Photophysical and Photocatalytic Properties of *β*-Sulfonatoporphycenes

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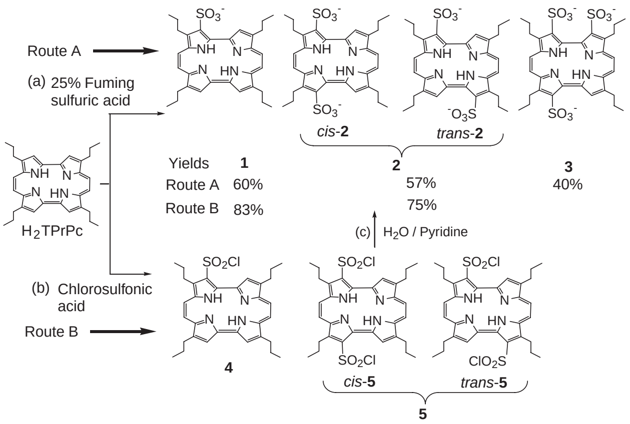
The photophysical properties and photooxidation ability of the *β*-sulfonatoporphycenes are reported. The photophysical parameters depend on the number of substitutions. The disulfonated porphycene **2** is expected to be a new photosensitizer due to its high catalytic activity and photostability.

Water-soluble porphyrins and their metal complexes have attracted much attention because of their various uses as photodynamic therapy photosensitizers,[1] fluorescent tumor markers,[2] and photooxidation catalysts[3] in aqueous media. There are also many reports concerning the photophysical properties[4] and photooxidation abilities[3] of water-soluble porphyrins.

On the other hand, porphycenes, the structural isomers of porphyrins first synthesized by Vogel et al.,[5] are considered to be superior photosensitizers for singlet oxygen generation due to their large absorption peaks in the visible region and suitable photochemical attributes.[6] In the previously submitted paper, we reported the syntheses of water-soluble porphycenes containing sulfonic acid groups.[7] Here, we report the photophysical properties of sulfonated porphycenes and the photodegradation of 2,4,6-trichlorophenol (TCP), which is a major pollutant,[8] using disulfonated porphycene **2** as a photosensitizer.

The sulfonated porphycenes were synthesized by the direct sulfonation[7] or chlorosulfonation[9] of 2,7,12,17-tetra-*n*-propylporphycene (H_2TPrPc) and followed by hydrolysis[10] as shown in Scheme 1. **2** and **3** exhibit a high water-solubility at pHs between 0 and 14. The details of the photophysical properties of the three sulfonatoporphycenes are discussed below. The photophysical parameters of the sulfonated porphycenes are summarized in Table 1.

The electronic spectra of the sulfonatoporphycenes were measured in CH_3OD and in H_2O. The Q-bands are red-shifted with the increasing number of sulfonic acid groups on the pyrrole groups of H_2TPrPc.



Scheme 1. Synthesis of sulfonated porphycenes (a) direct sulfonation of H_2TPrPc, (b) chlorosulfonation of H_2TPrPc, (c) hydrolysis of chlorosulfonated porphycenes.

Table 1. Photophysical parameters of sulfonated porphycenes

Compound	Solvent	λ^{a}_{max} /nm	$\lambda^{b}_{fluorescence}$ /nm	τ_s/ns[c]	Φ^{d}_{f}	Φ^{e}_{Δ}
1	CH_3OD	643	648	8.38	0.33	0.29
2	CH_3OD	653	657	3.94	0.17	0.25
2	H_2O	646	657	1.61	0.10	0.10[f]
3	CH_3OD	688	—	—	≈0	0.01
3	H_2O	686	—	—	≈0	≈0[f]

[a]Maximum of the lowest-energy absorption band. [b]Maximum of the fluorescence. [c]Life time of the singlet state. τ_s was measured by a HORIBA FluoroCube. Two components of the fluorescence-decay kinetics were observed. The main component was used to determine τ_s. [d]Quantum yield of fluorescence. [e]Quantum yield of singlet oxygen formation. Φ_Δ was measured by a HORIBA SPEX Fluorolog-NIR. [f]Solv., D_2O.

The absolute fluorescence quantum yields (Φ_f) of the sulfonated porphycenes were based on photoluminescent measurements using an integrating sphere. Compound **1** showed a strong fluorescence maximum at 648 nm with the quantum yield $\Phi_f = 0.33$ in air-saturated CH_3OD, and compound **2** also showed a fluorescence at 657 nm with the quantum yield $\Phi_f = 0.17$ in CH_3OD and $\Phi_f = 0.10$ in H_2O at neutral pH. These values are lower than that of H_2TPrPc ($\Phi_f = 0.36$) in toluene,[6a] but they are similar to that of the haematoporphyrin derivatives[11] ($\Phi_f = 0.09$) used as tumor markers. Thus, these sulfonated porphycenes appear to be potential agents for tumor diagnosis.[12] However, compound **3** does not show any fluorescence both in CH_3OD and in H_2O. The Φ_f value of the sulfonatoporphycenes decreased with an increase in the number of sulfonic acid groups. It appears that the *β*-substitutions result in deformation of the porphycene ring[13] due to steric repulsion. The resulting out-of-plane distortion of the porphycene macrocycle may increase the rate constants of the non-radiative decay.[14]

Steady-state $^1O_2$ phosphorescence detected at 1270 nm was used to determine the quantum yield of the singlet oxygen formation (Φ_Δ) for the sulfonatoporphycenes in air-saturated solutions. The Φ_Δ values were determined from the phosphorescence intensity, which were compared to the intensity obtained using heamatoporphyrin[4] ($\Phi_\Delta = 0.75$ in CH_3OD) and rose bengal[15] ($\Phi_\Delta = 0.75$ in D_2O) as standards.

The Φ_Δ values decreased with the increasing number of substitutions in a manner similar to the Φ_f values. The Φ_Δ values were as follows: in CH_3OD, $\Phi_\Delta = 0.29, 0.25$, and 0.01 for **1**, **2**, and **3**, respectively: in D_2O, $\Phi_\Delta = 0.10$ and 0 for **2** and **3**. **2** was observed to have low Φ_Δ and Φ_f values in water relative to methanol. An increase in the solvent polarity results in an increase of the non-radiative rate constants from the excited states, therefore Φ_Δ and Φ_f decrease as for aminoanthraquinones.[16]

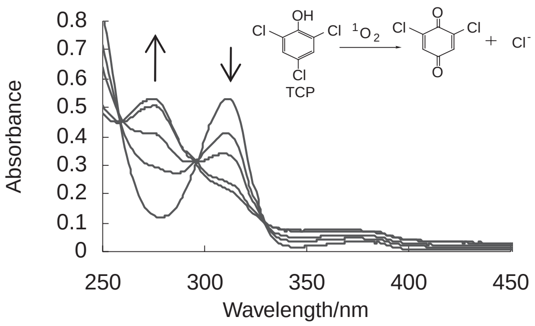


Figure 1. Electronic spectral changes observed during photodegradation of TCP in the presence of **2** in water at pH 10.

Table 2. Photodegradation of TCP in water[a]

Photo-sensitizer	TON[b]	Conversion /%	Yields/%	
			2,6-dichloro-benzoquinone	Cl^-
2	185	100	97	96
TPPS	115	73	70	71
none	0	0	0	0

[a] $[TCP] = 3.3 \times 10^{-3}$ M, $[sensitizer] = 7 \times 10^{-6}$ M, under air atmosphere with a 500-W tungsten lamp ($\lambda \geq 460$ nm) at room temperature. [b] Turnover number per 1 h.

To confirm the catalytic activity of **2**, the photodegradation of 2,4,6-trichlorophenol[8] (TCP, 3.3×10^{-3} M) was carried out under irradiation with visible light ($\lambda \geq 460$ nm). Figure 1 shows the spectral change observed during the photodegradation of TCP using **2** as a sensitizer every one hours. The spectral change shows decrease in the TCP absorption peak at 312 nm and formation of 2,4-dichlorobenzoquinone at 273 nm.[8] The turnover number based on **2** is 1.5 times greater than that of tetrakis(sulfonatophenyl)porphyrin (TPPS) as shown in Table 2, though the Φ_Δ value for **2** is lower than that for TPPS ($\Phi_\Delta = 0.51$, in water).[4] The high catalytic activity of **2** arises from its high absorption in the visible region. A chlorine ion was also detected as the product by the $Fe(NO_3)_3$ and $Hg(SCN)_2$ method. An almost quantitative yield of the chlorine ion was observed. Control experiments indicated that both light and **2** are essential for the degradation of TCP.

One of the important factors is the photostability of photosensitizers. We found that **2** is more stable than TPPS during photoirradiation. In order to compare the photostabilities of **2** and TPPS, photodecomposition experiments were carried out. The air-saturated water solutions containing a sensitizer (4.5×10^{-6} M) were irradiated with visible light ($\lambda \geq 460$ nm). The irradiation of the samples leads to a decrease in the absorption bands. After photoirradiation for 10 h, 51% of the TPPS had decomposed. On the other hand, only 4% of **2** had decomposed. The difference of the photostability is attributed to the structure of the macrocycle.

In conclusion, the photophysical properties of the sulfonated porphycenes were investigated and the photodegradation of TCP using **2** was carried out. The photophysical parameters are dependent on the number of sulfonic acid groups. **2** shows a higher catalytic activity and photostability compared to TPPS.

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10 **4**[9] and **5** were obtained in 83% and 75% yields, respectively. The hydrolysis of the chlorosulfonated porphycenes quantitatively proceeded.
4: UV-vis (in CH_2Cl_2): [λ_{max}/nm], 386, 577, 632, 669: MALDI-TOF-MS (dithranol matrix, m/z) $[M]^+$ 576.65. **5**: UV-vis (in CH_2Cl_2): [λ_{max}/nm], 386, 594, 644, 683: MALDI-TOF-MS (dithranol matrix, m/z) $[M]^+$ 674.77. The ratio of isomers (***cis*-2** and ***trans*-2**) was determined by peak integration of the ^{1}H NMR spectrum. Route A: ***cis*-2**:***trans*-2** = 1.8:1 Route B: ***cis*-2**:***trans*-2** = 2.5:1 Sample **2** synthesized by the Route B method was used for these experiments.

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