Organic LETTERS

Letter

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Gated Photochromic System of Diarylethene with a Photon-Working Key

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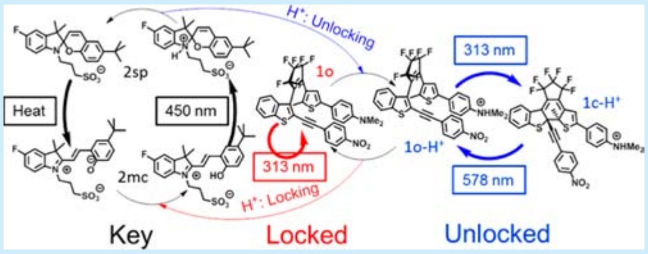
Supporting Information

ABSTRACT: Upon visible light irradiation, a thermally reversible photochromic acid generator merocyanine dye gives a proton to the dimethylamino group of a non-photochromic diarylethene in acetonitrile. The protonation rendered the non-photochromic diarylethene photochromic. Thus, the thermally irreversible photochromic nature of the diarylethene is activated without any physical contact or addition of any compound but only by photoirradiation to the merocyanine dye.

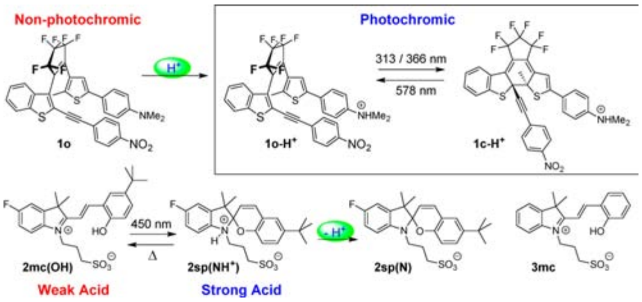


Photochromism is the reversible transformation between two or more chemical species induced by photon absorption.[1] Among such photochromic compounds, diarylethenes are known as one of the most studied families because of their superb fatigue resistivity and ease in fabricating their molecular structures.[2]

Photochemical changes in the structures of photochromic compounds induce switching of their physical, chemical, and bulk properties.[3] Their photochromic properties are sometimes modulated by some external stimuli. When a stimulus such as a chemical species,[4] a chemical reaction,[5] or change in circumstance[6] of the photochromic molecule deprives[4a−d,g,h,j,5a,e,6c] or provides[4e,f,i,k,5b−d,f,6a,b] the ability of photochromic reactions reversibly, it is called "gated photochromism". The most frequently used chemical species for the gated photochromism of diarylethenes is the proton,[4b,c,e,h] which works in many ways: protons can unlock decoloration,[4b] unlock coloration,[4e] lock decoloration,[4h] or lock coloration.[4c] Not only the lock/unlock systems with a proton but ALL gated photochromic reactions induced by a chemical species work by its addition to the system and its removal with the sequential addition of a scavenger such as, e.g., amines for protons. We hereby propose a gated photochromic system composed of **1** and **2** in acetonitrile, which works without addition of any chemical substances or scavenging agents but just by applying a third light irradiation in addition to the two lights necessary for photochromic reactions of the unlocked **1** (Scheme 1).

Recently, we reported the all-optical fine-tuning of the absorption band position for the closed form of a bisthienylethene, possessing two phenanthroline groups on both thiophene rings,[7] by generating a strongly acidic spiro form of spiropyran **2** (**2sp**) from the weakly acidic merocyanine form (**2mc**) by irradiation with 450 nm light.[8] This spiropyran, whose most stable state is the ring-opened merocyanine form, was designed by modification of Liao's sulfo-group-bearing water-soluble spiropyran **3**.[9−11] This modification increased the acidity of the spiro form by introducing a fluorine atom on the phenyl group of the indoline moiety and afforded higher solubility in the organic solvents by introducing a 2-methyl-2-propyl group (*tert*-butyl group) on the phenol ring. It should be noted that **2mc** can hardly give **2sp** by 313 nm light irradiation.[8] Therefore, the transformation of the open forms of diarylethenes to their closed forms can be carried out independent of acid generation. We now have a photochromic acid-generating agent **2** in hand that works in organic solvents.

Scheme 1. Concept of Gated Photochromism with the Photon-Working Key



As one of the ongoing projects in our laboratory, we have synthesized diarylethene **1** possessing a strong electron donor (dimethylaminophenyl) and a strong electron acceptor (nitrophenyl) on different aromatic groups. Its synthesis was carried

Received: August 20, 2016
Published: September 23, 2016

DOI: 10.1021/acs.orglett.6b02494
Org. Lett. 2016, 18, 5042−5045

out as shown in Figure SI-1.[12] This diarylethene **1o** was designed to have two side arms, which come in proximity to each other when it takes an antiparallel conformation.[13] However, **1o** showed sluggish photochromism in toluene with 366 nm light irradiation, which was evidenced by HPLC analysis. A certain part of the compound changed to several unidentified compounds in addition to **1c** when it reached the photostationary state (pss) after irradiation of more than 1 h (Figures SI-2 and SI-3).[12]

When **1o** was irradiated with 366 nm light in acetonitrile, **1o** did not show any change in its absorption spectra after 2 h (Figure 1), indicating neither photocyclization nor photodecomposition occurred. It has frequently been reported that polar solvents such as acetonitrile stabilize the nonreactive intramolecular charge-transfer (ICT)-type twisted excited state of diarylethenes,[14−16] which is generated by strong intramolecular donor−acceptor interactions. It should be noted that **1o** did not show fluorescence in acetonitrile. The strong interaction of the polar acetonitrile molecules with the excited state of **1o** prompted its nonradiative deactivation.[17]

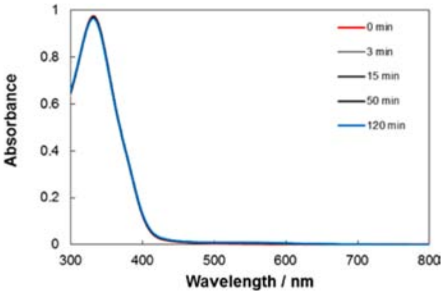


Figure 1. Absorption spectral change of **1o** in acetonitrile upon irradiation with 366 nm light. Concentration: 2.05×10^{-5} mol dm^{-3}. Light intensity: 0.400 mW cm^{-2}.

In order to obtain information on the interaction between the donor−acceptor side chains, we tried to prepare single crystals of **1o**. Under optimized conditions, brown-colored platelet crystals of **1o** suitable for X-ray crystallographic analysis were obtained from its hexane−chloroform solution.[18] The crystals have a chiral space group $P2_1$ where the donor−acceptor side chains adopt a $\pi-\pi$ stacking conformation with the interplanar distances between the cofacially oriented phenyl units of 353.8−358.0 pm.

The crystal lattice includes four independent molecules, all of which take antiparallel conformations. The cyclopentene ring bearing fluorine atoms showed severe multiple disorders; therefore, only the major conformations were modeled and refined.

It is natural that the (dimethylamino)phenyl group and the connected thiophene ring are not coplanar in order to avoid steric repulsion. However, in order to hold the parallel orientation of the two side arms, the nitrophenyl ring and benzothiophene ring connected by an ethyno bridge are also not coplanar, although no steric repulsion occurs when they become flat and coplanar. Although this twisting obviously sacrifices electronic stabilization of the conjugation, **1o** in the single crystal in turn gains stabilization from the $\pi-\pi$ stacking of the side arms in a molecule.

The structure of one of the four molecules is shown in Figure 2. To provide a better understanding of the crystal structure, the fluorine atoms of the primary conformer are shown as thermal ellipsoids and those of the secondary conformer are shown as green balls.

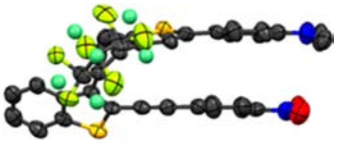


Figure 2. ORTEP drawing of the molecular structure of **1o** obtained by X-ray crystallographic analysis and shown with 50% probability of thermal ellipsoids. Fluorine atoms of the secondary conformer are shown as green balls. Hydrogen atoms are omitted for clarity.

The optimized conformation of **1o** at the ground state obtained by DFT calculations[19] in vacuum is shown in Figure 3a. It also proved that its HOMO is entirely located on the 5-[4-(dimethylamino)phenyl]thienyl side chain, while LUMO is exclusively on 2-[(4-nitrophenyl)ethynyl]benzothienyl side chain (Figure SI-4a,b).[12] Therefore, there is a strong donor−acceptor interaction between these side chains at the ground state of **1o**. In fact, the two side chains try to come closer by bending the otherwise straight nitrophenylethynly group, as shown in Figure 3a. This molecular deformation is different from that observed by X-ray crystallographic analysis in the densely packed crystals.

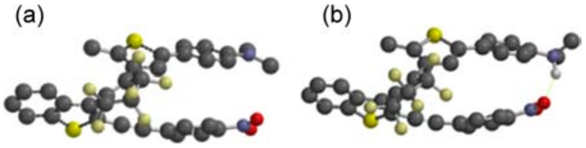


Figure 3. Optimized conformation of (a) **1o** and (b) **1o-H**$^+$ obtained by DFT calculations (B3LYP/6-31G*).

Since the loss of the photochromic nature of **1o** was caused by the interaction of two electronically opposite side arms as shown by DFT calculations, the transformation of the strongly electron-donating amino group into the inductively electron-withdrawing ammonium group led to remarkable changes in the photochromic nature of **1o**.[20] DFT calculations of the ammonium cation of **1o** (**1o-H**$^+$) (Figure 3b) showed that its HOMO and LUMO are located on the same side arm bearing the nitro group (Figures SI-4c,d).[12] Namely, the HOMO is located on the benzothienylethynyl part and the LUMO around the nitrophenylethynyl moiety. It should be noted that the distance between the hydrogen atom on the ammonium nitrogen atom and one of the oxygen atoms of the nitro group is 193.3 pm, forming a hydrogen bond between them. The shape of the nitrophenylethynyl group bends more than that in **1o**, resulting in both ends of the side arms being in proximity for secure hydrogen bonding. Judging from calculations of the molecular orbitals described above, it is strongly expected that the addition of a Brønsted acid results in a dramatic change in the photochromic nature of this molecule.

At first, an excess amount of trifluoroacetic acid (ca. 1000 equiv) was added to the acetonitrile solution of **1o** used in Figure 1. The shape of the absorption band changed remarkably.

As expected, **1o-H**$^+$ exhibited photochromism, as shown in Figure 4a,b. Irradiation of 366 nm light on the acetonitrile solution of **1o-H**$^+$ for 7 min generated an absorption band in the visible region ($\lambda_{\max}$ 546 nm), which is attributed to the generation of the protonated colored form **1c-H**$^+$. Irradiation of

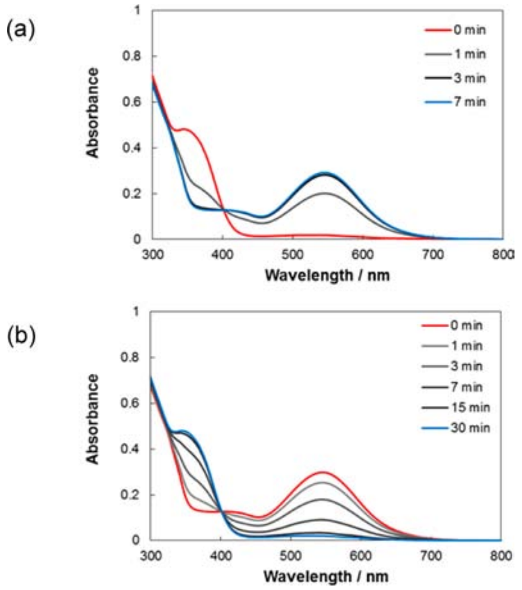


Figure 4. Absorption spectral change of **1o** in acetonitrile in the presence of ca. 1000 equiv of trifluoroacetic acid: (a) 366 nm light irradiation; (b) successive irradiation with 578 nm light to the pss solution of (a). Concentration: 2.05×10^{-5} mol dm^{-3}. Light intensity: 366 nm, 0.400 mW cm^{-2}; 578 nm, 2.20 mW cm^{-2}.

578 nm light on the resulting pss solution in turn generated the original **1o-H**$^+$ spectrum. Thus, it was demonstrated that **1** shows an ordinary acid-switchable "gated photochromism".

This set up the photon-gated primary photochromism of **1** controlled by the secondary photochromism of **2**, the thermally reversible photochemical acid generator. In order to generate a strong acid, 450 nm light is convenient where the absorbance of **2mc** is large but that of **1o** is negligible. Although 366 nm light is convenient for the ring closure of **1o**, it may induce the generation of **2sp** from **2mc**. Fortunately, it has already been evidenced[8] that **2mc** gives little **2sp** by 313 nm light irradiation. Therefore, 450 nm light can be used for the conversion of **2mc** to **2sp**, 313 nm light can be used for the generation of **1c-H**$^+$ from **1o-H**$^+$, and visible light such as 578 nm light can bring back **1c-H**$^+$ to **1o-H**$^+$.

Irradiation of 313 nm light on the equimolar mixture of **1o** and **2mc** in acetonitrile resulted in slight coloration due to the generation of small amounts of **1c-H**$^+$. It was presumed that the small amount of **2sp** generated by 313 nm light gave **1o-H**$^+$, which was cyclized to give **1c-H**$^+$ by 313 nm light simultaneously. When a 0.1 molar equiv of triethylamine existed in the solution, no coloration was observed after 5 min irradiation of 313 nm light to the mixture, as shown in Figure 5a.

When this solution was irradiated with 450 nm light for 4 min, the first photochromism of **2mc** (pK_a *ca.* 9.99[8]) generated a strong Brønsted acid **2sp** (pK_a ca. 3.97[8]), which transferred a proton to **1o** to generate **1o-H**$^+$ (pK_a ca. 4.16[8]) (Figure 5a). The successive irradiation of 313 nm light induced a rapid coloration resulting from the generation of **1c-H**$^+$ (Figure 5b). It is interesting to note that the absorption maximum of **1c-H**$^+$ generated by **2sp** in acetonitrile was 594 nm, while **1c-H**$^+$ obtained with trifluoroacetic acid was 546 nm. This may be due to the difference in the counteranion. The trifluoroacetate anion resides close to the proton on the ammonium group, while the alkylsulfonate anion exists out of the complexation sphere due to the extremely weak basicity of the sulfonate.

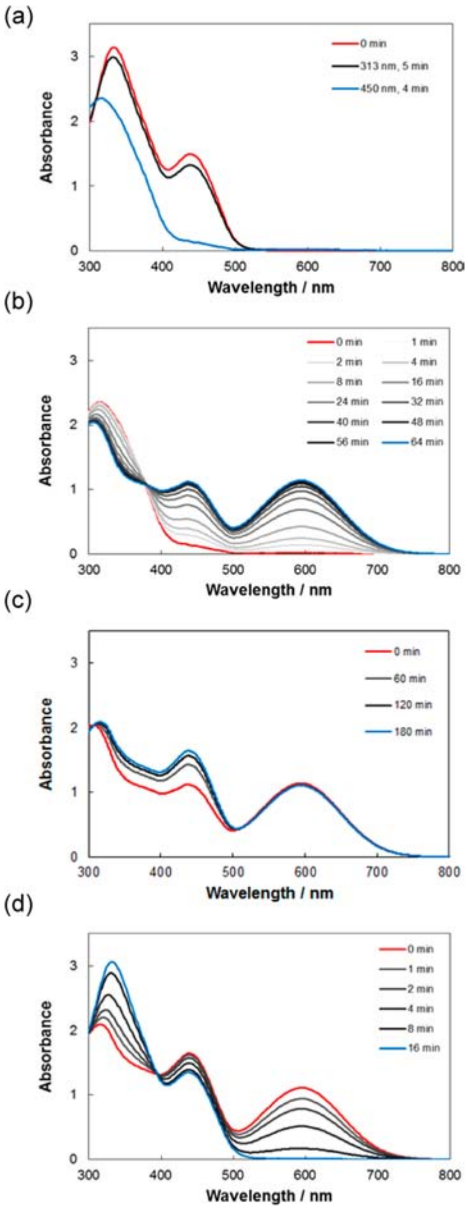


Figure 5. Absorption spectral change of **1o** and **2mc** in acetonitrile in the presence of triethylamine: (a) irradiation of 313 nm light (5 min), then 450 nm light (4 min); (b) successive irradiation to the solution of (a) with 313 nm light; (c) thermal change of **2sp** to **2mc** at room temperature; (d) irradiation of 578 nm light to the solution of (c). Concentration: **1o**, 2.50×10^{-5} mol dm^{-3}; **2mc**, 2.50×10^{-5} mol dm^{-3}; Et_3N, 2.50×10^{-6} mol dm^{-3}. Light intensity: (a) 313 nm, 0.400 mW cm^{-2}; 450 nm, 0.420 mW cm^{-2}; (b) 313 nm, 0.400 mW cm^{-2}; (d) 578 nm, 2.20 mW cm^{-2}.

A thermal back reaction of **2sp** to **2mc** was observed after irradiation of 313 nm light was discontinued by the slow increase of the absorption band at around 450 nm (Figure 5c). Irradiation of 578 nm light to this solution resulted in the complete transformation of **1c-H**$^+$ to **1o-H**$^+$ (Figure 5d). When **2sp** was completely changed to **2mc** after 3 h at room temperature, the photochromism of **1o** was locked again.

This phenomenon is repeatable, and no practical difference of absorption spectra was observed during the second cycle.

In summary, we have synthesized a new diarylethene **1o** possessing an electron-donating arm and an electron-withdrawing arm. These two side arms reside in proximity to each other when they take the antiparallel conformation, as evidenced by X-ray crystallographic analysis and DFT calculations.

In acetonitrile, **1o** did not show photochromism upon irradiation of 366 nm light. However, the addition of trifluoroacetic acid restored its photochromic nature, indicating that **1o** is a proton-gated photochromic compound.

Irradiation of 313 nm light to a solution of a **1o** and **2mc** mixture with small amounts of triethylamine in acetonitrile did not show photochromic reactions of both photochromic species. However, irradiation of 450 nm light to this solution to induce photochromism of **2mc** to **2sp** followed by the irradiation of 313 nm light resulted in the formation of **1c** as its protonated form **1c-H**$^+$. Irradiation of 578 nm light to the pss solution caused the complete disappearance of **1c-H**$^+$. The photochromism of **1o** was again locked when **2sp** reverted back to **2mc**. The thermally irreversible photochromism of **1** was thus unlocked and locked by the thermally reversible photochromism of **2** as the photon-working key. To the best of our knowledge, this acetonitrile solution of **1o** and **2mc** with triethylamine is the first all-optical, photon-working, gated photochromic system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02494.

Experimental details, synthetic procedures, DFT calculation results, and characterization of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant No. JP26107009 in Scientific Research on Innovative Areas "Photosynergetics". S.M. thanks Negin Baspar Giti Co., Ltd. for providing the scholarship for his work at YNU as part of his Ph.D. research activities. We are grateful to the Zeon Corp. for their generous gift of octafulorocyclopentene. We are also deeply indebted to Professor Yoshitaka Yamaguchi, YNU, for his valuable suggestions and support in solving the crystal structure of diarylethene **1o**. Thanks are also extended to the Analytical Instruments Center, YNU, for measurements of the mass spectra and the ^{1}H and ^{13}C NMR spectra.

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