Fluorescence On/Off Switching in Nanoparticles Consisting of Two Types of Diarylethenes

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INTRODUCTION

Photoresponsive materials have been widely studied in various fields because the properties of these materials can be modulated with noncontact upon photoradiation. Diarylethenes, which are one of the photochromic compounds, undergo thermally irreversible and fatigue-resistant photochromic reactions between the open-ring form and the closed-ring form upon alternating irradiation with ultraviolet (UV) and visible light. Diarylethene derivatives exhibit reversible fluorescence on/off switching accompanying the photochromic reactions. When diarylethene is in the open-ring form, the fluorophore exhibits fluorescence. On the other hand, when diarylethene is converted to the closed-ring form, the fluorescence is quenched because of an energy transfer from the excited-state fluorophore to the diarylethene closed-ring form. In the case of dyad systems consisting of a diarylethene derivative and a fluorophore, a low on/off contrast is often observed in a solution because the system remains still at a few of diarylethene open-ring forms at the photostationary state (PSS). In addition, high photocyclization conversion upon UV irradiation is required to quench the fluorescence completely because the fluorescence intensity decreases in proportion with the photocyclization conversion of diarylethene. The fluorescence switchable diarylethene systems having the efficient fluorescence on/off switching properties, such as high fluorescence on/off contrast and rapid switching speed, are desirable for applications in sensing materials, biomaterials for superresolution microscopy, bioimaging materials for single-molecule memory materials.

Recently, Fukaminato, Méthivier, and co-workers achieved extremely rapid and high fluorescence on/off contrast with full reversibility and high fatigue resistance using nanoparticles consisting of a diarylethene linked to a benzothiadiazole derivative. In the nanoparticles, a large number of the excited-state fluorophores are quenched by a single diarylethene closed-ring form because of the close intermolecular distance in high density. As a result, the fluorescence intensity dramatically decreased even in low photocyclization conversion of diarylethenes, which resulted in highly efficient fluorescence on/off switching properties. Although highly efficient fluorescence on/off switchable systems consisting of diarylethenes and fluorophores, such as dyad, polymers, silica nano-
particles, organic nanoparticles have been reported, a complicated multistep synthesis is required to construct the fluorescence switchable systems. If a more convenient system with highly efficient fluorescence on/off switching properties can be constructed, it will lead to the development of the fluorescence on/off switchable system and great contribution to the applications as described above.

Here, we have focused on nanoparticles consisting of two types of diarylethenes, 1,2-bis(3-methyl-5-phenyl-2-thienyl)-perfluorocyclopentene (1a), and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (2a), as shown in Scheme 1.

Diarylene 1a undergoes reversible photochromic reactions in n-hexane and exhibits blue fluorescence in the open-ring form with a fluorescence quantum yield ($\Phi_f$) of 0.017. The closed-ring form (1b) exhibits no fluorescence. On the other hand, crystals consisting of diarylene 1a exhibit strong fluorescence. Crystal 1a has two polymorphic forms (crystals 1a-α and 1a-β), which exhibit orange and yellow fluorescence ($\Phi_f = 0.52$ and 0.50), respectively. In addition, the open-ring form of crystal which is produced by the photochemical ring-opening reaction in the crystal of 1b exhibits green fluorescence ($\Phi_f = 0.15$).

In this work, first, the photochromic and fluorescence properties of single-component nanoparticles consisting of 1a, 1b, 2a, or 2b (NP1a, NP1b, NP2a, or NP2b) were investigated to reveal the optical properties of 1 and 2 in the nanoparticles. Next, double-component nanoparticles consisting of 1a, 1b, 2a, and 2b (NP1a/2a, NP1b/2a, NP1a/2b, and NP1b/2b) were fabricated to investigate the fluorescence on/off switching properties. The dependence of the fluorescence on/off switching properties of the nanoparticles on Förster distance and molar fraction was revealed.

### RESULTS AND DISCUSSION

**Photochromic and Fluorescence Properties of Nanoparticles Consisting of Diarylene 1.** Single-component nanoparticles of 1a and 1b were successfully fabricated by the reprecipitation method as described in the Experimental Section [dynamic light scattering (DLS) size distributions are shown in Figure S1]. Figure 1 shows the absorption and fluorescence spectra of NP1a and NP1b. The optical properties of NP1a and NP1b are summarized in Table 1, together with those of diarylene 1 in n-hexane and in the crystalline state. The absorption maximum wavelength ($\lambda_{abs}$) for NP1a was
observed at 387 nm, which is almost the same as that of 1a in n-hexane. On the other hand, the fluorescence maximum wavelength ($\lambda_{\text{fl}}$) for NP1a was observed at 596 nm, which was shifted toward longer wavelength than that of 1a in n-hexane ($\lambda_{\text{fl}} = 480$ nm). In addition, the fluorescence quantum yield ($\Phi_f$) of NP1a was determined to be 0.20. This value was much larger than that of 1a in n-hexane ($\Phi_f = 0.017$)\textsuperscript{34}. Moreover, NP1a did not undergo photocyclization reaction from the open-ring form to the closed-ring form upon irradiation with UV light. It was revealed that 1a in the nanoparticle behaves as a fluorophore.

On the other hand, the optical properties of NP1b were significantly different from those of NP1a. NP1b has the absorption band around 450 nm, as shown in Figure 1b. Upon irradiation with visible light (>500 nm), 1b in NP1b exhibited the ring-opening reaction from the closed-ring isomer to the open-ring isomer. The absorption band at 450 nm disappeared, and a sharp band around 400 nm appeared. Here, the open-ring isomer photogenerated from the closed-ring isomer is called 1a′, and the nanoparticle consisting of 1a′ is called NP1b′. NP1b′ did not undergo photocyclization reaction upon irradiation with UV light, as well as NP1a′. At the present work, the reason why 1a does not undergo photocyclization reaction in the nanoparticle state is not clear yet. Although NP1b′ exhibited no fluorescence upon excitation at 365 nm, NP1b′ exhibited green fluorescence, as shown in Figure 1d. $\lambda_{\text{fl}}$ was observed at 544 nm with $\Phi_f$ of 0.05. The fluorescence properties of NP1b′ are clearly different from those of NP1a′.

As mentioned above, crystal 1a has two crystalline polymorphic forms (crystals 1a-α and 1a-β). Crystals 1a-α and 1a-β exhibit the red-shifted strong fluorescence ($\lambda_{\text{fl}} = 601$ nm, $\Phi_f = 0.52$ for crystal 1a-α and $\lambda_{\text{fl}} = 570$ nm, $\Phi_f = 0.50$ for crystal 1a-β)\textsuperscript{35} in comparison with that of 1a in n-hexane ($\lambda_{\text{fl}} = 480$ nm, $\Phi_f = 0.017$)\textsuperscript{34}. In addition, crystal 1a′ exhibited green fluorescence with $\lambda_{\text{fl}} = 491$ nm and $\Phi_f = 0.15$.\textsuperscript{36} However, the fluorescence properties of these crystals are slightly different from those of the nanoparticles. This suggests that the nanoparticles are not in the crystalline state.

To reveal the state of the nanoparticles, powder X-ray diffraction (PXRD) measurement was performed. As shown in Figure S2, PXRD on NP1a and NP1a′ showed only a hollow pattern, which indicates that both NP1a and NP1a′ are in the amorphous state. In the excitation spectrum, NP1a has a small shoulder band in the region of 450–550 nm, whereas such a shoulder band was not observed in NP1a′, as shown in Figure S3. Crystals 1a-α and 1a-β also have the large band in the region of 450–550 nm in the reflection spectra, which is attributed to the aggregates with the intermolecular interaction of 1a.\textsuperscript{35} Therefore, NP1a′ is in the amorphous state containing a small part of the aggregates, whereas NP1a′ is no aggregate in the amorphous state.

Next, the fluorescence lifetimes of NP1a and NP1a′ were compared. Figure S4 shows the fluorescence decay curves of NP1a and NP1a′. Both NP1a and NP1a′ exhibited fluorescence decay with multiple components. The faster component of <1 ns is attributed to the fluorescence of a single molecule. On the other hand, the slower component of 1–5 ns is ascribed to the condensed state.\textsuperscript{38} NP1a′ has a rise component of 0.014 ns. The rise component may be because of an energy transfer from the excited energy in the single molecule to the condensed aggregate state. Thus, the nanoparticles consisting of diarylethene 1a exhibited orange or green fluorescence depending on the fabrication conditions of the nanoparticles.

**Figure 2.** Absorption spectral change of (a) NP1a ($d = 146 ± 37$ nm) and (b) NP1b ($d = 131 ± 27$ nm) in water/THF: the open-ring form (black solid line), the closed-ring form (blue solid line), and the PSS upon irradiation with 313 nm light (blue dashed line).

|      | $\lambda_{\text{ex}}$/nm | $\lambda_{\text{fl}}$/nm | $\Phi_f$ | $\tau_1$/ns | $\tau_2$/ns | $\tau_3$/ns | $\tau_4$/ns |
|------|-------------------------|-------------------------|--------|-------------|-------------|-------------|-------------|
| NP1a | 387                     | 595                     | 0.20   | 0.014 (79%, r$^1$) | 0.55 (6%)$^5$ | 2.4 (10%)$^5$ | 5.5 (5%)$^5$ |
| NP1b | 450                     |                         |        |             |             |             |             |
| NP1a′| 389                     | 544                     | 0.05   | 0.078 (25%)$^5$ | 0.33 (50%)$^5$ | 0.68 (24%)$^5$ | 4.4 (1%)$^5$ |
| 1a in n-hexane | 370$^7$ | 480$^7$ | 0.017$^7$ | 0.14 (93%)$^7$ | 0.42 (7%)$^7$ |             |             |
| 1b in n-hexane | 438$^8$ |             |        |             |             |             |             |
| crystal 1a-α$^5$ | 394, 509 | 601 | 0.52 | 1.9 (11%) | 4.6 (89%) | | |
| crystal 1a-β$^5$ | 398, 505 | 570 | 0.50 | 1.9 (14%) | 4.5 (86%) | | |
| crystal 1a$^5$ | 445 |             |        |             |             |             |             |
| amorphous 1a$^5$ | 407 | 589 | 0.17 | 0.30 (46%) | 0.84 (25%) | 3.1 (22%) | 5.6 (7%) |

$^1$Excited at 365 nm. $^2$Rise component. $^3$Excited at 400 nm and monitored at 600 nm. $^4$Excited at 400 nm and monitored at 540 nm. $^5$Reference 34. $^6$Reference 36. $^7$Reference 35.
(NP2b) upon photoirradiation (DLS size distributions are shown in Figure S5). Upon irradiation with 313 nm light, the colorless dispersion solution of NP2a turned blue, and the new absorption band appeared around 579 nm. The spectral change is ascribed to the photocyclization reaction. Upon irradiation with visible light, the solution color and absorption spectrum returned to the initial state. The photocyclization conversion upon irradiation with 313 nm light was determined to be 87%. The value is unexpectedly high although parallel and antiparallel conformers can coexist in NP2a. Diarylethene nanoparticles fabricated by the reprecipitation method are usually amorphous solids; in some cases, it may crystallize upon irradiation with microwave.24,38,39 To reveal the reason as to why the photocyclization conversion upon irradiation with 313 nm is high, the glass transition temperature of the amorphous solid materials was examined using differential scanning calorimetry (DSC) (Figure S6). DSC trace of 2a in the amorphous solid, which was prepared by melting crystal 2a followed by cooling to room temperature, exhibited a glass transition temperature at 21 °C, which is lower than room temperature (25 °C). Thus, the photocyclization conversion in the nanoparticles is high because the two conformers can interconvert with each other even in the nanoparticles. In addition, NP2b exhibited a similar photorefractive behavior to parallel alternation with UV and visible light. There was no difference in the spectral changes between NP2a and NP2b, which is because the antiparallel conformer can convert to parallel conformer in the nanoparticles, as mentioned above. It was revealed that diarylethene 2 undergoes the reversible photochromic reactions in the nanoparticle upon alternating irradiation with UV and visible light, even if the nanoparticle is fabricated from either of 2a and 2b.

Fluorescence On/Off Switching of Nanoparticles Consisting of Diarylenes 1 and 2. The fluorescence on/off switching accompanying the photochromic reactions of the double-component nanoparticles consisting of 1a, 1b, 2a, and 2b (NP1a/2a, NP1b/2a, NP1a/2b, and NP1b/2b) was investigated. The DLS size distributions of the nanoparticles are shown in Figures S7–S10. We determined the average diameters to be 100–170 nm and estimated the number of the molecules (sum of 1 and 2) per single nanoparticle to be $8.5 \times 10^6$ to $4.2 \times 10^6$ by assuming that the density of the nanoparticles is the same as those of 1 and 2 in the crystalline phase ($\approx 1.4$ g cm$^{-3}$). Figure 3a,b shows the absorption spectra of NP1a/2a and NP1b/2a, respectively, at the same molar fraction of 1 and 2. Two bands were observed around 385 and 285 nm in the initial absorption spectrum of NP1a/2a. The band around 385 nm is mainly attributed to 1a, and the band around 285 nm corresponds to those of 1a and 2a. Upon irradiation with 313 nm light, the absorption band of NP2b occurred around 580 nm. On the other hand, 1a did not undergo photocyclization reaction. The absorption band of 2b disappeared upon irradiation with visible light. Next, in the initial absorption spectrum of NP1b/2a, the absorption band of 1b was observed around 450 nm. Upon irradiation with visible light, the absorption band disappeared and the band of the photo-generated 1a (1a’) appeared. 1a’ in NP1a/2a also did not undergo photocyclization reaction, as well as 1a’ in NP1b/2a upon irradiation with 313 nm light. On the other hand, 2a underwent the photocyclization reaction upon irradiation with 313 nm. The photocyclization conversions of diarylethene 2a upon irradiation with 313 nm light were determined to be 83 and 78% for NP1a/2a and NP1b/2a, respectively.

The photochromic properties of NP1a/2b and NP1b/2b (NP1a/2b) were also investigated, as shown in Figures S11 and S12. They hardly changed in comparison with those of NP1a/2a and NP1b/2a (NP1a/2b). Therefore, it was revealed that the photochromic properties of the double-component nanoparticles can be explained by the summation of those of the single-component nanoparticles.

NP1a/2a and NP1a/2b exhibited orange and green fluorescence as shown in Figure 3c,d, respectively. The origin of the different color fluorescence between NP1a/2a and NP1a/2b is the same as that between NP1a and NP1a’. The fluorescence intensities quickly decreased upon irradiation with 313 nm light, as shown in Figure 4a. The fluorescence was completely quenched at the PSS. This is ascribed to an energy transfer from the excited state 1a (or 1a’) to 2b. Upon irradiation with visible light, the...
fluorescence intensities returned to their initial ones. Therefore, NP$_{1a/2a}$ and NP$_{1b/2a}$ exhibited the fluorescence on/off switching upon alternating irradiation with UV and visible light. There was no significant difference between NP$_{1a/2a}$ and NP$_{1b/2a}$ in the photocyclization reaction rate. On the other hand, the fluorescence on/off switching of NP$_{1a/2a}$ was faster than that of NP$_{1b/2a}$. Figure 4b shows the relative fluorescence intensity ($F/F_0$) relative to the photocyclization conversion of 2a. The $F/F_0$ values for NP$_{1a/2a}$ and NP$_{1b/2a}$ nonlinearly decreased with the increasing photocyclization conversion of 2a. This is due to quenching of the excited state energy of a lot of 1a (or 1a’) by a single 2b in the nanoparticles. The fluorescence for NP$_{1a/2a}$ and NP$_{1b/2a}$ was almost quenched when the photocyclization conversion was around 5 and 15%, respectively, which indicates that the number of 1a quenched by a single 2b in NP$_{1a/2a}$ is larger than that in NP$_{1b/2a}$. This is considered to be ascribed to the difference in Förster distance ($R_0$) between 1a (or 1a’) and 2b in the nanoparticles because the fluorescence on/off switching in this work is based on the Förster resonance energy transfer (FRET) from 1a (or 1a’) to 2b. The $R_0$ value can be described as follows:

$$R_0^6 = \frac{9\Phi_f (\ln 10) \kappa^2}{128\pi^6 n^3 N_A}$$  \hspace{1cm} (1)

where $\Phi_f$ is the fluorescence quantum yield of donor in the absence of the acceptor, $\kappa^2$ is the orientation factor, $N_A$ is the Avogadro constant, and $n$ is the refractive index of the medium. $f$ is an overlap integral and is estimated by using eq 2.

$$J = \int f_D(\lambda) e_A(\lambda) \lambda^4 \, d\lambda$$  \hspace{1cm} (2)

where $\lambda$ is the wavelength of the light, $e_A(\lambda)$ is the molar extinction coefficient of the acceptor, and $f_D(\lambda)$ is the normalized fluorescence spectrum of the donor. The $R_0$ values for NP$_{1a/2a}$ and NP$_{1b/2a}$ were determined to be 4.0 and 3.1 nm, respectively, based on eq 1 using the absorption coefficient of 2b in THF ($\varepsilon_{2b} = 587$ nm, $\varepsilon_{2b} = 17800$ M$^{-1}$ cm$^{-1}$) (Figure S13), the $\Phi_f$ values for NP$_{1a}$ and NP$_{1b}$, $\kappa^2 = 2/3$ of random orientations, and the refractive index of THF. This result indicates that a longer Förster distance results in a larger number of 1a (or 1a’) quenched by a single 2b and the faster fluorescence on/off switching.

Figure 4. (a) Photocyclization conversion and normalized fluorescence intensity excited at 410 nm relative to irradiation time with 313 nm light (0.4 mW cm$^{-2}$) for NP$_{1a/2a}$ (1a/2a = 1:1, $d = 131 \pm 26$ nm) (orange circles) and NP$_{1b/2a}$ (1b/2a = 1:1, $d = 167 \pm 37$ nm) (green circles) in water/THF (97:3). (b) Normalized fluorescence intensity excited at 410 nm relative to the photocyclization conversion for NP$_{1a/2b}$, NP$_{1b/2b}$, NP$_{1a/2a}$, and NP$_{1b/2a}$ in water/THF (97:3).

Figure 5. Reversible fluorescence on/off switching of (a) NP$_{1a/2a}$ (1a/2a = 1:1, $d = 131 \pm 26$ nm) and (b) NP$_{1b/2a}$ (1b/2a = 1:1, $d = 167 \pm 37$ nm) in water/THF (97:3) upon alternating irradiation with 313 nm light (for 30 s, 0.45 mW cm$^{-2}$ (a) and 60 s, 0.48 mW cm$^{-2}$ (b)) and visible light for 3 min (>500 nm).
Figure 5 shows repeating cycles of the fluorescence on/off switching of NP1a/2a and NP1a′/2a upon alternating the irradiation with UV and visible light, which could be repeated 50 times although decreases in 38 and 15% of the fluorescence intensity for NP1a/2a and NP1a′/2a, respectively, were observed after 50 cycles. To reveal the reason as to why the decrease in the fluorescence intensity of NP1a/2a was large in comparison with that of NP1a′/2a, first, we investigate the fluorescence intensity changes of NP1a and NP1a′ upon irradiation with 313 nm light (Figure S14). The fluorescence intensities hardly decreased after irradiation with 313 nm light for 25 min. The result revealed that the reason as to why the fluorescence intensities of NP1a/2a and NP1a′/2a decreased upon repeating cycles is not the degradation of 1a and 1a′. Next, a stability of 2 was investigated. The absorbance around 285 nm for NP1a/2a which is ascribed to 2a, slightly decreased after 50 repeating cycles (Figure S15). In addition, absorbance of 2b around 580 nm also decreased at the PSS. These results indicate that 2 in NP1a/2a is degraded upon repeating cycles of the fluorescence on/off switching. A previous study for fatigue resistance of 2 revealed that a photostable byproduct, which has an absorption maximum wavelength at 547 nm, is produced upon repeating the photocyclization reactions. Therefore, we could not confirm the byproduct in the absorption spectra because the amount of the byproduct produced by repeating the fluorescence on/off switching may be very small. A small amount of byproduct is sufficient to decrease the fluorescence intensity because a large number of the fluorophores are quenched by a single quencher in the nanoparticles. We considered the fact that the small amount of the byproduct quenched the fluorescence of 1a (or 1a′) in the nanoparticles. Furthermore, it is considered that the decrease in the fluorescence intensity of NP1a/2a was large in comparison with that of NP1a′/2a, which is because of the high efficiency of energy transfer from 1a to the byproduct in comparison with that from 1a′ to the byproduct due to the stronger fluorescence of NP1a′/2a in comparison with that of NP1a/2a. The fatigue resistance of the fluorescence on/off switching in this work is low. However, we could provide an important knowledge that it is necessary to select a highly fatigue-resistant diarylethene to improve the fatigue resistance of the fluorescence on/off switching in the aggregated states.

Next, the dependence of the fluorescence on/off switching properties on the molar fraction of 1 and 2 was investigated. Figures S16 and S17 show the absorption and fluorescence spectra of NP1a/2a and NP1b/2a with various molar fractions of 1 and 2. All of the nanoparticles underwent reversible photochromism and exhibited the fluorescence on/off switching upon alternating the irradiation with UV and visible light. The change of the F0/F value relative to the photocyclization conversion decreased with decreasing molar fraction of 2 as shown in Figure 6. In other words, the larger molar fraction of 2 results in the more efficient fluorescence on/off switching properties.

We have tried to quantitatively evaluate the dependence of the fluorescence on/off switching of the double-component nanoparticles on Förster distance and molar fraction. In a previous paper, a simplified model was proposed to quantitatively evaluate the amplified fluorescence on/off switching of the nanoparticles consisting of a diarylethene linked to a benzothiadiazole derivative. This model assumes that the fluorophore is not quenched when all diarylethenes are in their open-ring forms within R0 and completely quenched in all other cases. In the model, the relative fluorescence intensity

\[ \frac{F}{F_0} = (1 - \alpha_n) \]

\[ (F/F_0) \] is consistent with \[ (1 - \alpha_{CF})^n \], where \( \alpha_{CF} \) is the photocyclization conversion of diarylethene and \( n \) is the number of molecules within \( R_0 \). There are two types of molecules, that is, diarylethene-open- and closed-ring forms in the model. On the other hand, in this work, there are three types of molecules, that is, diarylenes 1a (or 1a′), 2a, and 2b at arbitrary ratio in the nanoparticles. Therefore, the model cannot be directly used for the nanoparticles in this work. Here, to quantitatively evaluate the dependence of the fluorescence on/off switching of the nanoparticles on Förster distance and molar fraction, the model was modified as follows

\[ F/F_0 = (1 - \beta \alpha_{CF})^n \]

where \( \beta \) is molar fraction of diarylethene 2 in the nanoparticles and \( (1 - \beta \alpha_{CF}) \) is the probability that a molecule in the nanoparticle is not 2b. The fitted curve based on eq 3 matched the experimental data for NP1a/2a and NP1a′/2b when the \( n \) value was 250, as shown in Figure 4b. Therefore, when the molar fraction of 1 and 2 in NP1a/2a and NP1a′/2b is the same (\( \beta = 0.5 \)), a single 2b quenched around 125 molecules of 1a (\( n \times (1 - \beta) \)) in the initial fluorescence quenching process. On the other hand, the n value was estimated to be 105 for NP1a/2a and NP1a′/2b which is smaller than that in NP1a/2a and NP1a′/2b. Therefore, the fluorescence on/off switching speed of NP1a/2a and NP1a′/2b is faster than that of NP1a′/2a and NP1a′/2b because the number of 1a quenched by a single 2b in NP1a/2a and NP1a′/2b is ca. 2.4 times larger than that in NP1a′/2a and NP1a′/2b because of the longer Förster distance. Therefore, the multicolor fluorescence properties of 1a in the nanoparticles revealed the dependence of the fluorescence on/off switching of the nanoparticles on Förster distance. Here, it was hypothesized that the density of the nanoparticles is the same as that in the crystalline phase of 1 and 2 \((\approx 1.4 \text{ g cm}^{-3})\), and the nanoparticles are evenly space distributed spheres. By using these hypotheses and the \( n \) values, the distances that 2b can quench 1a (or 1a′) were calculated to be 3.3 and 2.5 nm for NP1a/2a (and NP1a′/2b) and NP1a′/2a (and NP1a′/2b), respectively. The values are close to the \( R_0 \) values calculated by the Förster equation. This result indicates that the fluorescence on/off switching of the nanoparticles is mainly based on FRET process from 1a (or 1a′) to 2b although various energy-transfer processes, such as FRET, Dexter-type energy transfer, and energy migration, may contribute to the fluorescence quenching because the distance between the molecules is short enough to cause the energy-transfer processes.

FRET efficiency depends on the distance between a donor and an acceptor. However, we used eq 3 for the fluorescence on/off switching analysis of the nanoparticles because it is
difficult to make the model in consideration with the distance dependence. To determine if it is appropriate to use the model for the analysis, the fluorescence lifetimes of NP$_{1a/2a}$ at various photocyclization conversions were measured (Figure S18). NP$_{1a/2a}$ exhibited fluorescence decay with multiple components as well as NP$_{1a}$ (Table S1). The average fluorescence lifetime ($\tau_{\text{AVE}}$) values, which were calculated from these values according to $\tau_{\text{AVE}} = \Sigma(t_i \times \%)$, decreased with increasing photocyclization conversion. However, the change was much smaller in comparison with that of the fluorescence intensity. This result indicates that 2b almost quenched the fluorescence of 1a within $R_0$ in the nanoparticles and is close to the assumption in the model. Therefore, we concluded that it is available to use the modified model for the fluorescence on/off switching analysis of the nanoparticles.

In addition, the fitting curves calculated by eq 3 could match the all-experimental data of NP$_{1a/2a}$ and NP$_{1a/2b}$ at various molar fractions of 1 and 2 when the $n$ value was constant at 250 and the $\beta$ value was changed, as shown in Figure 6. Therefore, when molar fraction ($\beta$) for 2 was 0.5, 0.17, and 0.091, the number of 1a quenched by a single 2b was 125, 208, and 227, respectively, in the initial fluorescence-quenching process. This number increased with the decreasing molar fraction of 2. This is because the probability that other 2b molecules are present around 2b decreases with the decreasing molar fraction of 2. However, the change of the $F/F_0$ relative value to the photocyclization conversion increased with the increasing molar fraction of 2, as mentioned above. Therefore, a larger number of quencher, that is, 2b, leads to the apparent fluorescence on/off switching properties of the nanoparticles. However, in the case of single molecule in the nanoparticles, the opposite trend was observed. Thus, there is a trade-off relationship between the fluorescence on/off switching properties of the whole nanoparticle solution and the number of 1a quenched by a single 2b in the nanoparticles. As a result, we could quantitatively evaluate the dependence of the fluorescence on/off switching properties of the double-component nanoparticles consisting of 1 and 2 on Förster distance and molar fraction by using the modified model. We consider that 1a can be replaced by other simple fluorophore if the fluorophore is hydrophobic based on the results in this work. This convenient system with highly efficient fluorescence on/off switching properties will lead to the development of the fluorescence on/off switchable system and great contribution to the applications.

**CONCLUSIONS**

We fabricated single- and double-component nanoparticles consisting of diarylenes 1 and/or 2 to develop a convenient system with highly efficient fluorescence on/off switching properties. The nanoparticles consisting of 1a exhibited orange fluorescence with $\Phi_f = 0.20$. On the other hand, the nanoparticles consisting of 1b exhibited no fluorescence, and green fluorescence was observed with $\Phi_f = 0.05$ after irradiation with visible light. It was revealed that the nanoparticles consisting of 1 exhibited multicolor fluorescence depending on the fabrication conditions of the nanoparticles. Moreover, 2 underwent reversible photochromic reactions upon alternating irradiation with UV and visible light in the nanoparticle state. The double-component nanoparticles consisting of 1 and 2 exhibited the fluorescence on/off switching with rapid switching speed and high on/off contrast upon alternating irradiation with UV and visible light. In addition, the fluorescence on/off switching properties of the nanoparticles depended on molar fractions of 1 and 2, which is ascribed to the Förster distance. The longer Förster distance and larger molar fraction of 2 improved the fluorescence on/off switching properties, which was supported by a simplified model. As a result, we accomplished to construct the convenient and highly efficient fluorescence on/off switchable system using the double-component nanoparticles consisting of two types of diarylenes.

**EXPERIMENTAL SECTION**

**General.** $^1$H NMR spectra were recorded on a Bruker AV-300N spectrometer at 300 MHz. Deuterated chloroform (CDCl$_3$) was used as the solvent, and tetramethylsilane as an internal standard. High-performance liquid chromatography (HPLC) was performed using a Hitachi L-7150/L-2400 HPLC system equipped with a Kanto Chemical Mightysil Si 60 column. PXRD profiles were recorded on a Rigaku MiniFlex 600 diffractometer using Cu Kα radiation ($\lambda = 1.54184$ Å). The nanoparticle size was determined by the DLS (Sysmex Zetasiizer Nano ZS) analysis. DSC was performed using a Hitachi DSC7000X instrument. Absorption spectra were measured with a JASCO V-560 absorption spectrophotometer. Photoirradiation in solution was conducted using a 200 W mercury-xenon lamp (MORITEX MUV-202) as a light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin Yvon H10 UV) and glass filters. Fluorescence spectra were measured with a Hitachi F-2700 fluorescence spectrophotometer. Fluorescence quantum yields were determined with a JASCO FP-8300 fluorescence spectrophotometer equipped with a JASCO ILF-835 integrating sphere. All samples in solutions were deaerated by bubbling with argon gas for 5 min before the measurements.

**Fluorescence Lifetime.** Fluorescence lifetimes were measured using a time-correlated single-photon-counting (TCSPC) system. The experimental setup for the TCSPC has been described previously. Briefly, a Ti:sapphire oscillator (Spectra-Physics, Tsunami) was utilized as a pulsed light source. The operation wavelength, pulse width, and repetition rate were set to 800 nm, 70 fs, and 80 MHz, respectively. The fundamentals of the laser were converted to the second harmonics (400 nm) using a type I beta barium borate crystal and used to excite the samples. The repetition rate was reduced down to 8 MHz by using an electro-optic modulator (Conoptics, model 350), and the excitation intensity to the samples was typically 2.2 µW at 8 MHz. The detection of fluorescence at the magic-angle configuration was attained by utilizing a film polarizer and a Babinet-Soleil compensator. The fluorescence was detected using a photomultiplier tube (Hamamatsu Photonics, R3809U-50) equipped with a preamplifier (Hamamatsu Photonics, C5594) and a TCSPC module (PicoQuant, PicoHarp 300). For wavelength selection, a monochromator (Princeton Instruments, Acton 2150) was placed in front of the photomultiplier tube. The sample solutions were set in 1 cm path length of the quartz cells. The typical response time of the system was determined to be 40 ps full width at half maximum by detecting the scattered photons from a colloidal solution.

**Materials.** 1,2-Bis(3-methyl-5-phenyl-2-thienyl)-perfluorocyclopentene (1a) and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (2a) were prepared by the method described previously. The closed-ring isomers of 1a and 2a (1b and 2b) were prepared by irradiation with UV light
of the n-hexane solution and were isolated by HPLC equipped with a silica-gel column using n-hexane as the eluant.

Preparation of Nanoparticles. Nanoparticles were prepared by the precipitation method.43 NP1a or NP1b was prepared as follows: THF solution of 1a or 1b was prepared by dissolving 1a or 1b (1.9 mg) into THF (2.0 mL). The THF solution of 1a or 1b (300 μL) was quickly added to 10 mL of distilled water, followed by vigorous stirring for 30 min. The fabricated solution of NP1a or NP1b was used for the experiments just as it is. Double-component nanoparticles (NP1a/2a or NP1b/2b) were prepared as follows: the THF solution of 2a or 2b was prepared by dissolving 2a or 2b (3.8 mg) into THF (2.0 mL). The THF solution of 2a or 2b (10 μL) was quickly added to 4.0 mL of distilled water, followed by vigorous stirring for 30 min. The fabricated solution of NP1a or NP1b was used for the experiments just as it is.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00238.

PXRD patterns of NP1a and NP1a,i fluorescence spectra and excitation spectra of NP1a and NP1a,i fluorescence decay curve of NP1a and NP1a,i absorption and fluorescence spectra of NP1a/2b, NP1b/2b, NP1a/1a, and additional optical properties (PDF)

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Notes
The authors declare no competing financial interest.

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