

# **A Solid Reference System for Photosensitized $^1\text{O}_2$ Production**

## **Measurements**

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## **ABSTRACT**

The production of  $^1\text{O}_2$  via photosensitization by Methylene blue (MB) supported onto Nafion-Na films is characterized by measuring  $^1\text{O}_2$  emission at 1270 nm, as well as, using complementary techniques like UV-Visible absorption and emission, and fluorescence and triplet-triplet absorption decay. Quantum yield of  $^1\text{O}_2$  production ( $F_\Delta$ ) of was determined in this heterogeneous system ( $F_\Delta = 0.24 \pm 0.03$ ). Results are compared with the  $^1\text{O}_2$  generation by MB in solution and in methanol-swollen Nafion-Na films. Differences and similitudes are discussed in terms of factors that influence  $F_\Delta$  magnitude in solution and in solid media.

*Key words:* Singlet oxygen, heterogeneous media, photosensitization, quantum yield, methylene blue, Nafion.

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## INTRODUCTION

The lowest electronic excited state of molecular oxygen,  $O_2 (^1\Delta_g)$  or  $^1O_2$  in short, is a highly reactive species<sup>1</sup> with application in various fields such as organic synthesis,<sup>2</sup> wastewater treatment (decolorization),<sup>3</sup> medicine of cancer (photodynamic therapies)<sup>4</sup> and disinfection processes.<sup>5</sup> Singlet oxygen can be generated by several methods: chemical reactions, electric discharge, direct excitation and, most often, energy transfer from an electronic excited state of a so-called sensitizer molecule (*photosensitization*, predominantly from the first triplet state).<sup>1</sup> The latter processes occur with rate constants close to the diffusional limit.

In some applications, production of  $^1O_2$  by photosensitizers incorporated onto *solid supports* is more adequate than generation in homogeneous systems because of its advantages such as the easy removal, separation or recover of the sensitizer from the reaction medium after using the generated  $^1O_2$ , and the longer lifetimes of  $^1O_2$  in some polymer materials compared to those observed in water or hydroxylic solvents where the polymer-supported sensitizer is introduced for its sought effect.<sup>1</sup>

In order to find the optimum photosensitizing system for each application, quantification of the  $^1O_2$  production in different media is needed, i.e. knowledge of the quantum yields of singlet oxygen generation ( $F_\Delta$ ). While this issue is well solved in *homogeneous* systems (normally using a suitable standard, such as phenalenone, Rose Bengal or tetraphenylporphyrin, in the same solvent), there is no established reference in *heterogeneous* systems yet.<sup>6</sup> Obviously, a reference polymer-bound sensitizer must be readily available, cheap enough, easy to prepare and must provide reproducible results under a wide variety of experimental conditions.

The most commonly used techniques to measure  $F_\Delta$  are chemical trapping of  $^1O_2$ , photoacoustic methods and the  $^1O_2$  NIR phosphorescence measurements ( $\lambda_{em}^{max} = 1270$

nm). A suitable reference system with a known  $F_{\Delta}$  would be required to use the latter method in heterogeneous phase. Since we have got involved recently in a project aimed to carry out water disinfection using solar light and polymer-bound sensitizers, the objective of our initial work has been to find a robust solid-supported photosensitizing system that can be used as a reference for  $F_{\Delta}$  quantification. We will show that methylene blue (MB)-dyed Nafion<sup>®</sup> films fulfill the features to become a useful reference system, provided its  $^1\text{O}_2$  production is characterized thoroughly.

We chose Nafion as the sensitizer support because it is a chemically inert, transparent, gas-permeable ionomer material. Its microscopic structure comprises a hydrophobic skeleton of perfluorinated alkyl chains from which ramifications via an ether bond arise. These lateral chains are terminated with hydrophilic sulfonate groups resembling the polar heads of surfactant molecules.<sup>7</sup> Such a material seems to be ideal as a polymer support for  $^1\text{O}_2$  production via photosensitization because it has a high permeability to molecular oxygen ( $6.4 \times 10^{-12} \text{ cm mol s}^{-1}$ ),<sup>8</sup> does not absorb in the uv-visible region above 250 nm, and exchange of its native  $\text{H}^+$  counterions of the sulfonate groups by cationic sensitizers is extremely fast in polar solvents (particularly methanol). Moreover, many organic compounds can also be loaded in the hydrophobic domains of Nafion. In this way, we selected MB, a well known photosensitizer, because it absorbs in the uv-visible range, has a relatively high  $F_{\Delta}$  (0.51, in methanol)<sup>6</sup> and it is easily incorporated into the Nafion films due to its (mono)cationic nature. An additional reason to choose this couple as a reference system is that previous  $^1\text{O}_2$  trapping experiments in MB-doped Nafion films by anthracenes have shown that the polymer-bound sensitizer is more resistant to photodegradation by intense light than in solution.<sup>9</sup> We compared these results with the generation of  $^1\text{O}_2$  by MB in solution and in the Nafion-Na films swollen by methanol.

## EXPERIMENTAL

**Materials.** Methylene blue (Panreac, 98%) was used as received.  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  was obtained from commercial  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  (Aldrich, 99.95%) by dissolution in warm water and precipitation with a saturated  $\text{NH}_4\text{PF}_6$  aqueous solution. Methanol (SDS, HPLC grade) and perdeuteriated methanol (Cambridge Isotope Laboratories Inc., 99.8% D) were used as received. Acetonitrile (SDS, HPLC grade) was dried with 4 Å molecular sieves for seven days (Prolabo). Nafion<sup>®</sup>-117 perfluorinated membrane (Aldrich) and NaOH (Quimipur) were used to prepare the Nafion-Na samples. Argon (99.999%, Praxair, Madrid) and oxygen (99.95%, Praxair, Madrid) gases were employed to purge the samples.

**Film Preparations.** The Nafion membrane was cut into ca. 25 x 8 mm pieces. The rectangles were thoroughly washed with methanol. In order to exchange with  $\text{Na}^+$  for the original  $\text{H}^+$  counterion of the  $\text{SO}_3^-$  groups, the cleaned films were dip in methanolic NaOH solution (ca. 0.1 M) and stirred for 15 hours and washed again with methanol.<sup>7</sup> MB was incorporated into the Nafion-Na membranes by stirring each film into a separate vial containing the required concentration of the photosensitizer dye dissolved in methanol. The films were allowed to dry subsequently in open vials at room temperature. In this way, films of MB concentrations of 3.6, 1.4 and 0.93 mM were prepared. MB concentration of the different films was calculated with the number of moles incorporated and Nafion films volumes. The amount of MB was calculated measuring the absorbance of the solution used to dye the films before and after being in contact with them. The volumes of the films were calculated with the dimension of the rectangles and their thickness.

**Spectroscopic Characterization.** *Absorption spectra* were recorded in a UV-Visible Varian Cary 3 Bio spectrophotometer. The molar absorption coefficient ( $\epsilon$ ) of MB in Nafion-Na were determined by measuring the absorption of several films containing different amounts of the sensitizer. The film thickness (178  $\mu\text{m}$ ) was used as the optical pathlength to calculate absorption coefficient ( $\epsilon$ ).

The homogeneity of MB incorporation into the films was tested by recording the absorption profiles at 642 nm, the absorption maximum wavelength with film transport accessory.

*Fluorescence emission spectra* were recorded in a Perkin-Elmer LS50 spectrofluorometer. Nafion films were placed in the diagonal of a standard quartz cell of 10 x 10 mm (Hellma QS).

*Fluorescence emission lifetimes* of the sensitizer ( $t_f$ ) were measured with an Edinburgh Instruments FL-900 time-correlated single-photon counting (TC-SPC) spectrometer, equipped with a Peltier-cooled Hamamatsu R-955 red sensitive photomultiplier. Excitation was performed with a 405 nm pulsed diode laser (IBH Nanoled-07) and monitored near the emission maximum. The luminescence decay profiles were collected by accumulation of  $10^4$  counts at the peak channel. The signal was deconvoluted with the excitation pulse profile.

**Time-Resolved  $^1\text{O}_2$  Emission.** Kinetic profiles of the  $^1\text{O}_2$  phosphorescence at 1270 nm were used to measure  $^1\text{O}_2$  lifetimes ( $t_\Delta$ ) and to determine the quantum yield of singlet oxygen production ( $F_\Delta$ ) for the MB dyed Nafion-Na films.  $[\text{Ru}(\text{bpy})_3]^{2+}$  in air-equilibrated acetonitrile was used as the reference system ( $F_\Delta (\text{CH}_3\text{CN}/\text{air}) = 0.57 \pm 0.05$ ).<sup>10, 11, 12, 13, 14, 15, 16</sup>

Measurements were performed using an Edinburgh Instruments (UK) LP-900 ns laser flash photolysis system equipped with a frequency- doubled Nd:YAG laser (Minilite II, Continuum, CA) for excitation at 532 nm and an EI-P fast Ge photodiode for time-resolved near-infrared detection. An Ophir AN/2 energy meter with a thermopile head (Ophir Optronics Ltd., Israel) was employed to monitor the energy of the laser pulse ( $E_L$ ), which was varied from 200 to 1000  $\mu\text{J pulse}^{-1}$ . Solid and liquid samples were placed in a 1 mm optical pathlength quartz cell (Hellma) that could be conveniently placed in the Edinburgh Instruments diffuse reflectance accessory. The NIR emission was detected after passing through an interference filter centered at 1270 nm (77-nm FWHM, Spectrogon). Typically, 100 laser shots were averaged for each signal. The absorption of liquid and solids samples was checked before and after the  $^1\text{O}_2$  emission experiments. Measurements were performed with the dry films or while dip in  $\text{CH}_3\text{OH}$  or  $\text{CD}_3\text{OD}$ .

**Triplet Lifetime Measurements.** Transient absorption experiments were done in order to measure the triplet lifetime ( $t_T$ ) of MB in Nafion-Na by using the laser flash photolysis equipment described above. The source probe beam was a 450 W pulsed Xe lamp focused onto the sample cuvette. Triplet-triplet absorption decays were monitored at 420 nm with a fast PMT (Hamamatsu) and at 870 nm with the Ge photodiode. The monitoring light source was conveniently filtered after passing through the sample. The transient absorption decay profiles were fitted to an exponential function.

## RESULTS

**Spectroscopic Characterization.** Figure 1 shows the normalized absorption spectra of an air-dried MB dyed Nafion-Na film immediately after preparation and a week later. It

can be seen that the absorption spectrum changed during the first days. The absorption maximum is blue shifted and the shoulder near 610 nm is less pronounced. No further changes were observed upon storage the sensitizer-doped film in the dark for up to 10 months. The absorption profile shows that the film was homogeneously dyed.

### *Figure 1*

The spectroscopic parameters of the air-dried MB/Nafion films are summarized in **Table 1**. It can be seen that absorption and emission maxima in Nafion are blue shifted with respect to the values in methanol ( $I_{\text{abs}} = 652$  nm and  $I_{\text{em}} = 687$  nm, respectively). The MB emission decay profiles in air-equilibrated Nafion films are biexponential (see **Table 1**). This result agrees with the data for MB in water found in literature (0.37 (91%) and 0.82 (9%) ns).<sup>17</sup> The preexponential weighted mean fluorescence lifetime in air-equilibrated Nafion films is 0.4 ns. This value is similar to the reported value of 0.45 ns for MB in water-dipped Nafion films.<sup>18</sup>

### *Table 1*

**Triplet Lifetime Measurements.** **Figure 2** shows typical experimental decays of <sup>3</sup>MB in air-equilibrated Nafion. The triplet absorption measurements were carried out at 420 nm and 870 nm, where <sup>3</sup>MB absorbs strongly.<sup>16</sup> The triplet state lifetime obtained in both experiments was nearly the same, (average value  $38.6 \pm 1.2$ )  $\mu$ s.

### *Figure 2*

**Determination of  $t_D$  and  $F_D$ .** The emission profiles of the  $^1\text{O}_2$  generated by sensitization with MB in dried Nafion film (**Figure 3a** and **Figure 4**) were fitted to the following equation

$$I(t) = I(0)\left(e^{-t/t_\Delta} - e^{-t/t_T}\right) \quad (1)$$

where  $t_D$  and  $t_T$  are the lifetime of  $^1\text{O}_2$  and of the triplet sensitizer, respectively.

The  $^1\text{O}_2$  rise emission component is not observed when  $^1\text{O}_2$  is produced by either MB or  $[\text{Ru}(\text{bpy})_3]^{2+}$  in solution or by methanol equilibrated MB/Nafion films (see **Figure 3b** and **3c**). Therefore, in these cases an exponential decay function was employed.

*Figure 3*

**Figure 4** compares the  $^1\text{O}_2$  emission signal at 1270 nm produced by MB in a Nafion film when equilibrated with  $\text{O}_2$ , air or Ar. When the system was saturated with  $\text{O}_2$ , the signal showed a more rapid rise but the decay time is the same than under air. When saturated with Ar, the NIR signal disappears. Similar dependence of  $^1\text{O}_2$  emission profiles with the  $\text{O}_2$  concentration was found in the literature for photosensitization with 2-acetonaphthone in Nafion-K powders.<sup>19</sup>

*Figure 4*

**Table 2** summarizes the  $^1\text{O}_2$  and  $^3\text{MB}$  lifetime obtained after exponential fitting using equation 1.

*Table 2*



The integrated time-resolved  $^1\text{O}_2$  luminescence signal intensity ( $I_\Delta$ ) is proportional to the total number of photons emitted by the photogenerated  $^1\text{O}_2$  that, in turn, is proportional to the  $^1\text{O}_2$  luminescence quantum yield ( $F_e$ )

$$I_\Delta = \frac{K}{n^2} F_e E_L (1 - 10^{-A}) \quad (2)$$

where  $K$  is a constant that includes both geometric and electronic instrumental factors,  $n$  is the refractive index of the medium from which the  $^1\text{O}_2$  luminescence is originated,  $E_L$  is the energy of the laser pulse and  $A$  is the absorbance of the sample at the excitation wavelength (532 nm).

The  $^1\text{O}_2$  emission quantum yield can be written in terms of  $F_\Delta$ :

$$F_e = F_\Delta k_r t_\Delta \quad (3)$$

where the product of the rate constant for the  $^1\text{O}_2$  radiative decay ( $k_r$ ) and the lifetime of  $^1\text{O}_2$  ( $t_\Delta$ ) represents the fraction of  $^1\text{O}_2$  that, once formed, decays by emitting a NIR photon.

Combining equations (2) and (3):

$$I_\Delta = \frac{K}{n^2} F_\Delta E_L (1 - 10^{-A}) k_r t_\Delta \quad (4)$$

Equation (4) can be written in a short form:

$$I_\Delta^{E,A} = \frac{K}{n^2} F_\Delta k_r t_\Delta \quad (5)$$

where  $I_\Delta^{E,A}$  can be obtained after plotting  $I_\Delta$  as a function of  $E_L$  and then, the slope of this plot ( $I_\Delta^E$ ) as a function of  $(1 - 10^{-A})$ , see **Figure 5**.

*Figure 5*

If singlet oxygen measurements for the unknown sample ( $x$ : MB-dyed Nafion films) and the reference ( $R$ :  $[\text{Ru}(\text{bpy})_3]^{2+}$  in acetonitrile solution) are carried out under exactly the same geometrical and electronic detection conditions, the quantum yield of  $^1\text{O}_2$  production for the sample ( $F_\Delta^x$ ) can be obtained from the following equation:

$$F_\Delta^x = \frac{I_\Delta^{E,A^x} n_X^2 k_r^R t_\Delta^R}{I_\Delta^{E,A^R} n_R^2 k_r^x t_\Delta^x} F_\Delta^R \quad (6)$$

where  $t_\Delta^R$  and  $t_\Delta^x$  can be obtained by fitting an appropriate kinetic function to the  $^1\text{O}_2$  luminescence decay profiles (see above).

The values of  $k_r$  for the sample ( $k_r^x$ ) and the reference ( $k_r^R$ ), which are solvent dependent, are necessary in order to calculate  $F_\Delta^x$ . Values of  $k_r$  for  $^1\text{O}_2$  in liquid media are known to be a function of the solvent electronic polarizability. The empirical correlation found in the literature:  $k_r = 2.83 - 37.3(n^2-1)/(2n^2+1) + 128.2[(n^2-1)/(2n^2+1)]^2$  has been used.<sup>20</sup> The refractive index of Nafion ( $n = 1.335$ )<sup>21</sup> and acetonitrile ( $n = 1.344$ )<sup>22</sup> were used to calculate  $k_r$  in the respective media. In the case of measurements performed with the  $\text{CH}_3\text{OH}$  or  $\text{CD}_3\text{OD}$  swollen Nafion films, the limiting values of  $F_\Delta$  were estimated by using the refractive indexes of Nafion ( $n = 1.335$ )<sup>21</sup> and methanol ( $n = 1.328$ )<sup>22</sup> as the lowest and highest value expected for the sample.

The  $F_\Delta^x$  values calculated by using equation 6 are shown in **Table 3**.

*Table 3*

## DISCUSSION

If a polymer-supported sensitizer dye is to be used as a reference system for  $^1\text{O}_2$  production measurements in solid phase, it is essential to know properties such as the

new environment of sensitizer itself and its relationship with the  $^1\text{O}_2$  generation. MB solvation will reflect the environment where  $^1\text{O}_2$  generator,  $^3\text{MB}$ , will be produced. The absorption and emission spectra can be very useful to provide information about solvation around a probe. The MB emission maximum shifts to the red with increasing the polarity of the solvents (e.g. 678 nm in acetone, 684 nm in acetonitrile, 687 nm in methanol, all determined in this work and 691 nm in water<sup>17</sup>). The emission maximum wavenumber displays a linear correlation with  $\frac{\epsilon_r - 1}{2\epsilon_r + 2} - \frac{n^2 - 1}{2n^2 + 2}$  (**Figure 6**), a theoretical polarity scale derived by Lippert.<sup>23</sup> Since the emission band of MB in Nafion is located at 674 nm (**Table 1**), it can be concluded that MB dwells in a lower polar environment than in the rest of the solvents plotted in **Figure 6**. Niu et al.<sup>9, 18</sup> performed trapping experiments of  $^1\text{O}_2$  produced by MB in water-swollen Nafion-Na and concluded that the sensitizer is located at the interfacial zone of the film. As the position of the MB absorption maximum in air-equilibrated Nafion films and the preexponential weighted mean fluorescence lifetime are nearly the same than in water-swollen films it can be concluded that MB is placed in a similar environment in both cases. MB absorption maximum in methanol-swollen films is 652 nm, identical to that found in methanol solution so in this case MB seems to be in a methanol environment. The differences observed in the MB absorption spectra recorded immediately after the preparation of the dyed film and a week later evidences that MB distribution in the film changes during this time.<sup>7</sup> Taking into account that the position of the absorption maximum is blue shifted compared to polar solvents, it can be concluded that after equilibration MB is located into a less polar environment than in methanol. The shoulder observed near 610 nm can be attributed to the formation of MB dimers in polar media.<sup>17, 24, 25, 26, 27</sup> The ratio of the absorbance at 610 nm to the absorbance at the

maximum goes from 0.6 to 0.5 after equilibration (**Figure 1**). This result can be explained taking into account that Guadalupe et al.<sup>26</sup> estimated a dimerization constant for MB in Nafion-H films of  $130 \text{ M}^{-1}$  that is smaller than the constant in a polar solvent (in water, average value from literature  $3.8 \times 10^3 \text{ M}^{-1}$ ).<sup>24, 25, 26</sup>

The longer tired component fluorescence lifetime found in Nafion (1.7 ns, **Table 1**) compared to the lifetime found in water literature (0.82 ns)<sup>17</sup> is typical for a more viscous and rigid medium.

Considering the  $^1\text{O}_2$  emission profiles collected in **Figure 4** it can be concluded that the rise part of the signal reflects the  $^1\text{O}_2$  formation which depends on the  $\text{O}_2$  concentration and the decay portion can be attributed to  $^1\text{O}_2$  deactivation. The biexponential model (equation 1) to extract  $t_T$  and  $t_\Delta$  from the  $^1\text{O}_2$  emission experiments is an approximation that is valid under the condition  $t_T < t_\Delta$ ; otherwise a deconvolution between the triplet decay signal and  $^1\text{O}_2$  signal should be done.<sup>28, 29, 30</sup> The difference in the value of  $t_T$  obtained in the  $^1\text{O}_2$  emission experiments and the triplet-triplet absorption decay experiments can be due to the use of this approximation or to the fact that in the first case the number of channels used to fit the data was smaller than in the second case. The time scale used in the former experiments was chosen to adequately cover full  $^1\text{O}_2$  decay kinetics.

The rise contribution in  $^1\text{O}_2$  emission profiles observed in dried films can be explained considering that in more viscous environment oxygen diffusion is slower so the  $^1\text{O}_2$  precursor ( $^3\text{MB}$ ) is slowly quenched by oxygen and the  $^1\text{O}_2$  formation can be followed. The triplet decay experiments of MB in Nafion equilibrated in air show that the  $^3\text{MB}$  lifetime is long enough compared to the lifetime of  $^1\text{O}_2$  in this media to explain the rise contribution observed in  $^1\text{O}_2$  emission experiments. When the system is saturated with oxygen more oxygen is available and the quenching events with subsequent

sensitization occurs faster. In methanol-swollen films diffusion occurs faster than in the air-dried films and the rise time is not observed. Oxygen diffusion coefficient is two orders of magnitude smaller in Nafion than in solution ( $4.3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  in Nafion<sup>8</sup> versus  $2.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in ethanol<sup>31</sup>)

The values of  $t_\Delta$  obtained in different Nafion systems studied in this work (**Table 2**) can be rationalized applying the model proposed by Lee et al.<sup>19</sup> based upon the distribution of  $^1\text{O}_2$  between a solvent-like (internal) and a Nafion-like (external) phase. According to their model the observed  $^1\text{O}_2$  decay rate constant,  $k_d$ , ( $t_\Delta^{-1}$ ) for the system by the following equation:

$$k_d = \frac{f k_{\text{int}} K_{eq} + (1-f) k_{\text{ext}}}{f K_{eq} + (1-f)} \quad (7)$$

where  $f$  is the volume fraction occupied by the internal phase,  $k_{\text{int}}$  and  $k_{\text{ext}}$  are the  $^1\text{O}_2$  decay rate constant within the internal and external phase, respectively, and  $K_{eq}$  is the equilibrium constant of  $^1\text{O}_2$  between the two phases, expressed as the  $^1\text{O}_2$  concentration in the interior phase to the exterior phase. Introducing in equation 7 the values,  $K_{eq} = 0.21$ ,  $k_{\text{int}} = 2.5 \times 10^5 \text{ s}^{-1}$  and  $k_{\text{ext}} = 2.77 \times 10^3 \text{ s}^{-1}$ <sup>19</sup>, the value of  $k_d = 1.18 \times 10^4 \text{ s}^{-1}$  ( $t_\Delta = 85 \text{ }\mu\text{s}$ ) obtained in air dried Nafion films (**Table 2**) can be justified with a volume fraction of water of 0.153 that corresponds to a 5.5 molecules of water per sulfonate group. This result is in agreement with the number water molecules that justified the MB absorption maximum in this film (see **Figure 6**). The number of molecules of 2.6 obtained by Lee et al.<sup>19</sup> may be due to the point they used Nafion-K that absorbs smaller amounts of water.<sup>7</sup> A value of  $t_\Delta = 34 \text{ }\mu\text{s}$  for methanol-swollen Nafion films is obtained replacing in equation 7  $K_{eq} = 0.21$ ,  $k_{\text{int}} = 1.0 \times 10^5 \text{ s}^{-1}$ ,  $k_{\text{ext}} = 2.77 \times 10^3 \text{ s}^{-1}$ ,  $f = 0.6$ .<sup>47, 19</sup> The difference with the experimental value  $t_\Delta = 16 \text{ }\mu\text{s}$  (**Table 2**) can be explained taking into account

that the oxygen solubility in methanol is higher than in water<sup>32</sup> so the  $K_{eq}$  in methanol/Nafion system should be larger than in water/Nafion.

The  $F_{\Delta}$  value obtained in dry Nafion films (**Table 3**) is smaller than the value found in literature for methanol solution ( $F_{\Delta}^{\text{methanol}} = 0.51$ ).<sup>6</sup> Sometimes the cage effects can explain smaller  $F_{\Delta}$  in more rigid media than in solution because more collisions between quenchers, like the sensitizer itself, and  $^1\text{O}_2$  are allowed. In the case of Nafion films studied in this work this effect should not be important because the rate constant of quenching of  $^1\text{O}_2$  by MB ( $1 \times 10^3 \text{ M}^{-1} \text{ S}^{-1}$ , this work) is five orders of magnitude smaller than in methanol solution ( $2.3 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$ ).<sup>16</sup>

The  $F_{\Delta}$  can be written in terms of the quantum yield of sensitizer triplet state formation ( $F_T$ ), the proportion of sensitizer triplet state quenched by  $\text{O}_2$  ( $P_{\text{O}_2}^T$ ) and the fraction of this oxygen quenching reaction that yields to  $^1\text{O}_2$  ( $f_{\Delta}^T$ ):

$$F_{\Delta} = F_T P_{\text{O}_2}^T f_{\Delta}^T \quad (8)$$

The proportion of  $^3\text{MB}$  quenched by  $\text{O}_2$  ( $P_{\text{O}_2}^T$ ) is a function of the rate constant of quenching of MB triplet state ( $k_q^{\text{O}_2}$ ):

$$P_{\text{O}_2}^T = \frac{k_q^{\text{O}_2} [\text{O}_2]}{(t_T^0)^{-1} + k_q^{\text{O}_2} [\text{O}_2]} = t_T k_q^{\text{O}_2} [\text{O}_2] \quad (9)$$

where  $t_T^0$  is the MB triplet lifetime in the absence of  $\text{O}_2$  and  $[\text{O}_2]$  is oxygen concentration in the media.

A value of  $P_{\text{O}_2}^T$  (air) in polar solvents close to 1 was calculated with literature data ( $t_T^0 = 450 \mu\text{s}$ <sup>33</sup>,  $k_q^{\text{O}_2} = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ <sup>32</sup>,  $[\text{O}_2](0.21 \text{ atm}) = 2.1 \times 10^{-3} \text{ M}$ <sup>33</sup>).

Since the  $^3\text{MB}$  quenching rate constant by  $\text{O}_2$  ( $k_q^{O_2}$ ) in Nafion films is not available in literature it can be estimated from a Stern-Volmer equation:

$$\frac{1}{t_T} = \frac{1}{t_T^0} + k_q^{O_2} [\text{O}_2] \quad (10)$$

by using  $t_T$  obtained in the  $^1\text{O}_2$  emission experiments in air and  $\text{O}_2$  (**Table 2**) and the solubility of  $\text{O}_2$  in Nafion in both cases ( $3.1 \times 10^{-3} \text{ M}$  and  $1.49 \times 10^{-2} \text{ M}$ ).<sup>8</sup> The value obtained with this procedure is  $k_q^{O_2} = 1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . This rate constant can be used to calculate  $P_{O_2}^T$  (Nafion - air). This resulting value (0.85) is smaller than the  $P_{O_2}^T$  in methanol solution but is not small enough to justify the 50 % difference of  $F_\Delta$  observed in both media (**Table 3**). The lower  $F_\Delta$  in Nafion versus in methanol may arise from a smaller  $F_T$  or  $f_\Delta^T$  in the film. Under diffusion-controlled process, if all the triplet state quenching process by  $\text{O}_2$  drive to the formation of  $^1\text{O}_2$  (energy transfer process) a value of  $k_q^{O_2}$  equal to 1/9 of diffusion constant ( $k_{\text{diff}}$ ) is expected.<sup>13</sup> In this case the assumption of  $f_\Delta^T = 1$  is justified. The value of  $k_{\text{diff}}$ , when oxygen is one of the reaction partners, has been evaluated to be  $3.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in methanol.<sup>13</sup> As  $k_q^{O_2}$  in polar solvents ( $1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>32</sup> is close to  $k_{\text{diff}}/9$  ( $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) a value of  $f_\Delta^T$  close to the unity is expected. Considering than diffusion of oxygen in Nafion is 100 orders of magnitude smaller than in solution a value of  $k_{\text{diff}}$  10 or 100 times smaller will be expected. The value of  $k_q^{O_2} = 1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  should be close to the expected value of  $k_{\text{diff}}/9$  so in this case  $f_\Delta^T$  will be approximately 1 too. Increasing values of  $F_T$  for MB in increasing polarity solvents are found in literature (0.35, 0.43 and 0.52 in propylene carbonate, metoxyethanol and methanol, respectively).<sup>34</sup> Nafion, as is shown in **Figure**

**6**, is a less polar solvent than methanol so the smaller  $F_T$  expected in this medium should contribute to make  $F_\Delta$  smaller.

A quantum yield of singlet oxygen production when the Nafion film is equilibrated with  $O_2$  of 0.3 is predicted by using  $P_{O_2}^T(\text{air}) = 0.85$ ,  $F_\Delta(\text{air}) = 0.24$  and the proportion of  $^3\text{MB}$  quenched by  $O_2$  when the system is equilibrated with  $O_2$  ( $P_{O_2}^T(O_2) = 0.97$ ). This value agrees with the experimental value of 0.35 (**Table 3**).

Nevertheless, the  $F_\Delta$  obtained in methanol-swollen Nafion film is nearly the same than that found in literature for methanol solution (0.51).<sup>6</sup> This result means that the  $^1O_2$  produced in this case is mostly in the methanol phase. The disappearance of the rise contribution in  $^1O_2$  emission profiles, the magnitude of  $t_\Delta$  and the position of the absorption maximum of MB are other evidences that confirm that in this case  $^1O_2$  is generated and deactivated principally in a methanol environment.

After characterization MB dyed Nafion films we can conclude it is a suitable system to be used as a reference to determine  $F_\Delta$ .

## ACKNOWLEDGEMENTS

The authors thank the European Union (grants ICA4-CT-2002-10001 and ICA3-CT-2002-10028), for supporting this project.



**Table 1.** Absorption and emission parameters of MB in methanol and in air-dried Nafion-Na film.

| Medium             | $\lambda_{\text{abs}}$ (nm) | $\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ ) | $\lambda_{\text{em}}$ (nm) | $t_f$ (ns)                          |
|--------------------|-----------------------------|---|----------------------------|-------------------------------------|
| CH <sub>3</sub> OH | $652 \pm 2$                 | $80000 \pm 2000$                              | $687 \pm 2$                | 0.6                                 |
| Nafion             | $642 \pm 2$                 | $59000 \pm 3000$                              | $674 \pm 2$                | 0.2 (89%), 1.7 (11%) <sup>(a)</sup> |

(a) Values in parenthesis are the normalized pre-exponential factors of the fit.

**Table 2.**  $^1\text{O}_2$  lifetime ( $t_\Delta$ ) and  $^3\text{MB}$  lifetime ( $t_T$ ) in different media obtained by fitting the emission profiles to eq. 1.

| Medium                              | $t_D (\mu\text{s})^{(a)}$ | $t_T (\mu\text{s})^{(a)}$ |
|-------------------------------------|---------------------------|---------------------------|
| MB/Nafion-Na/air                    | 85                        | 20                        |
| MB/Nafion-Na/O <sub>2</sub>         | 90                        | 5                         |
| MB/Nafion-Na/CH <sub>3</sub> OH/air | 16                        | < 1                       |
| MB/CH <sub>3</sub> OH/air           | 10                        | < 1                       |

(a) Estimated error:  $\pm 20\%$ ; the dispersion of the data can be attributed to the water content in the film. ¿NO HABRIA QUE EXPLICAR POR QUE NO SE DA EL DATO EN LOS DOS ULTIMOS CASOS Y SE ESCRIBE SOLO <1? No entiendo!!

**Table 3.** Quantum yield of  $^1\text{O}_2$  production ( $F_\Delta$ ) by MB-dyed Nafion-Na films.

| Medium                           | $F_D$                       |
|----------------------------------|-----------------------------|
| Nafion-Na/air                    | $0.24 \pm 0.03$             |
| Nafion-Na/O <sub>2</sub>         | $0.35 \pm 0.05$             |
| Nafion-Na/CH <sub>3</sub> OH/air | $0.47(0.51) \pm 0.06^{(a)}$ |
| Nafion-Na/CD <sub>3</sub> OD/air | $0.47(0.50) \pm 0.06^{(a)}$ |

(a) The lowest value was calculated with the refractive index of Nafion ( $n= 1.335$ )<sup>21</sup> and the highest one with the refractive index of methanol ( $n= 1.328$ )<sup>22</sup> (see text).

## FIGURE CAPTIONS

**Figure 1.** Normalized absorption spectra of MB in an air-equilibrated Nafion-Na film. Spectra obtained immediately after preparation (---) and a week later (—) are shown. The inset shows the absorption profile at the absorption maximum (642 nm) of a MB-dyed (0.93 M) film (○) and a non-dyed film (□). The spectra are normalized with respect to the absorption maximum of the full line trace.

**Figure 2.** Triplet-triplet absorption decays of MB in air-equilibrated Nafion-Na film monitored at a) 870 nm and b) 420 nm. The MB concentration is 1.4 mM.

**Figure 3.** Emission profiles at 1270 nm of  $^1\text{O}_2$  generated by sensitization with MB in air-equilibrated: a) Nafion-Na, b)  $\text{CH}_3\text{OH}$  solution, c) Nafion-Na/ $\text{CH}_3\text{OH}$ . ¿PONEMOS LAS CONCENTRACIONES DE MB EN CADA CASO?No me parece

**Figure 4.** Emission profiles at 1270 nm of  $^1\text{O}_2$  produced by MB-doped Nafion-Na exposed to 100%  $\text{O}_2$  (□), air (○) and 100% Ar (—).

**Figure 5.** a) Integrated time-resolved  $^1\text{O}_2$  luminescence signal decay ( $I_\Delta$ ) as a function of the laser pulse energy ( $E_L$ ) produced by MB-dyed films of different absorbance at 532 nm: 0.066 (□), 0.105 (○), 0.278 (△), and by  $[\text{Ru}(\text{bpy})_3]^{2+}$  in acetonitrile (□). b) The slope of the previous plot ( $I_\Delta^E$ ) as a function of the absorbed photon flux ( $1 - 10^4$ ) for MB/Nafion (○) and  $[\text{Ru}(\text{bpy})_3]^{2+}$ /acetonitrile (□).

**Figure 6.** Energy of the MB emission maximum vs. the Lippert polarity function. The different points correspond to the following solvents: 1) water, 2) methanol, 3) acetonitrile, 4) acetone, 5) Nafion. The dielectric constant ( $\epsilon_r$ ) and the refractive index ( $n$ ) were taken from reference [22] except  $\epsilon_r$  of air-equilibrated Nafion that was taken for a water content of 6 molecules per sulfonate group of the film, the typical value for air-dried Nafion.<sup>35, 36</sup>

FIGURES

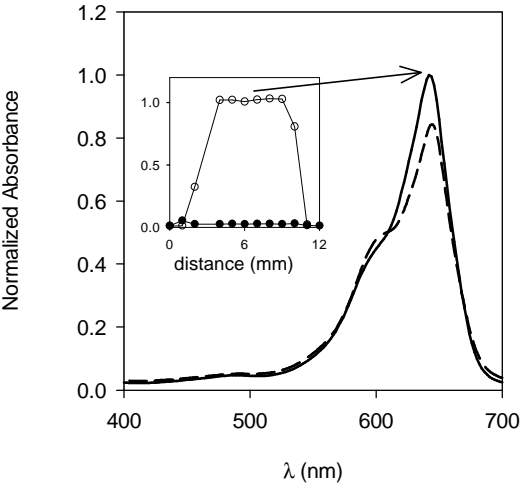


Figure 1

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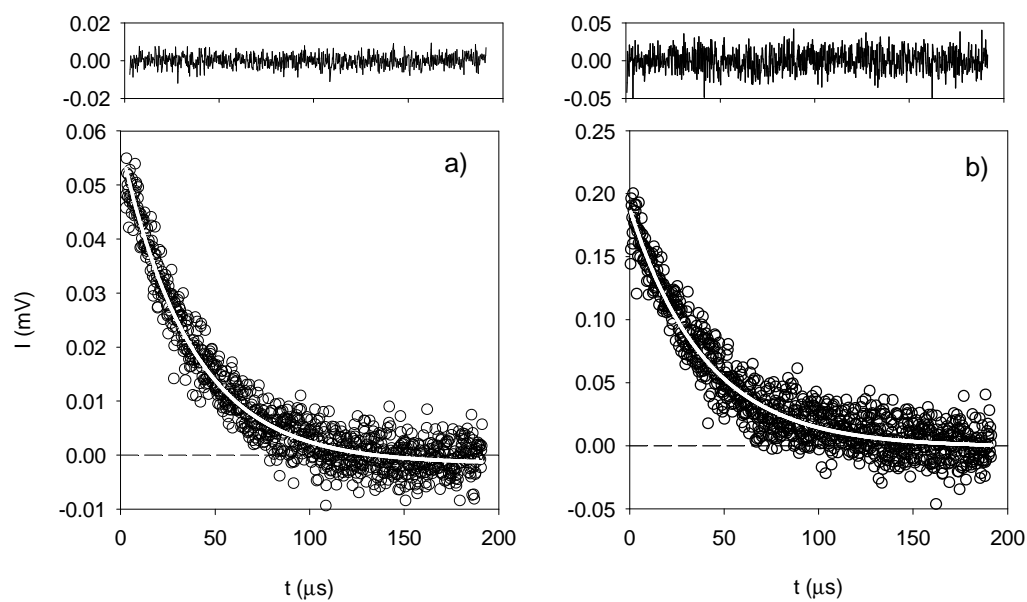


Figure 2

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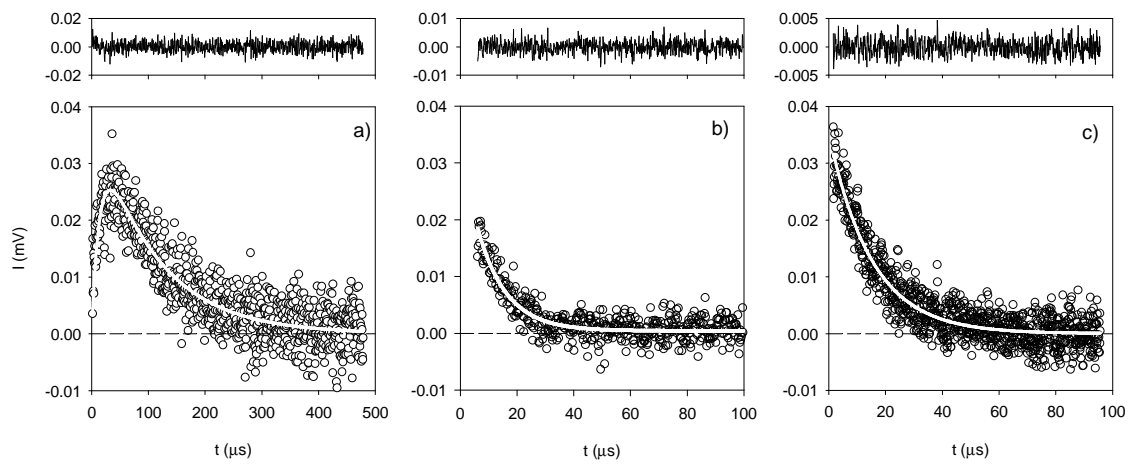


Figure 3

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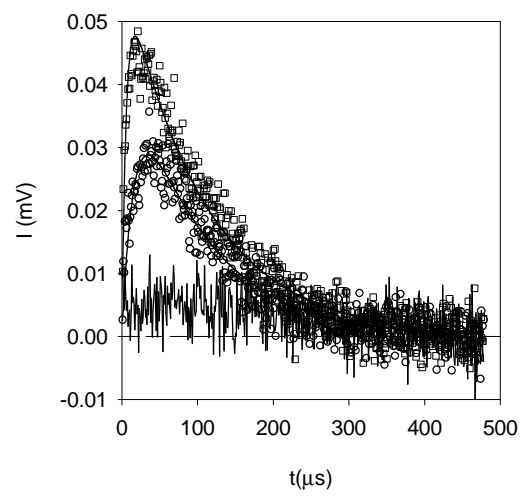


Figure 4

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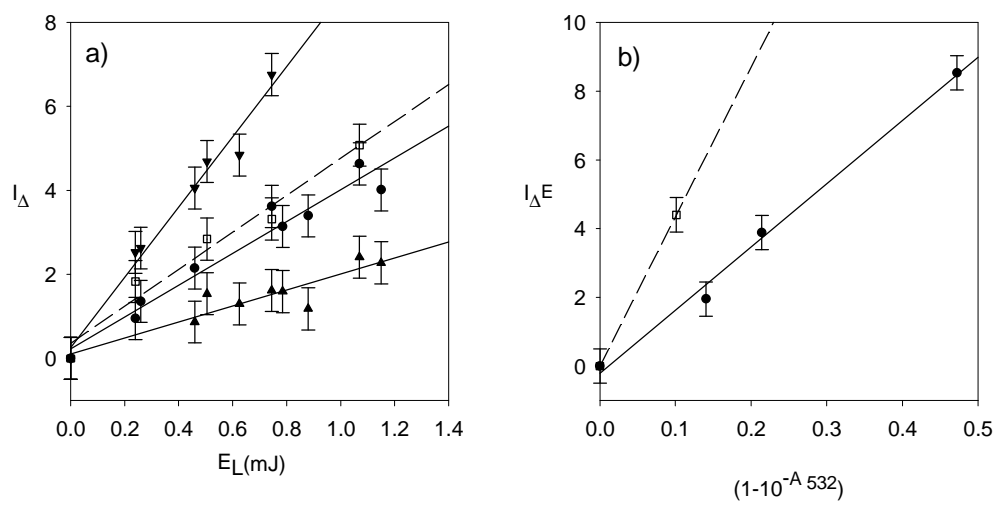


Figure 5

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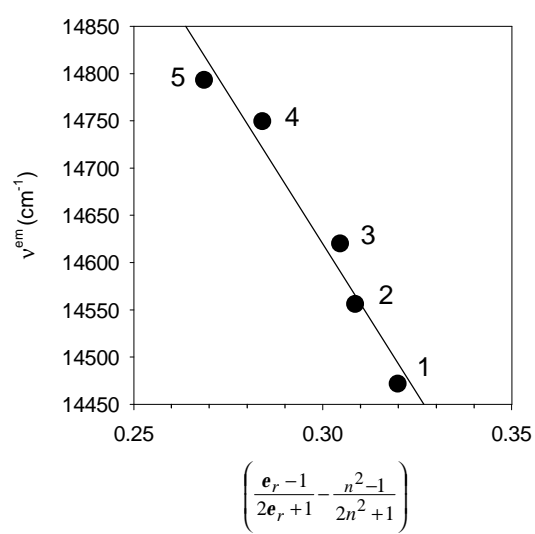


Figure 6

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would be counteracted by the decrease due to quenching of  $^1\text{O}_2$  by the sensitizer itself.

Unlike MB, Ru(II) polypyridyls are known to be efficient  $^1\text{O}_2$  generators and to have small quenching rate constants of  $^1\text{O}_2$  <sup>[9, 10, 13, 14, 15]</sup> (e.g.  $1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for  $[\text{Ru}(\text{bpy})_3]^{2+}$  in acetonitrile, this work).

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