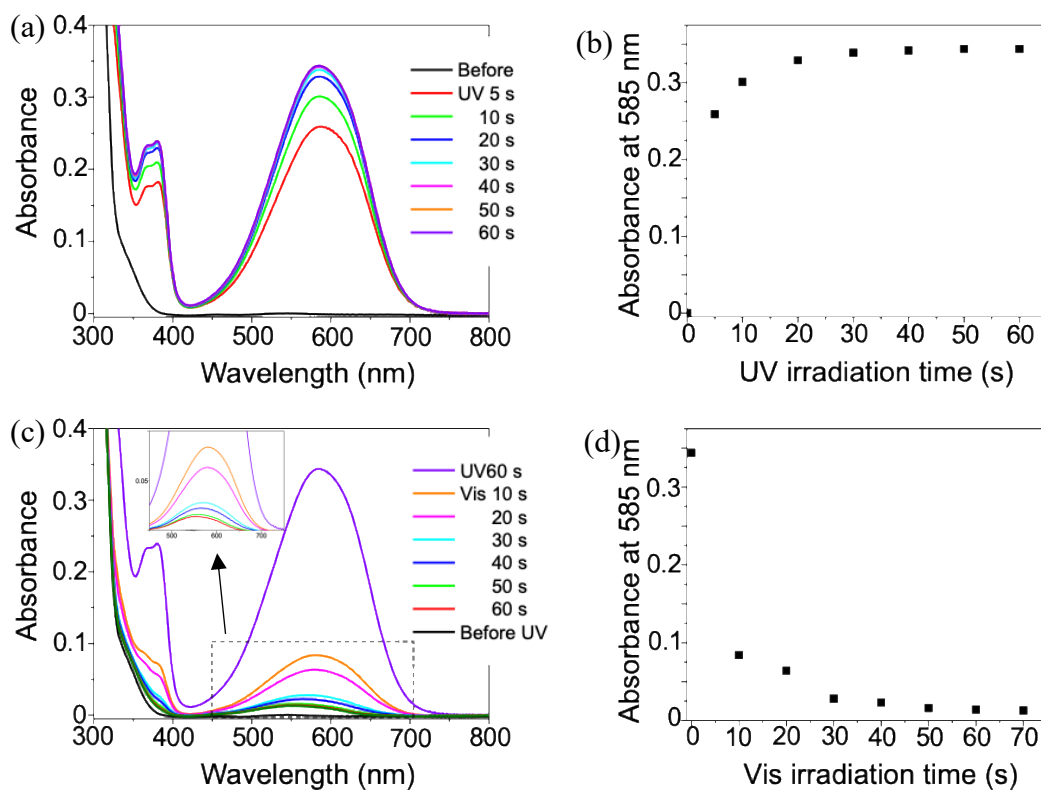


Figure S2. (a) Absorption spectra of DAE in a PMMA film upon UV irradiation. (b) Absorbance at 585 nm vs. UV irradiation time. (c) Absorption spectra of DAE in a PMMA film upon Vis irradiation after UV irradiation for 60 s. A inset is expanded view of the surrounded area. (d) Absorbance at 585 nm vs. UV irradiation time.

4. PL ON/OFF switching behavior of single QDs upon UV and Vis irradiation

The PL switching behavior strongly depended on the QDs. Here, representative switching behaviors, i.e., time traces and decay curves, obtained from three single QDs using **Conc.**

2 and **Conc. 3** are shown in Figure S3. The PL lifetimes before UV irradiation (τ_{ini}), after UV irradiation (τ_{UV}), and after Vis irradiation (τ_{Vis}) are shown in the Figures. The FRET efficiency, i.e., shortening of the lifetime upon UV irradiation, and recovery upon Vis irradiation were strongly dependent on the QDs. The obtained PL lifetime from these single QD measurements are summarized in Figure 4 and Table 1 in main text.

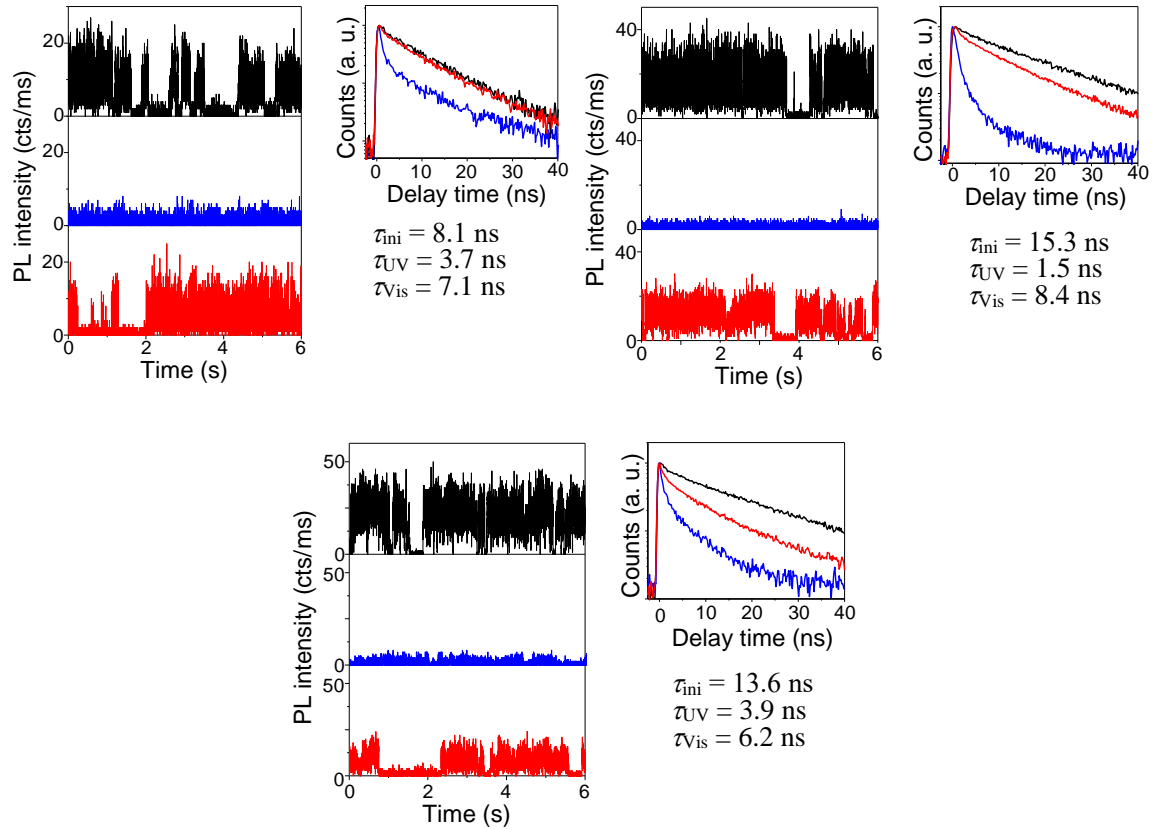


Figure S3. Time traces of the PL intensity and PL decay curves obtained from three single QDs upon UV and Vis irradiation. Black line: before UV irradiation, blue line: after UV irradiation, red line: after Vis irradiation.

Table S1. Average PL lifetimes of single QDs upon different UV irradiation time.

	Average lifetime (ns)		
	Conc.1	Conc.2	Conc.3
Before	–	13.4 ± 2.5	10.3 ± 3.4
UV (5 s)	–	5.1 ± 3.1	2.6 ± 2.1
Vis (60 s)	–	8.5 ± 2.8	5.8 ± 2.4
Before	17.0 ± 2.6	12.7 ± 3.9	10.5 ± 2.8
UV (10 s)	9.6 ± 3.3	2.4 ± 1.2	2.3 ± 1.1
Vis (60 s)	14.5 ± 2.3	6.4 ± 1.7	4.9 ± 1.8

Table S2. Average FRET efficiency and QD-DAE distance upon different UV irradiation time.

	FRET efficiency (%)		QD-DAE distance (nm)	
	UV 5 s	UV 10 s	UV 5 s	UV 10 s
Conc.1	–	44.1 ± 17.3	–	2.32 ± 0.28
Conc.2	61.7 ± 21.6	79.2 ± 14.0	2.07 ± 0.37	1.75 ± 0.25
Conc.3	75.4 ± 14.0	75.0 ± 16.4	1.82 ± 0.24	1.82 ± 0.28

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