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Efficient "*turn-off*" fluorescence photoswitching in a highly fluorescent diarylethene single crystal

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A highly fluorescent diarylethene single crystal was successfully designed and prepared. The crystal shows the efficient "*turn-off*" fluorescence photoswitching with a full reversibility. This might be originated from the amplified fluorescence quenching due to the intermolecular energy transfer process in densely packed and well-ordered single crystal.

Photoswitchable fluorescent materials have attracted much interest due to the suitability for several applications such as optical memories, displays, securities, inks, and probes for bioimaging including the super-resolution fluorescence imaging.[1-6] Typical organic fluorophores are emissive in dilute solutions, while their fluorescence intensity is usually suppressed in the solid state. Therefore, the application of fluorescent photoswitchable materials was seriously limited in the case of highly-concentrated assembled or solid states. To overcome such problem, the hybridization of a photochromic acceptor unit and a fluorescent donor unit in materials such as nanoparticles (NPs), quantum dots, polymer dots, or up-converting particles have been actively studied recently.[7-13] In addition, very recently, we successfully prepared highly fluorescent photoswitchable NPs purely made from a single component of a photochromic diarylethene derivative linked to a fluorescent benzothiadiazole (BTD) derivative (compound **3**, Fig. 1).[13] In the NPs of **3**, the remarkable efficient fluorescence photoswitching was observed, in which the fluorescence from the NPs was completely quenched by only a few % of the photogenerated closed-ring isomer. This result indicates a large number of the excited-state fluorophores are quenched by a single diarylethene closed-ring isomer because of the short intermolecular distance in a densely packed NP state. As a result, efficient and high-contrast fluorescence on/off switching could be achieved even at the low conversion yield. The powder X-ray diffraction (PXRD) measurement reveals that NPs of **3** are amorphous and the molecular orientation is random in the NPs. For efficient intermolecular energy transfer process, the well-ordered molecular orientation is ideal like as the light-harvesting photosynthetic center in nature.[14] Therefore, fluorescent photochromic diarylethene crystals are promising for the development of further efficient fluorescence photoswitchable materials. Nevertheless, only a few examples of the fluorescent diarylethene single crystal have been reported so far.[15-21] In many cases, efficient photoreactive derivatives show no or weak fluorescence, while highly fluorescent derivatives have no photoreactivity in the crystalline state. In such dilemma, 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene undergoes the reversible photochromic reactions and shows the "*turn-off*" mode fluorescence photoswitching even in the single crystalline state.[15,16] However, the fluorescence on/off contrast is not high due to the low photoconversion yield in the single crystalline state. Although only the "*turn-on*" mode fluorescent diarylethenes having benzo[*b*]thiophene-*S*,*S*-dioxide groups have executed high-contrast fluorescence photoswitching in the single crystalline state,[21] the efficient "*turn-off*" mode fluorescence photoswitchable diarylethene single crystal has never been accomplished up to now. Herein we firstly reported a highly fluorescent diarylethene single crystal with the efficient "*turn-off*" fluorescence photoswitching property.

In this study, we tried to prepare the single crystals of fluorescent diarylethene-BTD dyads (**1** and **2**) (Fig. 1) because dyad systems can be separated photochromic and fluorescence functions by each unit and maintained each performance with a high level. Based on this idea, in order to prepare the single crystal of fluorescent diarylethene-BTD dyads, we attempted to simply remove the bulky substituent (triphenylamine) from compound **3**. It is well known that the triphenylamine group is bulky and useful to prevent the π-π interaction and/or strong

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dipole-dipole interactions, which results in the highly fluorescence in the condensed phase. However, this bulkiness of triphenylamine group is not suitable to prepare the regular packed molecular rearrangement in the crystalline state. Therefore, we tried to reduce the bulkiness by replacing the triphenylamine group to the dimethylamine group (compound **2**) and the methyl group (compound **1**). Although we performed the crystallization of **2** from several solvents, unfortunately, only small precipitates were obtained and their crystallinity was not enough for X-ray crystallographic analysis in all cases. This results indicate that the substituent of fluorescence unit in **2a** is inadequate for the crystallization. On the other hand, single crystal **1a** was obtained as yellow plate upon slow evaporation of **1a** acetone solution at room temperature, which indicates the small methyl group effectively works to form a crystalline packing. Therefore, in this study, we focused on the detailed fluorescence photoswitching property of **1** in the single crystalline state.

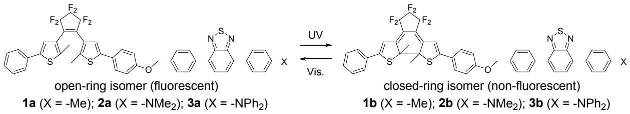

Fig. 1 Molecular structures and photochromism of diarylethene-BTD dyads **1**-**3**.

Diarylethene-BTD dyad **1** shows typical absorption and fluorescence spectral changes along with the photochromic reactions upon alternate irradiation with UV (365 nm) and visible (>450 nm) light in THF solution (Figure S1 in ESI). Before preparation of the single crystal of **1a**, we checked the fluorescence photoswitching property of **1a** in the NP state. The NP was prepared by the conventional reprecipitation method[22] from a THF solution of the closed-ring isomer **1b** isolated by HPLC to avoid the contamination of the photo-unreactive parallel conformation in the open-ring isomer **1a**. The detailed preparation method of NPs is described in ESI.

Reversible absorption spectral changes were observed in a suspension of NPs **1** upon alternate irradiation with 365 nm and >450 nm light, as shown in Fig. 2a and 2b. The conversion yield in NPs **1** under irradiation with 365 nm light was estimated to be 78%, which is almost similar to that in THF solution. In NPs **1a**, very interestingly, the green-coloured fluorescence was observed with relative high fluorescence quantum yield (Φ_f = 0.33) even though the bulky substituent was completely removed from the molecular framework. The inset of Fig. 2a represents the correlation plots of the fluorescence intensity of **1** as a function of the conversion yield upon irradiation with 365 nm light in THF solution as well as in a suspension of NPs. In THF solution, the fluorescence intensity was linearly changed depending on the conversion yield from the open- to the closed-ring isomer with reversible manner. On the other hand, the fluorescence photoswitching behaviour was definitely changed in NPs. The plots in NPs were nonlinearly changed against the conversion yield, in which the fluorescence was completely quenched when 5% of the closed-ring isomer was generated upon irradiation with 365 nm light. Upon irradiation with >450 nm light the fluorescence intensity was recovered perfectly both in THF solution and NPs state. These results are promising for the highly efficient fluorescence photoswitching properties of **1** even in the crystalline phase.

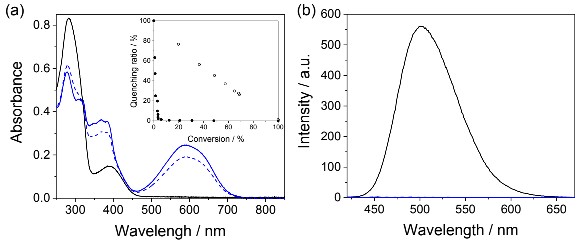

Fig. 2 (a) Absorption and (b) fluorescence spectral changes of a suspension of **1** nanoparticles along with photocyclization and photocycloreversion reactions; the open-ring isomer (solid-black line), the closed-ring isomer (solid-blue line), and PSS under irradiation with 365 nm light (dashed-blue line). Inset of Fig. 2(a): Plots of fluorescence intensity as a function of the conversion yield of **1a** in THF (open-circle) and in a suspension of nanoparticles (closed-circle).

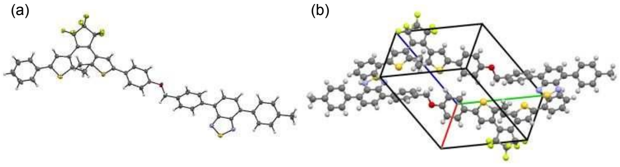

Fig. 3 (a) Molecular structure of **1a** and (b) molecular packing.

Single crystal **1a** was fabricated by recrystallization from dichloromethane/acetone mixture solution. Single crystal X-ray crystallographic analysis was successfully performed for **1a** and the results are summarized in Table S1 (see ESI). Crystal **1a** belongs to the triclinic $P\bar{1}$ space group. The crystal structure of crystal **1a** in an asymmetric unit and the molecular packing diagram are shown in Fig. 3. Crystal **1a** has two molecules in a unit cell and one molecule in the asymmetric unit. In the crystals, **1a** molecules adopt the photoreactive antiparallel conformation and the distance between the reactive carbon atoms is 3.54 Å, which is shorter than 4.2 Å. The conformation and the distance between the reactive carbon atoms fulfil the requirement for diarylethene molecules to undergo the photocyclization reaction in the single crystalline phase.[23] The molecular packing arrangement in the crystal shows **1a** molecules alternately packed each other and the linear distances of the adjacent fluorescence units along the three crystallographic a, b, and c axes are 11.551(2) Å, 12.862(3) Å and 15.172(3) Å, respectively, indicating negligible π-π interactions. This arrangement is especially suitable for the fluorescence property in the crystalline phase and efficient fluorescence quenching from the fluorescent open-ring isomer to the photogenerated closed-ring isomer because the photogenerated quencher (closed-ring isomer) exists close by the fluorescence unit.

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Photochromism of **1** in the single-crystalline phase was examined. Figure 4a shows photographs of photoinduced colour changes of the single crystal upon alternate irradiation with UV and visible light. The single crystal of **1a** is pale-yellow before photoirradiation. Upon irradiation with UV (365 nm) light, the crystal colour turns green, indicating the formation of the blue-coloured closed-ring isomer **1b** by photocyclization reaction in the crystal. This colour was thermally stable in the dark and bleached upon irradiation with visible (λ >450 nm) light. The fluorescence switching associated with the photochromic reactions was examined. Figure 4b shows photographs of fluorescence changes of the single crystal under dark field observation. Initially, the single crystal of **1a** emits strong greenish fluorescence (on state) with maxima at around 488 nm under irradiation with 438 nm light (Fig. S2). Upon irradiation with UV (365 nm) light, the fluorescence of the crystal suddenly disappeared (off state). Upon irradiation with visible (>450 nm) light, the greenish fluorescence appeared again (on state).

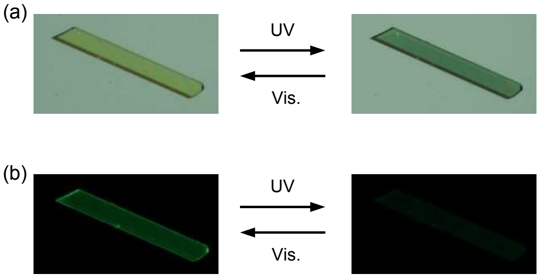

Fig. 4 Photographs of single crystal of **1a**: (a) photoinduced colour changes by irradiation with UV (λ = 365 nm) and visible (λ >450 nm) light and (b) photoinduced fluorescence changes under dark-field observation. The excitation wavelengths for the fluorescence detection were 438 nm.

Figure S2 shows the fluorescence spectral changes of the single crystal **1** along with photocyclization and photocycloreversion reactions. Typically, the photoconversion yield in the single crystalline state does not become high due to the inner-filter effect and the fluorescence on/off contrast is not good as reported previously. Therefore, this result indicates that the efficient fluorescence quenching takes place from the fluorescent open-ring isomer to the small amount of photogenerated closed-ring isomers in the crystal similarly to the nanoparticle. The crystals also exhibited fatigue resistance against repeated switching operations. The on/off fluorescence switching cycles upon alternate irradiation with UV and visible light could be repeated over 10 times without detectable deterioration (Fig. S3 in the ESI†). The fluorescence quantum yield (Φ_f) of single crystal **1a** was measured to be 0.21.

Regular packing and orientation of molecules in single crystals lead to the anisotropy of their optical properties. Dichroism of the single crystal of **1a** was examined with a polarization microscope. Clear polarization dependences for the absorption and fluorescence were observed (see ESI, Fig. S4), which indicates that the fluorescence from the single crystal is highly polarized because of the regular orientation of the molecules in the crystal. The observed anisotropy of the absorption and fluorescence spectra indicates that the photochromic reactions proceed in the crystal lattice and both the open-ring isomer **1a** and the photogenerated closed-ring isomer **1b** are oriented regularly in the crystal.

Fluorescence photoswitching behaviour in the single-crystalline state was further studied under the fluorescence microscope. Figure 5a shows fluorescence images of the single crystal of **1a** with area-selective UV-light irradiation. The excitation wavelength for the fluorescence imaging was 438 nm. Upon irradiation with very weak UV (390 nm) light through an objective lens to a certain area on the surface of the single crystal **1a** for 100 msec, the fluorescence signal of the irradiated area in the single crystal instantly disappeared and the intensity was down to the background level. This high-contrast fluorescence photoswitching was suggested to the efficient fluorescence quenching of **1a** attributed to the intermolecular FRET process in the regularly oriented single-crystals. In such oriented materials, it is anticipated that the long-range intermolecular FRET process takes place efficiently, and therefore a small number of photogenerated closed-ring isomers can quench the fluorescence of a large number of neighboring open-ring isomers. Furthermore, we found an interesting fluorescence recovery behaviour of the fluorescence quenching area under irradiation with 438 nm excitation light that can induce the photocycloreversion reaction. Under irradiation with 438 nm excitation light, the size of dark-area gradually decreased toward center with recovering the fluorescence signal (Fig. 5a and Movie S1). Figure 5c shows the intensity trajectories of points 1-5 marked in the figure. The fluorescence intensity of outside region (points 1 and 5) in the irradiation area quickly recovered to original level after stopping UV light irradiation. On the other hand, the fluorescence intensity of the center (point 3) and the middle regions (points 2 and 4) maintained the dark level for a while even after stopping UV light irradiation and then started to recover the fluorescence intensity. Usually, the fluorescence signal of dark area originated from the generation of non-fluorescent closed-ring isomers recovers uniformly under irradiation with visible light. As an example, the fluorescence photoswitching images of poly(methyl methacrylate) (PMMA) film containing **1a** (4 wt%) is shown in Fig. 5b (see Movie S2). Upon irradiation with UV (390 nm) light through an objective lens to a certain area on the surface of PMMA film containing **1a** for 2 sec, the fluorescence signal of the irradiated area was slightly decreased. However, the fluorescence on/off contrast was quite low compared to the single crystal **1a**. The fluorescence signal in the dark-area recovered uniformly under excitation with 438 nm light, which is common fluorescence recovery behaviour. Fig. 5d also shows the intensity trajectories of points 1-5 displayed in Fig. 5b. The fluorescence intensity of all points quickly recovered to original level after stopping UV light irradiation and no induction period was observed for all points.

The fluorescence recovery behaviour in single crystal **1a** might be explained by the following mechanism. The light

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intensity through an objective lens has Gaussian distribution and such distribution generates small distribution of conversion yield in the irradiation area, where the conversion yield becomes high as the position closes to the center. Such small difference of conversion yield is almost negligible in typical linear fluorescence photoswitching system such as a dye-doped polymer film. However, in the nonlinear system, the fluorescence intensity suddenly and largely changes based on a certain conversion yield. The conversion yield sequentially reaches to the critical point from outside to center in the irradiation area because the conversion yield becomes high with closing to the center part. As a result, the fluorescence recovery behaviour with decreasing the size of dark-area was observed. From these fluorescence photoswitching behaviour, there is no doubt that the efficient nonlinear fluorescence quenching takes place in the single crystal **1a**. Further detailed study of photophysical and photochemical measurements for single crystal **1** are under progress.

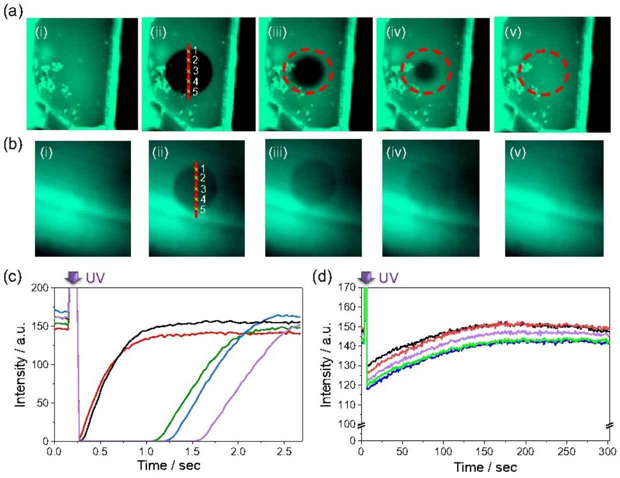

Fig. 5 Fluorescence images under excitation with 438 nm light of (a) single crystal **1a** and (b) PMMA film containing **1a** (4 wt%); (i) before UV (390 nm) irradiation, (ii)-(V) fluorescence recovery under 438 nm excitation light after stopping UV irradiation. (c),(d) Fluorescence intensity trajectories corresponding to points 1-5 marked in (a) and (b), respectively; Point 1; black, Point 2; blue, Point 3; purple, Point 4; green and Point 5; red.

In summary, we successfully designed and prepared a highly fluorescent diarylethene single crystal by removing the bulky group from triphenylamine substituent. Single crystal **1a** shows the high contrast "*turn-off*" fluorescence photoswitching with a full reversibility. This efficient fluorescence photoswitching might be attributed to the contribution of the efficient nonlinear fluorescence photoswitching based on the intermolecular energy transfer process in the densely packed crystalline phase. Such efficient fluorescent photoswitchable crystals find potential applications, such as in memory devices, sensors, electroluminescent displays, and bioimaging.

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Conflicts of interest

There are no conflicts to declare.

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