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Spectroscopic determination of very low quantum yield of singlet oxygen formation photosensitized by industrial dyes

Shoichi Yamaguchi*, Yutaka Sasaki

Center for Analytical Chemistry and Science, Inc., Yokohama Research Center, Mitsubishi Chemical Corporation,
1000 Kamoshida, Aoba, Yokohama 227-0033, Japan

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Abstract

We have measured the quantum yield Q_Δ of $^1\Delta_g$ molecular oxygen (singlet oxygen, $^1O_2$) formation photosensitized by some industrial dyes. As regards dyes and pigments for practical uses, it is widely believed that $^1O_2$ is a key intermediate in their photofading processes. Q_Δ for practical dyes, however, is generally very low, and it has been difficult to determine accurately Q_Δ for them. We have made a highly sensitive spectrometer for 1.27 μm $^1O_2$ phosphorescence detection, and determined Q_Δ for an azo dye as low as $(2.2 \pm 1.5) \times 10^{-5}$. This is the first demonstration of Q_Δ lower than 10^{-4}. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Singlet oxygen; Phosphorescence; Quantum yield; Azo dye; Photodegradation

1. Introduction

Molecular oxygen in the excited $^1\Delta_g$ state ($^1O_2$) is a highly reactive species, and has been regarded as one of the most important reaction intermediates in photobiology and photochemistry. $^1O_2$ is characterized by near-infrared (NIR) phosphorescence at 1.27 μm. Technological improvements in the detection of the $^1O_2$ NIR emission are very important from biochemical and medical viewpoints, because $^1O_2$ phosphorescence emitted from living systems is very weak [1]. An excellent technique of weak-phosphorescence detection is expected also in the field of industrial chemistry, because it is widely believed that $^1O_2$ plays an essential role in oxidative photofading processes of some industrial dyes and pigments in practical use [2–4]. Even though $^1O_2$ photosensitized by industrial dyes causes the photofading, the quantum yield Q_Δ of $^1O_2$ formation by these dyes is much lower than that by highly efficient photosensitizers such as porphin and terthiophene derivatives, whose Q_Δ ranges from 0.5 to 0.8 [5,6]. Actually all the Q_Δ values for industrial practical dyes reported to date lie in the region of 10^{-3} to 10^{-4} [4,5,7,8]. The measurements of $Q_\Delta < 10^{-3}$ have been realized only by the photochemical substrate consumption method.

There have been few works which apply spectroscopic methods of 1.27 μm phosphorescence detection to the determination of low Q_Δ. Stracke et al. [9], showed for the first time that it is possible to measure the $^1O_2$ phosphorescence spectrum photosensitized by rhodamine 6G (R6G), which is known as the most efficient laser dye and usually not regarded as a $^1O_2$ photosensitizer. We are going to show in this paper that Q_Δ for R6G is 8.3×10^{-3}. The intensity of the $^1O_2$ phosphorescence is proportional to the $^1O_2$ phosphorescence quantum yield as well as Q_Δ. Q_p in air-saturated acetonitrile is about 3×10^{-5} [10–14], and therefore the product $Q_\Delta Q_p$ is 2×10^{-7} in Stracke's R6G measurement. Schmidt and Tanielian have recently demonstrated that quantitative time-resolved measurements of the $^1O_2$ phosphorescence are possible under conditions of very strong quenching [15]. They obtained a $^1O_2$ phosphorescence decay curve with a good signal-to-noise ratio under the condition of $Q_\Delta Q_p = 3 \times 10^{-7}$. Beeby et al. have reported a novel electronic switch which eliminates obstructive fluorescence contributions from a $^1O_2$ phosphorescence decay curve [16].

The purpose of our present study is to establish a spectroscopic method of very low Q_Δ determination. We report the measurement of a $^1O_2$ phosphorescence spectrum photosensitized by industrial dyes for practical uses. We have made a highly sensitive spectrometer which is capable of even Raman spectroscopy. The spectrometer has enabled us to determine Q_Δ as low as 2.2×10^{-5} and $Q_\Delta Q_p$ as

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* Corresponding author. Tel.: +81-45-963-3155; fax: +81-45-963-4261.
E-mail address: shoichi.yamaguchi@nifty.com (S. Yamaguchi).

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7×10^{-10}. This is the first demonstration of Q_Δ lower than 10^{-4}.

2. Experimental section

RB (rose bengal, Aldrich), R6G (rhodamine 6G, Exciton, laser grade), DABCO (1,4-diazabicyclo[2.2.2]octane, Aldrich), and acetonitrile (Kanto Chemical, fluorometry grade) were used as received. Dyes **I** and **II** (Scheme 1) were manufactured and supplied by Mitsubishi Chemical and Orient Chemical, respectively. The concentrations of all the photosensitizers (RB, R6G, dyes **I** and **II**) in acetonitrile were so controlled that the absorbance at 532 nm was set to $1.95\,\mathrm{cm}^{-1}$. The sample solutions were kept in an open standard quartz cuvette of 1 cm × 1 cm × 4.5 cm. A beam from a diode-pumped continuous wave Nd:YVO_4 laser (Spectra Physics, Millennia Vi) illuminated the sample solution across the base of the cuvette. The wavelength of the excitation laser beam was 532 nm, and the average power was 0.20 W. The photoexcited area of the solution along the laser beam was imaged by an F-matched lens onto the entrance slit of a 33 cm single monochromator (Actes, CSM-330) with a grating of 600 grooves mm^{-1}. The luminescence was dispersed by the monochromator, and was detected by a liquid-nitrogen-cooled NIR photomultiplier tube (Hamamatsu, R5509-72) which had good spectral sensitivity in the wavelength region of 300 nm to 1.6 μm. The spectral slit width at 1270 nm was set to 16 nm. Wavelength calibration was done by using a mercury lamp and the Rayleigh and Raman scatterings of acetone excited by the fundamental (1064 nm) and the second harmonic (532 nm) of the Nd:YVO_4 laser. The laser beam was chopped by an optical chopper blade (Stanford Research, SR540) at approximately 2 kHz. The output of the photomultiplier tube was fed into a lock-in amplifier (NF Electronic, 5600A) with the chopper signal as a reference. The monochromator and the lock-in amplifier were controlled by a computer to record a spectrum. All the measurements were done at room temperature.

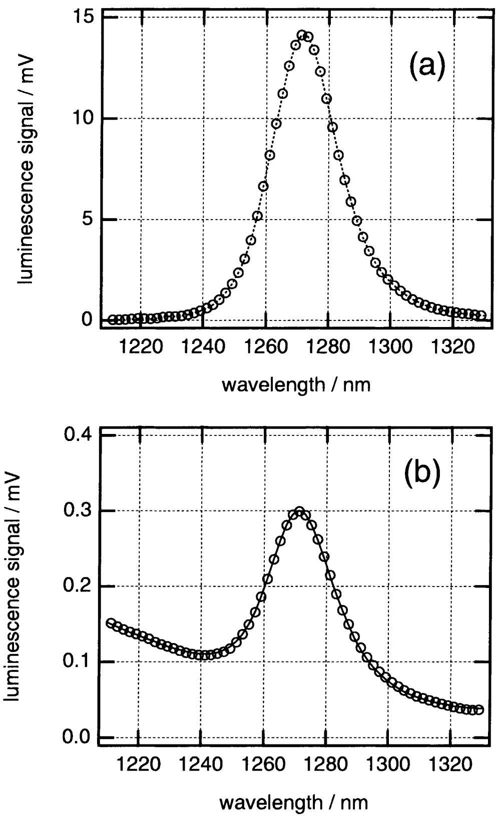
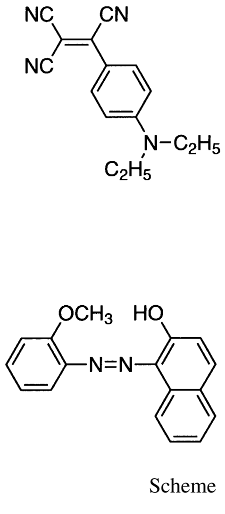


Fig. 1. $^1O_2$ phosphorescence spectra photosensitized by: (a) RB in aerated acetonitrile (open circles, data; dotted lines, only connecting the data points); (b) R6G in aerated acetonitrile (open circles, data; solid curve, fitting).



I

II

Scheme 1.

3. Results and discussion

Fig. 1a shows the $^1O_2$ phosphorescence spectrum photosensitized by RB in aerated acetonitrile. The peak at 1272 nm is assigned to the $^1\Delta_g \rightarrow {}^3\Sigma_g$ transition of O_2. The peak height is about 14 mV. The literature value of Q_Δ for RB in aerated acetonitrile is (0.54 ± 0.11)% [14], and we use it as the standard value in the present study.[1] The replacement of RB with R6G without changing the absorbance at 532 nm resulted in a spectrum shown in Fig. 1b. We can still clearly see the $^1O_2$ peak, though there are substantial background signals originated from R6G luminescence (fluorescence and phosphorescence). Stracke et al. first reported a R6G-photosensitized $^1O_2$ spectrum [9]. Our present data not only reproduce theirs but also have far better quality. The spectrum in Fig. 1b was fitted with a linear combination of

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[1] It is known that RB quenches $^1O_2$ sensitized by itself [9,16]. We do not take the effect of the $^1O_2$ quenching into account, because Q_Δ correction necessitated by the quenching effect is within the uncertainty of the standard value (0.54 ± 0.11)% and the present experimental uncertainty.

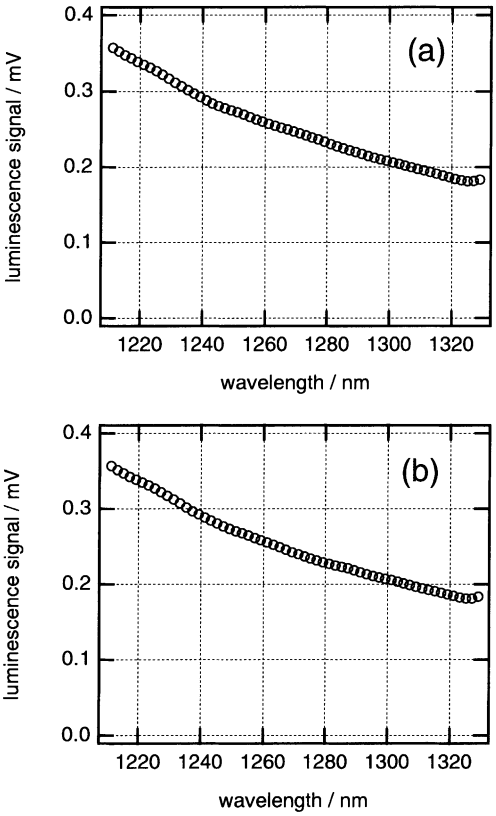

Fig. 2. Luminescence spectra (long-wavelength tail) of dye **I** in aerated acetonitrile: (a) in the absence of (DABCO); (b) in the presence of DABCO; DABCO = 4.6×10^{-3} mol dm^{-3}.

the $^1O_2$ spectrum by RB (Fig. 1a) and a parabolic base line. The fitting curve reproduces the data very well. The value of Q_Δ for R6G in aerated acetonitrile is obtained from the coefficient of the linear combination fitting as $(8.3 \pm 1.7) \times 10^{-3}$.

In Fig. 2a, we depict the luminescence spectrum obtained from dye **I**. There is no peak at 1.27 μm. The featureless spectrum in Fig. 2a is regarded as the long-wavelength tail of the dye **I** luminescence signals. The same measurement for dye **II** resulted in a similar featureless spectrum with no peak (data not shown). Though the spectrum in Fig. 2a does not have a $^1O_2$ peak, we believe that there is some contribution from $^1O_2$ photosensitized by dye **I** buried in the luminescence background. We made another sample solution which contained dye **I** and DABCO. The concentration of dye **I** in this solution was the same as above, and that of DABCO was 4.6×10^{-3} mol dm^{-3}. DABCO is an effective $^1O_2$ quencher [17], and we made sure that the presence of 4.6 mM DABCO reduced the phosphorescence signal of $^1O_2$ sensitized by RB in aerated acetonitrile to 0.7%. The luminescence from the solution of dye **I** with DABCO was measured in the same way, and is shown in Fig. 2b. The spectrum in Fig. 2b looks nearly identical with that in Fig. 2a, but we think that the former is not effectively contributed to by $^1O_2$. In harmony with this thought, we can see a peak at 1.27 mm in a difference spectrum shown in Fig. 3, which is obtained by subtracting the spectrum of dye **I** with DABCO (Fig. 2b) from that of dye **I** only (Fig. 2a). The peak is ascribed to $^1O_2$ photosensitized by dye **I**. This assignment has been confirmed by the fact that no peak was found in the difference spectra for dye **I** in nitrogen-saturated acetonitrile. The peak height in Fig. 3 is about 5 μV. The difference spectrum is well reproduced by the $^1O_2$ spectrum from RB (Fig. 1a) with a scaling factor. Q_Δ for RB multiplied by the scaling factor equals Q_Δ for dye **I**, which is calculated at $(1.7 \pm 0.5) \times 10^{-4}$. The same experimental procedure with longer accumulation time and the same data treatment for dye **II** resulted in a difference spectrum shown in Fig. 4. The $^1O_2$ peak height for dye **II** is about 0.6 mV. The standard $^1O_2$ spectrum (Fig. 1a) is multiplied by a scaling factor, and is drawn as a fitting curve in Fig. 4. Q_Δ for dye **II** in aerated acetonitrile is estimated at $(2.2 \pm 1.5) \times 10^{-5}$. This value is the lowest quantum yield of $^1O_2$ formation measured and reported so far to the best of our knowledge.

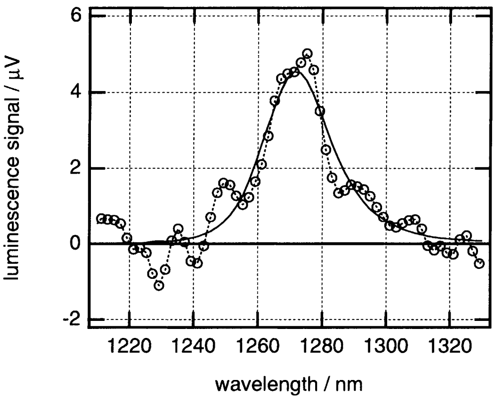

Fig. 3. Difference spectrum obtained by subtracting the spectrum of dye **I** with DABCO (Fig. 2b) from that of dye **I** only (Fig. 2a); open circles are data, and dotted lines only connect the data points; a solid curve indicates fitting.

Dye **I** is the most fundamental molecule among commercially used red styryl dyes for thermal-transfer printing. A lot of derivatives of dye **I** are now practically used. Dye **II** is

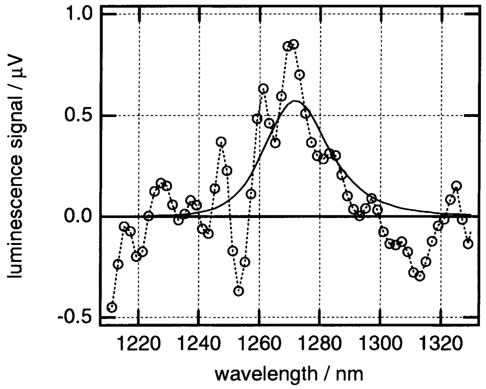

Fig. 4. $^1O_2$ phosphorescence spectrum photosensitized by dye **II** in aerated acetonitrile; open circles are data, and dotted lines only connect the data points; a solid curve indicates fitting.

one of arylazonaphthols which are most frequently used azo dyes, and shows keto (hydrazone)–enol (azo) tautomerism. The two tautomers were not selectively photoexcited in the present experimental condition. Time-resolved spectroscopic studies will be needed to elucidate which tautomer in the excited states is more likely to sensitize $^1O_2$. We know $^1O_2$ often plays an important role in the photofading of industrial practical dyes [4], but it is generally very difficult to fully understand photodegradation reaction mechanisms for low Q_Δ dyes. First of all, it is effective and useful to correlate Q_Δ with light-fastness data of many dyes for the development and screening of more light-durable dyes. Our new spectroscopic method of low Q_Δ determination is a powerful tool for this purpose. We are planning to improve the spectrometer by replacing the photomultiplier tube with a low-dark-noise one to improve the signal-to-noise ratio and lower the detection limit.

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