

Singlet oxygen quantum yields determined by oxygen consumption

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ABSTRACT

Quantifying singlet oxygen production from triplet photosensitizers typically requires spectroscopic techniques and specialty chemical traps. Herein we describe a novel method for determining the singlet oxygen quantum yield (Φ_{Δ}) of photosensitizers. The method utilizes the reaction between singlet oxygen and dimethyl sulfoxide (DMSO) to produce dimethyl sulfone. The rate of the reaction is measured by the pressure decrease that results from the consumption of oxygen from the headspace of a sealed system. It was found that the rate of pressure decrease was directly related to the singlet oxygen quantum yield. The Φ_{Δ} from known photosensitizers: fluorescein, Eosin Y, Eosin B, methylene blue, and tris(bipyridine)ruthenium (II) in DMSO were determined by the rate of pressure decrease using Rose Bengal as a relative standard. The singlet oxygen quantum yields of the photosensitizers in DMSO were found to be in agreement with the reported values for each photosensitizer determined using traditional spectroscopic methods.

1. Introduction

Chromophores with significant triplet yields have found utility in fields such as a photocatalytic water splitting, organic redox reactions, as well as in organic electronic applications [1–5]. Triplet-photosensitizers are chromophores that show a significant rate of intersystem crossing from a singlet-excited-state to produce a triplet-excited-state and can display phosphorescence. As compared to singlet-excited-states, triplet-excited-states typically are longer lived and can undergo energy transfers to other triplet-states such as ground state oxygen ($^3\text{O}_2$). Energy transfer from triplet-excited-states to $^3\text{O}_2$ produce singlet oxygen ($^1\text{O}_2$). $^1\text{O}_2$ is 94 kJ/mol higher in energy than $^3\text{O}_2$ and has found utility in organic synthesis due to its increased reactivity [6–8]. $^1\text{O}_2$ has been used in the oxidation of arenes, alkenes, and heteroatoms such as sulfur, nitrogen and phosphorous [9,10]. The production of $^1\text{O}_2$ can be quantified and used as a lower bound approximation for the triplet yield of a chromophore. Therefore, the measurement of $^1\text{O}_2$ quantum yields is crucial for the evaluation and optimization of systems employing triplet photosensitizers.

$^1\text{O}_2$ quantum yields are often used to approximate the triplet yield of a chromophore since directly measuring the triplet yield can be challenging. If the phosphorescence quantum yield (Φ_p) approaches unity the triplet yield can be approximated by measuring the emission quantum yield. However, most chromophores have competing radiative and non-radiative decay pathways making this method invalid. Advanced spectroscopic methods are required to directly quantify

triplet yields with non-radiative decay pathways [11,12]. In contrast, a wide variety of methods have been developed to determine the $^1\text{O}_2$ yield as an approximation of the triplet yield of a chromophore. $^1\text{O}_2$ formation is typically monitored directly by its phosphorescence around 1270 nm [13]. The phosphorescence can be quantified using a relative method, by comparing the emission integration of a known standard, or an absolute method using an integration sphere. Both methods rely on the excitation of the triplet photosensitizer and monitoring the phosphorescence of $^1\text{O}_2$. The phosphorescence of $^1\text{O}_2$ is typically very weak, with Φ_p ranging from 10^{-6} to 10^{-2} in common laboratory solvents, thus a very sensitive IR detector is required [13,14]. To avoid the need for an IR detector, reactions with an easily monitored spectroscopic signature have found utility as $^1\text{O}_2$ sensors.

A wide variety of chemical traps for $^1\text{O}_2$ have been used (Scheme 1) [7,15–17]. Among the most common are 9,10-disubstituted anthracene compounds and 1,3-diphenylisobenzofuran which react with $^1\text{O}_2$ to form endoperoxides and a diketone, respectively [18,19]. For both, the progress of the reaction is monitored by the change in absorbance of the compound by UV–vis absorption spectroscopy. Synthetic strategies have been used to provide different substituents at the 9 and 10 positions to increase solubility of anthracene traps in polar solvents [16,20]. Challenges can arise if the absorbance range of the photosensitizer in question overlaps with the chemical trap making these measurements difficult [21]. To overcome absorbance overlaps, the change in fluorescence from the chemical trap may also be monitored [21,22].

More specialized chemical traps have been developed to detect $^1\text{O}_2$

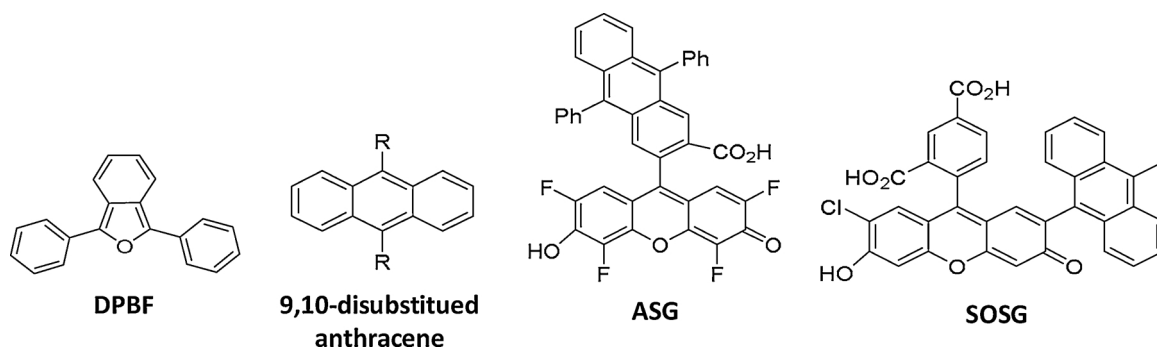
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Scheme 1. Structures of selected $^1\text{O}_2$ traps.

by visible fluorescence. These traps typically contain a fluorescein core structure with a 9,10-disubstituted anthracene substituent to trap the $^1\text{O}_2$ such as Aarhus Sensor Green (ASG) and the commercially available Singlet Oxygen Sensor Green (SOSG) [22,23]. SOSG has been shown to have great selectivity towards $^1\text{O}_2$ compared to other reactive oxygen species. However, complications arise since the endoperoxide of SOSG can itself create $^1\text{O}_2$ with a ϕ_Δ up to 0.20 when excited [23]. ASG and its endoperoxide have been shown to have a much lower ϕ_Δ , however, (to our knowledge) this sensor is not commercially available.

As describe above, most $^1\text{O}_2$ measurements monitor the concentration of the chemical trap rather than the oxygen itself. In this paper we propose that the amount of oxygen trapped from such reactions can be measured directly, which eliminates the need for specialty $^1\text{O}_2$ sensors with unique spectroscopic signatures. Irradiation of triplet chromophores in the presence of a chemical trap has been shown to result in the consumption of oxygen over time [7]. Production or consumption of gases can be monitored by the accompanying pressure change in a sealed system. Pressure sensors (transducers) are becoming common in many photochemistry labs to monitor photo-catalytic reactions such as water splitting to produce H_2 gas [24,25]. Gas producing reactions, such as water splitting, produce a pressure increase, while gas consuming reactions such as those with $^1\text{O}_2$ can be monitored by a pressure decrease.

Herein we describe a new method for determining the $^1\text{O}_2$ quantum yield using common laboratory chemicals that does not rely on spectroscopic measurements. We use the reaction of $^1\text{O}_2$ with dimethyl sulfoxide (DMSO). $^1\text{O}_2$ reacts with DMSO to afford dimethyl sulfone, resulting in the consumption of atmospheric oxygen over time that can be monitored by a corresponding pressure decrease within a closed system. The rate of pressure decrease was found to be directly related to the $^1\text{O}_2$ quantum yield of the chromophore in question.

2. Results and discussion

Measuring $^1\text{O}_2$ quantum yields typically relies on monitoring the reaction progress of singlet oxygen with a chemical trap, which is observed by a change in fluorescence or absorbance. Monitoring the consumption of oxygen, rather than the oxidation of these chemical traps, allows for the use of compounds that react with singlet oxygen but do not produce easily observable spectroscopic changes. DMSO was chosen as the singlet oxygen trap because it is commonly available in most research laboratories. Furthermore, DMSO is a polar aprotic solvent which can dissolve a wide range of chromophores. DMSO reacts with singlet oxygen in a 2:1 to stoichiometry to afford dimethyl sulfone (Scheme 2). Consequently, oxygen gas from the headspace is dissolved,

to restore equilibrium, resulting in a decrease in pressure over time.

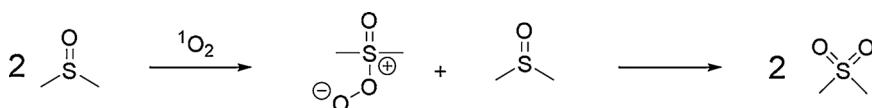
2.1. Oxygen consumption from Rose Bengal in DMSO

As a proof of concept, Rose Bengal, a well-known singlet oxygen sensitizer, was used as a reference to compare to other dyes. Solutions containing Rose Bengal (1×10^{-5} M, 10 mL) in DMSO were sealed in 50 mL reaction vessels containing 40 mL of atmospheric headspace. The reaction vessels were sealed with caps fitted with gage pressure sensors, that were read into a LabView™ program. The solutions were irradiated with red, green, and/or blue LEDs (to best match the absorption spectra of the photosensitizers) for five hours. The pressure change was recorded every two minutes for each sample resulting in 300 data points. The samples were consistently stirred at 500 rpm to assist in dissolving oxygen from the headspace.

A control sample containing only DMSO was monitored to account for the pressure changed caused by temperature increase from irradiation. The pressure change at each time point of the control sample was then subtracted from the samples containing dye. After averaging the triplicate data, a linear fit was applied to determine the rate of the pressure decrease. The linear fit from irradiating solutions of Rose Bengal in triplicate showed consistent pressure decrease plot with an average slope of $-2.248 (\pm 0.007) \times 10^{-5} \text{ psi}\cdot\text{s}^{-1}$. Applying a linear fit to the three individual samples resulted in linear fits with slopes within 7.5% of the average slope indicating good precision from this method.

The resulting pressure decrease over time shows a pseudo-zeroth order rate of oxygen consumption. The zeroth order plots are expected since both DMSO and the dissolved oxygen are in excess for the duration of the measurement and the concentration remains essentially unchanged. The rate of the pressure decrease is expected to be constant as long as there is no degradation to the photosensitizer and enough oxygen is dissolved to maintain the reaction, resulting in a linear decrease in pressure.

The gas composition of the headspace of the reaction vessels was analyzed by a Quantitative Gas Analyzer (QGA), before and after irradiation, to verify that only oxygen had been consumed. The concentration of the oxygen in the headspace after irradiation was nearly 2.7% less for each sample containing Rose Bengal than before. The average rate of decrease from the irradiated Rose Bengal samples was used as a relative standard for other photosensitizers, using the accepted singlet oxygen quantum yield of 0.76 as a reference as discussed below [26].



Scheme 2. Reaction of DMSO with singlet oxygen.

2.2. Calculation of singlet oxygen yields

The rate of oxygen consumption by Rose Bengal was compared to five other known photosensitizers to correlate the rate of pressure decrease from oxygen consumption to the singlet oxygen quantum yield. However, to accurately determine the quantum yields of the other dyes the absorption spectrum of the dye and the spectrum of the light source was considered through relative absorbance, I (Eq. (1)) [27]. Using I in the calculation of the singlet oxygen yields allows for the translation of results from the rate of pressure decrease from chromophores with different absorbance profiles irradiated using non-monochromatic light.

$$I = \int_{400\text{ nm}}^{900\text{ nm}} i(\lambda) (1 - 10^{-\text{Abs}(\lambda)}) d\lambda \quad (1)$$

The integral of i , the intensity of the light source at a given wavelength (λ), with respect to the absorbance of the dye (Abs) at the given wavelength was used to produce the absorbance intensity (I). The area was integrated from 400 nm to 900 nm in order to incorporate the full spectral range of the LEDs and encompass the absorbance range of the dyes.

$$\Phi_{\text{unknown}} = \frac{I_{\text{Rose Bengal}}}{I_{\text{unknown}}} \times \frac{k_{\text{unknown}}}{k_{\text{Rose Bengal}}} \times \Phi_{\text{Rose Bengal}} \quad (2)$$

The singlet oxygen quantum yield was calculated comparing the rate of pressure decrease (k) and relative absorbance of the dye relative to Rose Bengal (Eq. (2)) [27]. Utilizing the rate of pressure decrease rather than the total pressure decrease allows for results to be compared over different irradiation periods.

2.3. Experimental singlet oxygen quantum yields

The resulting calculated singlet oxygen quantum yields are summarized in Table 1 for fluorescein, Eosin Y, Eosin B, methylene blue and tris(bipyridine)-ruthenium(II) ($\text{Ru}(\text{bpy})_3$) using Rose Bengal as a reference. The calculated singlet oxygen quantum yields are in good agreement with previously reported values, considering the variability of literature values, for the photosensitizers in water or ethanol. All dyes produced pseudo-zeroth order plots of pressure decrease. The rate of the pressure decrease was determined by applying a linear fit across the average of triplicate samples. A sample of only DMSO was run simultaneously and the pressure change of this blank was subtracted from each photosensitizer sample before being averaged. All R^2 values were above 0.95, with the exception of fluorescein ($R^2 = 0.88$), indicating a good fit for the regression. The reported error values are obtained from the standard deviations of linear fits. Line segments can be used if the rates of oxygen consumption is not linear over the irradiation time.

The plots of the pressure decrease over time for the photosensitizers are shown in Fig. 2. The sensitivity of the method was demonstrated by using fluorescein, which has reported singlet oxygen quantum yield an order of magnitude less than Rose Bengal. The increase of temperature after irradiation with the LEDs did cause an initial increase in pressure,

Table 1
Calculated singlet oxygen quantum yields from rates of pressure decrease.

Photosensitizer	Slope (-1×10^{-5} psi / s)	Calculated Φ_{Δ}	Literature Φ_{Δ} in H_2O [26]	Literature Φ_{Δ} EtOH [26]
Fluorescein	0.24 ± 0.05	0.066 ± 0.001	0.03, 0.06	0.13, 0.03
Eosin Y	1.079 ± 0.004	0.611 ± 0.003	0.52, 0.57	0.60, 0.42
Methylene Blue	0.99 ± 0.04	0.490 ± 0.003	0.60, 0.52	0.52, 0.50
Eosin B	0.50 ± 0.04	0.370 ± 0.003	0.52	0.38
$\text{Ru}(\text{bpy})_3$	1.43 ± 0.02	0.656 ± 0.008	0.22 ^a	0.73 ^b
Rose Bengal	2.248 ± 0.007	N/A	Reference Value	0.76 [26]

^a Reported value in D_2O .

^b Reported value in CD_3OD .

even after subtraction of the pressure change from the blank solution, as observed in the pressure for fluorescein and methylene blue (Fig. 2). However, the five hour irradiation time was sufficient to see an overall decrease in pressure due to oxygen consumption even with the low singlet oxygen quantum yield of fluorescein.

Other fluorescein derivatives, Eosin Y and Eosin B, showed a more dramatic pressure decrease compared to fluorescein in line with their higher triplet yields. The importance of incorporating the relative absorbance, I , was demonstrated by comparing Eosin Y and Eosin B. The slope of pressure decrease of Eosin B was half that of Eosin Y despite similar triplet quantum yields. However, after incorporating the respective relative absorbance for both Eosin Y and Eosin B their singlet oxygen quantum yields were in good agreement with literature values. Methylene blue also showed a singlet oxygen quantum yield consistent from data previously reported in water. To accommodate the absorbance range of $\text{Ru}(\text{bpy})_3$, blue and green LEDs were used rather than the green and/or red LEDs, which were used to irradiate all the other photosensitizers. $\text{Ru}(\text{bpy})_3$ has been reported to have greatly varying singlet oxygen yields in different solvents. In methanol, the reported singlet oxygen yield for $\text{Ru}(\text{bpy})_3$ is 0.70, however, in water this yield diminishes to 0.22. We found the singlet oxygen yield for $\text{Ru}(\text{bpy})_3$ in DMSO was closer to that of methanol at 0.66.

2.4. Mixed solvent systems

The solvent of choice can have a great influence on the singlet oxygen quantum yield. The minimum amount of DMSO needed to observe a statistically significant pressure decrease was examined by mixing DMSO with ethanol. The addition of ethanol proved to be troublesome as the increase in vapor pressure made measurements difficult below 50% DMSO by volume. At 50% DMSO a solution containing Rose Bengal resulted in a net increase in pressure, however, after subtracting the respective blank solution containing 50% DMSO and 50% ethanol a pressure decrease with a slope of $-1.116 (\pm 0.006) \times 10^{-5} \text{ psi}\cdot\text{s}^{-1}$ was observed (SI Fig. 1). Solutions with 25% DMSO and 75% ethanol were attempted, however, fluctuations of the pressure resulted in inconsistent plots even after subtracting the control sample but careful temperature control could overcome this limitation.

2.5. Reaction of singlet oxygen with triphenylphosphine

To investigate the utility of this method with other substrates beyond DMSO the pressure change from the reaction of singlet oxygen with triphenylphosphine was also examined. The reaction of triphenylphosphine with singlet oxygen produces triphenylphosphine oxide in a similar 2:1 ratio as DMSO with singlet oxygen. Use of triphenylphosphine allows for dissolution in nonpolar solvents that DMSO may not be miscible in.

1-butanol was chosen as the solvent to accommodate the solubility of both Rose Bengal and triphenylphosphine and minimize vapor pressure. Irradiation of solutions of Rose Bengal (saturated triphenylphosphine, 0.08 M) resulted in a rate of pressure decrease of $-1.421 (\pm 0.004) \times 10^{-5} \text{ psi}\cdot\text{s}^{-1}$ (SI Fig. 2). Again, the pressure decrease over time was linear indicating a pseudo-zeroth order reaction rate. Triphenylphosphine is known to oxidize over time in normal atmospheric conditions, however, no indication of pressure change was apparent from the control sample containing only 1-butanol and triphenylphosphine over the course of the reaction.

2.6. Monitoring oxygen consumption by water displacement

To eliminate the need of pressure sensors; a manual method was developed that measures water displacement from oxygen consumption that can be assembled using simple equipment available in most labs (Fig. S5). The same pressure sensor tube with Rose Bengal in DMSO was used for a consistent irradiation area but it was fitted with a septa

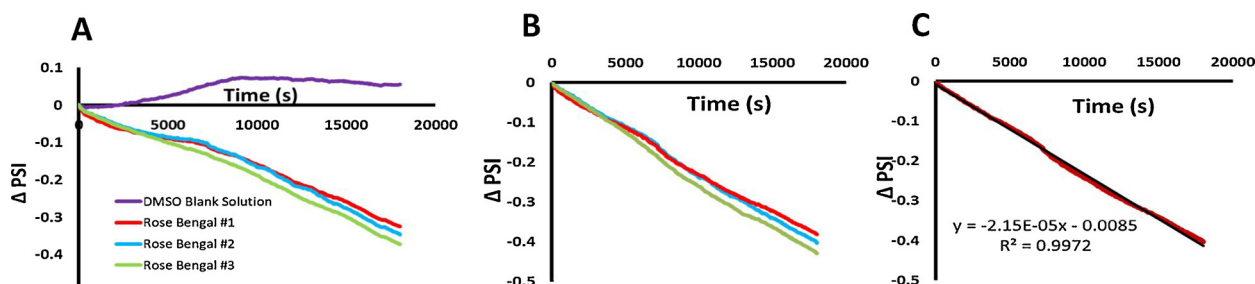


Fig. 1. A Uncorrected pressure change over time from irradiation of DMSO and triplicate solutions of DMSO containing Rose Bengal. B Adjusted pressure change of triplicate samples of Rose Bengal after subtracting the pressure change of the DMSO blank solution. C Average rate of pressure decrease over time of the triplicate samples of Rose Bengal (orange) and the linear fit (black).

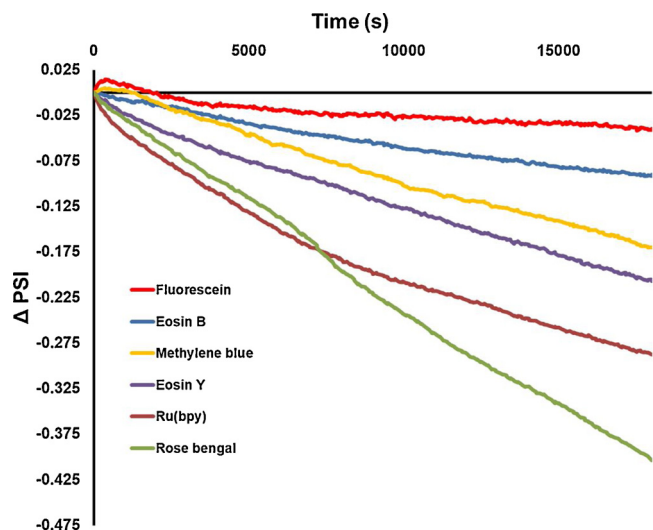


Fig. 2. The average pressure change over time for triplicate runs of 6 different photosensitizers irradiated by red, green, or blue LEDs in DMSO. The slope of the pressure change was monitored every 2 min for 5 h.

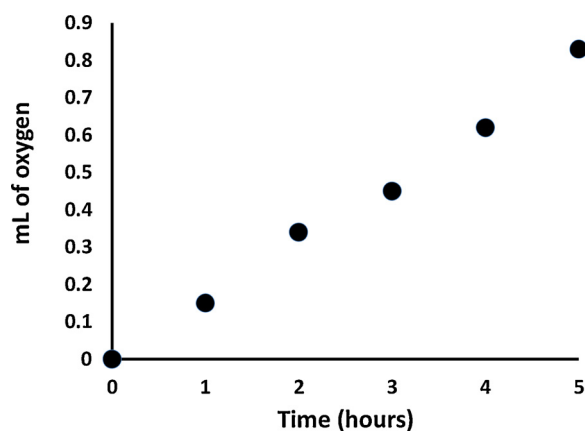


Fig. 3. Oxygen consumption over time of an irradiated solution of Rose Bengal in DMSO measured by the water displacement method.

instead of the pressure sensor cap. A hose with a needle puncturing the septa was connected to a 1 mL pipette submerged in a graduated cylinder of water. Air was injected through the septa of the reaction vessel to displace the water in the pipette such that the water level started at zero. The sample was irradiated with green LEDs and the oxygen consumption was monitored by the rise of the water in the pipette. The water level in the pipette was monitored every hour for five hours resulting in consumption of ~0.8 mL of oxygen (Fig. 3).

3. Conclusion

We have developed a method for determining the $^1\text{O}_2$ quantum yield of a triplet photosensitizer by monitoring the rate of pressure decrease upon irradiation of the photosensitizer in DMSO. The method can be performed in sealed systems under atmospheric conditions and does not require specialized chemical traps. Pseudo zeroth order plots of pressure decrease were shown for each photosensitizer. The rate of decrease in pressure was found to be related to the singlet oxygen quantum yield of the photosensitizer. The inclusion of the absorbance intensity term allows for the translation of results between dyes that absorb at different wavelengths and for different light sources. We focused on using DMSO to capture the singlet oxygen, however, the method can be adapted and used for a broad range of substrates that react with singlet oxygen. The need for pressure sensors can be substituted with a manual method by measuring the displacement of water over time. This method allows for the determination of singlet oxygen quantum yields without the need for specialty traps or spectroscopic measurements.

4. Materials and methods

4.1. Chemicals used

Rose Bengal, Eosin Y, Eosin B, methylene blue, tris(bipyridine)ruthenium (II) hexafluorophosphate, and fluorescein were obtained by commercial sources and used without further purification. Stock solutions of the dyes (10^{-5} M) were created in DMSO and stored in light free conditions. The pH was adjusted for Rose Bengal, Eosin Y, and fluorescein by adding NaOH (1 M) dropwise until no change in the UV-vis spectrum occurred.

4.2. Oxygen consumption measurements

Pressure sensor experiments were carried out in sealed 50 mL reaction vessels with Omega gage pressure sensors to monitor the pressure every two minutes for five hours using the TracerDAQ Stripchart program. Red, green, and blue LED ring lights lining a steal tube were used to evenly irradiate up to twelve samples held in a Radleys Carousel 12 cooled reaction station and stirred at 500 RPM (SI Fig. 3). The entire apparatus was covered in order to avoid irradiation from room lights. Samples of each photosensitizer (10 mL) were run in triplicate, with a single control solution containing only DMSO. The resulting rate was calculated from the average slope of the triplicate samples after subtraction of the pressure change of the blank solution.

4.3. Calculation of absorbance intensity (I)

The spectrum of the red, green, and blue LEDs, used to irradiate the samples, was measured using a Stellar Net Spectra Wiz in scope mode (SI Fig. 4). The absorbance spectrum of the dyes was collected on UV-

3600 Shimadzu UV–vis NIR spectrometer. The spectrums were used as detailed in Eq. (1) and the integral was determined using the Trapezoid Method.

4.4. Water displacement method

A pressure sensor tube containing Rose Bengal (10^{-5} M) in DMSO (10 mL) was set up as shown SI Fig. 5. The solution was irradiated with green LEDs and the water level in the pipette was monitored every hour.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jphotochem.2019.04.029>.

References

- [1] Z. Han, R. Eisenberg, Fuel from water: the photochemical generation of hydrogen from water, *Acc. Chem. Res.* 47 (2014) 2537–2544.
- [2] M.W. Kryman, K.S. Davies, M.K. Linder, T.Y. Ohulchanskyy, M.R. Detty, Selenorhodamine photosensitizers with the texas-red core for photodynamic therapy of Cancer cells, *Bioorg. Med. Chem. Lett.* 23 (2015) 4501–4507.
- [3] O. Shingo, I. Tomoya, H. Yuichirou, F. Shunichi, T. Kojima, Photocatalytic oxidation of organic compounds in water by using ruthenium(II)–pyridylamine complexes as catalysts with high efficiency and selectivity, *Chem. A Eur. J.* 19 (2013) 1563–1567.
- [4] L. Huang, J. Zhao, S. Guo, C. Zhang, J. Ma, Bodipy derivatives as organic triplet photosensitizers for aerobic photoorganocatalytic oxidative coupling of amines and photooxidation of dihydroxynaphthalenes, *J. Org. Chem.* 78 (2013) 5627–5637.
- [5] Y. Luo, H. Aziz, Correlation between triplet-Triplet annihilation and electroluminescence efficiency in doped fluorescent organic light-emitting devices, *Adv. Funct. Mater.* 20 (2010) 1285–1293.
- [6] D.R. Kearns, Physical and chemical properties of singlet molecular oxygen, *Chem. Rev.* 6 (1971) 395–427.
- [7] M.C. DeRosa, R.J. Crutchley, Photosensitized singlet oxygen and its applications, *Coord. Chem. Rev.* 233–234 (2002) 351–371.
- [8] J.E. Hill, M.K. Linder, K.S. Davies, G.A. Sawada, J. Morgan, T.Y. Ohulchanskyy, M.R. Detty, Selenorhodamine photosensitizers for photodynamic therapy of P-glycoprotein-expressing cancer cells, *J. Med. Chem.* 57 (2014) 8622–8634.
- [9] E. Baciocchi, T. Del Giacco, O. Lanzalunga, A. Lapi, Singlet oxygen promoted carbon-heteroatom bond cleavage in dibenzyl sulfides and tertiary dibenzylamines. Structural effects and the role of exciplexes, *J. Org. Chem.* 72 (2007) 9582–9589.
- [10] A.A. Ghogare, A. Greer, Using singlet oxygen to synthesize natural products and drugs, *Chem. Rev.* 116 (17) (2016) 9994–10034.
- [11] B. Amand, R. Bensasson, Determination of triplet quantum yields by laser flash absorption spectroscopy, *Chem. Phys. Lett.* 34 (1975) 44–48.
- [12] I. Hiromitsu, L. Kevan, Correlation between photoexcited triplet state yield and photoionization yield of chlorophyll a in frozen phosphatidylcholine vesicles studied by Electron spin resonance spectroscopy, *J. Phys. Chem.* (1989) 3218–3223.
- [13] A.U. Khan, M. Kasha, Direct spectroscopic observation of singlet oxygen emission at 1268 nm excited by sensitizing dyes of biological interest in liquid solution, *Proc. Natl. Acad. Sci. U. S. A.* (76) (1979) 6047–6049.
- [14] N. Hasebe, K. Suzuki, H. Horiuchi, H. Suzuki, T. Yoshihara, T. Okutsu, S. Tobita, Absolute phosphorescence quantum yields of singlet molecular oxygen in solution determined using an integrating sphere instrument, *Anal. Chem.* 87 (2015) 2360–2366.
- [15] A. Sivéry, F. Anquez, C. Pierlot, J.M. Aubry, E. Courtade, Singlet oxygen (1O_2) generation upon 1270 nm laser irradiation of ground state oxygen (3O_2) dissolved in organic solvents: simultaneous and independent determination of 1O_2 production rate and reactivity with chemical traps, *Chem. Phys. Lett.* (555) (2013) 252–257.
- [16] M. Botsivali, D.F. Evans, A new trap for singlet oxygen in aqueous solution, *J. Chem. Soc. Chem. Commun.* 24 (1979) 1114–1116.
- [17] V. Nardello, D. Brault, P. Chavalle, J.M. Aubry, Measurement of photogenerated singlet oxygen ($^1O_2(1\Delta(g))$) in aqueous solution by specific chemical trapping with sodium 1,3-cyclohexadiene-1,4-Diethanoate, *J. Photochem. Photobiol. B, Biol.* 39 (1997) 146–155.
- [18] H. Kotani, K. Ohkubo, S. Fukuzumi, Photocatalytic oxygenation of anthracenes and olefins with dioxygen via selective radical coupling using 9-mesityl-10-methylacridinium ion as an effective electron-transfer photocatalyst, *J. Am. Chem. Soc.* 126 (2004) 15999–16006.
- [19] L. Greci, On the use of 1, 3-diphenylisobenzofuran reactions with carbon and oxygen centered radicals in model and natural systems, *Res. Chem. Intermed* 19 (1993) 395–396.
- [20] G.R. Martinez, F. Garcia, L.H. Catalani, J. Cadet, M.C.B. Oliveira, G.E. Ronsein, S. Miyamoto, M.H.G. Medeiros, P.Di Mascio, Synthesis of a hydrophilic and non-ionic anthracene derivative, the N,N'-Di-(2,3-dihydroxypropyl)-9,10-Anthracenedipropylamide as a chemical trap for singlet molecular oxygen detection in biological systems, *Tetrahedron* 62 (2006) 10762–10770.
- [21] R. Ho-Wu, S.-H. Yau, T. Goodson III, Efficient singlet oxygen generation in metal nanoclusters for two-photon photodynamic therapy applications, *J. Phys. Chem. B* (2017) 10073–10080.
- [22] M. Marazzi, V. Besancenot, H. Gattuso, H.-P. Lassalle, S. Grandemange, A. Monari, Photophysics of the singlet oxygen sensor green chromophore: self-production of 1O_2 explained by molecular modeling, *J. Phys. Chem. B* (2017) 7586–7592.
- [23] S.K. Pedersen, J. Holmehave, F.H. Blaikie, A. Gollmer, T. Breitenbach, H.H. Jensen, P.R. Ogilby, Aarhus sensor green: a fluorescent probe for singlet oxygen, *J. Org. Chem.* 79 (2014) 3079–3087.
- [24] G. Li, M.F. Mark, H. Lv, D.W. McCamant, R. Eisenberg, Rhodamine-platinum dithiolate complex dyads as efficient and robust photosensitizers for light-driven aqueous proton reduction to hydrogen, *J. Am. Chem. Soc.* 140 (2018) 2575–2586.
- [25] H.N. Kagalwala, D.N. Chirdon, I.N. Mills, N. Budwal, S. Bernhard, Light-driven hydrogen generation from microemulsions using metallosurfactant catalysts and oxalic acid, *Inorg. Chem.* 56 (2017) 10162–10171.
- [26] F. Wilkinson, P. Helman, A. Ross, Quantum yields for the photosensitized formation of the lowest electronically excited singlet state of molecular oxygen in solution, *J. Phys. Chem. Ref. Data* 22 (1992) 1–126.
- [27] M. Hoebeke, X. Damoiseau, Determination of the singlet oxygen quantum yield of Bacteriochlorin a: a comparative study in phosphate buffer and aqueous dispersion of dimiristoyl-L- α -Phosphatidylcholine liposomes, *Photochem. Photobiol. Sci.* 1 (2002) 283–287.