Supplementary Material

Rate constant for the generation of $^1$O$_2$ 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 [¹O₂], eq 3’ becomes

\[
d[¹O₂]_t / dt = k₁ p [sen]_{l} [³O₂]_{l} - k₂ [¹O₂]_{l} [₁]_{l} = 0 \quad (3'')
\]

From eq 3’’
\[
[¹O₂]_{l} = k₁ p [sen]_{l} [³O₂]_{l} / k₂ [₁]_{l} \quad (3'''')
\]

By substituting 3’’’’ to eq 4, we obtain

\[-d[₁]_{l} / dt = k₁ p [sen]_{l} [³O₂]_{l} \quad (4')\]

As \( p, [sen]_{l} (≈ [sen]₀ = 0.12 \text{ mM}, \text{ initial concentration of the sensitizers}), \) and \([³O₂]_{l} (≈ [³O₂]_{s}, \text{ concentration of saturated } ³O₂) \) can be considered as constants, eq 4’ is solved as

\[[₁]_{l} = -k₁ p [sen]₀ [³O₂]_{s} t + C \quad (4'')\]

where \( C \) is a constant.

At \( t = 0, [₁]_{l} is [₁]₀ = 3.0 \times 10^{-2} \text{ [M]}, \) so that from eq 4’’

\[[₁]_{t} = -k₁ p [sen]₀ [³O₂]_{s} t + 3.0 \times 10^{-2} \quad (5)\]
[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 \((h)\) is calculated to be \(h = 10/(1.5^2 \pi)\) cm.

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

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

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

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

\[
[\text{sens}]_{\lambda,m} = \frac{60 \times 1.5 \times h E_{\lambda,m} \left(1 - 10^{-\varepsilon_{\lambda,m} c \lambda \sqrt{n^2 - m^2}}\right)}{h c N_A}
\]

where \(E_{\lambda,m}\) W/cm\(^2\) is the intensity of incident light (wavelength \(\lambda\)) at \(m\) th segment, \(c\) is the concentration of the sensitizer, \(h\) is Planck’s constant, \(C\) is the speed of light, \(\varepsilon_{\lambda}\) is the molar absorption coefficient of the sensitizer at wavelength \(\lambda\), and \(N_A\) is the Avogadro’s number.
Figure 4 shows the relationship between the light intensities of flat panel LED 395 (370-475 nm, $\lambda_{\text{max}}$ 400 nm) and LED 525 (455-600 nm, $\lambda_{\text{max}}$ 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 $\lambda$) at $m$ th segment (cf. Figure 2), $E_{\lambda m}$ W/cm$^2$, is

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

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

where $E_{\lambda 1.5}$ and $E_{\lambda 3}$ are the intensities of incident light (wavelength $\lambda$) 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

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

where $\lambda_1$ and $\lambda_2$ are the wavelengths of the both ends of the emission of LEDs, namely, $\lambda_1 = 370$ nm and $\lambda_2 = 475$ nm for the 395 nm LED, and $\lambda_1 = 455$ nm and $\lambda_2 = 620$ nm for the 525 nm LED.

Calculated $[\text{sen}]_0 p_{\text{max}}$ and $[\text{sen}]_0 p_{\text{min}}$ for $n = 1000$ are listed in Table S1. The $\varepsilon_\lambda$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 panel LEDs. The value $[\text{sen}]_0 p$ was obtained as an average of $[\text{sen}]_0 p_{\text{max}}$ and $[\text{sen}]_0 p_{\text{min}}$. 
Table S1. Minimum ([\text{sen}] p_{min}) and maximum ([\text{sen}] p_{max}) number of photons absorbed by the sensitizer per unit time.

| Sensitizer | Solvent | 395 nm LED (n=1000) | 525 nm LED (n=1000) |
|------------|---------|---------------------|---------------------|
|            | [\text{sen}] p_{min} (E/min) | [\text{sen}] p (E/min) | [\text{sen}] p_{min} (E/min) | [\text{sen}] p (E/min) |
| EY         | MeOH    | 6.705×10^{-6}       | 2.418×10^{-6}       | 2.419×10^{-6}       |
|            |         | 6.713×10^{-6}       | 2.420×10^{-6}       |                     |
| RB         | MeOH    | 6.200×10^{-6}       | 2.568×10^{-6}       | 2.569×10^{-6}       |
|            |         | 6.207×10^{-6}       | 2.571×10^{-6}       |                     |
| MB         | MeOH    | 3.250×10^{-6}       | 2.196×10^{-6}       | 2.197×10^{-6}       |
|            |         | 3.255×10^{-6}       | 2.198×10^{-6}       |                     |
| MB         | CH\textsubscript{2}Cl\textsubscript{2} | 3.173×10^{-6}  | 1.953×10^{-6}       | 1.955×10^{-6}       |
|            |         | 3.177×10^{-6}       | 1.956×10^{-6}       |                     |
| TPP        | CH\textsubscript{2}Cl\textsubscript{2} | 10.682×10^{-6} | 2.464×10^{-6}       | 2.466×10^{-6}       |
|            |         | 10.693×10^{-6}      | 2.467×10^{-6}       |                     |
| C\textsubscript{60} | CH\textsubscript{2}Cl\textsubscript{2} | 7.666×10^{-6}  | -                   | -                   |
|            |         | 7.675×10^{-6}       | -                   |                     |
| C\textsubscript{60} | Toluene | 7.714×10^{-6} | 1.178×10^{-6}       | 1.179×10^{-6}       |
|            |         | 7.723×10^{-6}       | 1.180×10^{-6}       |                     |

E = mol-photons