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Supporting Information

Photo-induced Damage of Cultured Cells on Diarylethene Thin Layers through Sulfur Dioxide Generation

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1 General Experimental Details

Cell culture experiment: NIH/3T3 (from Swiss mouse embryo tissue) and MDCK (Madin-Darby canine kidney) cells were used in this experiment. Light irradiation onto the photo-responsive culture substrates was carried out by using a PC-controlled microprojection system (DESM-01, Engineering System Co.) installed in an inverted research microscope (IX70, Olympus Co.).^{S1} Blue light with wavelength of 436 nm or near UV light with wavelength of 365 nm was irradiated onto arbitrary areas of the sample as observed through the same objective lens. Bright field images of the culture

surfaces were taken with a cooled CCD camera system (VB-7000, Keyence Co.) installed on the same microscope. JEOL JMS-GC mate IIR was used for identification by FAB-MS of the by-products of **10**. Shimadzu Gas Chromatograph-Mass Spectrometer GCMS-QP2010 Plus attached with a pyrolyzer PY-2020iD (Frontier Lab) was used for identification by mass spectrography of sulfur dioxide. GASTEC gas detector tube systems (gas sampling pump set GV-100S attached with sulfur dioxide detector tube (No. 5Lb, 1M005LbJ2) for sulfur dioxide) was used for measuring the concentration of sulfur dioxide gas. For the SO₂ gas generation, UV light was irradiated by using a UV hand lamp (TOPCON Fi-5L, 300 nm< λ <365 nm, main band at λ = 365 nm).



2. GC-Mass spectroscopy of UV generated substance in gas phase

Fig. S1. GC-Mass spectroscopy of UV generated substance in gas phase. The total mass profile vs retention time (min); blue line: total mass profile, red line: mass profile corresponding to $M^+=64$ (above). The mass spectrum at 1.6 min of the retention time on the red line (below). Detailed explanation is described in **6. Discussion about decomposition mechanism.**

3. Detection of sulfur dioxide by a gas detector



Fig. S2. Apparatus for the measurement of SO_2 gas generation. The beaker containing the hexane solution of 10 or 1c was sealed with cover glass and oil-based clay (for modelling and sculpting). Then the solution was irradiated UV lamp (Fi-5L) from the bottom. After the irradiation, the test tube of the gas detector was inserted through the clay and suctions were carried out to measure the SO_2 gas.



Fig. S3. Transmission spectrum of the bottom of the beaker.



Fig. S4. Detection of sulfur dioxide by a gas detector

Yellow domain indicates the detected amount of SO₂ gas. Isolated 20 mg of **10** or **1c** was dissolved in 5 mL of hexane and UV or visible light was irradiated for a limited period from the bottom, then the generated SO₂ gas was detected by a tube gas detector by suction. For the low concentration gas condition, suction times were increased for the detection. For the UV irradiation, a UV hand lamp (Topcon UV 21, 11W) was applied. For the visible light irradiation, Ushio Xe lamp (500 W) was used with cut-off filters (Toshiba colour filters) Y43 (λ >430 nm) and 48 (λ >480 nm).

1 **10:** UV (300 nm< λ <365 nm), 15 s, suction 4 times, 2 **1c:** UV (300 nm< λ <365 nm), 15 s, suction 4 times, 3 **10:** UV (300 nm< λ <365 nm), 30 s, suction twice, 4 **1c:** UV (300 nm< λ <365 nm), 30 s, suction twice, 5 **10:** UV (300 nm< λ <365 nm), 60 s, suction twice, 6 **1c:** UV (300 nm< λ <365 nm), 60 s, suction twice, 6 **1c:** UV (300 nm< λ <365 nm), 60 s, suction twice, 7 **10:** UV (300 nm< λ <365 nm), 120 s, suction twice, 8 **1c:** UV(300 nm< λ <365 nm), 120 s, suction twice, 9 **10:** UV (300 nm< λ <365 nm), 240 s, suction once, 10 **10:** UV (300 nm< λ <365 nm), 240 s, suction twice, 12 **1c:** Vis λ >430 nm, 240 s, suction twice, 12 **1c:** Vis λ >430 nm, 240 s, suction twice. (Standard measurement: suction twice)

4. Measurement of generated SO₂ gas by tuning the UV light intensity: Topcon UV hand lamp (Fi-5L) was used for SO₂ gas generation experiments. ND filters; Opto Sigma FNDU-50C02-50 and FNDU-50C02-20 were used for reducing the light intensity of UV light to 50% and 20%, respectively. And transmission spectra of the ND filters are shown in Figs. S5 and S6.

	10		1c	
	Detected	Calcd. SO ₂	Detected	Calcd. SO ₂
	concentration	amount	concentration	amount
	(ppm)	(mol)	(ppm)	(mol)
30 sec	0.20 (× 1)	$0.53 imes 10^{-6}$	0.10 (× 1)	$0.28 imes 10^{-6}$
1 min	0.70 (× 1)	$1.85\times10^{\text{-}6}$	0.47 (× 1)	$1.25\times 10^{\text{-6}}$
2 min	1.00 (× 1)	$2.75 imes 10^{-6}$	0.75 (× 1)	$1.98\times10^{\text{-}6}$
4 min	2.34 (× 2)	$6.25 imes 10^{-6}$	2.00 (× 2)	$5.25 imes 10^{-6}$

Table S1. Generated amount of SO₂ gas by gas detector without ND filters

Table S2. Generated amount of SO_2 gas by gas detector with 50%ND filter(FNDU-50C02-50)

	10		1c	
	Detected	Calcd. SO ₂	Detected	Calcd. SO ₂
	concentration	amount	concentration	amount
	(ppm)	(mol)	(ppm)	(mol)
1 min	0.40 (× 1/2)	$1.06 imes 10^{-6}$	0.20 (× 1/2)	$0.53 imes 10^{-6}$
2 min	0.80 (× 1/2)	2.11×10^{-6}	0.38 (× 1/2)	$0.99 imes 10^{-6}$
4 min	1.60 (× 1/2)	$4.22\times 10^{\text{-6}}$	0.90 (× 1/2)	$2.37 imes 10^{-6}$
6 min	2.50 (× 1/2)	$6.60 imes 10^{-6}$	1.50 (× 1/2)	$3.82\times10^{\text{-}6}$

	10		1c	
	Detected	Calcd. SO ₂	Detected	Calcd. SO ₂
	concentration	amount	concentration	amount
	(ppm)	(mol)	(ppm)	(mol)
1 min	0.30 (× 1/2)	$0.79 imes 10^{-6}$	0.18 (× 1/2)	$0.20\times 10^{\text{-}6}$
2 min	0.48 (× 1/2)	$1.25 imes 10^{-6}$	0.25 (× 1/2)	$0.28\times10^{\text{-}6}$
4 min	0.70 (× 1/2)	$1.84 imes 10^{-6}$	0.30 (× 1/2)	$0.37 imes 10^{-6}$
6 min	1.00 (× 1/2)	$2.57 imes 10^{-6}$	0.38 (× 1/2)	$0.99 imes 10^{-6}$

Table S3. Generated amount of SO_2 gas by gas detector with 20%ND filter(FNDU-50C02-20)



Fig. S5. Transmission spectra of the 50% ND filter (FNDU-50C02-50)



Fig. S6. Transmission spectra of the 20% ND filter (FNDU-50C02-20)

5. Fatigue resistance of the photochromism between 10 and 1c



Fig. S7 Repetition cycles of the photochromism between **10** and **1c** in hexane solution $(4.7 \times 10^{-5} \text{ mol } \text{L}^{-1})$. Initially the photostationary state (**10**:**1c**=34:66, depicted 0 in the figure) formed by UV light (300 nm< λ <365 nm, 12 W, UV hand lamp (Topcon Fi5L)). Then it was irradiated with visible light (Ushio Xe lamp, 500 W with cut off color filter (λ >480 nm)) for 20 min to recover the **10** solution. Then the UV light was irradiated for 6 min to form photostationary state (as depicted 1 in the figure). The absorbance of **1c** at 477 nm (λ_{max}) was reduced to 87% of the initial value. After repetition of 2, 3, and 4 cycles, the absorbance of the band was reduced to 60, 41, and 29% of the initial value, respectively. This is due to the decomposition of **10**.

6. Discussion about decomposition mechanism

In order to investigate the mechanism of the formation of SO_2 gas, we analyzed the product of the photoirradiation. S. I. Yang et al. has reported the fatigue resistant property of oxidized diarylethene is slightly inferior compared with un-oxidized diarylethene,^{S2} since the decomposition or by-product formation were anticipated. We monitored the photochromic reactions between 10 and 1c upon alternate irradiation with UV and visible light by ¹H NMR in CDCl₃ solution, and found the formation of small amount of by-products which shows the signals at 6.5 and 7.3 ppm, respectively (Fig. S8). In order to determine the generated gas accompanied by the formation of the byproducts, we irradiated the UV light (365 nm) to the chloroform solution of 10 in a closed-vessels, and photo-generated gas was analyzed by GC-Mass spectroscopy. The result is shown in Fig. S1. The large peak at 2.3 min of retention time is attributed to the chloroform of the solvent, and small peaks at 2.0 and 2.2 min are attributed to hexane (remained in previous measurement) and the (CH₃)₃Si-OH (origin from GC column), respectively. The peaks at 48 and 64 are attributable to SO and SO₂. From the solution, by-product 2 was obtained in 7% yield after UV irradiation for 10 h irradiation and isolated to determine the structure by ¹H NMR and X-ray analysis. The obtained structure is also shown in Scheme S1 and Fig. S12. However the products, generated after removal of SO₂ moiety could not be isolated, due to the formation of higher molecular weight by-products (Fig. S9). We also analyzed the by-products formed by heating **10** at 70 °C for 7 days in the dark (Fig. S10). The ¹H NMR showed the new signals attributed to the by-products at 6.86 ppm. And during the storage of the heated sample for 2 days at room temperature in the dark, another signal appeared at 3.49 ppm. Although we tried to isolate the products by HPLC, they were adsorbed on the silicagel and never obtained. Then we used the diffusion ordered spectroscopy (DOSY) NMR to identify the by-products (Fig. S11). The spectrum shows the formation of three kinds of by-products, two is smaller molecular weight by-products and the one is larger molecular weight by-products. The lower molecular weight products were evaporated even at room temperature under normal pressure indicating thiophene or butane analogues.



Fig. S8. ¹H NMR spectral changes of **10** upon alternate irradiation with UV (λ = 365 nm, 5 min) and visible (λ >410 nm, 10 min) light in CDCl₃. (A) Before UV irradiation, (B) after UV irradiation, (C) after visible light irradiation.



Fig. S9. FAB Mass spectra of the by-products of 10



Fig. S10. ¹H NMR spectral changes of **10** under a heating procedure. A) Before heating; B) upon heating at 70 °C in the dark for 7 days; C) stored in the dark at room temperature for another week after the situation of B.



Fig. S11. DOSY NMR spectra of the CDCl₃ solution of 10 after storage in hexane solution at 70 $^{\circ}$ C for 7 days in sealed tube.



Scheme S1. Obtained by-product 2 and expected compounds 3, 4 and 5



Fig. S12. Molecular structure of 2 determined by X-ray analysis

The by-product 2 was isolated and the structure was identified by ¹H NMR spectral measurement and X-ray single crystal analysis (Fig. S12).

Intensity data of crystal of **2** were collected by the ω scan with a width of 0.3 /frame on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo KR radiation ($\lambda = 0.71073$ Å) at 93 K. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects and decay. The cell constants were determined by the global refinement. The structure was solved by direct methods using SHELXS-9713 and refined by full-matrix least-squares on F2 using SHELXL-97.^{S3} The positions of hydrogen atoms were calculated geometrically and refined by the riding model.

Compound **2**: ¹H NMR (400 MHz, CDCl₃, 298 K): 1.30 (s, 3H), 2.14 (dd, 3H, *J*=3.0, 1.8 Hz), 2.56 (s, 3H), 2.57 (s, 3H), 4.32 (brs, 1H), 6.63 (m, 1H). Crystal Data for of **2**. $C_{17}H_{14}F_6O_2S_2$, monoclinic, P2(1)/c, a=9.9685(7) Å, b= 10.8630(7) Å, c=15.8102(11) Å, β = 98.9010(10), V = 1691.4(2) Å3, Z = 4, Dcalcd = 1.682 g /cm³, R1 (I > 2 σ (I)) = 0.0310, wR2 (I > 2 σ (I)) = 0.0844, T = 93(2) K; CCDC 926314. E. Kim *et al.* suspected the formation of compound **3** and **4**,^{S4} and **4** is a famous byproduct as reported by Kim,^{S4} Irie,^{S5} and Branda,^{S6} however **3** and **4** were not isolated in our study. In these structures, SO₂ moiety is still remained. Generation of sulfur dioxide gas should be accompanied by the formation of by-product with the molecular weight of 364 [428(M^+)-64(SO₂)]. Kobatake *et al.* reported the decomposition mechanism in which the elimination reaction of sulfur dioxide proceeds.^{S7} Considering their proposed mechanism, compound **5** is the suspected by-product. The compound have vinyl group and have the possibility to undergo photoinduced dimerization. The major product is shown by the mass spectra as the major peak at 727 which is considered as the fragment peak generated from the dimers (M^+ : 856).

The SO₂ gas formed in aqueous culture solution will change to form sulfurous acid. Due to the strong acidity will also give the damage to the cells. We measured the SO₂ gas detection by using a gas detector tube system. Same amount (20 mg, 4.7×10^{-5} mol) of **10** and **1c** were dissolved in methanol and the solution was coated to the bottom of 100 mL beakers. And the methanol was evaporated to form the film. One beaker is 10, and the other is 1c. 5 mL of water was added to the beakers having the 1o and 1c substrate to mimic the culture system. Two beakers were prepared containing 10 or 1c in 5 mL of hexane. And then UV light was irradiated for 4 min to the four beakers whose top side is closely sealed with oil based clay and a glass plate, then UV light was irradiated from the bottom of the beakers (Fig. S2). After irradiation, gas concentration was detected by using a gas detector. The result was summarized in Table S1. The SO₂ gas was detected only for hexane solution. Then we also observed the SO₂ gas detection experiment with changing the UV irradiation period 15, 30, 60, 120, and 240 s for the hexane solution of 10 and 1c, respectively. The content of SO₂ gas was increased with the periods of UV irradiation. And the yield of SO₂ gas after UV irradiation for 4 min was reached to 13.4%. In contract no SO_2 gas was detected upon irradiation to 1c the hexane solution of 1c in the same concentration with visible light (λ >430 nm). During the irradiation, 34% of 1c was turned to be 1o, however no by-products were obtained. Comparing the results of **10** and **1c**, SO₂ was generated only from **10**. Under continuous irradiation with 365 nm light, 1c generates 1o and 1o formed SO₂ gas. This leads the cell death under 365 nm to the solution of 1c. The SO₂ gas generation from thiophene 1,1-dioxide was already reported by Nakayama and his coworkers,^{\$8,\$9} and they

mentioned the gas formation proceeds even at room temperature. We also studied the gas formation from 2,5-dimethylthiopnene 1,1-dioxide and found the same gas generation at room temperature and enormous gas generation was observed under UV light irradiation. This also supports the rule that the generation ability of SO₂ gas is larger in shorter conjugation system.

Comparing the medium of water and hexane, detected amount of SO_2 gas from **1o** in hexane was larger than that in water. This result indicates that some amount of SO_2 gas dissolved into water, but no change of pH values was detected.

Upon UV irradiation, the cells cultured on the thin layer of diarylethene **10** were damaged significantly by UV (300-365 nm) light irradiation which brought apparent change in cell viability. Diarylethene **10** was confirmed to undergo photochromic reaction accompanied with decomposition to generate sulfur dioxide gas in the aqueous culture solution. This system will be applicable to a tool of cell screening and cell purification by killing adherent cells as they are cultured on a substrate by microprojection of incoherent 365 nm light. 2,5-Dimethilthiophene 1,1-dioxide also generates the SO₂ gas upon UV (300-365 nm) irradiation, however the compound has the absorption band at shorter wavelengths (λ_{max} : 292 nm, ε : 2.0×10³ M⁻¹cm⁻¹)(Fig. S13), and it decompose and generates SO₂ gas even in the dark at room temperature.^{S8,S9}



Fig. S13 Absorption spectrum of 2,5-dimethylthiophene *S*,*S*-dioxide in hexane $(4.21 \times 10^{-4} \text{ M}), (\lambda_{\text{max}}: 292 \text{ nm}, \varepsilon: 2.0 \times 10^{3} \text{ M}^{-1} \text{ cm}^{-1})$

7. Quantum yield of the production of SO₂

In order to obtain the quantum yield of the production of SO_2 , we analyzed the time dependence of the absorption spectra shown in Figure S8 by using the rate equation. In the following, we assume that one SO_2 molecule and one by-product are produced from the photo-excited **10**.

The rate equation for the current system is given by the following equations.

$$\frac{dP_{\rm o}}{dt} = -k_{\rm co}P_{\rm o} - k_{\rm bo}P_{\rm o} + k_{\rm oc}P_{\rm c} , \qquad (S1)$$

$$\frac{dP_{\rm c}}{dt} = k_{\rm co}P_{\rm o} - k_{\rm oc}P_{\rm c} \,, \tag{S2}$$

where P_0 and P_c are the probabilities to find a diarylethene molecule in **10** and **1c** state, respectively. The rate constants k_{co} , k_{oc} , and k_{bo} denote the rates for the cyclization, for the cycloreversion, and for the production of by-products, i.e., the production of SO₂. Thus, the probability to find by-product instead of **10** and **1c**, i.e., P_b is given by

$$P_{\rm b} = 1 - P_{\rm o} - P_{\rm c} \,. \tag{S3}$$

The rate constants are proportional to the power of laser. Also k_{co} , k_{oc} , and k_{bo} , are proportional to the quantum yield of cyclization, cycloreversion, and the production of by-products, respectively. We assume a monochromatic UV laser at the energy $\epsilon = \epsilon_0$ is continuously applied and the absorption spectra are obtained intermittently so that the P_o and P_c are not affected by the applied field for the determination of the absorption spectra.

Experimentally, the hexane solution of the open-ring isomer **10** was initially prepared. Thus, the initial conditions of the differential equations (S1) and (S2) are given by $P_0(t=0)=1$ and $P_c(t=0)=0$. Then, the solution of Eqs (S1) and (S2) is given by

$$P_{\rm o} = e^{\lambda_{\rm o}t} + \frac{k_{\rm oc} + \lambda_{\rm +}}{\sqrt{(k_{\rm co} + k_{\rm oc} + k_{\rm bo})^2 - 4k_{\rm oc}k_{\rm bo}}} \left(e^{\lambda_{\rm +}t} - e^{\lambda_{\rm -}t}\right),\tag{S4}$$

$$P_{\rm c} = \frac{k_{\rm oc}}{\sqrt{(k_{\rm co} + k_{\rm oc} + k_{\rm bo})^2 - 4k_{\rm oc}k_{\rm bo}}} \left(e^{\lambda_+ t} - e^{\lambda_- t}\right),\tag{S5}$$

where λ_+ and λ_- are given by

$$\lambda_{\pm} = \frac{1}{2} \Big\{ -(k_{\rm co} + k_{\rm oc} + k_{\rm bo}) \pm \sqrt{(k_{\rm co} + k_{\rm oc} + k_{\rm bo})^2 - 4k_{\rm oc}k_{\rm bo}} \Big\}.$$
 (S6)

The absorption spectra at the energy ϵ is obtained by the following equation.

$$A(\epsilon) = A_{\rm o}(\epsilon)P_{\rm o} + A_{\rm c}(\epsilon)P_{\rm c} + A_{\rm b}(\epsilon)P_{\rm b},\tag{S7}$$

where A_0 , A_c , and A_b are the absorption spectra of **10**, **1c**, and by-products, respectively. The absorption spectrum of **10** $A_0(\epsilon)$ can be obtained experimentally by $A(\epsilon)$ at t=0. If we know P_0 and P_c at a time $t = t_F$, the absorption spectra of $A_c(\epsilon)$ and $A_b(\epsilon)$ can be estimated by the following equations.

$$A_{\rm c}(\epsilon) = \frac{A(\epsilon, t=t_F) - A_o(\epsilon)P_o(t=t_F) - \left(A_{cr}(\epsilon) - A_o(\epsilon)\left(P_o(t=t_F) + P_{\rm c}(t=t_F)\right)\right)}{P_{\rm c}(t=t_F)},\tag{S8}$$

$$A_{\rm b}(\epsilon) = \frac{A_{cr}(\epsilon) - A_o(\epsilon) (P_o(t=t_F) + P_c(t=t_F))}{1 - P_o(t=t_F) - P_c(t=t_F)}.$$
(S9)

Here, $A(\epsilon, t = t_F)$ is the absorption spectrum at $t = t_F$. The absorption spectrum A_{cr} is experimentally determined by first irradiating the compound by a monochromatic UV laser starting from t = 0 to $t = t_F$, then switching the laser to the visible light and continuously irradiating the compound until photostationary state is achieved; the final absorption spectrum is A_{cr} .

As we have already shown in Eqs (S4) and (S5), the time dependences of P_0 and P_c are determined by k_{co} , k_{oc} , and k_{bo} . Those rate constants are used as parameters to reproduce the time dependence of the absorption spectrum $A(\epsilon, t)$. In the current system, we have previously determined the quantum yield of the cyclization and cycloreversion reactions ϕ_{co} and ϕ_{oc} . Therefore, we can obtain the quantum yield of the production of SO₂ ϕ_b using the determined values of k_{co} and k_{bo} .

$$\phi_b = \frac{k_{\rm bo}}{k_{\rm co}} \phi_{\rm co}.\tag{S10}$$

8. Influence of UV irradiation on MDCK cells on 1c coated substrate



Fig. S14. Influence of patterned UV irradiation (wavelength: 365 nm, intensity: 90 mW/cm²) on MDCK cells on **1c** coated substrate (0.3 μ g/cm²). Three same samples (a) (c) (e) were prepared. (b) 2 h later after UV irradiation for 4 min on the film of (a), (d) 2 h later after UV irradiation for 8 min on the film of (c), (f) 2 h later after UV irradiation for 12 min on the film of (e).

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