Dependence of Fluorescence On/Off Switching Properties of Nanoparticles Consisting of Two Types of Diarylethenes on Förster Distance and Molar Fraction

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Fluorescence switchable diarylethene systems having efficient fluorescence on/off switching properties, such as high fluorescence on/off contrast and rapid switching speed, are desirable for applications in sensing materials, bioimaging materials for super-resolution microscopy, and single-molecule memory materials.[1] Recently, Fukaminato, Métivier, 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.[2] However, a complicated multi-step synthesis is required to construct the fluorescence switchable systems. If more convenient system with highly efficient fluorescence on/off switching properties can be constructed, it will lead to 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 **1a** and **2a**, as shown in Figure 1. **1a** has three polymorphic forms, which exhibit strong orange, yellow and green fluorescence although all crystals do not undergo photocyclization reaction.[3,4] On the other hand, **2a** undergoes the reversible photochromic reactions in solution and the crystalline phase.[1] In this work, double component nanoparticles consisting of **1a** or **1b**, and **2a** (**NP$_{1a/2a}$**, and **NP$_{1b/2a}$**) 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.

NP$_{1a/2a}$ exhibited orange fluorescence with $\Phi_f = 0.20$. On the other hand, **NP$_{1b/2a}$** exhibited no fluorescence and green fluorescence was observed with $\Phi_f = 0.05$ after irradiation with visible light. The fluorescence intensities quickly decreased upon irradiation with 313 nm light. Upon irradiation with visible light, the fluorescence intensities returned to their initial ones. The fluorescence on/off switching of **NP$_{1a/2a}$** was faster than that of **NP$_{1b/2a}$**. Figure 2 shows the relative fluorescence intensity (F/F_0) relative to the photocyclization conversion of **2a**. The fluorescence for **NP$_{1a/2a}$** and **NP$_{1b/2a}$** was almost quenched when the photocyclization conversion became to 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 between **1a** and **2b** in the nanoparticles. In addition, the change of the F/F_0 value relative to the photocyclization conversion decreased with decreasing molar fraction of **2a**.

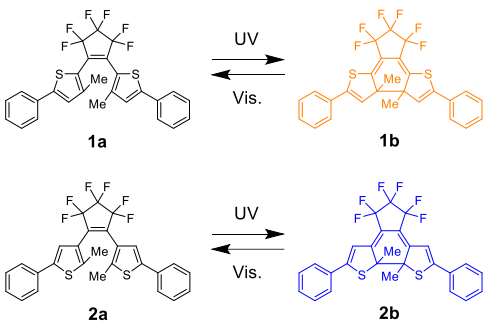

Figure 1. The molecular structures of diarylethenes used in this work.

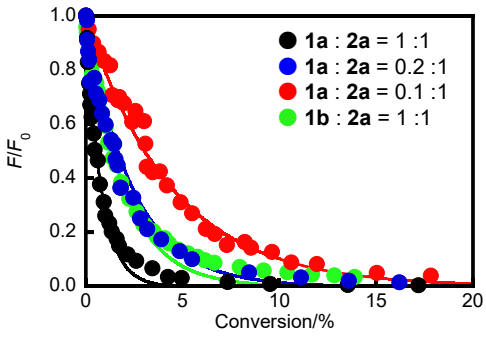

Figure 2. Normalized fluorescence intensity excited at 410 nm (F/F_0) as a function of the photocyclization conversion of nanoparticles consisting diarylethene **1** and **2** of in water/THF.

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[3] D. Kitagawa *et al*., *Dyes Pigm*., **2017**, *139*, 233-238.
[4] T. Nakahama *et al*., *Bull. Chem. Soc. Jpn*. **2018**, *91*, 153-157.