Supplementary Material

Rate constant for the generation of $^1O_2$ from commonly used triplet sensitizers: a systematic study on the wavelength effect using an ene reaction of 2,3-dimethyl-2-butene

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[1] Derivation of eq 5 from eqs 3′ and 4.

When we consider steady state of $[^1O_2]$, eq 3′ becomes

$$d[^1O_2]_t / dt = k_1\, p\, [\mathrm{sen}]_t [^3O_2]_t - k_2 [^1O_2]_t [\mathbf{1}]_t = 0 \qquad (3'')$$

From eq 3″

$$[^1O_2]_t = k_1\, p\, [\mathrm{sen}]_t [^3O_2]_t / k_2 [\mathbf{1}]_t \qquad (3''')$$

By substituting 3‴ to eq 4, we obtain

$$- d[\mathbf{1}]_t / dt = k_1\, p\, [\mathrm{sen}]_t [^3O_2]_t \qquad (4')$$

As p, $[\mathrm{sen}]_t$ ($\approx [\mathrm{sen}]_0$ = 0.12 mM, initial concentration of the sensitizers), and $[^3O_2]_t$ ($\approx [^3O_2]_s$, concentration of saturated $^3O_2$) can be considered as constants, eq 4′ is solved as

$$[\mathbf{1}]_t = - k_1\, p\, [\mathrm{sen}]_0 [^3O_2]_s\, \mathrm{t} + \mathrm{C} \qquad (4'')$$

where C is a constant.

At $t = 0$, $[\mathbf{1}]_t$ is $[\mathbf{1}]_0 = 3.0 \times 10^{-2}$ [M], so that from eq 4″

$$[\mathbf{1}]_t = - k_1\, p\, [\mathrm{sen}]_0 [^3O_2]_s\, t + 3.0 \times 10^{-2} \qquad (5)$$

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[2] Number of photons absorbed by the solution per unit time.

In our reactions, 10 mL of solutions were introduced in a cylindrical cell with 3.0 cm diameter. Therefore, the height of the solution in the cell (l_H) is calculated to be $l_H = 10/(1.5^2\ \pi)$ cm.

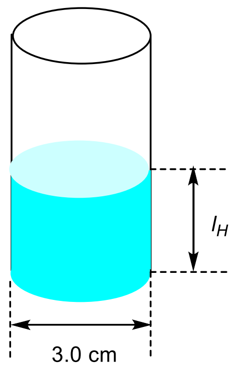

Figure 1. Cylindrical cell

Figure 2 shows the horizontal projection of the cylindrical cell. When the radius of the cell is divided into n segments, the optical path of the rectangular parallelepipeds at m th segment, l_m cm, is calculated to be

$$l_m = 2\sqrt{1.5^2 - \left(\frac{1.5}{n}m\right)^2}$$

$$= \frac{3}{n}\sqrt{n^2 - m^2}$$

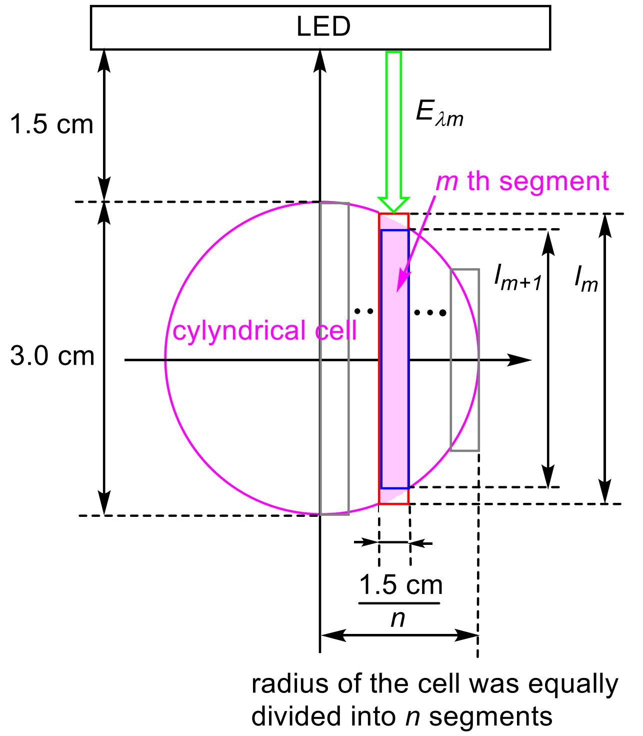

Figure 2. Horizontal projection of cylindrical cell

The number of photons (wavelength λ) absorbed by m th rectangular parallelepiped shown in Figure 3 in 1 min ($[\text{sens}]_0 p_{\lambda m}$) is,

$$[\text{sen}]_0 p_{\lambda m} = \frac{60 \times \frac{1.5}{n} l_H E_{\lambda m}\left(1 - 10^{-\varepsilon_\lambda c \frac{3}{n}\sqrt{n^2 - m^2}}\right)}{\frac{hC}{\lambda} N_A}$$

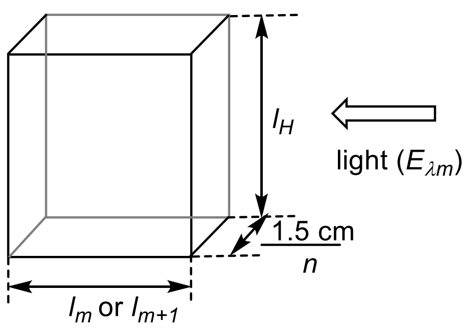

Figure 3. Rectangular parallelepiped of the solution at *m* th segment

where $E_{\lambda m}$ W/cm^2 is the intensity of incident light (wavelength λ) at m th segment, c is the concentration of the sensitizer, h is Planck's constant, C is the speed of light, ε_λ is the molar absorption coefficient of the sensitizer at wavelength λ, and N_A is the Avogadro's number.

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Figure 4 shows the relationship between the light intensities of flat panel LED 395 (370-475 nm, λ_{max} 400 nm) and LED 525 (455-600 nm, λ_{max} 518 nm), and distance from the LEDs. As shown in the figure, the light intensities decrease proportionally with the distance. Therefore, the intensity of incident light (wavelength λ) at m th segment (cf. Figure 2), $E_{\lambda m}$ W/cm^2, is

$$E_{\lambda m} = E_{\lambda 1.5} + (E_{\lambda 1.5} - E_{\lambda 3}) - (E_{\lambda 1.5} - E_{\lambda 3})/1.5 \times \left\{3 - \sqrt{1.5^2 - \left(\frac{1.5\,m}{n}\right)^2}\right\}$$
$$= 2\,E_{\lambda 1.5} - E_{\lambda 3} - (E_{\lambda 1.5} - E_{\lambda 3})/1.5 \times \left\{3 - \sqrt{1.5^2 - \left(\frac{1.5\,m}{n}\right)^2}\right\}$$

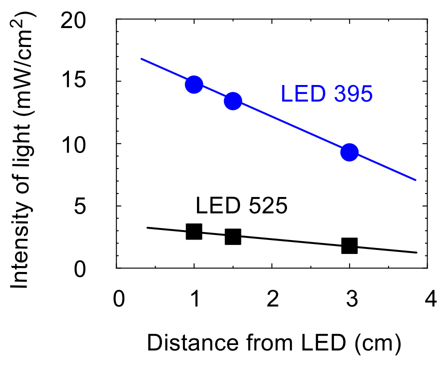

Figure 4. Intensity of light vs distance from LED

where $E_{\lambda 1.5}$ and $E_{\lambda 3}$ are the intensities of incident light (wavelength λ) at 1.5 and 3 cm from the LED, respectively.

Therefore, the total number of photons absorbed by the solution at m th segment of the cylindrical cell in 1 min ($[\text{sen}]_0 p$) falls between the volume of rectangular parallelepipeds having lengths l_m and l_{m+1} (cf. Figure 3), which is

$$[\text{sen}]_0 p_{min} = \sum_{\lambda_1}^{\lambda_2} \sum_{m=1}^{n} 2[\text{sen}]_0\, p_{\lambda m} < [\text{sen}]_0 p < \sum_{\lambda_1}^{\lambda_2} \sum_{m=0}^{n-1} 2[\text{sen}]_0\, p_{\lambda m} = [\text{sen}]_0 p_{max}$$

where λ_1 and λ_2 are the wavelengths of the both ends of the emission of LEDs, namely, λ_1 = 370 nm and λ_2 = 475 nm for the 395 nm LED, and λ_1 = 455 nm and λ_2 = 620 nm for the 525 nm LED.

Calculated $[\text{sen}]_0 p_{max}$ and $[\text{sen}]_0 p_{min}$ for n = 1000 are listed in Table S1. The ε_λ s in the above equations were calculated from the absorbance of each sensitizer that were measured by UV spectroscopy. $E_{\lambda 1.5}$ and $E_{\lambda 3}$ are the average emission intensities measured at 1.5 and 3 cm from the flat pannel LEDs. The value $[\text{sen}]_0 p$ was obtained as an average of $[\text{sen}]_0 p_{max}$ and $[\text{sen}]_0 p_{min}$.

Table S1. Minimum ($[sen]_0\,p_{min}$), maximum ($[sen]_0\,p_{max}$), and average ($[sen]_0\,p$) number of photons absorbed by the sensitizer per unit time.

Sensitizer	Solvent	395 nm LED (n=1000)		525 nm LED (n=1000)	
		$[sen]_0\,p_{min}$ $[sen]_0\,p_{max}$ (E/min)	$[sen]_0\,p$ (E/min)	$[sen]_0\,p_{min}$ $[sen]_0\,p_{max}$ (E/min)	$[sen]_0\,p$ (E/min)
EY	MeOH	6.705×10^{-6} 6.713×10^{-6}	6.709×10^{-6}	2.418×10^{-6} 2.420×10^{-6}	2.419×10^{-6}
RB	MeOH	6.200×10^{-6} 6.207×10^{-6}	6.204×10^{-6}	2.568×10^{-6} 2.571×10^{-6}	2.569×10^{-6}
MB	MeOH	3.250×10^{-6} 3.255×10^{-6}	3.253×10^{-6}	2.196×10^{-6} 2.198×10^{-6}	2.197×10^{-6}
MB	CH_2Cl_2	3.173×10^{-6} 3.177×10^{-6}	3.175×10^{-6}	1.953×10^{-6} 1.956×10^{-6}	1.955×10^{-6}
TPP	CH_2Cl_2	10.682×10^{-6} 10.693×10^{-6}	10.687×10^{-6}	2.464×10^{-6} 2.467×10^{-6}	2.466×10^{-6}
C_{60}	CH_2Cl_2	7.666×10^{-6} 7.675×10^{-6}	7.670×10^{-6}	-	-
C_{60}	Toluene	7.714×10^{-6} 7.723×10^{-6}	7.719×10^{-6}	1.178×10^{-6} 1.180×10^{-6}	1.179×10^{-6}

E = mol-photons

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