



## Photosensitizing properties of the porphycene immobilized in sol–gel derived silica coating films

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### ABSTRACT

Porphycene was covalently immobilized in a sol–gel silica film deposited on a glass plate, and the immobilized porphycene showed a photosensitizing property with recycling for the photo-oxidation of 1,5-dihydroxynaphthalene.

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The photosensitized production of singlet oxygen has significance in the areas of the photo-oxidation of organic compounds, DNA damage, and the photodynamic therapy of cancer.<sup>1,2</sup> Therefore, a variety of photosensitizers have been developed and their photochemical and photophysical properties extensively studied.<sup>3</sup> Among them, tetrapyrrolic compounds, such as porphyrin and phthalocyanine, are promising candidates for photosensitizers due to their unique photophysical properties.<sup>4–7</sup> During the course of these studies, the syntheses of porphyrin isomers have opened the door for developing new photosensitizers during these two decades.<sup>8–10</sup>

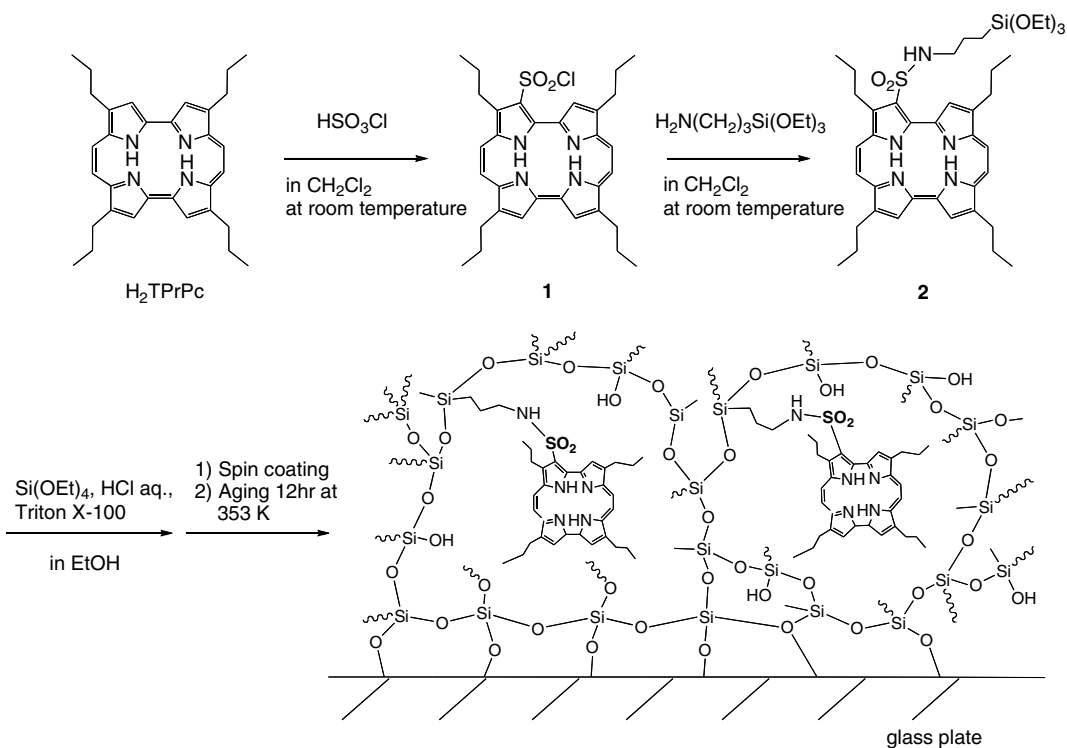
Porphycene, a structural isomer of porphyrin, first synthesized by Vogel and coworkers in 1986, shows a higher absorption than the porphyrin in the red spectral region due to its low symmetry.<sup>11,12</sup> This advantage of porphycene for photodynamic therapy has led chemists to extensively study its applications in this field.<sup>13–22</sup> Our group also reported the synthesis of water-soluble porphycenes having sulfonic groups, and its photosensitizing ability was examined in aqueous media.<sup>23,24</sup> The remarkable enhancement of the singlet oxygen production yield was also achieved by peripheral modification of the porphycene macrocycle with a heavy atom group, such as bromine.<sup>25</sup> The utility of tetraphenylporphycene in two-photon initiated photodynamic therapy was

also reported.<sup>26</sup> In this way, the development of a porphycene photosensitizer was achieved from various view points.

In this study, we report a gel film incorporating porphycene for development as an immobilized photosensitizer. Immobilization of a catalyst onto the various materials such as a polymer, metal, silica, and glass is a desirable approach for the establishment of ‘Green Chemistry’ since the catalyst is easily separated from the reaction medium and reused.<sup>27</sup> Among the immobilized methods, the sol–gel method is a convenient technique for the incorporation of various compounds into sol–gel films.<sup>28</sup> Furthermore, the prepared thin films are optically transparent in the visible region, which facilitates the photosensitization reaction within the gel film on a glass support. We now describe the synthesis, photochemical characterization, and photosensitizing properties of new organic–inorganic sol–gel materials incorporating the monofunctionalized porphycene.

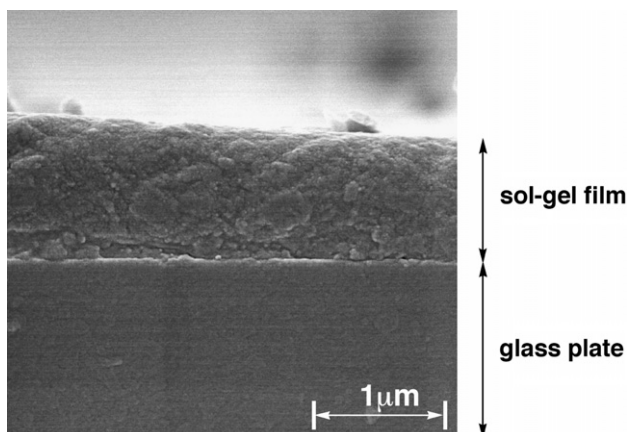
The porphycene derivative having a triethoxysilyl group (**2**) was synthesized as shown in Scheme 1. 2,7,12,17-Tetra-*n*-propylporphycene (H<sub>2</sub>TPrPc)<sup>11</sup> and 2,7,12,17-tetra-*n*-propylporphycene-3-sulfonyl chloride (**1**)<sup>20</sup> were synthesized by previously reported methods. The porphycene derivative (**2**) was synthesized by the reaction between **1** (1.1 × 10<sup>−5</sup> mol) and 1 equiv mol of 3-(triethoxysilyl)propylamine in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The amidosulfonation reaction was monitored by the UV–vis and MALDI-TOF-mass spectral changes and quantitatively proceeded within 1 h.<sup>29</sup> The solution was washed with H<sub>2</sub>O, dried over

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anhydrous  $\text{MgSO}_4$ , then evaporated under reduced pressure. This compound **2** was directly used for the following sol-gel process without purification due to its high reactivity.

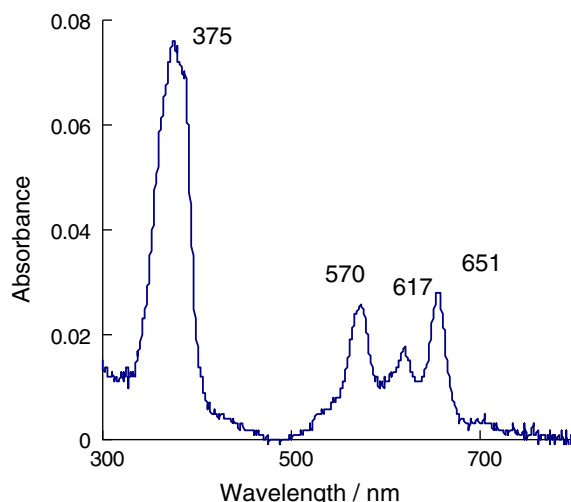
The sol-gel derived silica coated film containing the porphycene was prepared from tetraethoxysilane (TEOS) and **2** by an acid-catalyzed condensation reaction. A typical reaction condition is described as follows. To a solution of TEOS (0.62 g, 2.98 mmol) and triton X-100 (0.15 g) in 1.4 mL of  $\text{C}_2\text{H}_5\text{OH}$  was added a 0.1 M HCl aqueous solution (0.24 g) under air. The solution was further stirred for 24 h at room temperature. A 0.5 mL acetone solution of **2** ( $1.1 \times 10^{-5}$  mol) was then added and further stirred for 1 h. The resulting solution was deposited onto a freshly cleaned slide glass substrate<sup>30</sup> (Matsunami Glass Industries) by spin coating.<sup>31</sup> The silica gel film formed on the substrate was dried (aged) for 12 h at 353 K. Formation of the gel film was directly observed by a scanning electron micrograph (SEM) measurement as shown in



**Figure 1.** Cross-sectional SEM photograph for the gel film containing the porphycene.

Figure 1, and the thickness of the gel film was determined to be ca. 1000 nm.

The amount of the porphycene derivative in the gel film was determined by its UV-vis absorption spectrum. The absorption spectra of the gel film showed the typical shape for the porphycene,  $\lambda_{\text{max}}/\text{nm} = 375, 570, 617,$  and  $651$  as shown in Figure 2, and the spectrum is similar to that for **2** in  $\text{CH}_2\text{Cl}_2$ .<sup>29</sup> The total amount of the porphycene was estimated to be  $7.6 \times 10^{-10}$  mol/ $\text{cm}^2$  by the UV-vis measurement. The amount of the porphycene in the gel film did not change after being immersed in various solvents. This result indicates that the covalently bound porphycene was stably immobilized in the gel film. In contrast, we could definitely prepare the  $\beta$ -monosulfonated porphycene<sup>23</sup> doped gel film in a



**Figure 2.** UV-vis absorption spectrum of the gel film containing the porphycene.

**Table 1**  
Photophysical data of the porphycene derivative

Compound	Abs. $\lambda$ (nm)	Fluorescence, $\lambda$ (nm) <sup>a</sup>	$\Phi_f$ <sup>b</sup>
<b>2</b> <sup>c</sup>	372, 571, 616, 652	662	0.14
<b>2</b> <sup>d</sup>	375, 570, 617, 651	661	0.11

<sup>a</sup> Excitation at 380 nm.

<sup>b</sup>  $\Phi_f$ : Fluorescence quantum yield, excitation at 337 nm.

<sup>c</sup> Solvent, CH<sub>2</sub>Cl<sub>2</sub>.

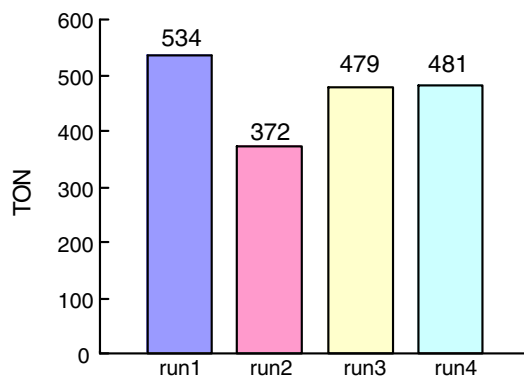
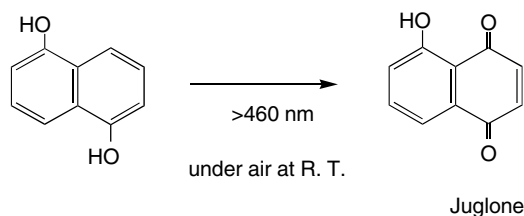
<sup>d</sup> In sol-gel modified silica plate.

similar manner, but the non-covalently bound porphycene disappeared after immersion in various solvents.

The photophysical data of the gel film are summarized in Table 1. The absolute fluorescence quantum yield ( $\Phi_f$ ) of the porphycene in the gel film was based on the photoluminescent measurement using an integrating sphere. The gel film showed a strong fluorescence maximum ( $\lambda_{fl}$ ) at 661 nm with the quantum yield of  $\Phi_f = 0.11$ .<sup>32</sup> This value is similar to that of **2** ( $\lambda_{fl} = 662$  nm,  $\Phi_f = 0.14$ ) in CH<sub>2</sub>Cl<sub>2</sub>. These results indicate that the immobilized porphycenes are homogeneously dispersed within the microporous cages and the electronic structure of the porphycene in the gel film was almost similar to that of **2** in solution. Thus, the immobilized porphycene existed in gel film without aggregation or stacking that causes static quenching of the excited state.

The photosensitizing property of the gel film was examined by ESR spin trapping experiment for singlet oxygen production. 2,2,6,6-Tetramethylpiperidine (TMP) was used as a probe molecule to react with singlet oxygen, yielding stable free radical nitroxide (2,2,6,6-tetramethylpiperidine oxide, TMPO), which can be easily detected by ESR. The gel film shows ESR signal typical for nitroxide radicals TMPO under irradiation by visible light ( $\lambda > 460$  nm) under air as shown in Figure 3.<sup>33</sup> Thus, the gel film containing porphycene acts as a photosensitizer for singlet oxygen production.

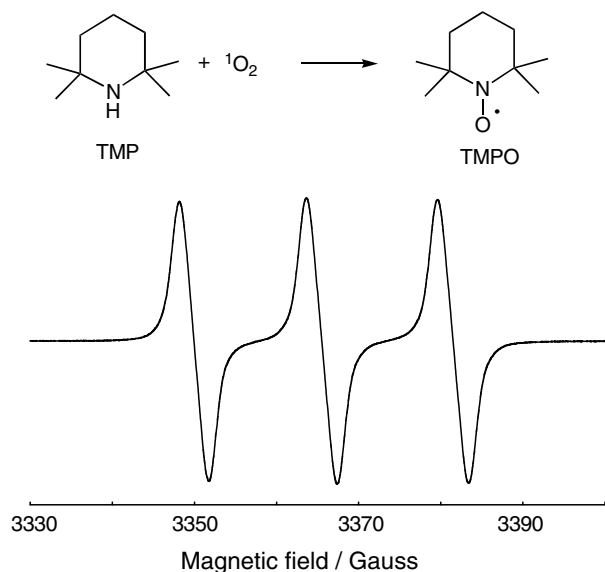
To confirm the catalytic activity of the gel film, the photo-oxygenation of the 1,5-dihydroxynaphthalene was investigated under irradiation by visible light ( $\lambda > 460$  nm).<sup>34</sup> As expected, the photo-reaction effectively proceeded and the oxygenated product, 5-hydroxy-1,4-naphthoquinone (Juglone), was obtained along with the spectral change at 427 nm, typical for Juglone.<sup>35,36</sup> The advantage of the porphycene over other photosensitizers including



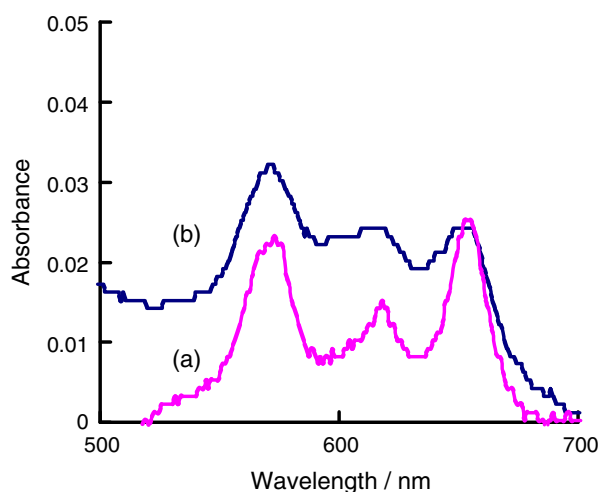
**Figure 4.** Turnover numbers (TON) for the recycled catalyses of the gel film containing the porphycene during 4 h reactions.

porphyrin in the photoreaction is due to its effective light absorption in the visible light.<sup>8,12,24</sup> After a 4 h reaction, the gel film was washed with CH<sub>3</sub>OH, and then reused for the successive reaction. The result of the recycled use of the gel film in the photo-oxygenation reaction is summarized in Figure 4. The reaction proceeded with almost the same efficiency in the 4th run, and the porphycene in the gel film did not undergo any bleaching during the reaction as shown in Figure 5.<sup>37</sup> The photo-oxygenation reaction using the gel film was additionally applied to 1-naphthol.<sup>38</sup> The turnover number toward product, 1,4-naphthoquinone was over 1200 based on bound porphycene.<sup>39</sup>

In summary, porphycene was stably immobilized in the silica gel film by covalent bonds using the simple sol-gel method in a one-pot procedure. The gel film generates singlet oxygen under visible light irradiation and shows a photosensitizing activity for the oxygenation of organic compounds and can be recycled.



**Figure 3.** ESR spectrum of nitroxide radical generated by irradiation of the gel film containing the porphycene in the presence of 2,2,6,6-tetramethylpiperidine (TMP).



**Figure 5.** UV-vis absorption spectra of the gel films containing the porphycene (a) before and (b) after recycled use.

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- Compound **2**: UV-vis (in CH<sub>2</sub>Cl<sub>2</sub>): [ $\lambda_{\max}$ /nm], 372, 383, 571, 616, 652; MALDI-TOF-MS (6-aza-2-thiothimine matrix,  $m/z$ ): [M+H]<sup>+</sup>, 762.7; HR MS (ESI-TOF,  $m/z$ ): calcd for C<sub>41</sub>H<sub>60</sub>N<sub>5</sub>O<sub>5</sub>SiS: [M+H]<sup>+</sup>, 762.4084. Found: [M+H]<sup>+</sup>, 762.4089.
- The slide glass substrate was cleaned by sonication in a 30% H<sub>2</sub>O<sub>2</sub> aqueous solution for 30 min followed by sonication in ethanol for 1 h at 303 K, and then dried with nitrogen gas.
- The sol-gel solution (10  $\mu$ L) was placed on the glass substrate and spun at 500 rpm for 10 s (1st) and then 2000 rpm for 10 s (2nd).
- The  $\Phi_f$  value was measured using an absolute photoluminescence quantum efficiency measurement system (Hamamatsu C9920-02) incorporating an integrating sphere. The gel film was deposited on a mica substrate.
- [TMP] = 0.2 M ( $5.9 \times 10^{-4}$  mol), [porphycene] =  $1.5 \times 10^{-9}$  mol (glass plate size  $0.8 \times 2.5$  cm with surface coverage  $7.6 \times 10^{-10}$  mol/cm<sup>2</sup>), solvent 3 mL CH<sub>2</sub>Cl<sub>2</sub> in air at room temperature with a 500 W tungsten lamp (TOSHIBA Y-46 filter,  $\lambda > 460$  nm).
- [1,5-Dihydroxynaphthalene] = 3.3 mM ( $9.9 \times 10^{-6}$  mol), [porphycene] =  $1.5 \times 10^{-9}$  mol (glass plate size  $0.8 \times 2.5$  cm with surface coverage  $7.6 \times 10^{-10}$  mol/cm<sup>2</sup>), solvent 3 mL CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (9:1, v/v) in air at room temperature with a 500 W tungsten lamp (TOSHIBA Y-46 filter,  $\lambda > 460$  nm).
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- The oxygenated product, 5-hydroxy-1,4-naphthoquinone (Juglone); GC-MS (EI,  $m/z$ ): [M]<sup>+</sup>, 174, UV-vis ( $\lambda_{\max}$ /nm), 427, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 6.94 (s, 2H), 7.27 (dd, 1H, Ph), 7.60–7.65 (m, 2H, Ph), 11.90 (s, 1H, OH).
- The intensity of the UV-vis absorption at 651 nm of the gel film was monitored during every run.
- [1-Naphthol] = 3.3 mM ( $9.9 \times 10^{-6}$  mol), [porphycene] =  $1.5 \times 10^{-9}$  mol (glass plate size  $0.8 \times 2.5$  cm with surface coverage  $7.6 \times 10^{-10}$  mol/cm<sup>2</sup>), solvent 3 mL CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (9:1, v/v) in air at room temperature with a 500 W tungsten lamp (TOSHIBA Y-46 filter,  $\lambda > 460$  nm).
- The oxygenated product, 1,4-naphthoquinone; GC-MS (EI,  $m/z$ ): [M]<sup>+</sup>, 158, UV-vis ( $\lambda_{\max}$ /nm), 334, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 6.96 (s, 2H), 7.74 (m, 2H, Ph), 8.06 (m, 2H, Ph).