

The turn-on type fluorescent photochromism of diarylmaimide-*S,S,S',S'*-tetraoxide

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Abstract

In recent years, fluorescence-switchable molecules have garnered significant attention as fluorescent dyes for super-resolution fluorescence microscopy, which is increasingly demanded in the field of biochemical imaging. Among such molecules, diarylethene-*S,S,S',S'*-tetraoxide derivatives have proven particularly promising due to their ability to achieve high contrast fluorescence switching. Diarylethenes incorporating perfluorocyclopentene as the ethene bridge have become the standard scaffold due to their excellent fatigue resistance and thermal stability. However, their inherently low polarity necessitates extensive functionalization with hydrophilic groups to render them suitable for use in aqueous environments, such as in fluorescent labeling for super-resolution fluorescence microscopy. To address this limitation, we designed a novel class of oxidized diarylmaleimide (DAM) derivative featuring a maleimide as the ethene moiety, offering increased polarity and synthetic flexibility. Specifically, DAM **1**, composed of 2,4-dimethyl-3-phenylthiophene and *N*-methylmaleimide, and its oxidized counterpart DAM **2**, bearing two *S,S*-dioxidized thiophene rings, were synthesized and characterized. DAM **1** exhibited reversible photochromism upon irradiation with 436-nm and 550-nm light, accompanied by weak turn-off fluorescence and a cyclization quantum yield that depended strongly on solvent polarity. In contrast, DAM **2** displayed switch between one-way and reversible two-way photoisomerization and exhibited turn-on fluorescence behavior. These findings suggest that DAM-based systems are promising alternatives to conventional perfluorocyclopentene-based diarylethenes for aqueous fluorescence imaging applications, owing to their improved polarity and tunable photoresponsive properties.

1 Introduction

Photochromism is the phenomenon in which a substance undergoes a reversible change in color when exposed to light. This change in color happens because the chemical structure of the substance alters under the influence of light [1–3]. There are two main types of photochromism: Only photochemically reversible type (P-type) and thermally reversible type (T-type). In P-type photochromism, the interconversion occurs only by light, while in T-type photochromism, the interconversion also occurs by heat.

Diarylethenes (DAEs) with two hetero 5-membered rings in the *cis* position as aryl groups are generally known as P-type photochromic compounds [4–6]. They undergo reversible photoisomerization between an open ring form (*o*-form), which contains a 1,3,5-hexatriene unit, and a closed ring form (*c*-form), which contains a 1,3-cyclohexadiene unit, upon light irradiation. Since the first P-type DAE was reported by Irie *et al.* in 1988 [7], DAEs have attracted significant attention due to their excellent fatigue resistance, thermal stability, and high quantum yields. Today, DAEs incorporating perfluorocyclopentene as the ethene moiety have become mainstream, however, various DAEs with alternative ethene moieties are also actively being investigated [6, 8–19].

Some DAEs are known to enable fluorescence on/off switching or fluorescence wavelength tuning upon isomerization due to differences in fluorescence emission properties between their *c*- and *o*-forms [8,

20–28]. DAE-*S,S,S',S'*-tetraoxide derivatives have recently attracted considerable attention as turn-on type fluorescence-switchable molecules, owing to their ability to achieve high contrast fluorescence switching [29]. Although various fluorescence-switchable oxidized DAE derivatives have been synthesized to date, the majority incorporate perfluorocyclopentene as the ethene moiety [8, 30–40]. Since the reports on oxidized DAE derivatives bearing alternative ethene moieties remain scarce [41–47], we undertook to investigate oxidized DAE derivatives with non-perfluorocyclopentene units.

In recent years, fluorescence-switchable oxidized DAE derivatives have been intensively studied by many research groups as fluorescent dyes for super-resolution fluorescence microscopy, which is increasingly demanded in the field of biochemical imaging [8, 20, 48–53]. However, when considering the application of the oxidized DAE derivatives for super-resolution fluorescence microscopy dyes, it was necessary to introduce substituents bearing highly polar hydrophilic groups onto the aryl moieties due to the low polarity of perfluorocyclopentene [50, 52, 54].

Therefore, we initiated the development of turn-on type fluorescent DAE-*S,S,S',S'*-tetraoxide derivatives featuring a simple structure that is low cost to synthesize, easy to handle, and readily identifiable. The aim of this study is to synthesize a novel, practical turn-on type fluorescence photoswitching DAE derivatives applicable to trace analysis, bioimaging. Herein, we report the synthesis of the diarylmaleimide-*S,S,S',S'*-tetraoxide derivative **2** which is anticipated to exhibit turn-on fluorescence photoswitching behavior, along with its precursor diarylmaleimide **1** (Scheme 1), as well as the results of their photochemical properties.

2 Results and discussions

2.1 Molecular design

The ethene moiety introduced in this study is a maleimide. Diarylmaleimides (DAMs) [55,56], which incorporate maleimide as the ethene core, have been extensively investigated [57-62]. DAM-*S,S*-dioxide derivatives, in which only one of thiophene rings is oxidized, have also been reported [63]. However, to the best of our knowledge, no examples of DAM-*S,S,S',S'*-tetraoxide derivatives, where both thiophene rings are oxidized, have been described, and there have been no reports regarding the turn-on fluorescence properties of the DAM-*S,S*-dioxide derivatives. The advantages anticipated from the use of maleimide are summarized as follows:

- (i) A higher molecular polarity can be achieved compared to that of perfluorocyclopentene.
- (ii) The strong electron-withdrawing nature of the maleimide unit facilitates selective oxidation of the thiophene rings in reactions using peroxide.
- (iii) In comparison with maleic anhydride[7,64], which is known for its highly polar structure, maleimide exhibits greater resistance to hydrolysis, enhanced stability, and improved handling properties in aqueous solvent.

(iv) The substituent on the nitrogen atom can be readily modified, allowing for the enhancement of hydrophilicity as well as the introduction of desired functionalities into DAMs [59-61,65-67].

In compounds **1** and **2**, the maleimide nitrogen bears a methyl substituent. This choice was based on the idea that a simplest and accessible derivative would be advantageous for initial development. This compound represents the first step toward the development of a series of *N*-substituted DAM derivatives. Regarding the structural design of the aryl moiety, which includes two methyl groups on the thiophene rings, this selection was based on previous reports indicating that substitution at the 4-position of the thiophene ring reduces the formation of by-products upon light irradiation and enhances photostability [68]. Furthermore, the structure was modeled after the well-established DAE based on perfluorocyclopentene, which is commercially available.

2.2 Synthesis

The synthetic route is summarized in Scheme 2. *N*-methyl-3,4-dibromomaleimide (**3**) was synthesized according to a reported procedure [69]. In consideration of the Migita-Kosugi-Stille coupling, which proceeds under almost neutral conditions, the aryl unit, 3,4-dimethyl-5-tributylstannylthiophene (**4**), was synthesized in 58% yield via tributylstannylation of 3,4-dimethyl-5-phenylthiophene, following previously reported procedures [70,71]. DAM **1o** was obtained in 35% yield by Migita-Kosugi-Stille coupling of **3** and **4** [70,71]. The DAM-*S,S,S',S'*-tetraoxide derivative **2o** was synthesized in 61% yield using *m*-chloroperbenzoic acid (*m*-CPBA), following an established method for the oxidation of DAE compounds [30,72]. More detailed synthetic procedures and compound characterization are provided in the ESI.

2.3 Photochromism of diarylmaleimide **1o**

A **1o** solution of toluene was irradiated with 436-nm light. A new absorption band between 450–700 nm ($I_{\max} = 548$ nm) appeared, accompanied by an increase in absorbance in the 350–450 nm region ($I_{\max} = 391$ nm) (Fig. 1a). The isobestic points were observed at 302, 418, and 439 nm. Apparently DAM **1** showed the photochromic ring closure to give **1c** via the 6p-electrocyclization reaction upon UV irradiation, since the change in the absorption spectra resembled that of the perfluorocyclopentene analog with the same aryl groups [73]. These absorption bands of **1c** decreased after irradiation with 550-nm light, and completely returned to the absorption spectrum of **1o**, indicating that a photocycloreversion (ring-opening) reaction occurred (Fig. S4a). The ring-opening reaction exhibited the same isobestic points as the ring-closing process, indicating that DAM **1** undergoes a clean and reversible photochromic transformation. The absorption spectrum of the solution containing **1c** remained almost unchanged after 2 days of standing at room temperature in the dark, confirming that **1** is the P-type photochromic compound.

To investigate the fluorescence properties of DAM **1**, the fluorescence spectrum of a toluene solution of **1o** was recorded under excitation at 460 nm; however, no distinct emission was observed (Fig. 1b). Upon closer examination of the 500-600 nm region, a faint fluorescence signal from **1o** was detected (Fig. S8a). When the excitation wavelength was set to 405 nm, the fluorescence was more clearly observed to

diminish as the ratio of the *c*-form increased upon irradiation with 436-nm light (Fig. S8b). In other words, DAM **1** exhibits turn-off type fluorescence-switching behavior.

In order to investigate the effect of solvent polarity [74] on photochromism of DAM **1**, solutions were prepared in dichloromethane (DCM) and ethanol in addition to toluene, and their photochromic behaviors were examined. The maximum absorption wavelength (λ_{\max}) of DAM **1**, its molar absorption coefficient (ϵ_{\max}) at that wavelength, the conversion ratio at the photostationary state under 436 nm irradiation (PSS₄₃₆), and the quantum yields for cyclization (F_{OC436}) and cycloreversion (F_{CO436} , F_{CO550}) are summarized in Table 1. Details of the calculations used to determine the quantum yields are shown in the ESI (Fig. S13-S16 and Table S1). These results indicate that DAM **1** exhibits solvent dependent behavior, with both the cyclization quantum yield and the conversion ratio at PSS decreasing as the solvent polarity increases. This solvent dependence is attributed to the formation of a twisted intramolecular charge transfer (TICT) photoexcited state, which is stabilized in polar solvents. [64,75] In contrast, the cycloreversion quantum yield was found to be independent of solvent, likely because the *c*-form adopts only a single, stable conformation that is unaffected by solvent polarity.

Table 1. Spectroscopic properties of **1** and **2** and quantum yields of the photochromic reaction

DAM	Solvent ($E_{\text{T}}(30)$ [kcal mol ⁻¹])	λ_{\max}^a [nm] (ϵ_{\max} [10 ³ dm ³ mol ⁻¹ cm ⁻¹])		Conversion ratio ^b [%]	Quantum yield ^c		Quantum yield ^d
		Open form	Closed form		Φ_{OC}	Φ_{CO}	
1	toluene (33.9)	396 (3.92)	548 (9.62)	76	0.26	0.10	0.05
	DCM (40.7)	397 (3.94)	549 (8.95)	44	0.05	0.06	0.04
	ethanol (51.9)	395 (3.56)	548 (8.00)	27	0.03	0.07	0.06
2	toluene (33.9)	321 (10.5)	413 (11.7)	> 99	0.30	-	-
	DCM (40.7)	320 (10.1)	408 (14.5)	> 99	0.24	-	-
	Ethanol (51.9)	313 (11.0)	402 (14.4)	95	0.11	3×10^{-3}	5×10^{-4}

a The absorption maximum at the longest wavelength was listed as λ_{\max} (maximum absorption wavelength).

b Conversion ratio of **1** at PSS₄₃₆ and that of **2** at PSS₃₆₅.

c **1**: Irradiation with 436-nm light. **2**: Irradiation with 365-nm light.

d **1**: Irradiation with 550-nm light. **2**: Irradiation with 436-nm light.

2.4 Photochromism of diarylmaleimide-*S,S,S',S'*-tetraoxide derivative **2o**

When the toluene solution of **2o** was irradiated with 365-nm light, no new absorption band appeared in the 550-700 nm region, in contrast to the case of **1o**. However, an increase in absorbance was observed around 350-500 nm, with a maximum at 413 nm and an isosbestic point at 349 nm, which was attributed to the formation of **2c** through the cyclization reaction (Fig. 1c). On the other hand, no increase in the ratio of the *o*-form was observed after prolonged irradiation with 436-nm light, and the cycloreversion reaction could not be confirmed (see Fig. S12a). This suggests that the cycloreversion quantum yield of **2c** is negligibly small, and one-way isomerization from **2o** to **2c** was observed.

To investigate the fluorescence properties of DAM **2**, fluorescence spectra were recorded using 460-nm excitation light while gradually increasing the proportion of *c*-form by irradiating a toluene solution of **2o** with 365-nm light. In the initial state of **2o**, no emission was observed. However, as the *c*-form content increased upon continued irradiation, yellow fluorescence emerged with a maximum intensity at 567 nm and became progressively more intense (Fig. 1d, Fig. 2). The absolute fluorescence quantum yield F_F was measured using a fluorescence spectrophotometer equipped with an integrating sphere, and the F_F of the toluene solution of **2c** was found to be 0.25.

As with **1**, to investigate the effect of solvent polarity on photochromism of DAM **2**, solutions of **2** were prepared in DCM and ethanol, in addition to toluene, and photoisomerization behavior was investigated for each. The I_{\max} in each solution of **2**, ϵ_{\max} at that wavelength, the conversion ratio at PSS₃₆₅, and the quantum yields for cyclization (F_{OC365}) and cycloreversion (F_{CO365} , F_{CO436}) are summarized in Table 1.

The cyclization quantum yields of **2** were significantly higher in medium- and high-polar solvents compared to those of **1**. Thus, the solvent dependence of the cyclization quantum yield was less pronounced for DAM **2** than for DAM **1**. As shown in Table 1, the cyclization quantum yield for **1** decreased markedly from 0.26 in toluene to 0.03 in ethanol (a reduction to less than one-eighth), whereas **2** showed a smaller decrease from 0.30 to 0.11 (about one-third). This reduced solvent sensitivity in **2** is likely attributable to oxidation of the thiophene ring, which diminishes its electron-donating ability and thereby suppresses the formation of the TICT photoexcited state [63].

Notably, although the cycloreversion reaction was not observed in toluene solution, it was observed in highly polar solvents such as ethanol (see Fig. S7, S12b), indicating that reversible (two-way) photoisomerization occurs under these conditions. To the best of our knowledge, while some oxidized DAE derivatives have been reported to exhibit solvent-polarity-dependent variations in their cyclization [76,77] and cycloreversion [78] quantum yields, no examples have yet been reported of oxidized DAE derivatives that enable polarity-dependent control over the cycloreversion quantum yield and allow switching between one-way and two-way photoisomerization, depending on whether the *c*-form undergoes ring-opening.

The low cycloreversion quantum yield observed for typical DAE-*S,S,S',S'*-tetraoxide derivatives is thought to arise from the formation of two intramolecular hydrogen bonds in the *c*-form between the pair of hydrogen atoms (H1 / H2; see Fig. S19) of methyl groups attached to the reactive carbon atoms and the oxygen atoms (O1 / O2; see Fig. S19) of the *S,S*-dioxide thiophene rings [79]. Furthermore, in the DAM-*S,S,S',S'*-tetraoxide **2**, four additional hydrogen bonds may be formed (see Table S3) between the hydrogen atoms (H3 / H4; see Fig. S19) and the oxygen atoms (O3 / O4; see Fig. S19) and between the hydrogen atoms (H5 / H6; see Fig. S19) and the oxygen atoms (O5 / O6; see Fig. S19). These interatomic distances are shorter than the sum of the van der Waals radii of the hydrogen (1.26 Å) and oxygen (1.64 Å) [80], suggesting the formation of hydrogen bonds. Accordingly, the differences in distances between O1 (2) and H1 (2), O3 (4) and H3 (4), as well as O5 (6) and H5 (6) suggest that stronger hydrogen bonds are formed at multiple sites in the *c*-form compared to the *o*-form. These intramolecular hydrogen bonds

are likely responsible for the suppression of the cycloreversion reaction in low-polarity solvents such as toluene and DCM. In contrast, in highly-polar protic solvents such as ethanol, intermolecular hydrogen bond can form between the oxygen atom of sulfone (S=O) or carbonyl (C=O) in **2c** and the hydroxy protons of ethanol molecules. This interaction disrupts the sextuple intramolecular hydrogen bonds, thereby facilitating the cycloreversion reaction of **2c**.

Regarding the fluorescence properties, the F_F of DAM **2** at the PSS₃₆₅ were 0.15 in DCM and 0.08 in ethanol, with corresponding emission maxima of 595 nm and 598 nm, respectively. Although the fluorescence quantum yield decreases with increasing solvent polarity, DAM **2** exhibits turn-on type fluorescence behavior, with the *o*-form being non-fluorescent and the *c*-form displaying fluorescence.

3 Conclusions

In this study, DAM **1o** bearing an *N*-methylmaleimide moiety as the ethene unit, and its oxidized derivative **2o**—featuring oxidation at both thiophene rings— were synthesized. DAM **1o** exhibited photochromism upon 436-nm and 550-nm light irradiation, and showed solvent-dependent behavior characterized by a decrease in photoisomerization conversion with increasing solvent polarity. It also displayed weak turn-off type fluorescence. In contrast, the oxidized DAM **2o** underwent one-way isomerization in low-polarity solvents, achieving nearly complete conversion to the *c*-form, while in protic high-polarity solvents such as ethanol, it exhibited reversible (two-way) isomerization, *i.e.*, photochromism. Thus, the isomerization mode—between one-way and two-way— can be selectively modulated by the choice solvent. Furthermore, unlike DAM **1o**, DAM **2o** demonstrated turn-on type fluorescence behavior. To enable future applications in super-resolution microscopy, efforts are currently underway to develop highly polar, oxidized DAM derivatives bearing strongly polar substituents on the nitrogen atom of the maleimide moiety, thereby enhancing their solubility in aqueous media.

Declarations

Supplementary Information

The online version contains supplementary material available at ###.

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Author contributions

The idea for this study was conceived by TU. All experiments and writing were performed by KN. All authors contributed to editing of the manuscript.

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Availability of data and materials

The data that supports the findings of this study are available in the supplementary material of this article.

Conflict of interest

The authors declare that they have no conflict of interest.

References

1. Bouas-Laurent, H., & Dürr, H. (2001). Organic photochromism. *International Union of Pure and Applied Chemistry*, 73(4), 639-665. <https://doi.org/10.1351/pac200173040639>
2. Dürr, H., & Bouas-Laurent, H. (Eds.) (2003). *Photochromism: Molecules and Systems* (Rev. ed.). Elsevier Science.
3. Feringa, B. L., & Browne, W. R. (Eds.) (2011). *Molecular Switches* (2nd ed.). Wiley-VCH.
4. Irie, M., (2021). *Diarylethene Molecular Photoswitches: Concepts and Functionalities*, Wiley-VCH.
5. Irie, M., (2000). Diarylethenes for Memories and Switches. *Chemical Reviews*, 100(5), 1685-1716. <https://doi.org/10.1021/cr980069d>
6. Irie, M., Fukaminato, T., Matsuda, K., & Kobatake, S. (2014). Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators. *Chemical Review*, 114(24), 12174-12277. <https://doi.org/10.1021/cr500249p>
7. Irie, M., & Mohri, M. (1988). Thermally Irreversible Photochromic Systems. Reversible Photocyclization of Diarylethene Derivatives. *The Journal of Organic Chemistry*, 53(4), 803-808. <https://doi.org/10.1021/jo00239a022>
8. Li, Z., Zeng, X., Gao, C., Song, J., He, F., He, T., Guo, H., & Yin, J. (2023). Photoswitchable diarylethenes: From molecular structures to biological applications. *Coordination Chemistry Reviews*, 497, 215451. <https://doi.org/10.1016/j.ccr.2023.215451>
9. Fukumoto, S., Nakagawa, T., Kawai, S., Nakashima, T., & Kawai, T. (2011). Syntheses and photochromic properties of diaryl acenaphthylene derivatives. *Dyes and Pigments*, 89(3), 297-304. <https://doi.org/10.1016/j.dyepig.2010.04.004>
10. Yamada, M., Sawazaki, T., Fujita, M., Asanoma, F., Nishikawa, Y., & Kawai, T. (2022). Tetrathienyl Corannulene Compounds with Highly Sensitive Photochromism. *Chemistry: A European Journal*,

- 28(49), e202201286. <https://doi.org/10.1002/chem.202201286>
11. Ferrer, M. B., Harada, D., Martin, C. J., Métivier, R., Allain, C., Nakatani, K., Louis, M., Kawaguchi, N., Yanagida, T., Yasuhara, K., & Kawai, T. (2024). Cascade Fluorescence Modulation in Photochromic Microcapsules. *ACS Applied Materials & Interfaces*, 16(42), 57626-57635. <https://doi.org/10.1021/acsami.4c09023>
 12. Morinaka, K., Ubukata, T., & Yokoyama, Y. (2009). Structurally Versatile Novel Photochromic Bisarylindenone and Its Acetal: Achievement of Large Cyclization Quantum Yield. *Organic Letters*, 11(17), 3890-3893. <https://doi.org/10.1021/ol901497t>
 13. Suzuki, K., Ubukata, T., & Yokoyama, Y. (2012). Dual-mode fluorescence switching of photochromic bithiazolylcoumarin. *Chemical Communications*, 48(5), 11838-11840. <https://doi.org/10.1039/c1cc16516j>
 14. Ogawa, H., Takagi, K., Ubukata, T., Okamoto, A., Yonezawa, N., Delbaere, S., & Yokoyama, Y. (2012). Bisarylindenols: fixation of conformation leads to exceptional properties of photochromism based on 6p-electrocyclization. *Chemical Communications*, 48(97), 11838-11840. <https://doi.org/10.1039/c2cc35793c>
 15. Herder, M., Eisenreich, F., Bonasera, A., Grafl, A., Grubert, L., Pätzelt, M., Schwarz, J., & Hecht, S. (2017). Light-Controlled Reversible Modulation of Frontier Molecular Orbital Energy Levels in Trifluoromethylated Diarylethenes. *Chemistry - A European Journal*, 23(15), 3743-3754. <https://doi.org/10.1002/chem.201605511>
 16. Glebov, E. M., Semionova, V. V., Lazareva, S. K., Smolentsev, A. B., Fedunov, R. G., Shirinian, V. Z., & Lvov, A. G., (2022). Solvent dependent photoswitching and emission of diarylethenes with a p-conjugated push-pull system. *Journal of Luminescence*, 241, 118472. <https://doi.org/10.1016/j.jlumin.2021.118472>
 17. Lvov, A. G., Yokoyama, Y., & Shirinian, V. Z. (2020). Post-Modification of the Ethene Bridge in the Rational Design of Photochromic Diarylethenes. *The Chemical Record*, 20(1), 51-63. <https://doi.org/10.1002/tcr.201900015>
 18. Kitagawa, D., Nakahama, T., Nakai, Y., & Kobatake, S. (2019). 1,2-Diarylbenzene as fast T-type photochromic switch. *Journal of Materials Chemistry C*, 7(10), 2865-2870. <https://doi.org/10.1039/C8TC05357J>
 19. Nakagawa, T., Kato, R., Iiyoshi, Y., Furuya, M., Kitano, T., Nakamura, R., Yokoyama, Y., & Ubukata, T. (2024). A chiral photoswitch based on enantiospecific interconversion between binaphthyl and helicoid skeletons. *Chemical Communications*, 60(39), 5149-5152. <https://doi.org/10.1039/d4cc00364k>
 20. Fukaminato, T., (2011). Single-molecule fluorescence photoswitching: Design and synthesis of photoswitchable fluorescent molecules. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 12(3), 177-208. <https://doi.org/10.1016/j.jphotochemrev.2011.08.006>
 21. Fukaminato, T., Ishida, S., & Métivier, R. (2018). Photochromic fluorophores at the molecular and nanoparticle levels: fundamentals and applications of diarylethenes. *NPG Asia Materials*, 10, 859-

881. <https://doi.org/10.1038/s41427-018-0075-9>
22. Pu, S.-Z., Sun, Q., Fan, C.-B., Wang, R.-J., & Liu, G. (2016). Recent advances in diarylethene-based multi-responsive molecular switches. *Journal of Materials Chemistry C*, 4(15), 3075-3093. <https://doi.org/10.1039/c6tc00110f>
23. Raymo, F. M., & Tomasulo, M. (2005). Fluorescence Modulation with Photochromic Switches. *The Journal of Physical Chemistry A*, 109(33), 7343-7352. <https://doi.org/10.1021/jp052440o>
24. Qi, Q., Li, C., Liu, X., Jiang, S., Xu, Z., Lee, R., Zhu, M., Xu, B., & Tian, W. (2017). Solid-State Photoinduced Luminescence Switch for Advanced Anticounterfeiting and Super-Resolution Imaging Applications. *Journal of the American Chemical Society*, 139(45), 16036-16039. <https://doi.org/10.1021/jacs.7b07738>
25. Ishida, S., Fukaminato, T., Kim, S., Ogata, T., & Kurihara, S. (2017). Sequential Red-Green-Blue (RGB) Fluorescence Color Photoswitching in Multicomponent Photochromic Fluorescent Nanoparticles. *Chemistry Letters*, 46(8) 1182-1185. <https://doi.org/10.1246/cl.170436>
26. Shimizu, K., Métivier, R., & Kobatake, S. (2020). Synthesis and fluorescence on/off switching of hyperbranched polymers having diarylethene at the branching point. *Journal of Photochemistry and Photobiology A: Chemistry*, 390, 112341. <https://doi.org/10.1016/j.jphotochem.2019.112341>
27. Ikariko, I., Deguchi, S., Fabre, N., Ishida, S., Kim, S., Kurihara, S., Métivier, R., & Fukaminato, T. (2020). Highly-stable red-emissive photochromic nanoparticles based on a diarylethene-perylenebisimide dyad. *Dyes and Pigments*, 180, 108490. <https://doi.org/10.1016/j.dyepig.2020.108490>
28. Nakagawa, T., Miyasaka, Y., & Yokoyama, Y., Photochromism of a spiro-functionalized diarylethene derivative: multi-colour fluorescence modulation with a photon-quantitative photocyclization reactivity. *Chemical Communications*, 54(26), 3207-3210. <https://doi.org/10.1039/c8cc00566d>
29. Jeong, Y.-C., Yang, S. I., Ahn, K.-H., & Kim, E. (2005). Highly fluorescent photochromic diarylethene in the closed-ring form. *Chemical Communications*, (19), 2503-2505. <https://doi.org/10.1039/b501324k>
30. Fukaminato, T., Tanaka, M., Kuroki, L., & Irie, M. (2008). Invisible photochromism of diarylethene derivatives. *Chemical Communications*, (33), 3924-3926. <https://doi.org/10.1039/b804137g>
31. Jeong, Y.-C., Park, D. G., Lee, I. S., Yang, S. I., & Ahn, K.-H. (2009). Highly fluorescent photochromic diarylethene with an excellent fatigue property. *Journal of Materials Chemistry*, 19(1), 97-103. <https://doi.org/10.1039/b814040e>
32. Uno, K., Niikura, H., Morimoto, M., Ishibashi, Y., Miyasaka, H., & Irie, M. (2011). *Journal of the American Chemical Society*, 133(34), 13558-13564. <https://doi.org/10.1021/ja204583e>
33. Takagi, Y., Kunishi, T., Katayama, T., Ishibashi, Y., Miyasaka, H., Morimoto, M., & Irie, M. (2012). Photoswitchable fluorescent diarylethene derivatives with short alkyl chain substituents. *Photochemical & Photobiological Sciences*, 11, 1661-1665. <https://doi.org/10.1039/c2pp25078k>
34. Morimoto, M., Sumi, T., & Irie, M. (2017). Photoswitchable Fluorescent Diarylethene Derivatives with Thiophene 1,1-Dioxide Groups: Effect of Alkyl Substituents at the Reactive Carbons. *Materials*, 10(9), 1021. <https://doi.org/10.3390/ma10091021>

35. Kashihara, R., Morimoto, M., Ito, S., Miyasaka, H., & Irie, M. (2017). Fluorescence Photoswitching of a Diarylethene by Irradiation with Single-Wavelength Visible Light. *Journal of the American Chemical Society*, *139*(46), 16498-16501. <https://doi.org/10.1021/jacs.7b10697>
36. Irie, M., & Morimoto, M. (2018). Photoswitchable Turn-on Mode Fluorescent Diarylethenes: Strategies for Controlling the Switching Response. *Bulletin of the Chemical Society of Japan*, *91*(2), 237-250. <https://doi.org/10.1246/bcsj.20170365>
37. Watanabe, K., Ubukata, T., & Yokoyama, Y. (2018). Photochromism and the fluorescence properties of bisbenzothienylethene and *S,S,S',S'*-tetraoxide derivatives with dual conjugated fluorescent groups on their side chains. *Photochemical & Photobiological Sciences*, *17*, 711-717. <https://doi.org/10.1039/c8pp00050f>
38. Barrez, E., Laurent, G., Pavageau, C., Sliwa, M., & Métivier, R. (2018). Comparative photophysical investigation of doubly-emissive photochromic-fluorescent diarylethenes. *Physical Chemistry Chemical Physics*, *20*(4), 2470-2479. <https://doi.org/10.1039/c7cp06541h>
39. Uno, K., Bossi, M. L., Belov, V. N., Irie, M. & Hell, S. W. (2020). Multicolour fluorescent "sulfide-sulfone" diarylethenes with high photo-fatigue resistance. *Chemical Communications*, *56*(14), 2198-2201. <https://doi.org/10.1039/c9cc09390g>
40. Iwai, R., Morimoto, M., & Irie, M. (2020). Turn-on mode fluorescent diarylethenes: effect of electron-donating and electron-withdrawing substituents on photoswitching performance. *Photochemical & Photobiological Sciences*, *19*, 783-789. <https://doi.org/10.1039/D0PP00064G>
41. Sumi, T., Kaburagi, T., Morimoto, M., Une, K., Sotome, H., Ito, S., Miyasaka, H., & Irie, M. (2015). Fluorescent Photochromic Diarylethene That Turns on with Visible Light. *Organic Letters*, *17*(19), 4802-4805. <https://doi.org/10.1021/acs.orglett.5b02361>
42. Ai, Q., Hong, S.-J., Khan, M. A., Ahn, K.-H. (2018). Turn-On Fluorescent Photochromic Disulfonylarylthiophenes: Effect of Sulfone Groups on Fluorescence and Conversion. *Bulletin of the Korean Chemical Society*, *39*(11), 1308-1314. <https://doi.org/10.1002/bkcs.11597>
43. Sysoiev, D., Procházková, E., Semenenko, A., Pohl, R., Shishkina, S., Klepetářová, B., Shvadchak, V., & Yushchenko, D. A. (2020). Di(benzothienyl)cyclobutenes: Toward Strained Photoswitchable Fluorophores. *ChemPlusChem*, *85*(9), 2084-2092. <https://doi.org/10.1002/cplu.202000481>
44. Wang, Z., Zhao, J., Li, H., Ai, Q., Cai, P., Si, J., Yao, X., Hu, X., & Liu, Z. (2022). Gated photochromic reactivity of diarylethenes with visible-light-triggered turn-on fluorescence. *Dyes and Pigments*, *204*, 110441. <https://doi.org/10.1016/j.dyepig.2022.110441>
45. Zhao, J., Wang, Z., Ai, Q., Li, H., Cai, P., Si, J., Yao, X., He, Q., Hu, X., & Liu, Z. (2022). Visible-light-triggered fluorescence "turn-on" diarylethenes: Computational molecular design and photophysical studies. *Journal of Luminescence*, *248*, 118973. <https://doi.org/10.1016/j.jlumin.2022.118973>
46. Hu, X., Zhao, J., Wang, Z., Li, H., Cai, P., Si, J., Yao, X., Ai, Q., & Liu, Z. (2022). Nonaromatic amine containing dibenzo[*b,d*]thiophene donor for D-A type visible-light driven fluorescence turn-on diarylethenes. *Dyes and Pigments*, *205*, 110571. <https://doi.org/10.1016/j.dyepig.2022.110571>

47. Lu, J., Yan, Q., Luo, M., Ren, J., & Wang, S. (2024). Synthesis of photoresponsive phenanthroimidazole-based *S,S*-dioxide dithienylethene for information storage and encryption. *Research on Chemical Intermediate*, *50*, 1929-1938. <https://doi.org/10.1007/s11164-024-05236-2>
48. Bates, M., Huang, B., Dempsey, G. T., & Zhuang, X. (2007). Multicolor Super-Resolution Imaging with Photo-Switchable Fluorescent Probes. *Science*, *317*(5845), 1749-1753. <https://doi.org/10.1126/science.1146598>
49. Arai, Y., Ito, S., Fujita, H., Yoneda, Y., Kaji, T., Takei, S., Kashihara, R., Morimoto, M., Irie, M., & Miyasaka, H. (2017). One-colour control of activation, excitation and deactivation of a fluorescent diarylethene derivative in super-resolution microscopy. *Chemical Communication*, *53*(29), 4066-4069. <https://doi.org/10.1039/c6cc10073b>
50. Roubinet, B., Weber, M., Shojaei, H., Bates, M., Bossi, M. L., Belov, V. N., Irie, M., & Hell, S. W. (2017). Fluorescent Photoswitchable Diarylethenes for Biolabeling and Single-Molecule Localization Microscopies with Optical Superresolution. *Journal of the American Chemical Society*, *139*(19), 6611-6620. <https://doi.org/10.1021/jacs.7b00274>
51. Li, C., Xiong, K., Chen, Y., Fan, C., Wang, Y.-L., Ye, H., & Zhu, M.-Q. (2020). Visible-Light-Driven Photoswitching of Aggregated-Induced Emission-Active Diarylethenes for Super-Resolution Imaging. *ACS Applied Materials & Interfaces*, *12*(24), 27651-27662. <https://doi.org/10.1021/acsami.0c03122>
52. Uno, K., Aktalay, A., Bossi, M. L., Irie, M., Belov, V. N., & Hell, S. W. (2021). Turn-on mode diarylethenes for bioconjugation and fluorescence microscopy of cellular structures. *Proceedings of the National Academy of Sciences*, *118*(14), e2100165118. <https://doi.org/10.1073/pnas.2100165118>
53. Kim, D., Aktalay, A., Jensen, N., Uno, K., Bossi, M. L., Belov, V. N., & Hell, S. W. (2022). Supramolecular Complex of Photochromic Diarylethene and Cucurbit[7]uril: Fluorescent Photoswitching System for Biolabeling and Imaging. *Journal of the American Chemical Society*, *144*(31), 14235-14247. <https://doi.org/10.1021/jacs.2c05036>
54. Roubinet, B., Bossi, M. L., Alt, P., Leutenegger, M., Shojaei, H., Schnorrenberg, S., Nizamov, S., Irie, M., Belov, V. N., & Hell, S. W. (2016). Carboxylated Photoswitchable Diarylethenes for Biolabeling and Super-Resolution RESOLFT Microscopy. *Angewandte Chemie International Edition*, *55*(49), 15429-15433. <https://doi.org/10.1002/anie.201607940>
55. Pal, M., Swamy, N. K., Hameed, P. S., Padakanti, S., & Yeleswarapu, K. R. (2004). A rapid and direct access to symmetrical/unsymmetrical 3,4-diarylmaleimides and pyrrolin-2-ones. *Tetrahedron*, *60*(18), 3987-3997. <https://doi.org/10.1016/j.tet.2004.03.036>
56. Yamaguchi, T., & Irie, M. (2004). Photochromic Properties of Diarylethene Maleimide Derivatives in Polar Solvents. *Chemistry Letters*, *33*(10), 1398-1399. <https://doi.org/10.1246/cl.2004.1398>
57. Ichimura, K., Watanabe, S., Kusakawa, K., & Ochi, H. (1980). Effects of Solvents, *N*-Substituents and Acids on the Photocyclization and the Fluorescence Behavior of Diphenylmaleimides. *Journal of the Chemical Society of Japan*, *1980*(6), 837-845. <https://doi.org/10.1246/nikkashi.1980.837>

58. Brenner, M., Rexhausen, H., Steffan, B., & Steglich, W. (1988). Synthesis of Arcyriarubin B and related bisindolylmaleimides. *Tetrahedron*, **1988**, 44(10), 2887-2892. [https://doi.org/10.1016/S0040-4020\(88\)90025-7](https://doi.org/10.1016/S0040-4020(88)90025-7)
59. Yamaguchi, T., Uchida, K., & Irie, M. (1997). Asymmetric Photocyclization of Diarylethene Derivatives. *Journal of the American Chemical Society*, *119*(26), 6066-6071. <https://doi.org/10.1021/ja970200j>
60. Krayushkin, M. M., Shirinyan, V. Z., Belen'kii, L. I., Shimkin, A. A., Martynkin, A. Y., & Uzhinov, B. M. (2002). Photochromic Dihetarylethenes: XVII. New Synthesis of Photochromic *N*-Alkyldithienylmaleimides. *Russian Journal of Organic Chemistry*, *38*(9), 1335-1338. <https://doi.org/10.1023/A:1021612131447>
61. Honda, A., Ueno, N., Fujiwara, K., Masuhara, H., & Miyamura, K. (2022). Cold crystallization and photo-induced thermal behavior of alkyl-derivatized diarylethene molecules. *RSC Advances*, *12*(34), 21926-21931. <https://doi.org/10.1039/D2RA03898F>
62. Fleming, C., Remón, P., Li, S., Simeth, N. A., König, B., Grøtli, M., & Andréasson, J. (2017). On the use of diarylmaleimide derivatives in biological contexts: An investigation of the photochromic properties in aqueous solution. *Dyes and Pigments*, *137*, 410-420. <https://doi.org/10.1016/j.dyepig.2016.10.023>
63. Ohsumi, M., Hazama, M., Fukaminato, T., & Irie, M. (2008). Photocyclization reaction of a diarylmaleimide derivative in polar solvents. *Chemical Communications*, (28), 3281-3283. <https://doi.org/10.1039/b802780c>
64. Irie, M., & Sayo, K. (1992). Solvent Effects on the Photochromic Reactions of Diarylethene Derivatives. *The Journal of Physical Chemistry*, *96*(12), 7671-7674. <https://doi.org/10.1021/j100198a035>
65. Ohsumi, M., Fukaminato, T., & Irie, M. (2005). Chemical control of the photochromic reactivity of diarylethene derivatives. *Chemical Communications*, (31), 3921-3923. <https://doi.org/10.1039/b506801k>
66. Nourmohammadian, F., Wu, T., & Branda, N. R. (2011). A 'chemically-gated' photoresponsive compound as a visible detector for organophosphorus nerve agents. *Chemical Communications*, *47*(39), 10954-10956. <https://doi.org/10.1039/c1cc13685b>
67. Cipolloni, M., Ortica, F., Yahyaoui, A. E., Heynderickx, A., Moustrou, C., & Favaro, G., (2009). New photochromic symmetrical and unsymmetrical bis(heteroaryl)maleimides: A spectrokinetic study. *Chemical Physics*, *358*(3), 258-264. <https://doi.org/10.1016/j.chemphys.2009.02.011>
68. Irie, M., Lifka, T., Uchida, K., Kobatake, S., & Shindo, Y. (1999). Fatigue resistant properties of photochromic dithienylethenes: by-product formation. *Chemical Communications*, (8), 747-750. <https://doi.org/10.1039/A809410A>
69. Štrbac, P., & Margetić, D. (2022). Complementarity of solution and solid state mechanochemical reaction conditions demonstrated by 1,2-debromination of tricyclic imides. *Beilstein Journal of Organic Chemistry*, *18*, 746-753. <https://doi.org/10.3762/bjoc.18.75>

70. Deng, X., & Liebeskind, L. S. (2001). A Contribution to the Design of Molecular Switches: Novel Acid-Mediated Ring-Closing–Photochemical Ring-Opening of 2,3-Bis(heteroaryl)quinones (Heteroaryl = Thienyl, Furanyl, Pyrrolyl). *Journal of the American Chemical Society*, *123*(31), 7703-7704. <https://doi.org/10.1021/ja0106220>
71. Saito, E., Ako, T., Kobori, Y., & Tsuda, A. (2017). Switching of the p-electronic conjugations in the reduction of a dithienylethene-fused *p*-benzoquinone. *RSC Advances*, *7*(5), 2403-2406. <https://doi.org/10.1039/c6ra27001h>
72. Jeong, Y.-C., Han, J. P., Kim, Y., Kim, E., Yang, S. I., & Ahn, K.-H. (2007). Characterization and photophysical properties of sulfur-oxidized diarylethenes. *Tetrahedron*, **2007**, *63*(15), 3173-3182. <https://doi.org/10.1016/j.tet.2007.02.007>
73. Irie, M., Sakemura, K., Okinaka, M., & Uchida, K. (1995). Photochromism of Dithienylethenes with Electron-Donating Substituents. *Journal of Organic Chemistry*, *60*(25), 8305-8309. <https://doi.org/10.1021/jo00130a035>
74. Reichardt, C. (1994). Solvatochromic Dyes as Solvent Polarity Indicators. *Chemical Reviews*, *94*(8) 2319-2358. <https://doi.org/10.1021/cr00032a005>
75. Kobatake, S., Terakawa, Y., & Imagawa, H. (2009). Solvent effect on photochromism of a dithienylperfluorocyclopentene having diethylamino group. *Tetrahedron*, *65*(31), 6104-6108. <https://doi.org/10.1016/j.tet.2009.05.053>
76. Gillanders, F., Giordano, L., Díaz, S. A., Jovin, T. M., & Jares-Erijman, E. A. (2014). Photoswitchable fluorescent diheteroarylethenes: substituent effects on photochromic and solvatochromic properties. *Photochemical & Photobiological Sciences*, *13*, 603-612. <https://doi.org/10.1039/c3pp50374g>
77. Morimoto, M., Takagi, Y., Hioki, K., Nagasaka, T., Sotome, H., Ito, S., Miyasaka, H., & Irie, M. (2018). A turn-on mode fluorescent diarylethene: Solvatochromism of fluorescence. *Dyes and Pigments*, *153*, 144-149. <https://doi.org/10.1016/j.dyepig.2018.02.016>
78. Barrez, E., Laurent, G., Pavageau, C., Sliwa, M., & Métivier, R. (2018). Comparative photophysical investigation of doubly-emissive photochromic-fluorescent diarylethenes. *Physical Chemistry Chemical Physics*, *20*(4), 2470-2479. <https://doi.org/10.1039/c7cp06541h>
79. Taguchi, M., Nakagawa, T., Nakashima, T., & Kawai, T. (2011). Photochromic and fluorescence switching properties of oxidized triangle terarylenes in solution and in amorphous solid states. *Journal of Materials Chemistry*, *21*(43), 17425-17432. <https://doi.org/10.1039/c1jm12993g>
80. Batsanov, S. S. (2001). Van der Waals Radii of Elements. *Inorganic Materials*, *37*(9), 1031-1046. <https://doi.org/10.1023/A:1011625728803>

Schemes

Schemes 1 and 2 are available in the Supplementary Files section.

Figures

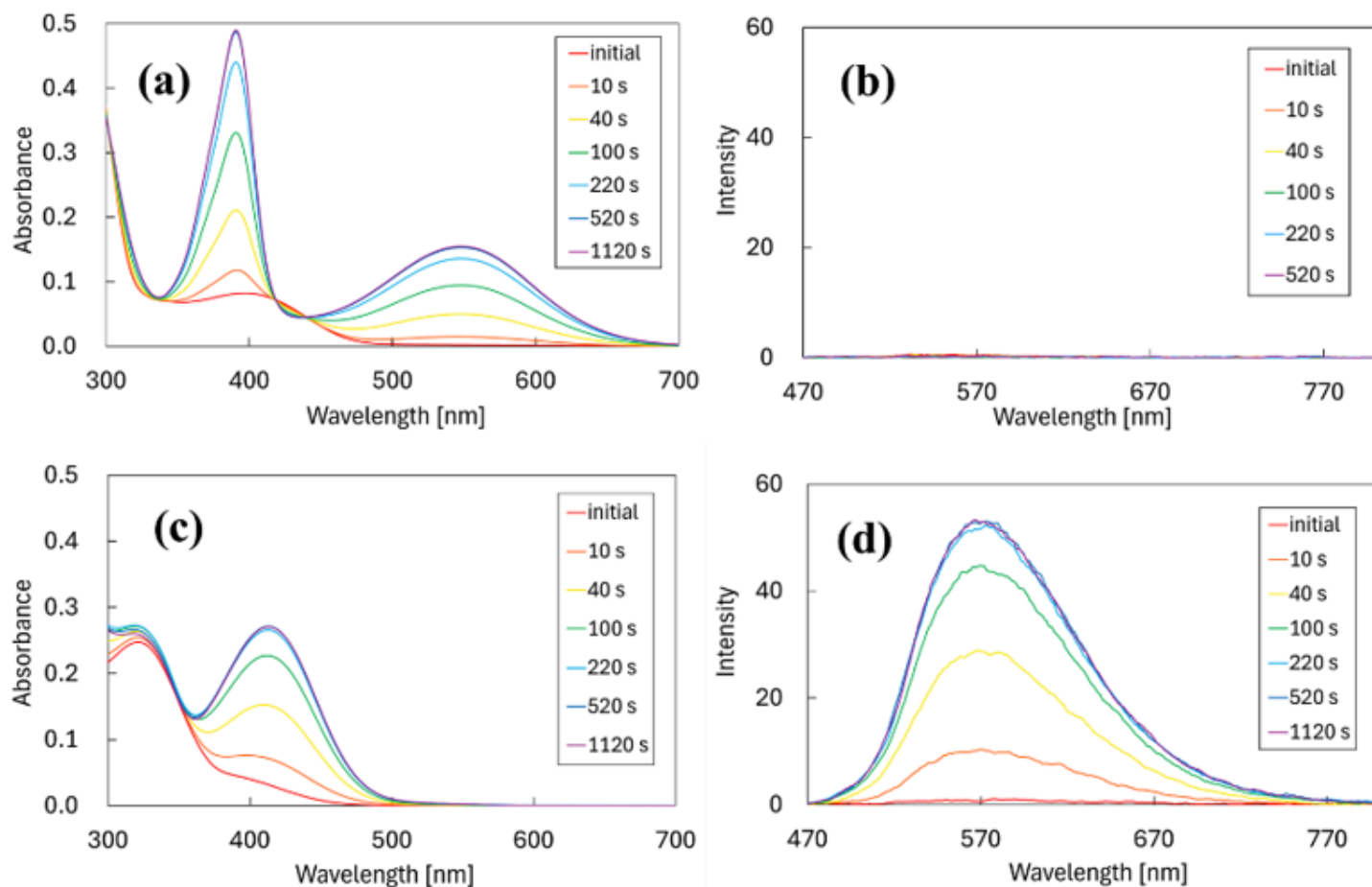


Figure 1

Spectral change in absorbance (**a, c**) and fluorescence excited at 460 nm (**b, d**) of **1o** (**a, b**, 2.1×10^{-5} mol dm^{-3}) and **2o** (**c, d**, 2.3×10^{-5} mol dm^{-3}) in toluene upon irradiation (**a**, 436 nm, 1.5 mW cm^{-2} ; **b**, 436 nm, 2.0 mW cm^{-2} ; **c, d**, 365 nm, 2.0 mW cm^{-2})

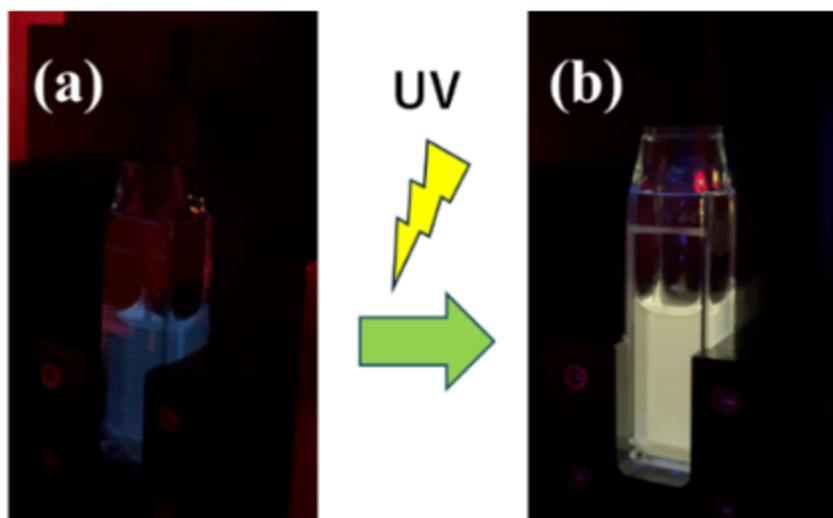


Figure 2

Fluorescence of (a) **2o** and (b) PSS₃₆₅ of **2** in ethanol. Concentration: 2.3×10^{-5} mol dm⁻³. Irradiation and Excitation: 365 nm

Supplementary Files

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