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## Singlet Oxygen Chemistry in Water: A Porous Vycor Glass–Supported Photosensitizer

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Singlet molecular oxygen [ $^1\text{O}_2$  ( $^1\Delta_g$ )] is generated cleanly in aqueous solution upon irradiation of a heterogeneous complex, *meso*-tetra(*N*-methyl-4-pyridyl)porphine (**1**) adsorbed onto porous Vycor glass (PVG). The cationic photosensitizer **1** tightly binds onto PVG and gives a stable material, which does not dissociate **1** into the surrounding aqueous phase. The production of  $^1\text{O}_2$  was measured by monitoring the time-resolved  $^1\text{O}_2$  ( $^1\Delta_g$ ) phosphorescence at 1270 nm. Indirect analysis of  $^1\text{O}_2$  generation was also carried out with the photooxidation of *trans*-2-methyl-2-pentenoate anion, which afforded the corresponding hydroperoxide. Sensitizer-**1**-impregnated PVG gives rise to a new singlet oxygen generator but more importantly provides a heterogeneous system for use in water.

## 1. Introduction

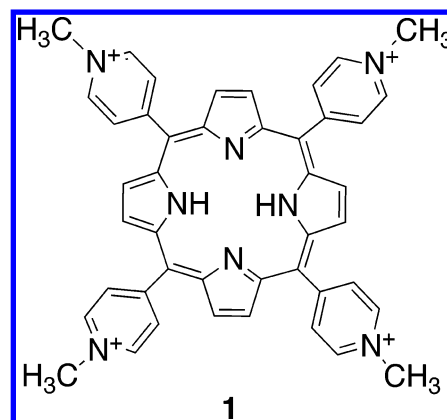
Singlet oxygen [ $^1\text{O}_2$  ( $^1\Delta_g$ )] has a lifetime of microseconds to milliseconds and can diffuse a distance from where it was generated.<sup>1,2</sup> Remarkably,  $^1\text{O}_2$  can diffuse across a cell membrane<sup>3,4</sup> and even serve as a signaling molecule.<sup>5–7</sup> The first report of  $^1\text{O}_2$  as a diffusible intermediate came from Kautsky and de Bruijn in 1931,<sup>8</sup> in which tryptaflavine (a sensitizer) and leucomalachite green (an oxygen-acceptor compound) were adsorbed separately on silica gel beads (Scheme 1). Upon photolysis in the presence of  $\text{O}_2$ ,  $^1\text{O}_2$  was generated on a  $\text{SiO}_2$  bead and diffused to another (separate)  $\text{SiO}_2$  bead where it was trapped by leucomalachite green.<sup>8–10</sup> Kautsky's "through space" experiment was similar in many respects to the Paneth/Hofeditz lead mirror experiments (thermal decomposition of  $\text{PbEt}_4$ ),<sup>11</sup> which provided evidence for free ethyl radicals in the gas phase.<sup>12–14</sup> Other researchers have since conducted similar heterogeneous  $^1\text{O}_2$  studies. The first heterogeneous photosensitizer (covalently bound) was polymer Rose Bengal synthesized by Neckers et al. in 1972.<sup>15–17</sup> Polymer Rose Bengal was based on Merrifield beads with its origins traced directly to solid-phase peptide synthetic chemistry.

Silica gel, polymers, alumina, and zeolites have been used as solid supports for  $^1\text{O}_2$  photosensitizers.<sup>18</sup> However, these solid supports<sup>18a–c</sup> are often used to generate  $^1\text{O}_2$  in the presence of organic solvents, or in the absence of solvent altogether.

Additional studies could be directed toward  $^1\text{O}_2$  chemistry in water, and the search for alternative solid supports. We sought a system that does not require covalent attachment of the sensitizer to the solid but nonetheless binds the two together tightly. Because porous Vycor glass (PVG) develops a negative  $\zeta$  potential in water (indicating an anionic surface), cations bind tightly.<sup>19,20</sup> Neutral molecules can also bind to PVG<sup>21–27</sup> but

do so more weakly than cations. By taking advantage of the cation-binding ability of PVG in water,<sup>19,20,28–32</sup> one can imagine a similar PVG binding of a cationic photosensitizer. Raftery et al. have used PVG as a solid support for photocatalysts, such as a  $\text{TiO}_2$  monolayer.<sup>33,34</sup> To date, no reports exist on heterogeneous  $^1\text{O}_2$  photooxidations with PVG as a solid support. *Meso*-tetra(*N*-methyl-4-pyridyl)porphine (**1**) was selected in our study because it is a  $^1\text{O}_2$  photosensitizer<sup>2</sup> known to photodynamically inactivate *E. coli*.<sup>35</sup> Anions tend not to bind to PVG. Thus, PVG might also yield specificity for  $^1\text{O}_2$  reactions with anions rather than cations and neutral compounds in the bulk aqueous phase.

We report that cation **1** binds to the PVG anionic silanol sites to give an adsorbed complex. Singlet oxygen is photochemically generated at the solid–liquid interface, and then,  $^1\text{O}_2$  diffuses into the aqueous medium. An anionic alkene is readily oxidized by  $^1\text{O}_2$  in the surrounding aqueous solution.



## 2. Experimental Section

**2.1. Materials and Instrumentation.** Reagents were obtained commercially [*meso*-tetra(*N*-methyl-4-pyridyl)porphine tetratosylate, *meso*-tetra(4-sulfonatophenyl)porphine dihydro-chloride, *trans*-2-methyl-2-pentenoic acid, sodium hydroxide, magnesium

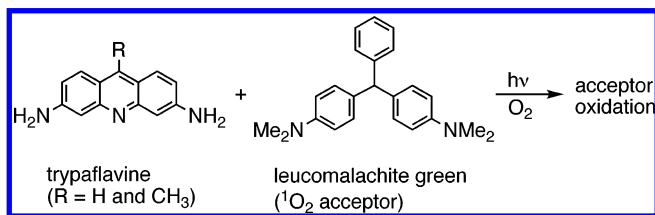
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## SCHEME 1



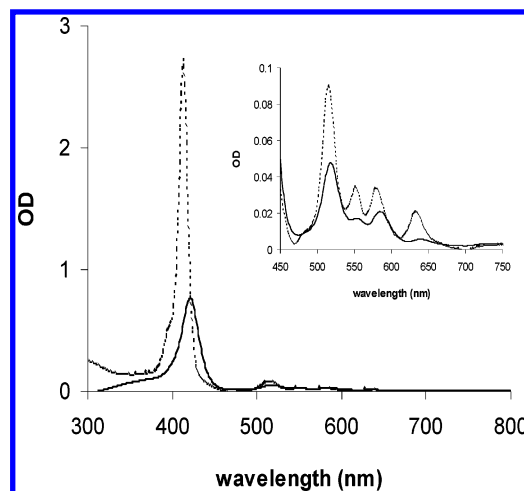
sulfate, triphenylphosphine, *p*-toluene sulfonic acid (TsOH), and adipic acid] and used without further purification. The solvents used (methanol, absolute ethanol, deuterium oxide-*d*<sub>2</sub>, and chloroform-*d*<sub>1</sub>) were of spectroscopic or equivalent grade and were used as received. Deionized water was obtained from a U.S. Filter Corporation deionization system. PVG samples (Corning 7930, pore size = 40 Å) were dried in a Fisher Scientific Isotemp muffle furnace at 500 °C and then stored in a desiccator under a vacuum (30 mmHg). Pieces of PVG were in the shape of disks (11.0 mm in diameter and 2.0 mm in thickness) or squares (1.5 cm<sup>2</sup> and 1.0–1.5 mm in thickness). Samples were irradiated with a *Q*-switched Nd:YAG laser (532 nm, 3–4 ns, 30 mJ, Polaris II-20, New Wave Research Merchantek Products). A liquid-N<sub>2</sub>-cooled germanium photodetector (Applied Detector Corporation) was used for the determination of quantum yields of <sup>1</sup>O<sub>2</sub>. The steady-state generation of <sup>1</sup>O<sub>2</sub> was conducted with a Rayonet photoreactor with Sylvania F8T5/CW 8 W bulbs that emit at ~425–650 nm. Mass spectrometry data were acquired on an Agilent Technologies 6890N GC/MS instrument with a 5973 mass selective detector (MSD) and a HP-5MS column. UV–visible spectra were collected on a Hitachi UV–vis U-2001 instrument. NMR data were collected on a Bruker DPX400 NMR instrument.

**2.2. Measurements.** The adsorption process was achieved by placing a 0.28 g PVG sample into 24.7 mL of a 1.0 × 10<sup>-5</sup> M solution of **1** in deionized water. The amount of photosensitizer adsorbed onto PVG was calculated from the difference in absorbance of the solution before introduction of PVG and the absorbance of the same solution after the PVG's removal [at the λ<sub>max</sub> value of **1** (422 nm)]. The number of moles of photosensitizer adsorbed per gram of PVG was calculated using eq 1

$$n_{\text{adsorbed}}/\text{g of PVG} = \{[(A_i - A_f)/A_i] \times n_i\}/\text{g of PVG} \quad (1)$$

in which *A*<sub>i</sub> is the absorbance of the solution prior to introduction of PVG, *A*<sub>f</sub> is the absorbance of the solution after the impregnation interval and removal of the PVG, *n*<sub>i</sub> is the number of moles of sensitizer prior to impregnation, *n*<sub>adsorbed</sub> is the number of moles adsorbed onto the PVG, and *g* of PVG is the weight of the PVG in grams.<sup>29</sup> Typically, PVG samples were loaded with 1.0 × 10<sup>-6</sup> mol of **1**/g of PVG. Colorless PVG was converted to deep red on adsorption of **1** after 48 h. The moles of hydronium ion were calculated from the pH of the surrounding aqueous solution. The experiments were carried out at room temperature and with O<sub>2</sub>-saturated solutions. The phosphorescence of <sup>1</sup>O<sub>2</sub> at 1270 nm was measured as previously described.<sup>36</sup> The initial <sup>1</sup>O<sub>2</sub> intensity is extrapolated to *t* = 0. The data points of the initial 3–4 ns are not used due to electronic interference signals from the detector. The intensity of the pulses at 532 nm was controlled between 20 and 30 mJ. The quantum yield for production of <sup>1</sup>O<sub>2</sub> in homogeneous solution is calculated according to eq 2.

$$\Phi_{\Delta \text{ sample}}/\Phi_{\Delta \text{ reference}} = S_{\text{sample}}/S_{\text{reference}} \quad (2)$$

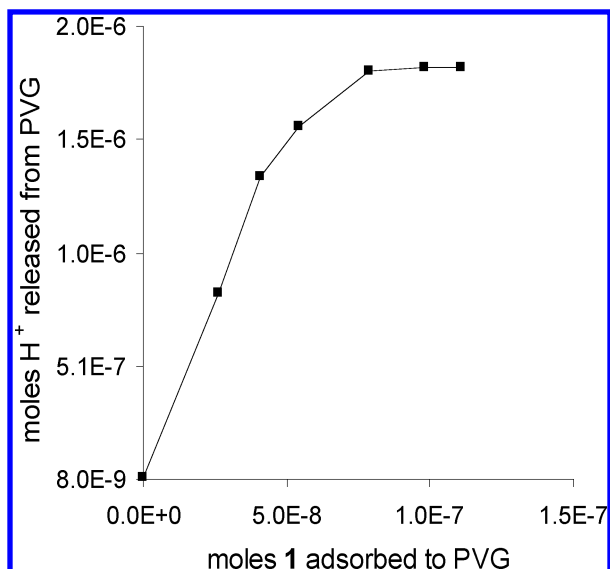


**Figure 1.** Absorption spectra of *meso*-tetra(4-sulfonatophenyl)porphine (dashed line) and **1** (solid line) in H<sub>2</sub>O solution. The inset is an expanded view of the visible portion of the spectra, in which the two compounds are optically matched at 532 nm.

Here, Φ<sub>Δ sample</sub> and Φ<sub>Δ reference</sub> are the <sup>1</sup>O<sub>2</sub> quantum yields for samples and the reference. *Meso*-tetra(4-sulfonatophenyl)porphine was used as a reference sensitizer, in which its absorbance was optically matched with that of **1** at 532 nm (Figure 1). *S*<sub>sample</sub> and *S*<sub>reference</sub> represent the slopes obtained from the plot of initial intensity of <sup>1</sup>O<sub>2</sub> via the absorbance at an excitation wavelength of 532 nm for the sample and the reference, respectively.

**2.3. *Meso*-tetra(*N*-methyl-4-pyridyl)porphine (**1**).** The purity of the tosylate of **1** was determined to be 99% based on NMR (integration of peaks in its <sup>1</sup>H NMR spectrum) and greater than 95% based on HRMS: <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz) δ 1.50 (s, 12H), 4.63 (s, 12H), 6.43 (bs, 8H), 7.01 (bs, 8H), 8.78 (d, *J* = 4.6 Hz, 8H), 8.83–9.08 (bs, 8H), 9.14 (d, *J* = 4.6 Hz, 8H). <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz) δ 155.0, 141.6, 138.7, 136.9, 130.8, 126.1, 122.3, 113.3, 46.1, 17.1. Mass spectrum (EI); *m/z* = 676.31 (100), 677.31 (48), 678.31 (12.5), 677.30 (3.0), 679.32 (1.7). HRMS calcd for (C<sub>44</sub>H<sub>36</sub>N<sub>8</sub>)<sup>2+</sup> 338.1522 (the base peak represents the loss of four tosylate fragments and two protons), found 338.1525. Literature: <sup>1</sup>H NMR (D<sub>2</sub>O) δ 9.19 (d, 8H), 9.03 (bs, 8H), 8.71 (d, 8H), 4.77 (s, 12H) at pD 7.0.<sup>37</sup> <sup>1</sup>H NMR (DMSO) δ 9.47 (d, 8H), 9.18 (s, 8H), 8.97 (d, 8H), 4.72 (s, 12H).<sup>38</sup>

**2.4. Heterogeneous Photooxidation of *Trans*-2-methyl-2-pentenoate Anion (**2**).** Compound **1** (7.5 × 10<sup>-7</sup> mol) adsorbed onto 1.58 g of PVG was combined with 20 mL of *trans*-2-methyl-2-pentenoic acid (0.25 mmol) and NaOH (0.35 mmol) in deionized H<sub>2</sub>O. Presumably *trans*-2-methyl-2-pentenoic acid is a stronger acid and is selectively deprotonated affording **2**, since the PVG silanol groups are reported to be p*K*<sub>a</sub> ~ 9.<sup>39</sup> Dioxygen was bubbled into the solutions. Photooxygenation was carried out for 4 h at room temperature with the Rayonet reactor. Aliquots of the H<sub>2</sub>O reaction were mixed with D<sub>2</sub>O for NMR analysis. 3-Hydroperoxy-2-methylene pentanoic acid (**3**) was detected as the sole product: <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.91 (t, *J* = 7.5 Hz, 3H), 1.66 (m, 2H), 4.75 (t, *J* = 6.5 Hz, 1H), 5.56 (s, 1H), 5.94 (s, 1H). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.71 (m, 2H), 4.82 (t, *J* = 6.4 Hz, 1H), 6.01 (s, 1H), 6.54 (s, 1H) [note that 1.66 (in D<sub>2</sub>O) and 1.71 (CDCl<sub>3</sub>) represent ABX3 multiplets]. HRMS calcd for (C<sub>6</sub>H<sub>9</sub>O<sub>4</sub>)(M - H<sup>+</sup>) 145.0506, found 145.0506. The percent yield was determined by comparison of the integrated methyl protons of **3** with the methylene protons of adipic acid (internal standard) by <sup>1</sup>H NMR spectroscopy. Upon addition of triphenylphosphine (0.08 M), **3** converted to 3-hydroxy-2-methylene pentanoic acid (**4**),

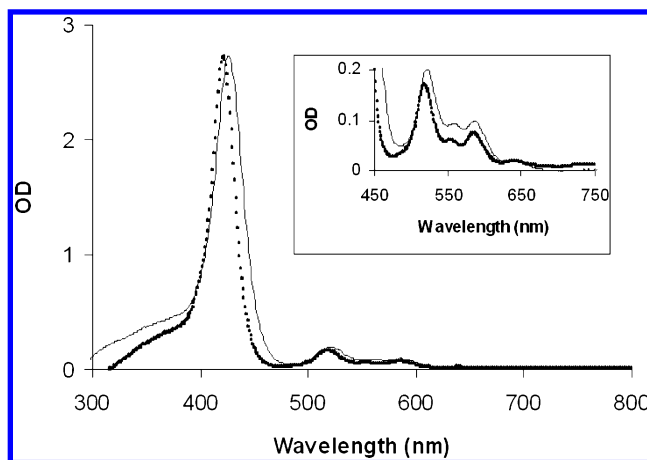


**Figure 2.** Plot of the moles of H<sup>+</sup> ions arising from PVG silanol deprotonation calculated from the decrease in pH of the aqueous solution during the adsorption of **1** onto PVG. Each point is taken at a 30 min increment over a total of 3 h.

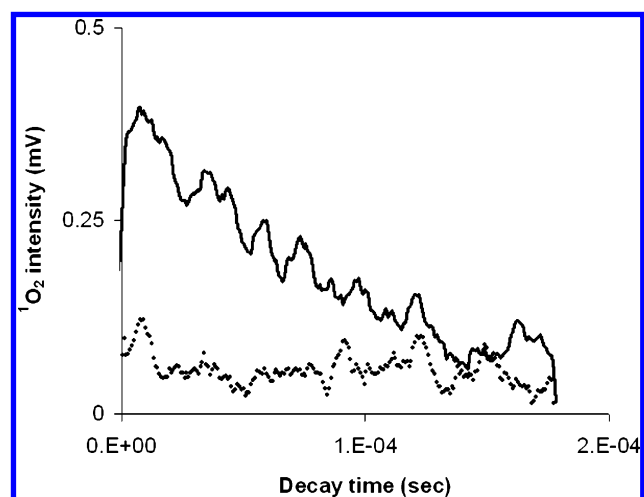
a known compound.<sup>40</sup> Our data agreed with the literature value: <sup>40</sup> <sup>1</sup>H NMR (D<sub>2</sub>O) δ 1.19 (t, *J* = 7.1 Hz, 3H), 1.54 (m, 2H), 4.44 (t, *J* = 6.0 Hz, 1H), 5.45 (s, 1H), 5.76 (s, 1H) (note that 1.54 represents an ABX3 multiplet).

### 3. Results and Discussion

**3.1. Adsorption of Photosensitizer 1.** In aqueous solution, cation **1** adsorbs onto PVG and forms a complex. After 48 h, we find that  $1.0 \times 10^{-6}$  mol of **1** adsorbed onto 1 g of PVG. Three experiments were conducted to examine aspects of the adsorption process. First, an experiment was carried out in order to determine whether a decrease in pH in the surrounding solution coincides with the adsorption of **1** onto PVG. A concurrent decrease in pH of the aqueous solution is found (plotted as the appearance of moles of H<sup>+</sup> ions, Figure 2), which suggests that cation **1** exchanges onto the anionic silanol sites. The adsorption of **1** over 3 h corresponded to a pH reduction from 6.12 to 4.14. Figure 1 shows that cationic **1** replaces hydronium ions on the PVG silanol groups. The initial mole ratio of **1** adsorbed/H<sup>+</sup> dissociated is 1:32 (after 30 min). After 3 h, an equilibrium is established and reveals that every mole of **1** adsorbed leads to the release of 15 mol of H<sup>+</sup> from PVG. Perhaps this decrease in the ratio relates to a tendency for reprotonation of some silanol anion sites over time. Second, to determine if the counterion (TsO<sup>-</sup>) is coadsorbed onto the anionic surface, a 1.69 g PVG sample was placed in 25.0 mL of  $1.01 \times 10^{-5}$  M **1** and the aqueous phase was monitored by UV spectroscopy. Adsorption of **1** was accompanied by the appearance of  $3.9 \pm 0.05$  mol of equivalent tosylate ion in solution ( $\lambda_{\max} = 260$  nm) measured by a prior constructed calibration curve. The spectroscopic analysis suggested that less than 5% TsO<sup>-</sup> counterion coadsorbs onto PVG, and that the majority of TsO<sup>-</sup> remains in the surrounding aqueous solution likely because of the Coulombic interaction disfavoring association of the anion with the anionic silanol surface of PVG. Similarly, Cr<sup>3+</sup>, Fe<sup>3+</sup>, and Cu<sup>2+</sup> are known to cation exchange onto PVG with less than 3% coadsorption of the Cl<sup>-</sup> counterion.<sup>29</sup> Third, repeated washing with water failed to detect **1** by UV-visible absorption (the detection limit of **1** is  $3.1 \times 10^{-7}$  M at  $\lambda_{\max} = 422$  nm). One may assume the worst case, i.e.,



**Figure 3.** Normalized absorption spectra of **1-ads** and **1**: (1) the solid line is of **1-ads** in air, in which uncoated PVG was used as a blank, and (2) the dashed line is an H<sub>2</sub>O solution of **1**, in which H<sub>2</sub>O was used as a blank. The inset is an expanded view of the visible portion of the spectra.



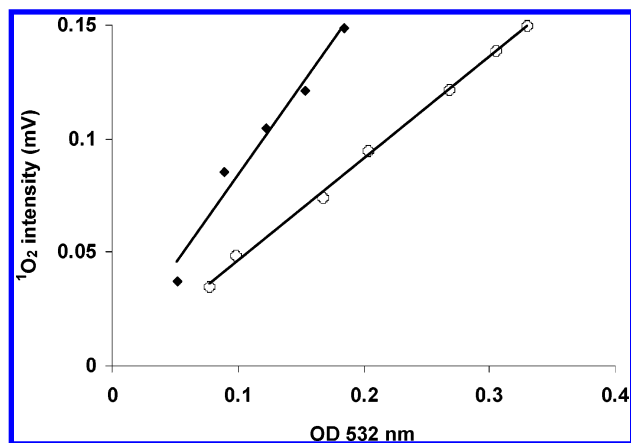
**Figure 4.** Singlet oxygen phosphorescence (1270 nm) decay from **1-ads** carried out in H<sub>2</sub>O (dots) and D<sub>2</sub>O (solid line). The above traces have been corrected, in which an uncoated PVG sample served as a blank and was subtracted from the background.

desorption below the detection limit of  $\sim 3 \times 10^{-7}$  M **1** of our UV instrument. However, this conclusion is probably incorrect because a control experiment showed that  $3 \times 10^{-7}$  M **1** does not lead to the <sup>1</sup>O<sub>2</sub> chemistry in sections 3.3 and 3.4. The experimental data lead us to conclude that the adsorbed **1** remains attached to PVG throughout the sensitization and photochemical processes. Thus, the PVG-attached sensitizer is referred to as **1-ads** hereafter.

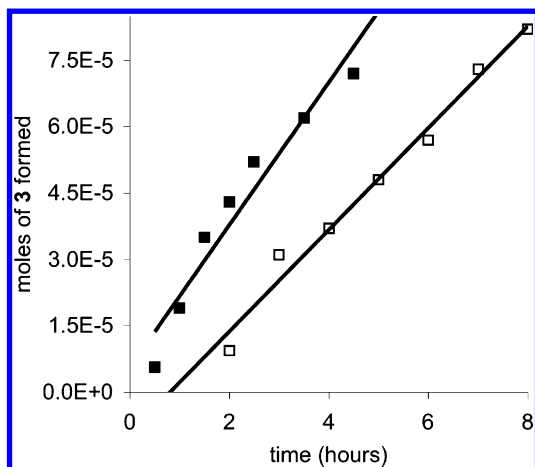
**3.2. Spectroscopic Properties of PVG-Adsorbed 1.** Figure 3 shows normalized UV-visible spectra of **1-ads** (in air) and **1** (in H<sub>2</sub>O). The spectra are very similar. The  $\lambda_{\max}$  value of **1-ads** in air is 419 nm. The  $\lambda_{\max}$  value of **1** in H<sub>2</sub>O is 422 nm. There appears to be only a slight decrease of the 500–600 nm absorption of heterogeneous **1** compared to homogeneous **1**. The absorption of **1-ads** consists of a band in the visible region between 500 and 700 nm, indicating that it may be excited upon the absorption of light in this range. The similarity between the two spectra suggests the **1-ads** may have similar properties to serve as a <sup>1</sup>O<sub>2</sub> photosensitizer.

**3.3. Detection of Singlet Oxygen.** In D<sub>2</sub>O, unlike H<sub>2</sub>O, <sup>1</sup>O<sub>2</sub> luminescence is easily detected at 1270 nm from the 532 nm irradiation of **1-ads** (Figure 4). The generation of <sup>1</sup>O<sub>2</sub> is based on a bimolecular sensitization reaction, represented by the



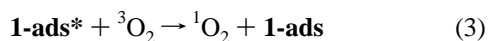


**Figure 5.** Time-resolved quantum yield measurement.  $^1\text{O}_2$  emission intensity as a function of absorbance in  $\text{D}_2\text{O}$  with an excitation wavelength of 532 nm. The solid squares represent *meso*-tetra(4-sulfonatophenyl)porphine dihydrochloride with  $\Phi_{\Delta} = 0.63$  in  $\text{D}_2\text{O}$ . The open circles represent free **1** measured to be  $\Phi_{\Delta} = 0.43 \pm 0.07$  in  $\text{D}_2\text{O}$ .



**Figure 6.** Photooxidation of *trans*-2-methyl-2-pentenoate anion by **1-ads** as a function of irradiation time in  $\text{D}_2\text{O}$  [solid squares ( $y = 2 \times 10^{-5}x + 6 \times 10^{-6}$ ;  $r^2 = 0.9394$ )] and  $\text{H}_2\text{O}$  [hollow squares ( $y = 1 \times 10^{-5}x + 9 \times 10^{-6}$ ;  $r^2 = 0.9832$ )].

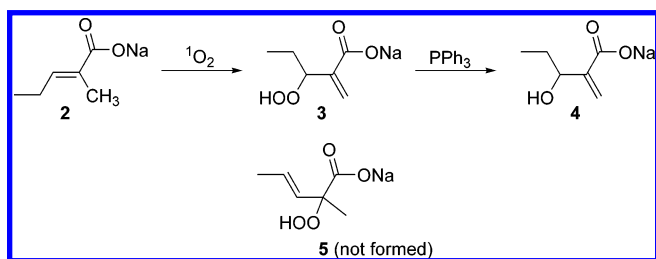
reaction between the electronically excited sensitizer, **1-ads**<sup>\*</sup>, and the acceptor,  $^3\text{O}_2$ . It is possible that **1-ads**<sup>\*</sup> is quenched by  $\text{O}_2$  which is adsorbed itself or, simply,  $\text{O}_2$  collides with excited **1-ads**. The formation of  $^1\text{O}_2$  is predominantly a triplet quenching process (eq 3).



The 1270 nm luminescence decay is exponential, and the lifetime of  $^1\text{O}_2$  in  $\text{D}_2\text{O}$  is found to be 65  $\mu\text{s}$ , which matches the literature value.<sup>41</sup> After  $^1\text{O}_2$  is generated, its diffusion into the surrounding solution can take place. Ogilby et al.<sup>4</sup> suggested that if one assumes a typical diffusion coefficient for oxygen,<sup>42</sup>  $D$ , in liquid of  $\sim 3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , then the distance traveled by  $^1\text{O}_2$  is approximately 62  $\mu\text{m}$  in  $\text{D}_2\text{O}$ . The difficulty in detecting  $^1\text{O}_2$  in  $\text{H}_2\text{O}$  arises from its short lifetime (3.1  $\mu\text{s}$ )<sup>43</sup> due to efficient electronic to vibronic energy transfer between the two.<sup>44</sup>

Figure 5 shows  $^1\text{O}_2$  emission intensity over a range of absorbances for **1** in homogeneous  $\text{D}_2\text{O}$  solution. The literature value of  $\Phi_{\Delta}$  for the reference sensitizer *meso*-tetra(4-sulfonatophenyl)porphine dihydrochloride is 0.63 in  $\text{D}_2\text{O}$ .<sup>45</sup> Thus,  $\Phi_{\Delta}$  for the formation of  $^1\text{O}_2$  from **1** is  $0.43 \pm 0.07$  in  $\text{D}_2\text{O}$ , using *meso*-tetra(4-sulfonatophenyl)porphine dihydrochloride as

## SCHEME 2



a reference. Triplet–triplet annihilation appears to be negligible at absorbances ranging from 0.03 to 0.60 from excitation at 532 nm, as indicated by the  $^1\text{O}_2$  intensity showing a linear correlation with the absorption of the complexes. Because there is no reference sensitizer–PVG complex, we were not able to determine the  $\Phi_{\Delta}$  value for the formation of  $^1\text{O}_2$  with **1-ads**. PVG-adsorbed **1** appears to retain its photosensitization property in aqueous solution. Unlike porous silicon nanocrystals,<sup>44,46,47</sup> PVG is not found to produce  $^1\text{O}_2$  in  $\text{D}_2\text{O}$  in the absence of adsorbed **1**. Furthermore, the 1270 nm luminescence of  $^1\text{O}_2$  in  $\text{H}_2\text{O}$  appears at the noise level of the instrument. However, we show that  $^1\text{O}_2$  is formed in  $\text{H}_2\text{O}$  by indirect trapping experiments. The results described next show that  $^1\text{O}_2$  produced in the **1-ads** photosensitized reaction can react with *trans*-2-methyl-2-pentenoate anion (**2**).

**3.4. Photooxidation of *Trans*-2-methyl-2-pentenoate Anion (**2**).** Unlike the aerobic UV irradiation of PVG reported to form superoxide,<sup>48</sup> the visible light irradiation of **1-ads** generates  $^1\text{O}_2$ , which can diffuse out of the silica matrix, and is then trapped by a *trans*-2-methyl-2-pentenoate anion (**2**) in a surrounding aqueous solution. The **1-ads** sensitized photooxidation of **2** affords one product, hydroperoxide **3** (Scheme 2). The reaction is monitored by NMR. No other products were detected, which would be expected if superoxide were present. Formation of **3** and not regioisomer **5** indicates that the methyl protons are more acidic, in which the resulting double bond is conjugated with the carboxylate group. Hydroperoxide **3** reacted with triphenylphosphine and converted to alcohol **4**, also characterized by NMR. The yield of **3** was dependent on whether the **1-ads** sensitized photooxidation of **2** was conducted in  $\text{D}_2\text{O}$  or  $\text{H}_2\text{O}$ . Figure 6 shows that this  $^1\text{O}_2$  “ene” reaction is found to be about 2 times faster in  $\text{D}_2\text{O}$  than  $\text{H}_2\text{O}$ . Hydroperoxide **3** was formed more rapidly in  $\text{D}_2\text{O}$  than  $\text{H}_2\text{O}$  (cf. 16.9 to 3.9%) after 2 h. In  $\text{H}_2\text{O}$ , photooxygenation of **2** with **1-ads** formed **3** in 32.8% yield after 8 h. The results support the conclusion that the reaction of  $^1\text{O}_2$  with **3** occurs in the surrounding  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  solution. Previous data led to a similar conclusion that alkene oxidation is more efficient in  $\text{D}_2\text{O}$  than  $\text{H}_2\text{O}$ .<sup>35</sup> The results establish the feasibility of carrying out the heterogeneous sensitization process with **1-ads** in which  $^1\text{O}_2$  is released into surrounding  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ .

## 4. Conclusion

PVG is a cation-binding solid. We took advantage of this binding property to examine PVG as a support for the cationic photosensitizer **1**. Sensitizer **1** adsorbs to PVG and gives a stable material, which does not dissociate in water at room temperature. Singlet oxygen is generated in the surrounding aqueous solution upon irradiation of the adsorbed complex. The excited state of **1-ads** is quenched by  $\text{O}_2$  to give  $^1\text{O}_2$ , which can be detected in the surrounding aqueous solution. The heterogeneous system described in this paper could have application in ridding wastewater of *E. coli*.

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