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Publication Date 11 Jul 2019

Article Type Full Research Paper

Supporting Information File 1 Supporting information.pdf; 189.9 KB

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Photochromic diarylethene with turn-off fluorescent switching property

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Abstract

Background: Diarylethenes are well-known photochromic compounds, which undergo cyclization and cycloreversion reactions between open- and closed-ring isomers. Recently, diarylethene derivatives with photoswitchable fluorescent properties were prepared. They are applicable for imaging and bio-imaging. On the other hand, new system called “excited state intramolecular proton transfer (ESIPT)” is reported. In the system, absorption and emission bands are divided due to the proton transfer, hence it showed strong fluorescence even in the crystalline state. We aimed to construct the photochromic system incorporating the ESIPT mechanism.

Results: A diarylethene incorporating a fluorescent moiety that exhibit excited state intramolecular proton transfer (ESIPT) behavior was prepared. The ESIPT is one of the examples which express the mechanisms of aggregation-induced emission (AIE). This compound emits orange fluorescence with a large Stokes shift derived from ESIPT in aprotic solvents such as THF or hexane, while it exhibits only photochromic reaction in protic solvents such as methanol. In addition, it shows turn-off type fluorescence switching in an aprotic solvent and in crystals. The fluorescence is quenched as content of closed-ring isomers increases upon UV light irradiation.

Conclusions: A diarylethene containing ESIPT functional group was prepared. It showed fluorescent turn-off behavior during photochromism in aprotic solvents as well as crystalline state upon UV light irradiation. Furthermore, it showed AIE in THF/water mixtures with blue-shift of the emission.

Keywords

diarylethene; fluorescent switching; turn-off fluorescence; AIE; ESIPT

Introduction

Diarylethenes are well-known photochromic molecules and are widely applied to molecular switches and systems [1,2]. Recently, the photo-switching of fluorescence signals by using diarylethene switches has attracted much attention because of the potential in various optoelectronic applications [3]. For example, fluorescence switching for molecular level recording [4], multiple-fluorescence for logic circuit [5] as well as biological applications [6] and super-resolution microscopy for bio-imaging

[7,8]. The fluorescence switching in solid state is attracting much attention from both scientific and technological points of view, such as sensors, electroluminescent displays, memory devices [9].

On the other hand, molecular aggregation also affects the intensity of fluorescence [10, 11]. Some material shows fluorescence by aggregation (aggregation-induced emission (AIE)), while the others decay the fluorescence by aggregation (aggregation-caused quenching (ACQ)). The luminogenic materials with AIE have attracted much interest since Tang *et al.* reported the AIE concept [12]. The introduction of photo-switching ability in the system will be interesting for creating new AIE system. In addition, organic photochromic crystals are inherently capable of photo-reversible luminescence switching because the electronic structures of photochromic molecules reversibly change upon photoisomerization [13,14]. However, such fluorescent system in condensed phase emitted fluorescence often absorbed in adjacent molecules, therefore a large Stokes shift is indispensable for such system.

A photoinduced proton transfer through an intramolecular hydrogen bond is termed the excited-state intramolecular proton transfer (ESIPT), which is a remarkably fast process (rate constant $k \approx 1 \times 10^{13}$ s^{-1}) comparable to the internal conversion [15,16]. Emission from the ESIPT state is characterized by a large Stokes' shift (8,000-11,000 cm^{-1}), which enables yellow luminescence by UV-excitation [17,18]. Mutai *et al.* reported an ESIPT luminescence of an imidazo[1,2-a]pyridine derivative, in which remarkable fluorescence was observed and no overlapping from the absorption band due to the large Stokes shift of the fluorescence [19].

Herein, we prepared a diarylethene incorporating the imidazo[1,2-a]pyridine moiety with ESIPT ability and reported the fluorescence switching of the system.

Results and Discussion

The diarylethene **1o** having ESIPT moiety was prepared by coupling reaction of asymmetric diarylethene **3** [20] and 6-bromo-2-(2’-methoxyphenyl)imidazo[1,2-a]pyridine **4** [21] followed by ether cleavage according to Fig. 1.

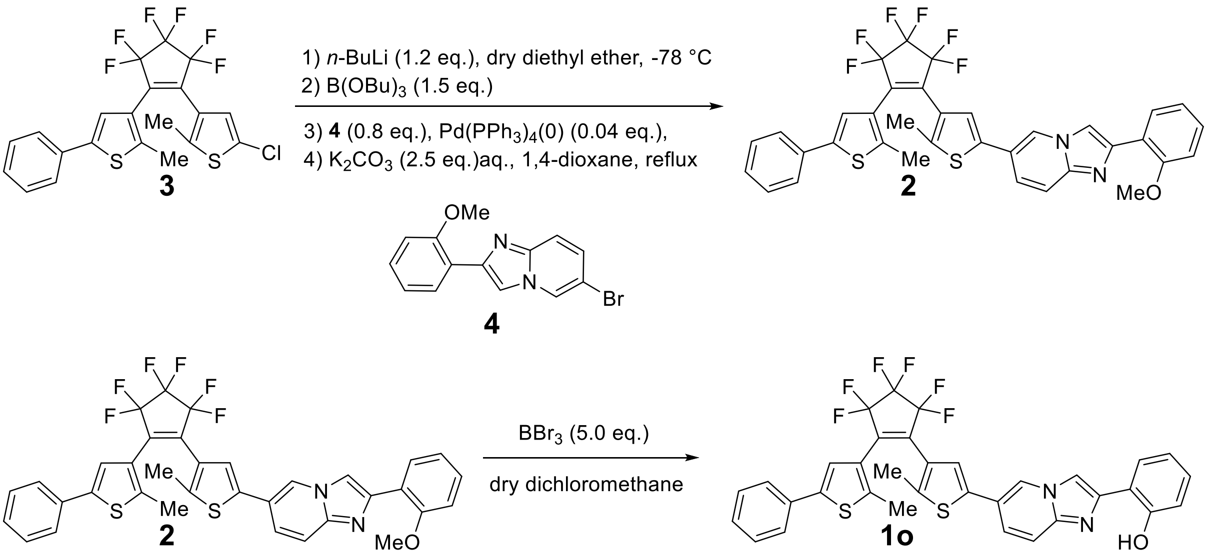

Figure 1: Synthetic procedure for a diarylethene (**1o**).

The photochromic reaction and spectral changes are shown in Figs. 2 and 3. The photochromic absorption spectral changes in THF are shown in Fig. 3. Upon UV light irradiation to the solution of **1o**, the color changed to blue with increasing the absorption band at 587 nm of the closed-ring isomer **1c**, then disappeared the color by visible light irradiation and reproducing the absorption spectra at 285 nm in **1o**. The cyclization and cycloreversion reactions of **1** were measured in THF and methanol. The results were summarized in Table 1.

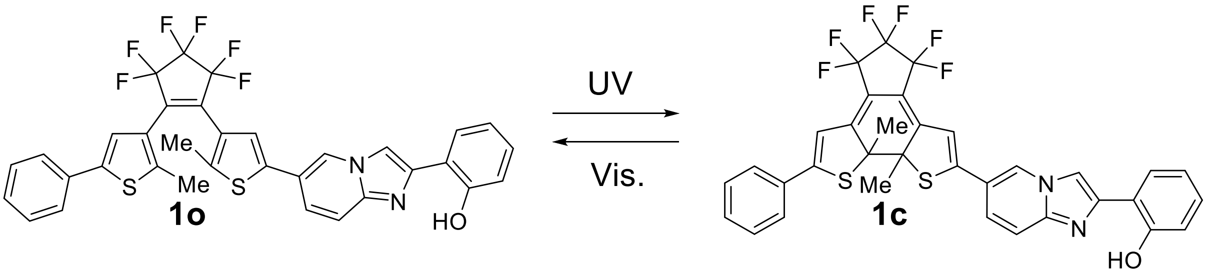

Figure 2: Photochromic reaction of diarylethene **1o** having an ESIPT moiety.

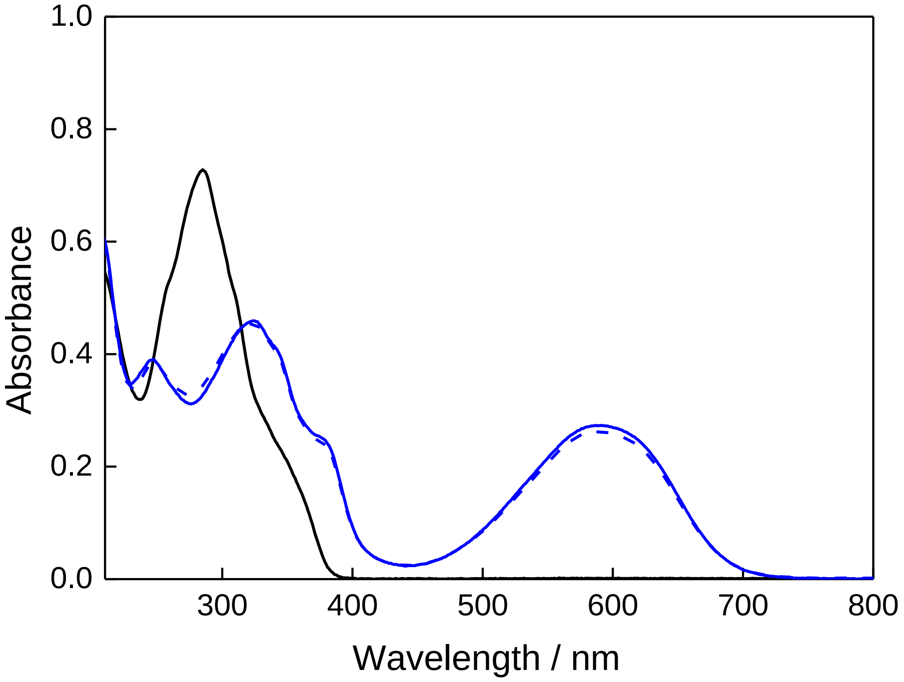

Figure 3: Absorption spectral changes of diarylethene **1o** having an ESIPT moiety in THF (c = 1.3 × 10^{-5} M). Black solid line: **1o**, Blue solid line: **1c**, Blue broken line: photostationary state under irradiation with 313 nm light (**1o**: **1c** = 4.2: 95.8) (irradiation. for 30 s).

The quantum yields of cyclization and cycloreversion reactions of **1o** in THF are obtained to be 0.31 and 6.2 x 10^{-3}, respectively. They are a little bit smaller than those of simple diarylethene switches having thiophenes as aryl groups [22]. It may be due to the connection with an ESIPT moiety. Only slight changes were observed in absorption spectra as well as photochromic quantum yields in two solvents.

Table 1: Photochromic properties of a diarylethene **1** in methanol and THF.

compounds	λ_{max}/nm (ε/10^4 M^{-1} cm^{-1})		$\Phi_{o\to c}$ (313 nm)	$\Phi_{c\to o}$ (577 nm)
	Open-ring isomer	Closed-ring isomer		
1 (in THF)	285 (5.7)	587 (2.1)	0.31	0.0062
1 (in methanol)	283 (5.5)	584 (2.0)	0.34	0.0073

In the protic solvents including methanol, **1o** and **1c** did not emit fluorescence, while only **1o** emitted in aprotic solvent i.e. in hexane orange fluorescence with fluorescence quantum yield of ($\Phi_f = 0.027$). The fluorescent emission spectra of **1o** in several solvents were shown in Fig. 4 and λ_{max} of emission spectra and fluorescence quantum yields in the solvents were summarized in Table 2. Generally, the fluorescence quantum yields decreased with increasing the permittivity of the solvents. No fluorescence was observed for methanol and acetonitrile solutions, indicating the suppression of ESIPT, because the solvents were used without dehydration.

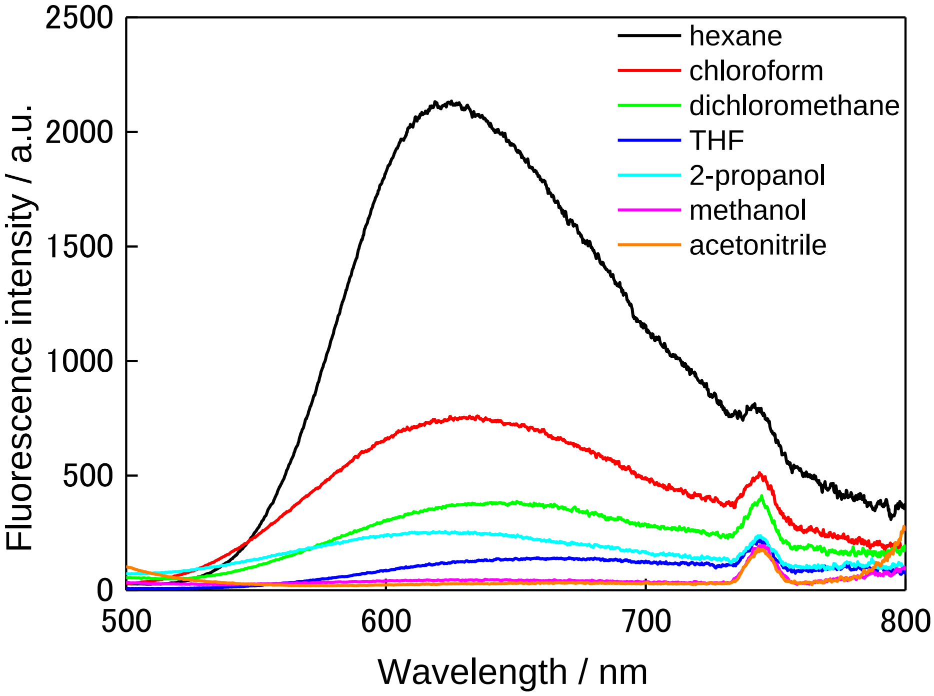

Figure 4: Fluorescent spectra of **1o** in several solvents (λ_{ex} = 370 nm). Hexane (black line), chloroform (red line), dichloromethane (green line), THF (blue line), 2-propanol (pale blue line), acetonitrile (pink line), methanol (orange line).

Table 2: Emission maxima of the fluoresce spectra and the relative fluorescence quantum yields Φ_f in several solvents.

solution	$\lambda_{max}{}^a$ / nm	$\Phi_f{}^a$	Permittivity / F m^{-1}	refractive index [23]
Hexane	625	0.027	2.0	1.3727
Chloroform	635	0.013	4.8	1.4459
THF	670	0.002	7.5	1.4050
Dichloromethane	650	0.006	9.1	1.4242
2-propanol	623	0.004	18	1.3776
Methanol	-	-	33	1.3288
Acetonitrile	-	-	37	1.3442

$^a\lambda_{ex}$ = 370 nm.

The intensity of the fluorescence decreased gradually upon UV light irradiation accompanied with the formation of **1c**, because from the ESIPT moiety to the closed-ring isomer (Figure 5) [24].

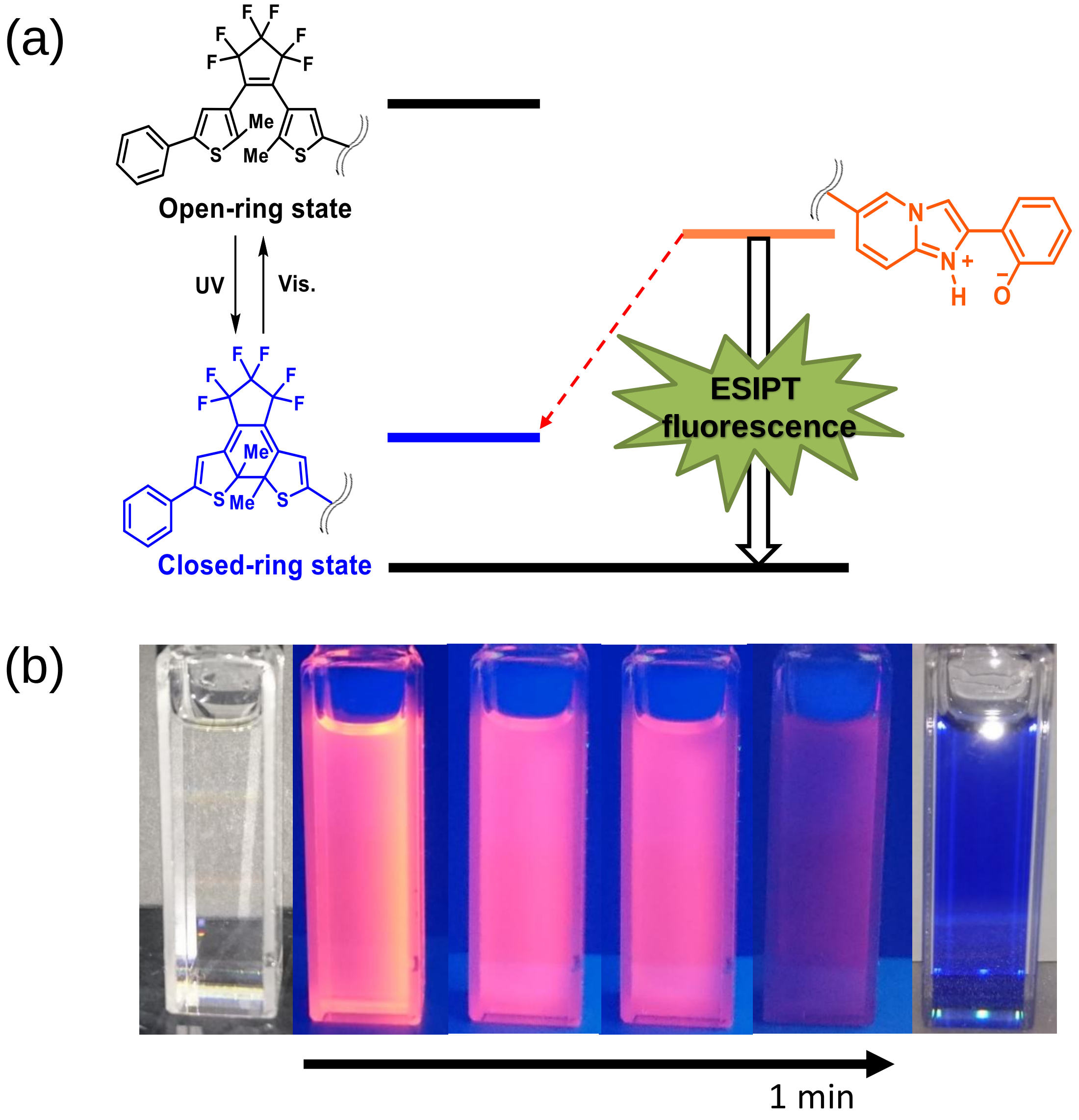

Figure 5: (a) The energy diagram of ESIPT process of **1**. (b) ESIPT fluorescence quenching upon UV light (λ = 313 nm) irradiation of **1o** in THF solution. The fluorescence is quenched by photo-generated closed-ring isomer (**1c**).

The wavelengths of absorption (Table 3) and fluorescence (Table 4) were obtained computationally by using the density functional theory (DFT) and the time-dependent DFT (TDDFT). The excitation wavelengths as well as the emission wavelength qualitatively agrees with the experimental results. It is also interesting to note that we did not obtain the structure with the proton transfer for the ground state. For the optimized structure at the first excited state, **1c** with the proton transfer is much less stable than **1c** without the proton transfer (the energy difference is 11.1 kcal/mol). In contrast, we obtained the structures of **1o** only with the proton transfer.

Table 3: Excitation energies for **1o** and **1c** in THF.

	Excited State	Excitation energies (λ)	Oscillator strength
1o	1	3.38 eV (366 nm)	0.2108
	2	3.48 eV (356 nm)	0.2089
1c	1	1.97 eV (630 nm)	0.6744
	2	2.53 eV (490 nm)	0.0308

Table 4: Emission energies for **1o** and **1c** in THF.

	Excited State	Emission energies (λ)	Oscillator strength
1o	1	1.69 eV (735 nm)	0.0027
	2	2.31 eV (538 nm)	0.3004
1c	1	1.39 eV (887 nm)	0.5519
	2	2.23 eV (555 nm)	0.0471

To the THF solution of **1o**, water was gradually added, and the intensities and color changes of the fluorescence were monitored. By adding the water with 10 vol%, fluorescence dramatically reduced, by the addition of 80 vol%, color of fluorescence changed to orange and the intensity increased. In the mixture of 90 vol% water and 10 vol% THF the fluorescence band was blue-shifted, and the color changed to yellow, and the intensity was enhanced. Such blue shit of ESIPT fluorescence was already reported and it is ascribed to suppression of the stabilization of the excited zwitterionic species through solvent rearrangement and/or further conformational changes of the substrate [19].

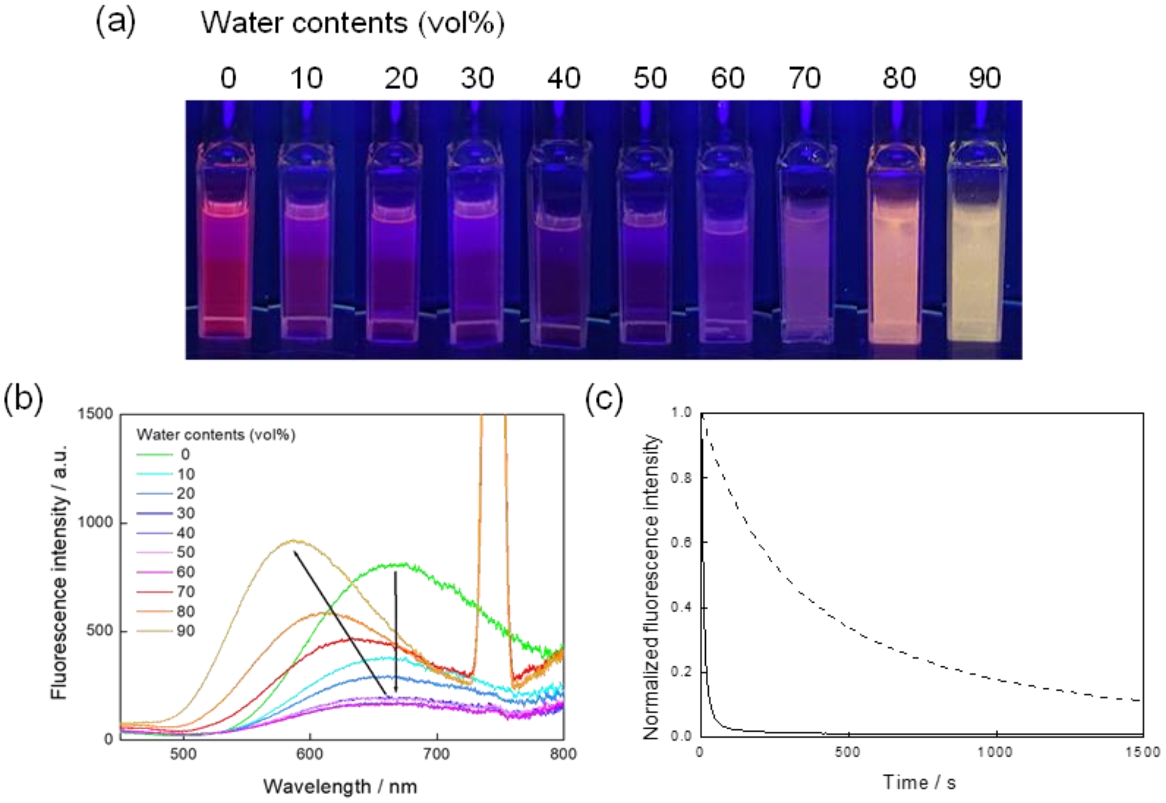

Figure 6: (a) Fluorescence photographs of solutions/suspensions of **1o** (1.2×10^{-4} M) in THF/water mixtures with different water contents under UV light (λ = 365 nm) irradiation. (b) The spectra of **1o** solutions (λ_{ex} = 370 nm). (c) The fluorescence quenching of THF 100 vol% (water 0 vol%) solution at 670 nm (broken line) and that of THF/water = 10: 90 (v/v%) at 585 nm (solid line).

The X-ray analysis data of a single crystal of **1o** was shown in Fig. S1 and Table S1. The distance between two reactive carbon atoms was obtained to be 3.534 Å, which is less than 4.2 Å. It indicates the molecule is photoreactive in crystalline state [25].

In the crystalline state, **1o** emitted green fluorescence (Φ_f = 0.031) as shown in Fig. 7b. The color is more blue-shifted color compared with the mixed solution (THF/water = 10: 90 (v/v%)). The fluorescence also quenched with formation of **1c** upon UV light irradiation, indicating turn-off type fluorescent switch (Fig. 6c, 7e) [26, 27]. The crystal did not show any vapochromism, while a dramatic fluorescent spectral change green to pink were observed when the UV light irradiating crystal **1o** was dropped chloroform (Movie).

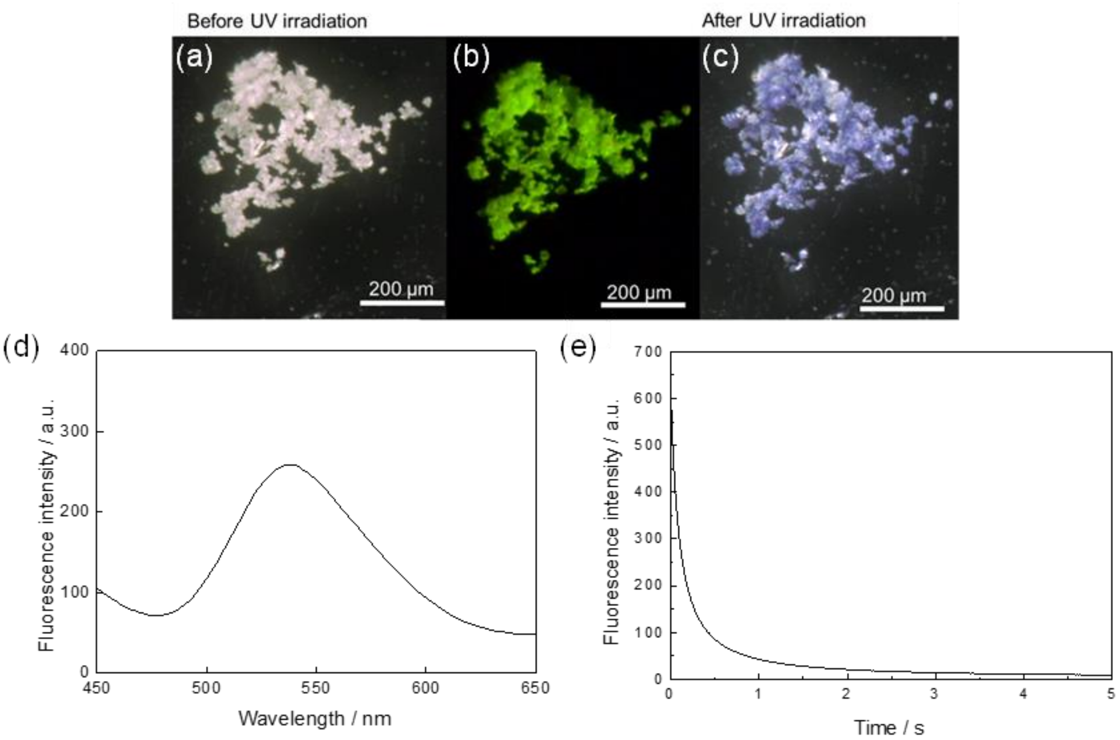

Figure 7: (a) Crystals of **1o** before UV light irradiation, (b) Green fluorescence of **1o** observed under UV light (λ = 365 nm) irradiation, (c) Cycloreversion proceeded to form **1c** with suppression of the fluorescence, (d) Fluorescence spectra of **1o** in crystalline state (λ_{ex} = 370 nm, λ_{max} = 537 nm), (e) The fluorescence quenching of **1o** in crystalline state (λ_{ex} = 370 nm, λ_{em} = 537 nm).

The rate of fluorescence quenching ($\tau_{1/2}$ is less than 0.2 s) in the crystalline state is much faster than those observed in solutions. This is attributed the degree of condensation is much higher in crystalline state. The mechanism of the fast quenching is expected to be related to the amplification of photo-switching of a photochromic organic nanoparticle system as well as the crystalline system reported by Fukaminato [26,27]. The detailed study of the amplification will be carried out in the future.

Conclusion

In summary, we prepared a new diarylethene derivative having ESIPT functional moiety. It shows the pink fluorescence upon UV light irradiation. Prolonged irradiation with UV light, the emission suppressed accompanied with proceeding photocyclization reaction. This is turn-off type fluorescence. The fluorescence was also suppressed in protic and polar solvents because of prohibit of ESIPT. In the THF/water mixed solvents, when the content of water increased to 10-60 vol%, the fluorescence was quenched; however, strong fluorescence and blue-shift of emission band was observed above 80 vol% of water content. This is attributable AIE effect. The effect was much more remarkable in crystalline state. The emission can be switchable by diarylethene moiety. The effect was also observed in the crystal. The crystal of **1o** emits green fluorescence, and the emission was also suppressed by forming closed-ring isomer. The crystal shows pink fluorescence once chloroform droplets were dropped on the crystal. The system will be useful for sensors and color indicators.

Experimental

General: Starting materials were commercially available and were used without further purification. Melting points were determined on a Yanaco MP-500D melting point apparatus and are uncorrected. ^{1}H (400 MHz), ^{13}C (100 MHz), ^{19}F NMR (376 MHz) spectra were recorded on a JEOL JNM-400 spectrometer at ambient temperature. The splitting patterns are designated as follows: s (singlet); d (doublet); dd (double doublet); t (triplet); q (quartet); m (multiplet) and br (broad). Chemical shifts are denoted in δ (ppm) referenced to the residual protic solvent peaks. Coupling constants *J*, are denoted in Hz. Mass spectra were recorded on a MALDI-Spiral-TOF-MS mass spectrometer with DCTB (10 mg/mL in $CHCl_3$) as a matrix. Absorption and emission spectra were monitored on Hitachi U-4150 spectrophotometer and Hitachi F-7100 fluorescence spectrophotometer, respectively. Fluorescence quantum yields in several solvents were obtained as comparison with that of 9,10-bis(phenylethynyl)anthracene in hexane (Φ_f = 1.0) [28]. The luminescence quantum yields of crystalline solids were measured using a JASCO ILF-533 integral sphere attached to a JASCO FP-6600 spectrofluorophotometer. Mixture of microcrystalline compounds (2 mg) and powdered sodium chloride (1 g) were put into a 5-mm quartz cell, which was then placed in the integral sphere. The quantum yield was calculated using an installed software. Solid-state absorption spectrum was obtained by Kubelka-Munk conversion of a diffractive reflectance spectrum of the above mixture measured on a JASCO FP-6600 spectrofluorophotometer equipped with ILF-533 integral sphere. KEYENCE VHX-500, VH-S30, VH-Z20 were used to monitor the crystals. For the UV light irradiation, KEYENCE UV-400, UV-50H (λ = 365 nm), SPECTRONICS CORPORATION WESTBURY. NEW YORK. USA SPECTRO LINE HIGHEST ULTRAVIOLET

INTENSITY GUARANTEED (100 V, 40 A, λ = 313 nm) and AS ONE Handy UV Lamp SLUV-4 (λ = 365 nm) were used. For visible light irradiation, 500W USHIO SX-UI501XQ Xenon lamp attached with Toshiba color filters (Y-48, Y-44, and UV-29) was used.

Gaussian09 program package [29] was used for geometry optimizations with DFT for ground states and subsequent TDDFT calculations. For the calculation of the fluorescence, the geometry optimizations were performed for the first excited state obtained by TDDFT. The hybrid B3LYP functional [30-32] was adopted to exchange-correlation term of DFT. The gaussian 6-31G(d,p) basis set was adopted to all calculations. As for the solvent effect, polarizable continuum model (PCM) [33] was employed for THF.

X-ray crystallographic analysis for crystal of **1o** was carried out at BL40XU beamline of SPring-8. Si(111) channel cut monochromator was used and the wavelength and the size of X-ray beam were 0.81106 Å and 150 × 150 mm (square), respectively. The diffraction data was collected by oscillation method using EIGER detector at 173 K. The data were corrected for absorption effects by multi-scan method with ABSCOR [34]. The structure was solved by the direct method and refined by the full-matrix least-squares method using the SHELX-2014/7 program. The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. (CCDC 1920569).

Synthesis:

Diarylethene (2)

To a 50 mL three neck flask containing 1.15 g (2.40 mmol, 1.0 eq.) of 1-(2-methyl-5-phenylthien-3-yl)-2-(5-chloro-2-methylthien-3-yl)perfluorocyclopentene (**3**) [20] and 15 mL of diethyl ether anhydrous, 2.20 mL (3.52 mmol, 1.5 eq.) of 1.6 N *n*-BuLi hexane solution was added followed by stirring for 1 h at -10 °C on ice-salt bath under argon gas atmosphere. Then, 0.96 mL (3.58 mmol, 1.5 eq.) of $B(OBu)_3$ was added and the temperature of the mixture was allowed to warm to room temperature and stirred for 1 h. After ascertaining the formation of boronic acid by TLC, 5 mL of H_2O was added, and solvent was removed in vacuo. To a 200 mL three necked flask, the boronic acid, 0.90 g (6.51 mmol, 2.7 eq.) of K_2CO_3, 0.72 g (2.37 mmol, 1.0 eq.) of 6-bromo-2-(2'-methoxyphenyl)imidazo[1,2-a]pyridine (**4**) [21], 0.11 g (0.09 mmol, 0.04 eq.) of $Pd(PPh_3)_4(0)$, and 80 mL of mixture of 1,4-dioxane/H_2O (3: 1) were added, and refluxed for 16 h. After reaction was over, the mixture was cooled down to room temperature. Then the mixture was extracted with 40 mL of diethyl ether for four times. The combined organic layer was washed with 400 mL of water twice and dried over sodium sulfate anhydrous. After the filtration, solvents were removed in vacuo. The residue was purified by silica gel chromatography (eluent: hexane and followed by a mixture of hexane and ethyl acetate (98: 2)) to obtain 0.42 g of **2** as a pale-blue oil in 26% yield. The oil was purified with GPC followed by silica gel chromatography (eluent: hexane and followed by a mixture of hexane/diethyl ether (7: 3) to obtain 0.31 g (0.47 mmol) of **2** as bluish viscous solid in 19% yield.

2 : ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.40 (dd, *J* = 7.7, 1.7 Hz, 1H), 8.32 (s, 1H), 8.23 (s, 1H), 7.64 (d, *J* = 9.3 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.41-7.28 (m, 6H), 7.24 (s, 1H), 7.11 (ddd, *J* = 7.6, 7.4, 1.0 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 4.01 (s, 3H), 2.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 156.9, 143.7, 142.6, 142.2, 141.5, 141.4, 138.4, 133.4, 129.2, 129.2, 129.2, 129.1, 129.0, 128.9, 128.1, 126.1, 125.9, 125.7, 125.6, 123.9, 123.0, 122.5, 122.2, 121.7, 121.2, 119.4, 117.5, 113.2, 111.0, 55.5, 14.7, 14.77. ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ = -113.1 (s, 2F), -113.3 (s, 2F), -135.0 (s, 2F). HRMS (MALDI-TOF) *m/z* Calcd. for $C_{35}H_{24}F_6N_2OS_2$: 666.1234, Found: 652.1228.

Diarylethene (1o)

To a 5 mL of dichloromethane anhydrous solution containing 0.21 g (0.31 mmol, 1.0 eq.) of diarylethene **2**, 1.5 mL (1.5 mmol, 5.0 eq.) of 1.0 M BBr_3 dichloromethane solution was added on dryice - methanol bath (-78 °C) under argon gas atmosphere, and stirred over night at room temperature. After the reaction was over, saturated sodium bicarbonate aqueous solution was added to stop the reaction. To the mixture, 70 mL of water was added and the mixture was extracted with 30 mL of chloroform for four times. Combined organic layer was washed with saturated sodium bicarbonate aqueous solution and water, successively, then dried over sodium sulfate anhydrous. After the filtration, solvents were removed in vacuo. The residue was purified by silica gel chromatography (eluent: chloroform) to obtain 0.08 g (0.12 mmol) of **1** as colorless prism shaped crystals in 41% yield.

1o: m.p. 215.0-215.8 °C, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 12.5 (s, 1H), 8.33 (s, 1H), 7.89 (s, 1H), 7.62 (d, *J* = 9.3 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.5, Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.42 (dd, *J* = 9.3, 1.7, Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.33-7.23 (m, 4H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 157.4, 146.3, 142.8, 142.6, 142.1, 141.4, 137.7, 133.4, 130.1, 129.2, 129.2, 128.2, 126.3, 125.9, 125.9, 125.8, 125.8, 124.6, 123.7, 122.5, 121.5, 120.7, 119.2, 117.9, 117.0, 116.1, 107.3, 14.7, 14.7. ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ = -113.1 (s, 2F), -113.3 (s, 2F), -135.0 (s, 2F). HRMS (MALDI-TOF) *m/z* Calcd. for $C_{34}H_{22}F_6N_2OS_2$: 652.1078, Found: 652.1072.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP26107012 in Scientific Research on Innovative Areas “Photosynergetics”, the CREST program (JPMJCR17N2) of the Japan Science and Technology Agency. We thank Ms Y. Nishikawa (NAIST) for conducting the mass-spectroscopic measurement. The synchrotron radiation experiments were performed using the BL40XU beamlines of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2019A1110).

References

1. Feringa, B. L.; Browne, W. R. *Molecular Switches*; Wiley-VCH: Weinheim, 2011.

2. Irie, M; Fukaminato, T.; Matsuda, K.; Kobatake, S. *Chem. Rev.* **2014,** *114,* 12174–12277.

3. Fukaminato, T.; Ishida, S.; Métivier, R. *NPG Asia Materials* **2018**, *10*, 859–881.

4. Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002,** *420,* 759–760.

5. Pu, S.; Ding, H.; Liu, G.; Zheng, C.; Xu, H. *J. Phys. Chem. C* **2014**, *118*, 7010−7017.

6. Chen, Y. Xie, N. *J. Mater. Chem*. **2005**, *15*, 3229–3232.

7. Arai, Y.; Ito, S.; Fujita, H.; Yoneda, Y.; Kaji, T.; Takei, S.; Kashihara, R.; Morimoto, M.; Irie, M.; Miyasaka, H. *Chem. Commun.* **2017**, *53*, 4066-4069.

8. Kashihara, R.; Morimoto, M.; Ito, S.; Miyasaka, H.; Irie, M. *J. Am. Chem. Soc.* **2017**, *139*, 16498−16501.

9. Morimoto, M.; Kashihara, R.; Mutoh, K.; Kobayashi, Y.; Abe, J.; Sotome, H.; Ito, S.; Miyasaka, H.; Irie, M. *CrystEngComm* **2016**, *18*, 7241-7248.

10. Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2015***, 115,* 11718–11940.

11. Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361–5388.

12. Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.*, **2001**, 1740–1741.

13. Fukaminato, T.; Kobatake, S.; Kawai, T.; Irie, M. *Proc. Jpn. Acad., Ser. B*, **2001**, *77*, 30–35.

14. Williams, D. E.; Rietman, J. A.; Maier, J. M.; Tan, R.; Greytak, A. B.; Smith, M. D.; Krause J. A.; Shustova, N. B. *J. Am. Chem. Soc.* **2014**, *136*, 11886–11889.

15. Barbatti, M.; Aquino, A. J. A.; Lischka, H.; Schriever, C.; Lochbrunner, S.; Riedle, E. Phys. Chem. Chem. Phys. 2009, 11, 1406–1415.

16. Lochbrunner, S.; Schultz, T.; Schmitt, M.; Shaffer, J. P.; Zgierski, M. Z.; Stolow, A. J. Chem. Phys. 2001, 114, 2519–2522.

17. Ormson, S. M.; Brown, R. G. Prog. React. Kinet. 1994, 19, 45–91.

18. Khan, A. U.; Kasha, M. Proc. Natl. Acad. Sci. U. S. A. 1983, 80, 1767–1770.

19. Mutai, T.; Tomoda, H.; Ohkawa, T.; Yabe, Y.; Araki, K. *Angew. Chem., Int. Ed.* **2008**, 47, 9522–9524.

20. Browne, W. R.; de Jong, J. J. D.; Kudernac, T.; Walko, M.; Lucas, L. N.; Uchida, K.; van Esch, J. H.; Feringa, B. L. *Chem. Eur. J.* **2005**, *11*, 6430–6441.

21. Mutai, T.; Ohkawa, T.; Shono, H.; Arai, K. *J. Mater. Chem. C,* **2016,** *4,* 3599–3606.

22. Sumi, T.; Takagi, Y.; Yagi, A.; Morimoto, M.; Irie, M. *Chem. Commun.* **2014**, *50*, 3928-3930**.**

23. Lide, D. R. CRC Handbook of Chemistry and Physics (95th edition), CRC Press, New York, 3-1, **2015**.

24. Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature*, **2002**, *420*, 759-

760.

25. Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun.* **2002**, 2804-2805.

26. Su, J.; Fukaminato, T.; Placial, J.-P.; Onodera, T.; Suzuki, R.; Oikawa, H.; Brosseau, A.; Brissert, F.; Pansu, R.; Nakatani, K.; Metivier, R. *Angew. Chem. Int. Ed*. **2016**, *55*, 3662-3666.

27. Ishida, S.; Kitagawa, D.; Kobatake, S.; Kim, S.; Kurihara, S.; Fukaminato, T. *Chem. Commun.* **2019**, *55*, 5681-5684.

28. Demeter, A. *J. Phys. Chem. A* **2014**, *118*, 9985−9993.

29. Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.

30. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

31. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100.

32. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

33. Tomasi, J.; Mennucci, B.; Cammi, R.; *Chem. Rev.*, **2005**, *105*, 2999-3094.

34. Higashi, T. ABSCOR Rigaku Corporation, Tokyo, Japan, **1995**.